CHEMISTRY:
THE MODERN APPROACH

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PREFACE

Welcome to Chemistry: The Modern Approach. This book invites you on a fascinating journey through the complex and captivating world of chemistry, highlighting the vital role it plays in our everyday lives. From the smallest atoms to the vastness of chemical reactions, this science helps us understand the foundation of everything around us. We begin with the fundamentals—introducing the key concepts and principles that are essential for understanding chemistry. From the basic structure of atoms to the bonds that hold molecules together, these foundational topics pave the way for exploring more advanced areas.

As you move through the chapters, you'll encounter the latest advancements in the field. We delve into nanotechnology's role in chemistry, uncovering its transformative impact across various industries. You'll also explore green chemistry and its sustainable applications, emphasizing the importance of environmentally friendly practices in addressing global challenges. Further, this book covers advances in materials chemistry, catalysis, and spectroscopy techniques—showcasing the cutting-edge research that's shaping the future of the field. Medicinal chemistry, with a focus on drug design and development, highlights the essential role chemistry plays in healthcare. You'll also find discussions on the latest developments in organic and organometallic chemistry, which are critical to both industry and research. Environmental chemistry and pollution control are examined to illustrate how chemistry can be a powerful tool in mitigating human impact on the planet. Finally, the book concludes with advances in organic compound synthesis, demonstrating the creativity and innovation involved in crafting new molecules.

Chemistry: The Modern Approach is not just a textbook; it's a celebration of the wonders of chemistry. Through vivid examples and practical applications, this book seeks to inspire a deep appreciation for the role chemistry plays in shaping our world.

October 2024

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Introduction of Nanotechnology in Chemistry

Yasmeen JUNEJO

Mehmet OZASLAN

1. Introduction

Nanotechnology, a multidisciplinary field that converges at the intersection of physics, chemistry, biology, and engineering, has revolutionized various scientific domains, including chemistry. At its core, nanotechnology involves the manipulation and control of matter on an atomic and molecular scale, typically within the range of 1 to 100 nanometers. This nanoscale dimension endows materials with unique physical, chemical, and biological properties that differ significantly from their bulk counterparts. The profound implications of these properties have opened new avenues in chemical research and industrial applications (Bayda et al., 2019; Elnashaie et al., 2015; Stefan & Monchaud, 2019; Whitesides, 2005).

The term "nanotechnology" was first coined by Norio Taniguchi in 1974, but the conceptual foundation was laid by physicist Richard Feynman in his famous 1959 lecture, "There's Plenty of Room at the Bottom." Feynman envisioned the possibility of manipulating individual atoms and molecules, a vision that has since become a reality. Over the past few decades, advancements in instrumentation, such as the development of the scanning tunneling microscope (STM) and the atomic force microscope (AFM), have enabled scientists to observe and manipulate matter at the nanoscale with unprecedented precision (Bayda et al., 2019; Elnashaie et al., 2015).

Nanomaterials exhibit a plethora of unique properties that arise due to their high surface area to volume ratio, quantum confinement effects, and the presence of surface atoms with unsaturated bonds. These properties include enhanced reactivity, quantum effects, mechanical strength, and optical properties. The increased surface area of nanoparticles leads to a higher proportion of atoms being exposed to the surrounding environment, resulting in enhanced chemical reactivity. This property is particularly advantageous in catalysis, where nanoparticles can act as highly efficient catalysts in chemical reactions. At the nanoscale, quantum mechanical effects become significant, leading to discrete electronic states. This can result in unique optical, electronic, and magnetic properties, which are not observed in bulk materials. For instance, quantum dots exhibit size-dependent fluorescence, making them useful in imaging and sensing applications. Nanomaterials such as carbon nanotubes and graphene exhibit extraordinary mechanical strength and flexibility, making them ideal candidates for reinforcing materials in composites and other structural applications. Nanoparticles can also exhibit unique optical properties, such as surface plasmon resonance (SPR), which is the collective oscillation of electrons on the surface of metallic nanoparticles. This phenomenon is exploited in various applications, including biosensing and imaging (SAFDAR et al.; Safdar et al., 2019; Stefan & Monchaud, 2019; Whitesides, 2005).

The integration of nanotechnology into chemistry has led to significant advancements in various sub-disciplines. In catalysis, nanocatalysts are employed to enhance the efficiency and selectivity of chemical reactions. For example, gold nanoparticles have been found to catalyze the oxidation of carbon monoxide to carbon dioxide at room temperature, a reaction that is not catalyzed by bulk gold. In analytical chemistry, nanotechnology has revolutionized analytical techniques by enabling the development of highly sensitive and selective sensors. Nanomaterials such as graphene and carbon nanotubes are used in the fabrication of electrochemical sensors for detecting trace amounts of analytes in complex matrices. In environmental chemistry, nanomaterials are utilized for environmental remediation, including the removal of pollutants from water and air. For instance, nanoscale zero-valent iron particles are used for the remediation of contaminated groundwater. In pharmaceutical chemistry, nanoparticles are engineered to deliver drugs to specific targets within the body, improving the efficacy and reducing the side effects of therapeutic agents. Liposomes, dendrimers, and polymeric nanoparticles are some of the nanocarriers used in drug delivery systems (JUNEJO & ÖZASLAN, 2023; Junejo & Safdar, 2019; Junejo et al., 2019; JUNEJO et al.; Tunio et al., 2024).

The future of nanotechnology in chemistry holds immense promise, with ongoing research focused on developing novel nanomaterials and exploring new applications. However, several challenges need to be addressed to fully realize the potential of nanotechnology. These include the scalability of nanomaterial production, the reproducibility of nanomaterial properties, and the assessment of potential health and environmental risks associated with nanomaterials. In conclusion, nanotechnology has ushered in a new era in chemistry, enabling the manipulation of matter at the atomic and molecular levels to create materials with unprecedented properties. As research in this field continues to advance, the integration of nanotechnology in chemistry is expected to lead to innovative solutions for some of the most pressing challenges in science and technology.

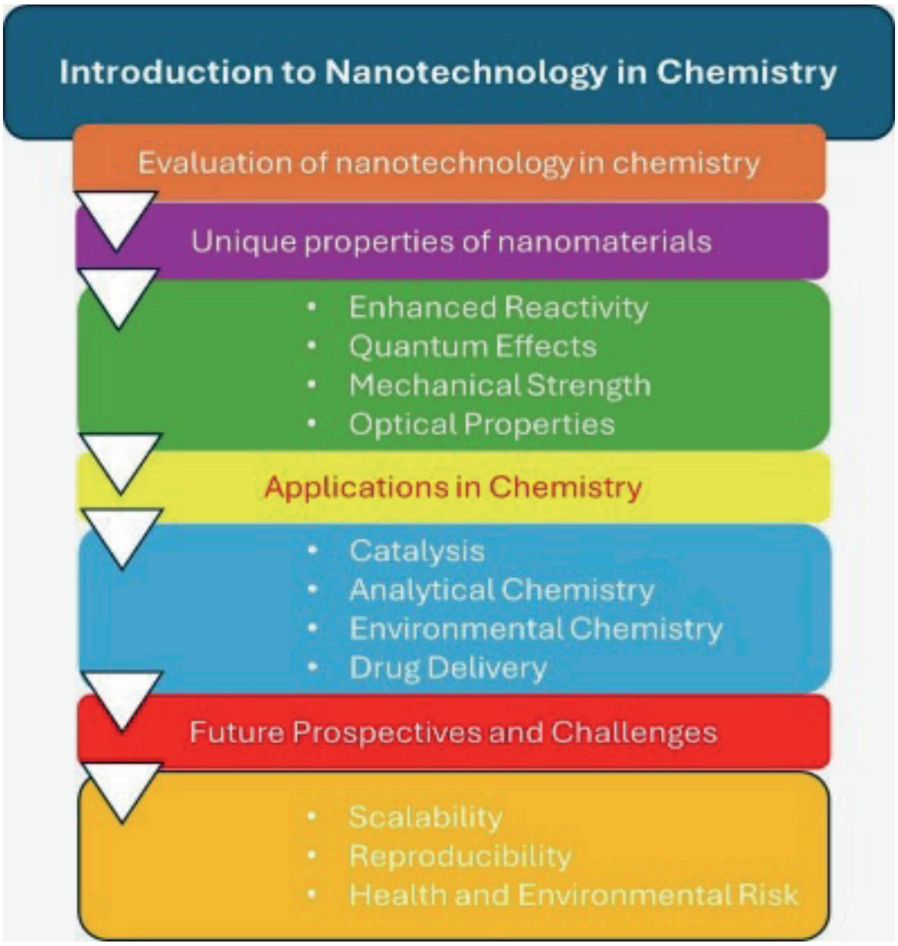

Figure 1: Overview of the Nanotechnology in Chemistry

2. Unique Properties of Nanomaterials

Nanomaterials exhibit a range of unique properties that arise due to their nanoscale dimensions. These properties include enhanced reactivity, quantum effects, mechanical strength, and optical properties. Understanding these properties is essential for exploiting nanomaterials in various chemical applications.

i. Enhanced Reactivity

At the nanoscale, materials have a significantly higher surface area to volume ratio compared to their bulk counterparts. This increased surface area results in a higher proportion of atoms being exposed to the surrounding environment, leading to enhanced chemical reactivity. This property is particularly advantageous in catalysis, where nanoparticles can act as highly efficient catalysts, accelerating chemical reactions and increasing selectivity (Junejo & Safdar, 2019; JUNEJO et al.; SAFDAR et al.).

ii. Quantum Effects

When the size of a material is reduced to the nanoscale, quantum mechanical effects become significant. These effects lead to discrete electronic states and can result in unique optical, electronic, and magnetic properties that are not observed in bulk materials. For instance, quantum dots, which are semiconductor nanoparticles, exhibit size-dependent fluorescence, making them useful in imaging and sensing applications (Blonder, 2010; Comini et al., 2013; Elnashaie et al., 2015).

iii. Mechanical Strength

Nanomaterials such as carbon nanotubes and graphene exhibit extraordinary mechanical strength and flexibility. Carbon nanotubes, for example, have a tensile strength much higher than that of steel while being lightweight. This property makes them ideal candidates for reinforcing materials in composites and other structural applications (Blonder, 2010; JUNEJO & ÖZASLAN, 2023; Junejo & Safdar, 2019; Nasrollahzadeh et al., 2019).

iv. Optical Properties

Nanoparticles can exhibit unique optical properties, such as surface plasmon resonance (SPR). SPR is the collective oscillation of electrons on the surface of metallic nanoparticles when they are excited by light at specific wavelengths. This phenomenon is exploited in various applications, including biosensing, imaging, and medical diagnostics (O'Connor & Hayden, 2008; SAFDAR et al.).

Table1 Unique Properties of Nanomaterials

	Property	**Description**	**Example Applications**
1	Enhanced Reactivity	Increased surface area leads to higher reactivity.	Catalysis, environmental remediation
2	Quantum Effects	Discrete electronic states lead to unique optical, electronic, and magnetic properties.	Quantum dots for imaging and sensing
3	Mechanical Strength	Exceptional tensile strength and flexibility.	Reinforcement in composites, structural materials
4	Optical Properties	Surface plasmon resonance and other optical effects.	Biosensing, imaging, medical diagnostics

This table provides a summary of the unique properties of nanomaterials and their example applications, highlighting the significance of these properties in various fields of chemistry.

3. Applications of Nanotechnology in Chemistry

Nanotechnology has profoundly impacted various sub-disciplines within chemistry, leading to significant advancements and innovative applications. Here are some key applications of nanotechnology in chemistry:

i. Catalysis

Nanocatalysts are used to enhance the efficiency and selectivity of chemical reactions. Due to their high surface area and unique electronic properties, nanoparticles can act as highly efficient catalysts. For example, gold nanoparticles catalyze the oxidation of carbon monoxide to carbon dioxide at room temperature, a reaction not catalyzed by bulk gold. This property is exploited in industrial processes, environmental remediation, and energy conversion (JUNEJO & ÖZASLAN, 2023; Junejo & Safdar, 2019; Junejo et al., 2019; JUNEJO et al.; SAFDAR et al.; Safdar et al., 2019).

ii. Analytical Chemistry

Nanotechnology has revolutionized analytical techniques, enabling the development of highly sensitive and selective sensors. Nanomaterials such as graphene, carbon nanotubes, and quantum dots are used in fabricating electrochemical sensors, biosensors, and fluorescent probes. These sensors can detect trace amounts of analytes in complex matrices, making them invaluable in environmental monitoring, medical diagnostics, and food safety (Junejo & Safdar, 2019; Junejo et al., 2019; Kaehler, 1994; Nasrollahzadeh et al., 2019; Stefan & Monchaud, 2019).

iii. Environmental Chemistry

Nanomaterials are utilized for environmental remediation, including the removal of pollutants from water and air. Nanoscale zero-valent iron particles, for instance, are used to remediate contaminated groundwater by reducing toxic contaminants. Nanotechnology also aids in developing materials for pollutant detection and degradation, contributing to cleaner and safer environments (Junejo & Safdar, 2019; Junejo et al., 2019).

iv. Drug Delivery

In pharmaceutical chemistry, nanoparticles are engineered to deliver drugs to specific targets within the body, improving efficacy and reducing side effects. Liposomes, dendrimers, and polymeric nanoparticles are some of the nanocarriers used in drug delivery systems. These carriers can encapsulate drugs, protect them from degradation, and release them at the desired site, enhancing therapeutic outcomes (JUNEJO et al.; Seeman, 2003; Stefan & Monchaud, 2019).

Table 2: Applications of Nanotechnology in Chemistry

	Application Area	**Description**	**Example Applications**
1	Catalysis	Nanocatalysts enhance reaction efficiency and selectivity due to high surface area and unique properties.	Industrial processes, environmental remediation, energy conversion
2	Analytical Chemistry	Nanomaterials enable the development of highly sensitive and selective sensors.	Environmental monitoring, medical diagnostics, food safety
3	Environmental Chemistry	Nanomaterials are used for the removal of pollutants and environmental remediation.	Water and air purification, pollutant detection and degradation
4	Drug Delivery	Nanoparticles are engineered to deliver drugs to specific targets, improving efficacy and reducing side effects.	Targeted drug delivery, controlled drug release, cancer therapy

Nanotechnology holds great promise for chemistry, offering a range of innovative solutions and improvements, but it also faces several challenges. Here's a summary of the future prospects and challenges in this field:

Future Prospects

a) Advanced Material Development: Nanotechnology can enable the creation of new materials with unique properties, such as superstrength, lightweight, or highly specific reactivity.

This includes the development of nanocomposites, nanostructured materials, and smart materials.

b) Catalysis and Reaction Efficiency: Nanocatalysts can enhance the efficiency of chemical reactions by increasing the surface area available for reactions. They can be used in green chemistry to develop more sustainable processes with fewer by-products.

c) Improved Drug Delivery Systems: Nanoparticles can be engineered to deliver drugs more precisely to targeted cells or tissues, improving the efficacy and reducing side effects of treatments. This is particularly useful in cancer therapy and personalized medicine.

d) Environmental Remediation: Nanotechnology can be applied to clean up pollutants from water and soil through processes such as adsorption, degradation, or transformation of contaminants. Nanomaterials can also be used in sensors for detecting environmental toxins.

e) Enhanced Analytical Techniques: Nanotechnology can improve the sensitivity and resolution of analytical methods. For example, nanoscale sensors and probes can detect very low concentrations of substances, enabling more precise measurements in chemical and biological systems.

f) Energy Storage and Conversion: Nanomaterials can improve the performance of batteries, fuel cells, and solar cells by enhancing their energy storage capacity and conversion efficiency. This can lead to more efficient and sustainable energy solutions.

Challenges

a) Safety and Toxicity: The potential toxicity of nanoparticles is a significant concern. Their small size can lead to unforeseen interactions with biological systems, and understanding their long-term health and environmental impacts is crucial.

b) Scalability and Cost: Producing nanomaterials and implementing nanotechnology at a large scale can be expensive and technically challenging. Scaling up from laboratory research to industrial production requires careful planning and investment.

c) Regulation and Standardization: There is a need for clear regulatory guidelines and standards for nanomaterials to ensure their safe use and to facilitate their commercialization. This includes developing standardized methods for assessing their safety and efficacy.

d) Ethical and Social Implications: The use of nanotechnology raises ethical and societal concerns, such as privacy issues related to nanoscale sensors and potential environmental impacts. Addressing these concerns requires interdisciplinary dialogue and public engagement.

e) Integration with Existing Technologies: Combining nanotechnology with existing technologies can be complex. Ensuring compatibility and optimizing performance while maintaining cost-effectiveness is a challenge.

f) Interdisciplinary Collaboration: Successful development and application of nanotechnology often require collaboration across multiple disciplines, including chemistry, physics, biology, and engineering. Building effective interdisciplinary teams and communication channels is essential for overcoming these challenges.

Finally, nanotechnology in chemistry presents exciting opportunities for innovation and advancement, but addressing these challenges is crucial for realizing its full potential.

5. Conclusion

In conclusion, the integration of nanotechnology into chemistry represents a transformative leap forward with the potential to revolutionize various fields, from materials science and catalysis to drug delivery and environmental remediation. By harnessing the unique properties of nanomaterials, chemists can develop innovative solutions that enhance efficiency, performance, and sustainability across numerous applications.

However, this promising future is accompanied by significant challenges. The safety and toxicity of nanomaterials require thorough investigation to ensure their responsible use. Additionally, scaling up production, managing costs, and establishing regulatory frameworks are essential steps towards the practical implementation of nanotechnology. Ethical considerations and interdisciplinary collaboration further underscore the complexity of advancing this field.

Ultimately, while nanotechnology holds immense promise for addressing many of the pressing challenges in chemistry and beyond, its successful realization depends on overcoming these obstacles. It is a dire need of continued research, development, and dialogue among scientists, policymakers, and the public will be crucial in shaping a future where nanotechnology can be safely and effectively integrated into society.

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GREEN CHEMISTRY AND SUSTAINABLE APPLICATIONS

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Green chemistry has emerged as a pivotal approach in addressing environmental concerns and promoting sustainability in chemical processes and industries. The goal of green chemistry is to do this by rationally designing chemical and processes based on a set of measurement and principles that have been developed over the previous many decades. Several political, social, economic, and technological aspects need to change in concert for green chemistry to realize its full potential. Tran materialization and dematerialization initiatives within the chemical industry are advanced by the conceptual and technological framework offered by green chemistry. In addition to other sustainability criteria the concepts of green chemistry aid in locating areas that merit innovation. Green chemistry guarantees that new technologies minimize unintentional risks and offers insight into the ramifications of new technologies and it differs from other technical development that concentrate nearly only on application by taking into account both the consequences for new technology and its application. This viewpoint encourages the multidisciplinary design and development of new technologies that are integrated with sustainable concepts. Overall, this book chapter underscores the pivotal role of green chemistry in fostering sustainable development and offers insights into its potential to address global environmental challenges while promoting economic growth and societal well-being.

2.1 Introduction

Green chemistry has been around for more than three decades, as a framework for contributing to the broad scope of global sustainability. American Chemical Society journals are a great place for these scientists to share their latest finding and serve as a resource for the chemistry community and beyond to understand current issues and envision solutions. We think this is a good time to highlight some of the top articles on the broad theme of green chemistry. that are being published today through a Virtual Issue of selected works from nine ACS chemistry and engineering journals (Sheldon et al., 2018; Zimmerman et al., 2020). The global economy has grown astronomically over the 20th century, and the industrialized world's quality of living has continued to rise. On the other hand, the amount of water consumed worldwide has quadrupled since the mid-1900s. The market for wood-based building materials has increased. The amount of wood needed to generate heat has quadrupled. The demand has raisedsix fold for raw materials for paper and wood pulp. Over the past 50 years, the amount of marine fish consumed has grown fivefold. There has been a consistent decline in farmland quality as a result of intensive livestock husbandry (Kar et al., 2021). More than a thousand creatures or plants are in danger of going extinct every year. Since the start of the industrial era, the atmospheric content of carbon dioxide has been progressively declining until it has reached zero. The atmospheric concentration of carbon dioxide has been continuously rising since the start of the industrial era (greenhouse effect). To put it another way, rising living standards and resource exploitation have come at a cost, with environmental pollution continuing to rise and natural resources being used to the furthest extent possible (Sheldon et al., 2022; Ganesh et al., 2021).

Green chemistry offers a conceptual and technology framework that advances the chemical enterprises dematerialization and transmaterialization efforts. Innovation opportunities are identified by the application of sustainability indicators and the concepts of Green chemistry and also take care to minimize unintentional risk associated with new technology and provide insight into their ramifications. Green chemistry stand out from other technological trends that focus mainly on application by also considering the broader implications of new technologies. This perspective promotes the multidisciplinary design and development if innovations that adhere to sustainable principles. By evaluating both the applications and potential impacts green chemistry fosters the creation of technologies that support sustainability from multiple angles (Brandt, 2002).

Green chemistry tools and metrics help businesses evaluate their products through a "triple bottom line of environmental, economic and social factors. This approach promotes the creation of safer control costs. Regulatory advantages for green solutions could further incentivize their use. The adoption of green chemistry and sustainable practices is proving that green technologies can be economically competitive (Hofer & Bigorra, 2007). Green chemistry to be most effective it must be done at the design phase of a new chemical or process. When building a new chemical or product there are many opportunities for deeper forms of innovation, such as overhauling the production system which can start with small surface design changes and progress to full system redesign. Over the past fifteen years the biggest developments have occurred in chemical even though green chemistry fosters innovation throughout the chemical supply chain (Mulvihill et al., 2011; Sheldon, 2018).

The terms "green chemistry" and "minimum impact chemistry" were previously interchangeable, the EPA's initiatives led to the global adoption of the term "green chemistry" to refer to the design of chemical processes and products that minimize or completely eliminate waste generation and avoid the use of toxic or hazardous substances. It was dubbed "benign by design chemistry" at first. There are two approaches to approach the connection between analytical and green chemistry. Green chemistry is controlled and justified by the study of analytical chemistry. Here, analytical chemistry proves to be a useful instrument in verifying the environmentally friendly outcome of a chemical product or technology. However, chemical analysis techniques produce waste and need energy, solvents and reagents (Koel & Kaljurand, 2006; Horváth, 2018).

However, in many instances, the samples being analyzed are complex mixtures with interfering matrices that prevent the use of waste reducing methods. Identifying alternatives solvent is a crucial step towards adopting greener methodologies. In order to increase the sensitivity, selectivity, and reliability of the analysis while cutting down on analysis time the primary goal of this method should not only be the replacement of these solvents bur also the introduction of an extra benefit from their various features (Korany et al., 2017). Energy utilization is generally reduced by the use of instrumental methods, particularly when the process is highly automated and requires a little sample. An effective use of energy is made possible by the hyphenation of multiple techniques for sample treatment, component separation or combination of separation and complex detection methods. When a microwave treatment or even just microwave heating is used in the procedure more energy can be saved. Several sample procedures may also be significantly impacted by an ultrasonic irradiation. Another very green approach in analytical chemistry is the development of photochemical techniques (Chen et al., 2020).

The majority of the above mentioned method also provides safer chemicals and various chemical techniques for sample derivatization and chemical modification are still employed in many sample preparation and treatment scenarios. The creation of new techniques should include the search for less hazardous substances and waste-generation procedures. Electrically drive separation techniques are the most convenient for using the "green" concepts of analytical chemistry because they use less solvent and sample (Clarke et al., 2018).

2.2 History of Green Chemistry

The U.S. Environmental Protection Agency (EPA) introduced the term “green chemistry” to promote sustainable advancement in chemistry and chemical technology across government, academia and industry. Concurrently, the annual U.S. President Green Chemistry Challenge (PGCC) was launched in 1995. Following this, Europe established similar awards. Additionally, the International Union of pure and Applied Chemistry (IUPAC) formed a working party on green chemistry (Ali et al., 2020). The Green Chemistry Institute (GCI) which was established with branches across several nations to promote communication between academia, industry and government and research institute was established nearly a year this IUPAC initiative. In the meantime, academia conference on green chemistry, which was first held in Washington in 1997, has become an annual event. The first book and publications on green chemistry were published in the 1990s; two well-known journals in this field are green chemistry published by the Royal Society of Chemistry (RSC) and journal of Clean Processes and products published by Springer-Verlag. Nonetheless, a few other journals have also included section on green chemistry including Journal of Chemical Education and the Environmental Science and Technology (De Marco et al., 2019; Ali et al., 2020).

2.3 Principles of Green Chemistry

The pressing environmental challenges of the 21st century, including climate change, pollution, and resources depletion, demand innovative solutions that align economic growth with environmental sustainability. Green chemistry, also known as sustainable chemistry, represents a fundamental shift in how chemical process and products are designed, aiming to minimize or eliminate the use and generation of hazardous substances. Green chemistry is guided by twelve principles that provide a framework for designing safer chemicals processes (Table 2.1) (Khajuria et al., 2022; Ardila-Fierro & Hernández, 2021).

Table 2.1 The twelve (12) foundational principles of green chemistry

S.No	Principle	Description
1	Eliminate waste	It’s more beneficial to prevent waste than to process it after it occurs.
2	Design safer chemicals and products	Chemical products should be manufactured to perform their desire role with minimal toxicity.
3	Element efficiency	Synthesis should be optimizing to incorporate all materials used into the final products.
4	Develop safer chemical synthesis	When feasible, synthetic procedures should be designed to use and create materials with minimal or no toxicity to human or the environment.
5	Non-hazardous solvent and auxiliaries	Reduce the need for auxiliary substances such as separation agent or solvents and ensure their safety when they must be used.
6	Enhance energy efficiency	Analyze the environmental and economic effects of energy consumption in chemical processes and minimize them. Whenever possible carry out synthetic procedures at standard temperature and pressure.
7	Apply renewable feedstock	Use renewable raw materials or feedstock’s instead of non-renewable ones when technically and economically feasible.

S.No	Principle	Description
8	Minimize use of chemical derivatives	Reduce or eliminate derivatization (e.g., protection, non-permanent alteration and blocking group) when feasible to prevent the use of extra reagents and the generation of waste.
9	Reduced the risk of accidents	To reduce the risk of chemical accidents, examples, leaks, explosion and fire certain compound and their forms should be used in chemical operation.
10	Employ catalysts instead of Stoichiometry reagents	Whenever feasible, catalytic reagents are preformed over stoichiometric reagents.
11	Monitor in real time to avoid contamination	To prevent harmful substances from forming analytical methodologies must be developed further for real-time in process monitoring and control.
12	Synthesized chemical substances and products for degradation after use	Ensure that chemical products degrade into benign substances after their function and do not remain in the environment for extended periods.

2.4 Benefits of Green Chemistry

Green chemistry not only minimizes waste production but also offers effective solutions in the realms of economy and energy efficiency. It plays a crucial role in reducing the risk of accident by incorporating safety measures into the early stages of chemical reactions. Overall, this is a novel strategy to protect the environment and public health; it is actively utilized in many different contexts and will actively contribute to preventing environmental pollution in our nation (Sajid, & Płotka-Wasylka, 2022; Armenta et al., 2019). Green chemistry offers numerous advantages. The benefits to human health, the environment and the economy were listed in Table 2.2.

Table 2.2 The role of green chemistry in advancing health, environmental protection, and economic efficiency

Area	Benefits
Human Health	Enhanced environmental conditions, reduced discharge of toxic chemicals, leading to fewer respiratory health issues. Enhanced water quality, minimized discharge of toxic chemicals resulting in cleaner water for drinking and recreation. Safer food: elimination of persistent toxic chemicals that can contaminate the food chain, use of pesticides that target specific pests and degrade rapidly after application. Enhanced safety in products, new and safer products will become available for commerce, some items (pharmaceutical) will be produced with less waste and other products (cleaning solutions and pesticides) will serve as safer replacements for existing options. Increased safety for chemical industry employees, less use of dangerous materials, fewer protective outfits needed and reduced risk of incident such as explosion and fire.

Area	**Benefits**
Environment	The environment contains fewer poisonous chemicals, reducing exposure to plants and animals. Reduced reliance on landfills, particularly hazardous waste landfills. Reduced risk of climate change, smog development and ozone layer depletion. Chemical substances enter the environment through deliberate application (pesticides) unintended emissions or through disposal. Green chemicals aims to either convert to more environmentally friendly products or are recycled for further use
Economy and business	Enhanced efficiency of chemical reactions, consuming less feedstock to produce the same amount of product. Reduced waste generation, hazardous waste disposal, avoiding costly remediation, and end of pipe treatments More efficient processes, reducing energy and water usage, boosting plant capacity, and facilitating rapid manufacturing. Facilitate the replacement of commercial feedstock with waste Improved efficiency, requiring less product to perform the same task Improved marketability and sales with the display of a safer product label. Enhanced competition within the chemical industry and among their customers. Minimized reliance on petroleum products, decreasing consumptions and avoiding risk and cost variability

2.5 Sustainable Applications in Green Chemistry

Sustainable application in Green chemistry focuses on developing processes and products that minimize environmental impact. This involves using renewable resources, reducing energy consumption, and minimizing waste generation. Green chemistry aims to design efficient chemicals processes that prioritize safety and sustainability without compromising product quality or performance (Gawlik-Kobylińska et al., 2020; Cao & Su, 2021). By integrating principles such as atom economy and benign solvents, it seeks to promote eco-friendly alternatives across industries, fostering a more sustainable future (Figure 2.1).

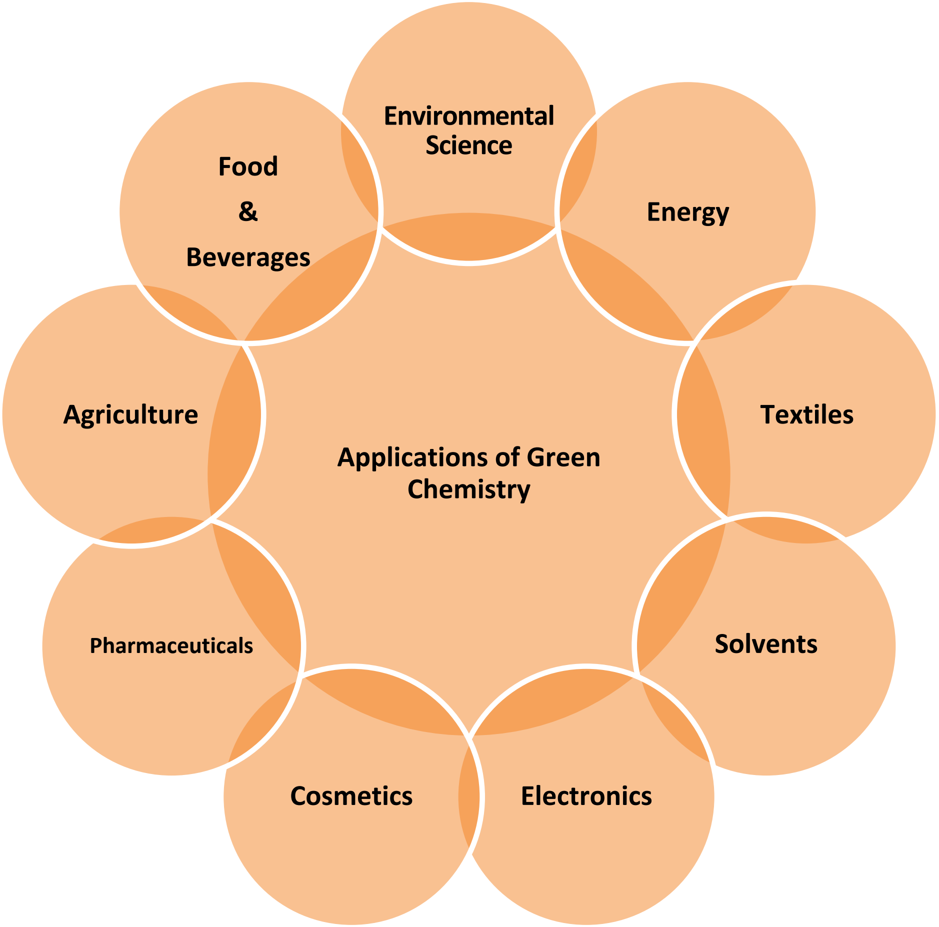

Figure 2.1 Innovative applications of green chemistry in various fields

2.5.1 Pharmaceuticals

Wasted or expired medication, as well as excess medication excreted by people and animals, end up in municipal sewage effluent treatment facilities. Several European nations' surface waters have been shown to contain pharmaceuticals since the 1980s, including clofibrate, antibiotics, cytostatic medications, and several analgesics and some products remain in the environment and end up finding their way back into drinking water. In addition to endangering human health, genotoxic chemicals can also impact environmental organism. It is reasonable to infer that bacterial populations are the area of aquatic ecosystem most impacted by the discharge of effluents containing antibiotic since drugs interfere principally with bacterial metabolism (Castiello et al., 2023). Also, infections that are challenging to treat arise from resistance to specific medications. Humans eat antibiotics and they are employed in fish farming, cattle production, and poultry production. Over the past 50 years, the usage of these medications has increased which has led to the genetic selection of more pathogenic bacteria. Animal excrement which contains unmetabolized pharmaceuticals, contaminate soil, and ground water when it is put to agriculture fields as manure or fertilizer. Depending on how mobile the excreta are it can also impact aquatic and terrestrial creatures by leaching from the fields (Pacheco-Fernández & Pino, 2019).

The disposal of solid waste in landfills by industrial effluent treatment facilities may result in the leaching of unmetabolized pharmaceuticals into groundwater (Polshettiwar & Varma, 2007). Seventy percent of the drugs supplied to fish in fish farms that are misused are discharged into the environment, primarily into the sediments surrounding the fish farms. The majority of drugs' modes of action in fish, animals, and humans are poorly understood. Additionally unknown are many potential adverse affects or side effects on nontarget receptor species as well as any potential synergistic effects from medication combination. Humans ingest the meat from poultry and animals, which include growth booster, antibiotic and other veterinary medications (Campos et al., 2019).

In aquatic creatures, estrogens both natural and synthetic cause harmful consequences such feminization and hermaphroditism. A drug's photostability, binding and adsorption capacity, rate of disintegration and water solubility all effects how long it will last in sediment or soil. On the other hand, highly mobile medications are carried by surface runoff, drainage water, and groundwater, and they frequently seep into groundwater. Pharmaceuticals with high absorption rates typically accumulate in soil or sediment (Zimmerman et al., 2020). In Germany, the sewage treatment plant effluent contained 80% of 32 drugs, with concentration levels of the order of 6 µg/L, that belong to the classes of lipid regulators, beta blockers, antiphlogistics, psychiatric drug, sympathomimetics, and antiepileptic drugs. Additionally, 0.165 mg/L of clofibric, a lipid regulating agent was found in drinking, ground, and river water (Piontek et al., 2018).

In the UK, both drinkable water and groundwater included medications such as diazepam, methaqualone, and antibiotics called penicilloyl. Pharmaceuticals, hormones, and other organic wastewater pollutants were discovered in surface water in a 2002 U.S. Geological Society countrywide investigation. River silt, river water, and drinking water in Italy were discovered to include many medications, animal growth boosters, and antibiotics at the nanogramme level, in addition to ceftriaxone and tilmicosin. There was not enough of the discovered concentrations to have any pharmacological impact, many orders of magnitude lower. However, it's unknown what consequences people would have if exposed to these pharmaceuticals all their lives (Lasso et al., 2021).

2.5.2 Green solvents

The discharge of hazardous compounds into the environment is a key problem in the context of sustainability. This is one area where green chemistry can make a big difference. For example, solvents are used extensively in government, commercial and academia. Industrial solvents are employed in a variety of chemical process operation processes, including reactants, separation, carrier, degreasing, reaction, crystallization, and cleaning. Different kinds of solvents that are often utilized including hazardous air pollutants, toxic, flammable, and volatile organic compound. They also provide significant risks to process safety, environmental, management, waste, human and other health, and safety factors (Pacheco-Fernández & Pino, 2019; Häckl & Kunz 2018). Green solvents often referred to as biosolvents, are solvents derived from the processing of crops that are less harmful to the environment. The majority of chemical operations use petrochemical solvents, which have detrimental effects on the environment. Green solvents were developed as an environmentally acceptable replacement for petrochemical solvents.

A green solvent that is produced by digesting maize is ethyl lactate, for instance, lactic acid's ester is called ethyl lactate. As well as, being 100% biodegradable easily recyclable, non-ozone depleting, noncarcinogenic, noncorrosive, and lactate ester solvents are widely utilized in the coating and paint industry. High boiling point, high solvency power, low surface tension, and low vapor pressure make ethyl lactate a particularly appealing solvent for the coating industry (Perna et al., 2020). It works very well as a paint stripper and graffiti remover and it is a desired coating for metal, wood and polystyrene surfaces. A far safer work environment has resulted from replacing solvents like xylene, acetone, and toluene with ethylene lactate. Among ethyl lactates other uses is as a superior cleaner for the polyurethane resins can be dissolved by ethyl lactate due to its strong solvency power. Solid fuels adhesives, oil, and grease, may all be effectively removed from a range of metal surfaces because to ethyl lactate's exceptional cleaning capabilities. Since chlorinated solvents are no longer needed ethyl lactate is a very important tool (Vanda et al., 2018).

2.5.3Environmental Science

The scientific community has gradually shifted its approach to addressing environmental protection regulations during the 1990s. This transformation within the chemical industries and research and development labs has given rise to green chemistry. In recent years, green chemistry has become a widely acknowledged and accepted alternative for achieving sustainable development. As its name suggests, green chemistry is a scientific approach that complies with environmental protection regulations in a safer way than the conventional cleaning chemical that was in use before to the 1900s (Cue et al., 2009).

In order to comply with pollution regulatory boards' guidelines while employing conventional trash treatment or recycling technologies, industries are frequently required to pay high costs. Legislative committees are also now more closely examining the potential negative impacts of a greater variety of chemicals due to the aggravating environmental issues. For this reason, end-of-pipe cleanup has given way to green chemistry and environmentally safer production processes. This is due to the combined effect of current environmental safety regulations, growing scientific understanding of previously unknown toxic chemicals and their long-term effects on the biota, and industry financial interests. Because green chemistry may help bridge the gap between ecoefficiency and economic growth, it is becoming increasingly important (Campos et al., 2019). Process efficiency has undergone a paradigm change as a result of the increased environmental concern. These days, the emphasis is on the atom economy factor and the environment coefficient factors rather than the conventional chemical yields. When defining waste as everything that is created aside from the intended product the atom economy factor may be defined as the amount of waste generated per kilograms of product (Anastas & Eghbali, 2010).

One easy way to create two different roots for a given product is to use the atom economy calculation. To calculate it, divide the molecular weight of the desired product by the total molecular weight of all chemicals generated in the processes included in the stoichiometric equation. It can alternatively be defined by some writers as the total number of reactant atoms that are transformed into desired product atoms throughout a reaction. Stoichiometric reagent processes are less atom-efficient than catalytic processes. For example, conventional oxidations utilizing oxidants such permanganate or chromium reagent increase atom-economies when substituted with cleaner catalyzed oxidation (Wilson & Schwarzman, 2009).

In 2000, the United States alone emitted around 7.1 billion pounds of over 650 hazardous substances into the environment. The roughly 75,000 chemicals that are used commercially in the US are not even close to being represented by this inventory. Even though certain chemicals have been in use for several decades, their effects on human health and the environment are still mostly unknown (Campos et al., 2019). The U.S. industry spends about $10 billion per year on environmental R&D. A prefect process has a single step is easy to understand, atom efficiency, safe, creates no waste, employ renewable resources is acceptable to the environment has a total yield and only takes a few easy steps for separation. A perfect product would use the least amount of energy and safe, recyclable, packaging, and entirely biodegradable. In general, the public pays very little attention to the ideal user and instead concentrate on the procedure and final result. The perfect consumer is one who considers the environment, reuses; consumers little, recycle, and are aware of the environment impact of the products they purchase. The ideal user also supports “green” activities (Chanshetti, 2014).

2.5.4 Agriculture

Green chemistry in agriculture focuses on applying sustainable and environmentally friendly practices to agriculture processes and products. It aims to reduce the use of harmful chemicals, minimize waste, conserve resources, and enhance the overall sustainability of farming. By integrating green chemistry principles, agriculture can become more efficient and less harmful to the environment and human health (Perlatti et al., 2014; Withers et al., 2015). Traditional agriculture relies heavily on synthetic pesticides and fertilizers, which can lead to soil degradation, water contamination, and harm to non target species including humans. Green chemistry promotes the development and use of bio-based and biodegradable pesticides and fertilizers. These alternatives are designed to be effective against pests and provide nutrient to crop while minimizing environmental impact. Bio-pesticides are derived from natural material such as bacteria, plants, and certain minerals. For example neem oil extracted from the neem tree is a natural pesticide that is effective against a wide range of pests.Bio-fertilizers include microorganism like nitrogen fixing bacteria and mycorrhizal fungi, which enhances soil fertility and plant growth by making nutrient more available to plant (Bryan et al., 2018).

Green chemistry plays a crucial role integrated pest management (IPM) by providing safer chemicals alternatives and promoting practices that reduce the need for chemicals interventions. For examples, pheromone traps use synthetic pheromones to lure and trap pests, reducing the need for broad-spectrum pesticides. Botanical insecticides made from plant extracts can target specific pests with minimal impact on beneficial insects and the environment. Green chemistry promotes practices that maintain and enhance soil fertility while minimizing erosion and degradation. This includes the use of organic amendments such as compost and biochar which improve soil structure ware retention and nutrient availability. Cover cropping is another practice supported by green chemistry. Cover crops such as legumes and grasses are grown off seasons to protect the soil from erosion, suppress weeds, and enhance soil organic matter. These crops can also fix nitrogen in the soil reducing the need for synthetic nitrogen fertilizers (Morin-Crini et al., 2019).

Agriculture activities can significantly impact water resources through runoff and leaching of chemicals. The green chemistry reduces these impacts by promoting efficient water use and minimizing the contamination of water bodies. Drip irrigation system deliver water directly to the plant roots, reducing water use and minimizing runoff. Slow release fertilizers and controlled release pesticides are designed to release their ingredients gradually reducing the risk of leaching into water sources. Green chemistry in agriculture also emphasizes the use of renewable energy sources and resources efficient practices. For examples, biofuels derived from agriculture residues and dedicated energy crops can provide a sustainable alternative to fossils fuels. Solar powered irrigation system and wind turbines can help farmers reduce their reliance on non-renewable energy sources (Shirmohammadli et al., 2018; Campos et al., 2019).

Genetically modified organisms (GMOs) have the potential to contribute to sustainable agriculture by enhancing crop yields, improving resistance to pests and disease and reducing the need for chemicals input. For instance, Bacillus thuringiensis (Bt) crops which are genetically modified to produce a bacterial protein toxic to certain insects, can reduce the need for chemical insecticides. However, the use of GMOs must be carefully managed to avoid issued such as the development of pest resistance and the impact on non-target species. Green chemistry promotes the use of plant growth regulators and natural plant hormones to enhance crop growth and resilience. These substances can improve crop yields and quality without the negative impacts associated with synthetic chemicals. For example, biostimulants which include seaweed extract, humic substances and beneficial microorganism can enhance plant growth and stress tolerance. They work by stimulating natural processes in plant improving nutrient uptake and enhancing resistance to abiotic stresses such as drought and salinity (Kummerer, 2007; Ahmed et al., 2017).

2.5.5 Food and Beverages

Food safety has become an increasingly pressing issue for society in recent year due to improvements in people's quality of life and increased consumer and organizational concern. In food supply chain, the unprocessed ingredients, storage procedures preparation, processing, and packing might contaminate food items (Pallone et al., 2018). Thus, it would appear that research on food contamination detection technologies is very crucial. Before detection pretreatments for analyte extraction and preconcentration are crucial because of the complexity of food samples and the low concentration of food pollutant.

In this sense, the extraction of analytes at trace levels is demonstrate to be highly effective by microextraction method as liquid-liquid microextraction, and solid phase microextraction. However, employing hazardous organic solvents for extraction typically halogenated hydrocarbons does not align with the principle of green chemistry. Because HDESs have good hydrophobicity and dissolving capability they have been explored as great possible alternatives to the standard solvents in microextraction (Płotka□Wasylka et al., 2018). In fact, it is rather unexpected that the adaptability of HDESs makes up for some of the extraction process's drawbacks when substituting the organic solvents with HDESs, aside from boosting the advantages of quick operation, high selectivity, high sensitivity and low cost. One of the most often used microextraction methods in conjunction with HDESs is dispersive liquid-liquid microextraction (DLLME). This method increases the mass transfer and extraction efficiency by using the distributed droplets that the extraction solvents in the water samples create.

Nevertheless, several constraints persists including the requirement for an additional solvent for the dispersion the challenge of finding the trace extraction solvent and the energy expenditure associated with phase separation (Valduga et al., 2019). To guarantee that food meets quality standards for color, flavor, and shelf life, food additives are essential. The primary concern with food safety meanwhile is that certain illicit businesses misuse food additives for their financial gain. Overconsumption and improper application of food additives may be extremely dangerous for human health. Every single country establishes the recommended daily intake value of each addition fro safer purposes. Thus, there is an urgent demand for precise and trustworthy analytical methodologies (Cannavacciuolo et al., 2022).

Food packaging may increase shelf life and keep food from being contaminated. The main risk associated with food packaging is the leaking of toxic substances from the materials used for packaging, which also contributes to contamination of food products. When consumed with food, harmful pollutants can have a negative impact on health (Płotka□Wasylka et al., 2018). This raises the bar for the identification of these dangerous elements. Because of their light weight, low cost, and superior process ability, plastics are the most often used materials for packaging, which helps lower the expenses associated with food processing and shipping. Plastic materials are thought to make up around 50% of food packaging. Plastics have had many additives added to them to improve their functionality and toughness. Plasticizer, UV absorbent, antioxidant, and bisphenol compounds are only a few of the hazardous raw chemicals and additives found in plastic packaging that have been extracted and detected using HDESs.Some additives are completely prohibited as food additives due to their toxic nature. However, international use of these banned additives continues to pose a serious food safety concern (Efenberger-Szmechtyk et al., 2018; Farrán et al., 2015).

2.5.6 Cosmetics

A cosmetic item can be termed “green” whenever it contains plant-based active components, such minerals and plants, rather than chemically synthesized equivalents. It is preferable if it is manufactured using environmentally friendly, plant-friendly processing techniques in accordance with organic crops. To minimize the environmental effect, it is recommended to grow these cosmetics at zero km or on land close to the manufacturing laboratories, or to use sustainable modes of transportation. Different green goods have different qualities. It is essential to distinguish between organic, natural, and natural origin substances (Secchi et al., 2016; Mohamed, 2015). Chemical substances classified as natural components have not been refined or handled using mechanical, gravitational, or human techniques, nor have they been refined using naturally occurring solvents. They can also be removed from the air using any technique, dissolved in water, or heated to remove water. Naturally derived ingredients are those that come from plants, minerals, or animals and have undergone chemical processing or mixing with other ingredients; they do not include petroleum-or fossil fuel-derived ingredients or ingredients that have been bio-manufactured through the use of processes like fermentation, condensation, esterification, or saponification to increase their performance or make them more sustainable (Dini & Laneri, 2021).

In 2020, the skincare and cosmetics sector needed to quickly change to satisfy the changing needs of a fickle and discriminating consumer base. Finding a balance between the natural and chemical components of cosmetics was the main problem. Notwithstanding the market's volatility, several patterns and associated industries exhibit encouraging signs of revival (Wan et al., 2022; Morin-Crini et al., 2019). In the realm of green cosmetics new trend have emerged recently such as nutricosmetics a nutritional supplement applied to the hair, nails, and skin to achieve beauty from inside. Three scientific fields of study pharmaceuticals, food, and personal care have produced nutricosmetics, sometimes known as beauty supplements. These can be firm or soft gel, pills, capsules, syrup, candies, or sachets that enhance personal care and include a concentrated form of vitamins, hyaluronic acid, minerals, or plant extracts. However, there is no dedicated regulatory framework for nutricosmetics at either the EU or USA levels (Saxena et al., 2017).

Beauty supplements are governed by the same regulations as dietary supplements; however, this work includes revisions to the nutrition matrix of cosmetics significance, bioactive molecules that may be used in cosmetics formulations, environmentally friendly technology for producing bioactive cosmetics ingredients and analytical techniques beneficial for dosing and purifying the active ingredients in vegetable and animal matrices. We aim to shed light on the nutricosmetic market waiting for a specific regulation for green cosmetics to help consumers make informed choices (Qidwai et al., 2018).

The manufacture and promotion of cosmetics and personal hygiene items is referred to as the "global beauty market." The average annual growth rate of this industry over the past 20 years has been 4.5%, indicating a tendency towards rising demand, particularly in the developing economies of Asia and Latin America. The scenario is also marked by the continuous appearance of new items, which is a result of the expansion of increasingly stringent criteria of beauty (Kuang et al., 2016). Nonetheless, public concern over the use of dangerous chemicals in cosmetics and the rise of ethical issues surrounding the cosmetics sector helped to propel the market for organic cosmetics. Naturally occurring cosmetics and organic products are typically linked to the "green" label, which is applied to goods that are environmentally friendly and manufactured according to certain guidelines. Common claims made in the context of green cosmetics are those that guarantee the goods are created in compliance with the Green Chemistry principles. It is described as the use of a set of guidelines that lessens or eliminates the use of hazardous compounds in the creation, production, and use of chemicals in order to limit the danger to the environment and public health (Barbulova et al., 2015; Dubey et al., 2022).

2.5.7 Energy

An energy source is considered renewable if it is replenished by natural processes at a rate equal to or faster than its consumption. A subcategory of sustainable energy is energy except for geothermal and tidal power, the majority of renewable energy sources eventually come from solar radiation. Utilizing the energy of the sun, photosynthesis processes plants to generate biomass, which is used as energy (Ratti, 2020). The Wind is the source of wind energy and also produced by the uneven heating caused by the sun of the atmosphere. Rain is a prerequisite for hydropower, yet rain is reliant on sunlight’s ability to evaporate water. Solar energy is the source of even fossils fuels, as they were originally formed from plant matter. Energy resources can be used straight away or converted into more practical kinds of energy. Windmills, water, and geothermal energy are a few examples of direct usage as are sun ovens. Biomass encompasses any type of plant or animal tissue including straw, dung, wood, and other natural resources that have the capacity to store energy. The energy contained in biomass can be extracted either by directly burning the material or by using microorganism to convert it into biogas (Weaver et al., 2017).

It has been projected that by 2040, the expected 10 billion people on Earth will require annual global energy consumption of 935 EJ, or 3000 W energy/per person. The technological potential of the world's winds is estimated to be five times that of the present energy consumption, or forty times that of the current electricity demand. At an elevation of 80 meters, this takes up 12.7% of the total land area. Natural gas supplies are expected to remain stable for the next fifty years, after which they are likely to be depleted. Nuclear energy which has only met 2% of our energy needs so far, is projected to be completely phased out by 2050 (Ostergaard et al., 2020; Gielen et al., 2019).

Developing and improving technologies for renewable energy sources, such as bioenergy, wind and solar, can reduce reliance on fossils fuels and decrease carbon emission. Green power is the term used to describe energy generated from renewable resources, which have a lower environmental impact than fossil fuels. Thus, green power includes electricity from small hydropower facilities, geothermal, solar, biomass, and wind farms. An endless supply of energy that refills swiftly is renewable energy (Güney, 2019). Energy doesn't pollute the environment or discharge harmful elements into the atmosphere, yet hydroelectric dams inflict harm to the surrounding vegetation and land area. Certain renewable energy methods have negative environmental effects. While hydroelectric dams may erect obstacles in the way of fish migration—a major issue in the Pacific Northwest where salmon numbers have been decimated wind turbines also pose a risk to soaring birds. Large tracts of land are needed for biomass and biofuel production. Distributing the collection across a wide region is necessary to transform the comparatively low-intensity energy that renewable energy sources supply into usable energy (Kuang et al., 2016). Figure 2.2 shows the different sources of energy used in different field such as, renewable energy (Biodiesel, hydropower, ocean waves, geothermal, solar/wind, and biomass while nonrenewable energy (crude oil, natural gas, coal, and nuclear).

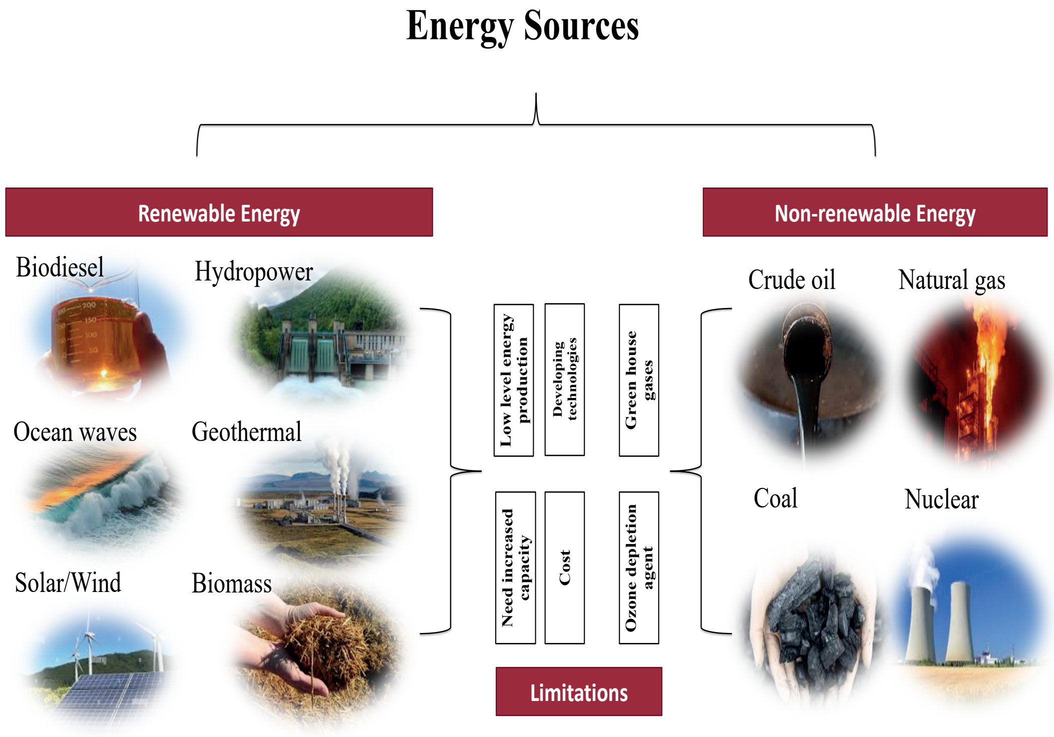

Figure 2.2 Types and categories of energy sources

2.5.8 Textiles Industry

The production of textiles uses a significant amount of water. The main contaminants found in textile effluent include recalcitrant organics, soaps, salts, color, toxicants, detergents, surfactant, inhibitory and chlorinated compounds. The hardest component of textile waste water to treat is dye, which can change on a daily or even hourly based on the campaign (Nimkar, 2018). Due to the low COD/BOD ratio (less than 0.3) it is often challenging to treat textile industry wastewater using traditional biological methods. Two of the harshest processes that lead to the production of hazardous wastewater are desizing and scouring (Sun et al., 2021).

A combination of biochemical and chemical/physical processes appears to be promising in degrading such an effluent. The main issue is the presence of dyes in the wastewater since they are poisonous and recalcitrant. The dyes can be successfully degraded by both anaerobic and aerobic processes, but the best appears to be a combination of both. Treatment with living cells does not seem to be as effective as dye adsorption by dead cell (Barbulova et al., 2015).

In order to preserve energy, water, chemicals, and time while maintaining the performance features of the original alkaline scour systems, Novozymes developed an enzymatic technique (BioPreparation) for treating cotton textiles. According to field tests, substituting caustic scours or merging distinct scouring and dyeing processes into one might save water expenses for textile mills by 30–50% (Saxena et al., 2017). From scouring to finishing, 162 knitting mills typically utilise 89 million m3 of water annually. 27–45 million m3 of water would be saved annually with the new method. Comparing this technique to the traditional sodium hydroxide method also results in a 25% and 40% reduction in the biological and chemical oxygen requirements. Cost reductions of at least 30% would result from the switch. There are several benefits of using biomass instead of nonrenewable petroleum resources to make chemicals, such as reduced or zero net CO2 emissions (Sahu & Singh, 2019; Felgueiras et al., 2021).

Global production of dyes and pigments amounts to around 10,000 distinct types, with a yearly market volume exceeding 7 × 105 tonnes. A range of structural variations exist for dyes, including anthraquinone-based, azo, reactive, dispersion diazo, acidic, basic, and metal-complex dyes. In the visible spectrum, all absorb light. Just 2% of the colors generated are released into the wastewater directly (Lei et al., 2017). Furthermore, 10% is wasted while colouring textiles. Numerous dyes have been proven via studies to be extremely hazardous to the environment, mutagenic, and carcinogenic. Due of the intense color of untreated dye effluent, less sunlight can reach it, which inhibits photosynthesis. They negatively impact flora and wildlife, are harmful to fish and other mammals, and stop the growth of microorganisms. They can induce bowel cancer and problems in the brain development of fetuses since they are carcinogenic. The color of the textile dye effluent can be removed using a variety of chemical and physical techniques. One unresolved issue meanwhile, related to how to dispose of the precipitate or sludge. Adsorbent addition offers a number of benefits such as reduced toxic effects on microorganism due to the adsorption of harmful chemical and improved sludge-settling properties (Saxena et al., 2017; Uddin, 2021).

2.5.9 Electronics

The enormous global scientific and engineering work that has supported the growth of the modern solid-state electronic industry started with the development of the integrated circuit in 1959, which is largely attributed to the work of Jack Kilby (Texas Instruments Inc., Texas, USA) and Robert Noyce (Fairchild Semiconductor International, Inc., California, USA). Electronic technology has advanced at a rate that is exponential since Moore's Law was accepted as the basis for advancement (Zhu et al., 2016). In response, electronics technology has been used worldwide in an ever-growing variety of complicated consumer, medical, space, industrial, and military applications due to the frequent availability of computer chips that are either more powerful or less expensive. Modern electronics provide enormous social and economic benefits; nearly every endeavor undertaken by humans is impacted by solid state electronics to some extent.

The worldwide consumer electronics industry is predicted to reach over 1793 billion USD in 2024, having been valued at roughly 1180 billion USD in 2018 (Hsu et al., 2019). Electronics trash (e-waste) is produced in large quantities when the sheer number of electronics devices and related semiconductor devices, including silicon solar cells, is coupled with the quick turnover of older technology that is replaced in a short amount of time. Consider the 20-50 million tones of consumer electronics that are reportedly thrown out annually around the world's current municipal solid garbage is represented by this (Kang et al., 2015). The increasing number of semiconductor based gadgets including rooftop photovoltaic cells, being distributed globally are contributing to the growing amount of e-waste from consumer electronics. It is predicted that by 2020 there will be 35000 tonnes of solar waste rising to 60 million tonnes by 2050, despite the fact that these devices have a far longer lifespan than consumer electronics (Marr & Marr, 2016). In the absence of measures to gather, recycle, and reduce our dependency on conventional solid-state electronic devices, the quantity of e-waste will have a significant and negative impact on the environment. Furthermore, burning plastic releases volatile substances that are classified as category 1 carcinogen, such as dioxin derivatives, polychlorinated biphenyls, and polychlorinated dibenzofuran. When e-waste is disposed of in landfills, large amounts of dangerous elements including arsenic, mercury, chromium, and lead can leach into soils and streams from semiconductor equipment (Hakola et al., 2020).

Green electronics which replaces some semiconductor electronics related functions and device structure with more ecologically friendly alternatives is becoming more popular as a means of reducing the amount of e-waste produced and its associated environmental impact. European Standards EN13432 states that under specific defined conditions of humidity, temperature, and oxygen concentration at least 90% of all materials used in green electronics must be transformed by fungi or microorganism into harmless components such as biomass, water, and carbon dioxide within 6 months of abandonment (Kang et al., 2015; Lei et al., 2017). The use of degradable materials offers additional, although specialized, benefits for a variety of applications beyond the elimination (or at least reduction) of harmful elements in the processing procedures and end products of green electronic technologies. In the context of green electronics the use of biodegradable or biocompatible materials may also be helpful in the creation of medical implants by reducing the need for surgical device removal after diagnosis, therapy, or monitoring thereby improving patient outcomes. Additionally, there is growing interest in biocompatible and biodegradable electronics materials due to the development of wearable electronics especially on flexible substrate (Liang et al., 2019; El-Seedi et al., 2019).

2.6 Future Perspectives

- A global awareness of environmental issues grows the importance of green chemistry continuous to increase. Green chemistry aims to design chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Despite significant advancement the field faces ongoing challenges and opportunities for growth.

- Interdisciplinary collaboration and cooperation are needed to realize the full potential of green chemistry and engineering. Implementing real time monitoring and control systems can enhance the efficiency and safety of chemical processes. Future perspectives include integrating advanced analytical techniques and digital technologies (process analytical technology and AI) into green chemistry.

- Catalysts play a crucial role in making chemical process more efficient and sustainable. Innovation in biocatalysis, nanocatalysis and photocatalysis could lead to significant reduction in energy consumption and waste generation.

- Transition from fossils-based feedstock to renewable ones is essential for sustainable chemistry. The developing efficient method to convert biomass, CO2 and other renewable resources into valuable chemical and materials.

- The creation of safer compounds will go more quickly if high-throughput screening and predictive toxicity models are developed further. Solvents are often a significant source of waste and environmental impact in chemical processes.

- Public education campaigns will encourage informed consumer behaviour and assist reduce green washing. Data on chemical safety should be accessible to the public through reform of chemical policies. Improving chemical production and product development requires supply chain transparency.

2.7 Challenges in Green Chemistry

- One of the significant barriers to the adsorption of green chemistry is economic viability. Developing and scaling up green processes and materials can be costly, and industries may be reluctant to invest without clear financial benefits.

- Developing green processes that are scalable and economically viable for industrial applications is a significant challenge. Ensuring that green products and materials meet or exceed the performance of traditional counterparts is essential for adoption.

- Renewable feedstock can be more expensive and less consistent in quality compared to fossils based resources. Significant investment in research and development is required to develop new green technologies and processes which may not yield immediate returns.

- Effective regulatory and policy frameworks are essential to promote green chemistry. However, inconsistent regulations and lack of incentives can hinder progress. Complex and varying regulations across regions can pose challenges for the development and commercialization of green chemicals and processes. Insufficient incentives for adopting green chemistry practices such as tax breaks or subsidies can deter industries from making the transition.

- Raising awareness and educating stakeholders about the benefits and practices of green chemistry is crucial for its adoption. There is a need for comprehensive education and training programs in green chemistry for students, researchers and industry professionals. Moreover, increasing public awareness about the environmental and health benefits if green chemistry can drive demand for sustainable products and processes.

Conclusion

The global public perception views the chemical industry as highly polluting with concern about the safety, health, and environmental impacts of chemical products and manufacturing. Despite a significant reduction in emissions since the mid-1980s, this perception persists influenced by increased data accessibility through NGOs and awareness of the incomplete understanding of the long-term effects of many industrial chemicals. Innovation such as finding new use for CO2, biomass and advancements in biotechnology are seen as solutions to these problems, safer processes, offering waste reduction, lower energy and raw material usage.The adoption of life cycle analysis by all industries is essential, alongside the promotion of responsible consumers who reduce recycle and reuse products.This approach contrasts with the prevalent use and throw culture in the US and Europe, which needs reconsideration for sustainable development. Products should be evaluated for sustainability based on their net energy release.Furthermore, Green chemistry characterized by continual improvement, innovation, and interdisciplinary research require significant financial and collaborative support from government, industries and NGOs.Achieving environmentally benign chemical processes and product is crucial for preserving the world for future generation. Without government intervention green chemistry and greenhouse gas emission reduction will remain theoretical rather than practical.

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MATERIALS CHEMISTRY: PROPERTIES AND APPLICATIONS

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1. Introduction To Material Chemistry

Life in the 21st century relies heavily on various advanced materials. We often take for granted the micro- and nanoscale components that make up everyday items like microwaves, laptops, cell phones, tablets, and modern transportation. Yet, we seldom appreciate the materials behind these technological advances (Heilbron, 2003; Wright & Sommerdijk, 2018). Materials can be broadly defined as any solid-state substance or device used to meet societal needs, from basic building materials like glass, wood, and aluminum to nanoscale components that may not yet be widely utilized. A general classification of various types of materials is illustrated in Fig. 1.1. Classification of materials can be ambiguous; for instance, thin films under 1 µm may be classified as 2-D nanomaterials if thinner than 100 nm. Liquid crystals have properties between amorphous and crystalline phases, and composites often include both inorganic and organic elements (Brush, 1988; Shirota, 2000). Materials chemistry broadly focuses on the relationships between the atomic, ionic, or molecular structures of materials and their physical and chemical properties. This encompasses fields like polymer chemistry, solid-state chemistry, and surface chemistry. The discipline involves analyzing the structure and properties of current materials, creating and characterizing new materials, and employing advanced computational methods to understand both existing and yet-to-be-fabricated materials (Fahlman, 2023). The field has evolved significantly over the past few decades, driven by advances in technology and a deeper understanding of molecular and atomic interactions. Materials chemists utilize principles from chemistry, physics, and engineering to create materials that meet specific functional requirements, leading to innovations in various industries such as electronics, healthcare, energy, and environmental science (Cahn, 2001)(Ozin et al., 2009). The significance of materials chemistry is multifaceted, encompassing its impact on scientific progress, technological advancements, and societal development. One of the core contributions of materials chemistry is its ability to convert raw materials into advanced functional materials with tailored properties. This transformation is critical for the development of high-performance products that enhance efficiency, durability, and functionality across various applications.

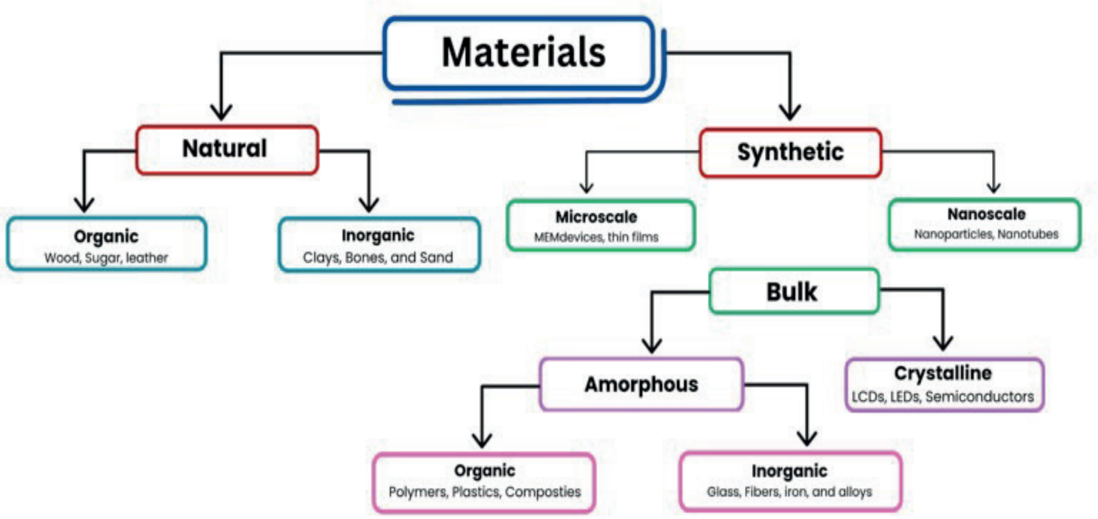


Figure 1. General classification of various types of materials

Materials chemistry is central to the development of new energy solutions. For instance, the quest for sustainable energy sources has led to the creation of high-efficiency photovoltaic cells, which convert sunlight into electricity. These solar cells are often based on novel materials such as perovskites, which have shown remarkable efficiency improvements in recent years (Grätzel, 2001). Additionally, materials chemistry plays a crucial role in the development of energy storage systems, such as batteries and supercapacitors, which are essential for the integration of renewable energy sources into the power grid (Bruce et al., 2008). In the healthcare sector, materials chemistry has led to significant advancements in medical diagnostics and therapeutics. The development of biocompatible materials has revolutionized the design of medical implants and prosthetics, advancing patient wellness and quality of life. Furthermore, materials chemists have developed advanced drug delivery systems that can target specific sites within the body, enhancing the effectiveness of treatment while minimizing side negative consequence (Langer & Peppas, 2003). Environmental protection is another area where materials chemistry has a profound impact. The creation of materials that can remove pollutants from air and water, such as advanced filtration membranes and catalytic converters, is crucial for mitigating environmental contamination. Materials chemistry also contributes to the development of sustainable materials and processes that reduce the environmental footprint of industrial activities (Anastas & Warner, 2000).

Moreover, materials chemistry is integral to the advancement of electronics and information technology. The miniaturization of electronic components and the development of new materials for semiconductors, such as graphene and other two-dimensional materials, have enabled the continued progression of Moore's Law and the creation of faster, more efficient electronic devices (Novoselov et al., 2004). The interdisciplinary nature of materials chemistry fosters collaboration among chemists, physicists, engineers, and biologists, leading to a holistic approach to solving complex scientific and technological challenges. This collaborative effort is essential for the continuous development of innovative materials and technologies that drive economic growth and improve the quality of life globally. This chapter delves into the essential aspects of materials chemistry, encompassing synthesis and fabrication techniques, characterization methods, and the diverse properties of materials. It underscores the importance of understanding the relationships between structure and properties and explores practical applications across various industries. The objective is to provide a comprehensive view of materials chemistry, highlighting both foundational principles and the latest advancements in the field.

The chapter begins with an introduction to materials chemistry, including its significance and scope. It then explores synthesis and fabrication techniques, discussing common methods such as chemical vapor deposition, sol-gel processing, and hydrothermal synthesis, as well as fabrication techniques for different types of materials like thin films, nanoparticles, and composites. This is followed by a section on characterization techniques, covering various methods such as spectroscopy, microscopy, diffraction, and thermal analysis, and their applications in probing material properties at different length scales. The chapter also examines the mechanical, electrical, magnetic, thermal, optical, and chemical properties of materials. An exploration of structure-property relationships follows, illustrating how material structure influences properties, with examples from different classes of materials and discussions on defects, microstructure, and phase transitions. Finally, the chapter highlights practical applications of materials chemistry in industries such as electronics, healthcare, energy, environment, and structural materials.

The primary objectives of this chapter are to provide a foundational understanding of materials chemistry, introduce key synthesis and fabrication techniques, explain various characterization methods and their applications, examine the diverse properties of materials, explore the relationship between material structure and properties, and highlight practical applications of materials chemistry in different industries. Additionally, it aims to inspire further research and innovation in the field. This chapter is intended for a diverse audience, including students at the undergraduate and graduate levels in chemistry, materials science, and related fields, researchers engaged in materials research and development, industry practitioners such as engineers and technologists working in sectors that utilize advanced materials, educators seeking comprehensive resources for teaching materials chemistry, and general readers with an interest in the advancements and applications of materials science.

Materials chemistry is a dynamic and essential field that continues to drive innovation and address critical global challenges. This chapter aims to provide readers with a thorough understanding of the principles, methods, and applications of materials chemistry, equipping them with the knowledge to appreciate its significance and potential. Through detailed discussions and illustrative examples, readers will gain insights into how materials chemistry shapes our world and what future developments might hold.

2. Synthesis and Fabrication Techniques

This chapter dives into the fundamental methods for creating and shaping materials at the heart of material chemistry. We will explore various synthesis techniques, delve into fabrication methods for different material types, and discuss crucial considerations for controlling the final properties of your material.

2.1 Overview of Common Synthesis Methods

2.1.1 Chemical Vapor Deposition (CVD): Precursor chemicals are converted into a solid phase onto a substrate through reactions or decomposition. In chemical vapor deposition (CVD), vapor-phase compounds, typically mixed with an inert carrier gas, undergo a reaction at a heated surface, resulting in the formation of a solid film (POWELL et al., 1966)(Wahl et al., 2014). The significance of CVD lies in its versatility to deposit a wide range of elements and compounds at relatively low temperatures and atmospheric pressure. It allows for the formation of amorphous, polycrystalline, epitaxial, and uniaxially oriented polycrystalline films with high purity. Key aspects of CVD include the chemical reactions, the thermodynamics and kinetics of the reactors, and the transport of material and energy to and from the reaction site. Below is a list of examples of common types of chemical reactions used in CVD (Frey & Khan, 2015).

- **Pyrolysis:** The simplest CVD process, pyrolysis, involves the decomposition of a gaseous compound on a hot surface, resulting in the deposition of a stable residue.

Examples include: Deposition of pyrolytic graphite from methane (CH_4) at a substrate temperature of 2200°C, Deposition of silicon from monosilane (SiH_4) within the temperature range of 800–1350°C, and Deposition of nickel from nickel carbonyl [$Ni(CO)_4$] at approximately 100°C (Tavares et al., 2008).

- **Reduction:** Hydrogen is the most commonly used reducing agent in CVD processes. Examples include deposition of silicon through the hydrogen reduction of silicon tetrachloride ($SiCl_4$) at approximately 1000°C, and deposition of tungsten via the hydrogen reduction of tungsten hexafluoride (WF_6) at around 800°C. Additionally, hydrogen reduction is employed to enhance the pyrolytic process by removing unwanted byproducts as gaseous hydrogen compounds, requiring less energy for their removal.
- **Oxidation:** Silicon dioxide films can be formed through the oxidation of silane (SiH_4) in the presence of oxygen (O_2).
- **Nitridation:** Silicon nitride films can be deposited by reacting silane (SiH_4) with ammonia (NH_3) in a chemical vapor deposition process.
- **Carbidization:** Titanium carbide deposition occur via titanium tetrachloride ($TiCl_4$) and methane (CH_4) reaction at a substrate temperature of 1850°C.
- **Chemical-transport reaction:** In these processes, the targeted material is conveyed from the source to the substrate, where it forms a film, is governed by a difference exists in the equilibrium constants of the reactant source and the carrier phase, and between the substrate and the carrier phase, when each is maintained under varying thermal condition.
- **Spray pyrolysis:** This technique involves dissolving the reagents in a carrier liquid, which is then sprayed on a heated substrate as fine droplets. Upon contact with the hot surface, the solvent dissipates, and the leftover constituents interact to form the intended material. For example, cadmium sulfide films can be produced by spray pyrolysis of a solution containing thiourea and cadmium chloride in water, substrate temperature optimized at 300°C (Chamberlin & Skarman, 1966).

2.1.2 Sol-Gel Processing: Liquid precursors form a colloidal suspension (sol) that transforms into a gel network and then a solid material. The sol-gel method is effective for modifying substrate surfaces, offering the key advantage of achieving high surface area and stability. The properties of sol-gel materials depend on the experimental conditions. The process consists of two main reactions: (1) hydrolysis of the precursor in acidic or basic conditions, and (2) polycondensation of the hydrolyzed products (Pena-Pereira et al., 2012). The key factors contributing to the widespread use of this method are its relative simplicity compared to other coating processes and its ability to significantly improve metallic biomaterial coating layers on the substrate (J. X. Zhang et al., 2011). To prepare the solution (sol), calcium and phosphorus precursors (CaP) are typically combined with distilled water and pure ethanol, which act as solvents (Costa et al., 2012). Ethanol is primarily employed to dissolve phosphorus precursors, such as phosphorus pentoxide or triethyl phosphite. Subsequently, a small amount of water is added to facilitate the hydrolysis of the sol (Kessler et al., 2006). Similarly, to dissolve the calcium precursor, typically calcium nitrate, ethanol is used. The resulting solution is then added drop by drop to the hydrolyzed phosphorus solution (Singh, 2012). Finally, the solution is refluxed at various temperatures to evaporate the solvents. This process is repeated until the solution reaches the desired viscosity, becoming a sol-gel. The chemical composition of the precursors significantly affects the temperature needed for apatite formation and the related chemical activities (Amerinatanzi et al., 2017). Due to its simplicity, the sol-gel process is inexpensive and highly adaptable to various coating compositions and sample geometries. Additionally, it provides a strong adhesive coating layer, ensuring a robust substrate-coating bond (Qu & Wei, 2008). The dip coating process consists of three steps: dipping, withdrawing, and drying. Samples are immersed in the prepared solution and then withdrawn at a constant speed to achieve a uniform thickness across the substrate's surface.

The sol-gel method is easy, cheap, and provides excellent coatings, leading to its growing applications. Enhancing adhesion and preventing delamination are crucial but under-studied. Research on new precursors and their effects on corrosion resistance and adhesion is needed. Key parameters like pH, solvents, aging, temperature, molar ratios, hydrolysis kinetics, curing, and crack formation during drying and heat treatment should be studied to better control coating properties (D. Wang & Bierwagen, 2009). Current sol-gel methods face limitations due to lengthy preparation, aging, and curing times, and the risk of phase separation during heat treatment, particularly in hybrid coatings. Optimizing both new and existing sol-gel processes is necessary. Sol-gel coatings can be applied via dip coating, spraying, and spinning. A new method, electrochemical deposition, controls pH, colloid concentration, and deposition voltage and time, providing reliable coatings for complex geometries with controllable compositions (Toki et al., 1988). Most sol-gel materials like TEOS (Tetraethyl Orthosilicate) and TMOS (Tetramethyl Orthosilicate) are toxic and expensive. A better solution is to use environmentally friendly materials like silicates and titanates, which have good coating properties. Adding metal particles to the sol can increase coating toughness and thickness. Zinc and magnesium particles, in particular, offer excellent corrosion protection for coated substrates (Philipp & Schmidt, 1984).

2.1.3 Hydrothermal Synthesis: Hydrothermal synthesis utilizes high-temperature and high-pressure water environments to create crystalline materials. Hydrothermal processing yields nanocrystalline inorganic materials through a direct precursor-product correlation, enabling versatile material synthesis without additional structure-directing agents (Whittingham, 1996). In brief, this synthesis method capitalizes on the solubility of most inorganic substances in water under high temperatures and pressures, followed by crystallization from the fluid. Water at elevated temperatures is crucial for the transformation of precursor materials, as implied by the method's name. The synthesis method, commonly referred to as solvothermal, utilizes water as well as other solvents, aligning with the general process principle. Additives may be introduced to modify the properties of pure hydrothermal water. Polar solvents (e.g., NH3, aqueous solutions containing HF or other acids or bases) or even non-polar solvents (e.g., pure, supercritical CO2) can be employed to broaden the method's applicability. However, these solvents may present challenges such as toxicity and corrosion issues for autoclave materials, potentially compromising the simplicity and elegance of the original process (Schäf et al., 2005).

Hydrothermal processing allows for systematic adjustment of both physical and chemical parameters to establish a direct correlation between precursor and product. However, the method is complex due to numerous interacting parameters (Byrappa & Yoshimura, 2001). In-situ observation of the process remains challenging and has not been satisfactorily addressed yet.

Temperature significantly influences the kinetics of product formation and the thermodynamic stability of the product phase. Pressure is crucial for solubility and the supersaturation range, directing the crystallization process and affecting the thermodynamic stability of the product phase (e.g., excessively high synthesis pressure can lead to the crystallization of denser phases). The external pressure mode is preferred to mitigate the influence of temperature-driven autogeneous pressure, making low temperature-high pressure syntheses possible, known as high-pressure hydrothermal synthesis (HPHS). Time is also crucial, with kinetically stable phases favored in short-term processes and thermodynamically stable phases typically formed in long-term experiments, corresponding to the chosen temperature-pressure regime. This phenomenon arises from re-dissolution and recrystallization of formed phases. Additionally, factors like convection within the reaction vessel and the state of aggregation of precursor materials (e.g., macroscopic crystals, nanocrystalline phases, or glass) must be considered to effectively control the process parameters (Schäf et al., 2005).

2.2. Fabrication Techniques for Different Materials

2.2.1 Thin Films: Thin films are layers of material with thicknesses ranging from several nanometers to micrometers, created by the precise condensation of atoms, molecules, and ions onto substrates. This process is achieved either directly through physical methods or via chemical and electrochemical reactions (Chopra & Kaur, 1983). Due to the numerous benefits of using thin films in batteries, solar cells, and various electronics, a wide range of techniques has been developed for their fabrication. The fabrication techniques for thin films can be divided into two categories: (1) gas phase methods and (2) liquid phase methods as outlined in Table 1.

Table 1. List of some well-established techniques for fabricating thin films.

Gas phase methods	Liquid phase methods
1. Magnetron sputtering	1. Electrospray deposition
2. Pulsed laser deposition	2. Electrochemical deposition
3. Atomic layer deposition	3. Sol-gel method
4. Chemical vapor deposition	4. Molecular precursor method

In this context, gas-phase fabrication techniques deposit materials sourced from small particles of bulk solids or vaporized chemical precursors. In contrast, liquid-phase fabrication techniques entail a reaction between a substrate and a chemical precursor in liquid form (Lu & Nagai, 2019).

2.2. Nanoparticles: Different synthesis methods can produce various types of nanostructures, which are defined by having at least one or two dimensions within the 1–100 nm range. Nanoparticles can be synthesized through several techniques, such as co-precipitation, hydrothermal synthesis, sputtering, sol-gel processing, ultrasound treatment, microwave synthesis, and inert gas condensation. These methods are capable of producing both dry particles and nanoparticles dispersed in liquid. Nanostructures can be formed either by assembling them from individual atoms or by reducing the size of microparticles to the nanoscale (Rane et al., 2018). Methods such as wet chemical synthesis, hydrothermal synthesis, and ultrasonic processing allow for precise control over the size, shape, and surface properties of nanoparticles (Jamkhande et al., 2019).

2.2.3 Composites: A typical composite material comprises two or more distinct materials combined and bonded on a macroscopic scale. Generally, a composite material includes reinforcement elements (such as fibers, particles, flakes, or fillers) embedded within a matrix (which can be polymers, metals, or ceramics). The matrix maintains the structure and shape, while the reinforcement elements enhance the mechanical properties of the composite. When properly designed, the combined material exhibits superior strength compared to the individual components (Nagavally, 2016).

There are various methods for fabricating composite components. Some, like injection molding, are adapted from other fields, while others are specifically developed to address unique design or manufacturing challenges. The choice of method depends on the materials, part design, and intended application. Composite fabrication processes typically involve molding to shape the resin and reinforcement. A mold tool is essential to form the resin/

fiber combination into the desired shape before and during curing.

Various techniques are used for the fabrication of composites tailored to application needs, including hand lay-up, filament winding, resin transfer molding (RTM), and autoclave processing (Nagavally, 2016; Summerscales, 1991). Hand lay-up is cost-effective and versatile, ideal for large structures like boat hulls, though labor-intensive and less consistent. Filament winding, perfect for cylindrical shapes like pipes, offers high precision but is limited to rotationally symmetric components. RTM, a closed-mold process, produces high-quality parts with excellent surface finishes, suitable for aerospace and automotive industries, though it requires expensive tooling and longer cycle times. Autoclave processing, used for critical aerospace components, delivers the highest quality composites with minimal void content, but is costly due to the high expenses of autoclaves and tooling. Each technique balances mechanical properties, production volume, and cost (Nagavally, 2016).

2.3. Considerations for Controlling Material Properties

Controlling material properties is a critical aspect of materials science and engineering, as it directly impacts the performance, reliability, and durability of materials in various applications. Several factors must be considered to effectively control and optimize material properties, including precursor selection, reaction conditions, processing parameters, environmental conditions, and testing methods.

2.3.1 Precursor Selection

The tarting materials play a crucial role in determining the ultimate composition and characteristics of the material. Choosing the appropriate precursors can determine the purity, phase, and elemental constituents of the synthesized material. For instance, in the synthesis of advanced ceramics, the choice of precursors affects the grain size, porosity, and mechanical strength of the final product (Callister, 1997). High-purity precursors are often preferred to minimize impurities that could negatively affect the material's performance (Lark-Horovitz & Johnson, 1959).

2.3.2 Reaction Conditions

Temperature, pressure, and reaction time are critical factors that influence crystallinity, morphology, and defect concentration in materials. For example, variations in annealing temperature can affect the grain size and phase distribution in metals, thereby impacting their mechanical properties (Shaba et al., 2021). Similarly, in polymer synthesis, reaction conditions such as temperature and catalyst concentration can dictate the molecular weight distribution and, consequently, the mechanical and thermal properties of the polymer (Rudin, 1989).

2.3.3 Processing Parameters

Fabrication techniques like deposition rate, solution concentration, and processing temperature play crucial roles in shaping the final material. In thin-film deposition, the deposition rate and substrate temperature can affect the film's thickness, crystallinity, and surface roughness (Acosta, 2021). For composite materials, the concentration of the matrix and reinforcement phases, along with the curing temperature, can significantly influence the composite's mechanical strength and thermal stability (Bouhfid et al., 2019).

2.3.4 Environmental Conditions

Environmental conditions during processing and in-service environments can significantly impact material properties. Factors such as temperature, humidity, and exposure to chemicals or radiation need to be controlled to achieve the desired performance of materials.

For instance, metals exposed to high temperatures during processing can experience grain growth, which might reduce their mechanical strength (Akbarpour & Kim, 2015). In polymers, prolonged exposure to UV radiation can lead to photo-oxidative degradation, affecting their mechanical properties and color (Luyt & Malik, 2019).

2.3.5 Testing and Characterization

Accurate testing and characterization are essential to understand and control material properties. Techniques such as tensile testing, hardness testing, scanning electron microscopy (SEM), and X-ray diffraction (XRD) provide valuable insights into the mechanical, microstructural, and compositional attributes of materials (C. Suryanarayana, 1998). By thoroughly characterizing the material, engineers can identify any deviations from the desired properties and make necessary adjustments in the processing or material selection.

2.3.6 Alloy Design and Composition Control

Alloy design is a sophisticated approach to controlling material properties by precisely manipulating the composition of metallic elements. Progress in computational materials science has facilitated the development of high-performance alloys customized to meet specific application requirements. The addition of elements such as carbon, manganese, and vanadium in specific proportions can significantly enhance the wear resistance, hardness, and toughness of steels (Han et al., 2021). Moreover, modern techniques like additive manufacturing allow for the creation of functionally graded materials, where the composition varies gradually to optimize performance at different sections of the component.

2.3.7 Surface Treatments

Surface treatments are another crucial consideration for controlling material properties, especially in applications where surface interactions play a significant role. Techniques such as surface hardening, coating, and plating can enhance surface properties like wear resistance, corrosion resistance, and friction characteristics. For instance, nitriding or carburizing can significantly increase the surface hardness of steel components, thereby extending their service life in demanding applications (Bell, 1991).

2.3.8 Residual Stresses and Defects

Managing residual stresses and minimizing defects are important for maintaining the integrity and performance of materials. Residual stresses, which can arise from differential cooling rates during processing, can lead to distortion, cracking, and premature failure. Techniques such as stress-relief annealing, and controlled cooling can help mitigate these stresses (Schajer & Ruud, 2013). Additionally, identifying and reducing defects such as porosity, inclusions, and cracks through improved processing techniques and quality control measures is vital for ensuring material reliability.

2.3.9. Thermomechanical Treatments

Thermomechanical treatments combine thermal and mechanical processing to refine grain structures and enhance material properties. Processes such as rolling, forging, and hot isostatic pressing (HIP) can improve the mechanical strength, toughness, and fatigue resistance of materials. For instance, thermomechanical processing of titanium alloys can result in a fine, uniform microstructure that enhances their performance in aerospace applications (Alluaibi & Cojocaru, 2018).

3. Characterization Techniques

3.1 Overview of Characterization Methods

Characterization techniques are essential tools in material science, providing detailed information about the composition, structure, and properties of materials. These methods can be broadly categorized into spectroscopy, microscopy, diffraction, and thermal analysis.

3.1.1 Spectroscopy: Spectroscopy techniques, such as infrared (IR), nuclear magnetic resonance (NMR), and Raman spectroscopy are employed to identify chemical compositions and molecular structures. IR spectroscopy detects and analyzes the absorption of infrared radiation by molecules, thereby identifying the specific functional groups present in a material (B. H. Stuart, 2005). NMR spectroscopy utilizes the magnetic properties of nuclei to determine the structure and dynamics of molecules (Marion, 2013). Raman spectroscopy involves the scattering of light by molecular vibrations, providing a fingerprint of molecular structure (Andre Lyon et al., 1998).

3.1.2 Microscopy: Microscopy techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy, and atomic force microscopy (AFM), allow visualization of materials at various scales. Optical microscopy uses visible light to magnify images of small objects, useful for biological samples and general imaging (Huang & Murphy, 2004). SEM provides high-resolution images of surfaces using a focused electron beam, revealing topographical and compositional information (de Assumpcão Pereira-da-Silva & Ferri, 2017). TEM transmits electrons through a thin sample, providing atomic-scale resolution of internal structures (Williams & Carter, 1996). AFM utilizes a cantilever featuring a sharp tip to scan surfaces at the nanoscale, measuring topography and mechanical properties (Giessibl, 2003).

3.1.3 Diffraction: X-ray diffraction (XRD) and electron diffraction are essential techniques for determining crystallographic structures. XRD involves directing X-rays at a material and analyzing the resulting diffraction pattern to identify phases and measure lattice parameters (Ali et al., 2022). Electron diffraction, often used in conjunction with TEM, provides information on crystal orientation and defects (Bendersky & Gayle, 2001).

3.1.4 Thermal Analysis: Thermal analysis techniques, including techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), investigate how the properties of materials vary with temperature. DSC measures heat flows associated with phase transitions, such as melting and crystallization (Haines et al., 1998). TGA monitors weight changes as a material is heated, indicating thermal stability and composition. DMA assesses mechanical properties like modulus and damping as a function of temperature and frequency (Prime et al., 2009).

3.2. Principles and Applications of Various Techniques

Each characterization technique is based on specific principles and is suited for probing different material properties.

3.2.1 Spectroscopy

3.2.1.1 Infrared (IR) Spectroscopy:

Principle: IR spectroscopy is based on the absorption of infrared light by molecules, causing vibrations in the molecular bonds. When IR radiation passes through a sample, certain wavelengths are absorbed, corresponding to the vibrational frequencies of the bonds in the molecules. The resulting IR spectrum represents the absorbed light as a function of wavelength or frequency (B. Stuart, 2021).

Mechanism: Different functional groups in a molecule absorb characteristic frequencies of IR radiation, allowing for identification of these groups. For instance, a carbonyl group (C=O) typically absorbs strongly near 1700 cm -1. The IR spectrum acts as a molecular fingerprint that can be used to identify and quantify different components in a sample.

Applications: Used for identifying functional groups in organic and inorganic compounds, studying chemical bonding, and analyzing complex mixtures in fields like pharmaceuticals, polymers, and environmental science.

3.2.1.2 Nuclear Magnetic Resonance (NMR) Spectroscopy:

Principle: NMR spectroscopy exploits the magnetic properties of certain atomic nuclei. When placed in a strong magnetic field, nuclei such as ^1H or ^13C absorb and re-emit electromagnetic radiation at characteristic frequencies, dependent on the local chemical environment (Andre Lyon et al., 1998).

Mechanism: The resonance frequency of a nucleus in a magnetic field is influenced by the surrounding electron cloud, which provides information about the molecular structure. The resulting NMR spectrum displays chemical shifts, multiplicity (splitting patterns due to spin-spin coupling), and integration (relative number of nuclei contributing to each signal).

Applications: Widely used in organic chemistry and biochemistry to determine molecular structure, study dynamics, and investigate molecular interactions.

3.2.1.3 Raman Spectroscopy:

Principle: Raman spectroscopy is based on the inelastic scattering of light (Raman scattering). When monochromatic light (usually from a laser) interacts with a sample, most photons are elastically scattered (Rayleigh scattering). A small fraction of photons is inelastically scattered, experiencing a shift in energy corresponding to vibrational modes of the molecules (Ferrari et al., 2004).

Mechanism: The Raman effect results in a spectrum that offers insights into rotational, vibrational, and other low-frequency modes within a system. The shifts in the scattered light frequency are specific to the molecular vibrations, providing a complementary technique to IR spectroscopy.

Applications: Used for characterizing molecular structures, studying chemical compositions, and investigating material properties in fields such as chemistry, materials science, and biology.

3.2.2 Microscopy

3.2.2.1 Optical Microscopy:

Principle: utilizes visible light and lenses to magnify and observe small objects. The resolution is limited by the wavelength of light, typically around 200 nm for visible light (Huang & Murphy, 2004).

Mechanism: Light emitted from a source is concentrated onto the sample using objective lenses, and the transmitted or reflected light is collected to form an image. Advanced techniques like fluorescence microscopy use specific wavelengths to excite fluorescent molecules, providing detailed images of biological specimens.

Applications: Commonly used in biological sciences for examining cell structures, tissues, and microorganisms. Also used in materials science for studying microstructures of metals and polymers.

3.2.2.2 Scanning Electron Microscopy (SEM):

Principle: SEM utilizes a concentrated beam of high-energy electrons to scan the surface of a sample. The interactions between the electrons and the sample atoms produce signals that are detected to form detailed images (Goldstein et al., 2018).

Mechanism: Upon striking the sample, the electron beam generates secondary electrons, backscattered electrons, and characteristic X-rays. Secondary electrons yield details regarding surface topography, whereas backscattered electrons provide contrast based on composition. X-ray signals can be used for elemental analysis.

Applications: Extensively used for high-resolution imaging of surfaces, studying microstructures, and compositional analysis in materials science, nanotechnology, and biological sciences.

3.2.2.3 Transmission Electron Microscopy (TEM):

Principle: TEM operates by passing a beam of electrons through an ultra-thin sample. The transmitted electrons are focused to form an image with atomic-scale resolution (Howe et al., 2012).

Mechanism: The electron beam interacts with the sample, leading to scattering based on the atomic structure. The scattered electrons are collected to produce an image, which can show detailed crystallographic and morphological information. Techniques like electron diffraction and high-resolution TEM (HRTEM) further enhance structural analysis.

Applications: Used for atomic-scale imaging of materials, studying crystallography, and investigating defects and interfaces in materials science and nanotechnology.

3.2.2.4 Atomic Force Microscopy (AFM):

Principle: AFM employs a cantilever equipped with a sharp tip to scan across the surface of a sample. The forces between the tip and the sample surface cause deflections of the cantilever, which are measured to create a topographical map (BLANCHARD, 1996).

Mechanism: As the tip scans across the surface, interactions such as van der Waals forces, electrostatic forces, and mechanical contact cause the cantilever to bend. A photodiode detects the laser beam reflected off the backside of the cantilever to measure these deflections with high precision.

Applications: Used for nanoscale imaging of surface topography, mechanical property measurement, and manipulation of nanostructures in materials science, biology, and nanotechnology.

3.2.3 Diffraction

3.2.3.1 X-ray Diffraction (XRD):

Principle: XRD is based on the constructive interference of X-rays that are scattered by the periodic atomic planes in a crystalline material. The angles and intensities of the diffracted beams reveal information about the crystal structure. (Ali et al., 2022).

Mechanism: When X-rays hit a crystal, they are diffracted in specific directions defined by Bragg's law ($n\lambda = 2d \sin\theta$), where n is an integer, λ is the wavelength, d is the distance between atomic planes, and θ is the diffraction angle. The resulting diffraction pattern is analyzed to determine lattice parameters, phase identification, and crystallite size.

Applications: Widely used for identifying crystalline phases, determining crystal structures, studying polycrystalline materials, and analyzing thin films and coatings in materials science and chemistry.

3.2.3.2 Electron Diffraction:

Principle: Electron diffraction relies on the wave nature of electrons. When a beam of electrons interacts with a crystalline sample, the electrons are diffracted, producing patterns that can be analyzed to gain structural information (Ali et al., 2022).

Mechanism: Similar to X-ray diffraction, the electrons are scattered by the periodic atomic structure, creating diffraction patterns that provide information about crystal orientation, interatomic spacing, and defects. Techniques like selected area electron diffraction (SAED) in TEM are commonly used.

Applications: Used for crystallographic analysis of small volumes, nanocrystalline materials, and defects in materials science and solid-state physics.

3.2.4 Thermal Analysis

3.2.4.1 Differential Scanning Calorimetry (DSC):

Principle: DSC measures the heat flow into or out of a sample during heating or cooling, providing information about thermal transitions such as crystallization, melting, and glass transitions (Haines et al., 1998).

Mechanism: The sample and a reference are exposed to a precisely controlled temperature program. The heat flow needed to keep both the sample and reference at the same temperature is recorded. Detecting endothermic (heat-absorbing) and exothermic (heat-releasing) events enables the analysis of phase transitions and thermal characteristics.

Applications: DSC is employed to investigate the thermal characteristics of polymers, pharmaceuticals, and various materials, encompassing melting points, crystallization behavior, and glass transition temperatures.

3.2.4.2. Thermogravimetric Analysis (TGA):

Principle: TGA computes the variation in mass of a sample as it is undergoes thermal energy increment, apprise about thermal strength, composition, and decomposition operations (Prime et al., 2009).

Mechanism: The sample is positioned on a balance with a conditional atmosphere (inert or reactive). As the temperature elevated, evaporation caused mass change, decomposition, or oxidation are monitored. The outcome TGA curve imply weight changes as a repercussions of temperature.

Applications: Utilized to examine the thermal stability and chemical composition of analysis, analyze decomposition kinetics, and study the effects of additives in polymers and composites.

3.2.4.3 Dynamic Mechanical Analysis (DMA):

Principle: DMA characterize the mechanical durability of a material as it is deformed in the course of periodic stress, providing information about viscoelastic behavior, modulus, and damping (Placet & Foltête, 2010).

Mechanism: The sample is subjected to an oscillating force, and the following distortion (strain) is analyzed. The storage modulus (elastic response), loss modulus (viscous response), and damping factor (tan δ) are determined as functions of temperature and frequency.

Applications: Examine the viscoelastic behavior of polymers, composites, additionally biological materials, including glass transition temperatures, relaxation processes, and mechanical performance.

3.3. Importance of Characterization in Understanding Structure-Property Relationships

Characterization techniques are indispensable for understanding the structure-property relationships in materials. By elucidating the detailed structure of materials, these techniques enable the optimization of material properties for specific applications. For example:

Material Design: Tailoring materials with specific properties by understanding how atomic or molecular structures influence macroscopic behaviors. For instance, controlling the degree of crystallinity in polymers can significantly impact their mechanical strength and thermal properties (Chung, 2017).

Quality Control: Ensuring materials meet specified standards and perform reliably in industrial settings. Techniques like XRD and SEM are routinely used to monitor manufacturing processes and assess material quality (Ali et al., 2022).

4. Properties of Materials

Metals have properties like mechanical, thermal, electrical resistivity, and optical properties. As with people, various materials respond differently to different conditions and the reactions determine their application in our daily lives and particular uses. Like suits, scientists and engineers owe it to it to understand these characteristics and design materials that are suitable for our technological requirements (Askeland et al., 2003). The understanding of material characteristics is the fundamental starting point of designing durable yet lightweight structures for constructions and vehicles, as well as sophisticated technological products, and medical equipment. When we explore and even try to manipulate these attributes, what we find is a world teeming with possibilities, which adds to the ever-growing potential in every single aspect of our lives. Materials are solid-state substances or technology that can satisfy current, or future wants in society. The concept of property requires clarification: when materials are used, they undergo certain reactions due to the external forces which come into contact with them. For instance, a substance can become deformed by external forces and a smooth metal surface can reflect light. An attribute is an inherent characteristic of an object that determines its identity and the manner in which it responds to a certain treatment. Usually, the property definitions are set without paying attention to the shape or size of the material under consideration (Mittemeijer, 2010).

Materials can be categorically assigned into six core groups established on their significant qualities: mechanical, electrical, thermal, magnetic, optical, and deteriorative. Strength, toughness, and elastic modulus (stiffness) are mechanical characteristics that help define a relationship between deformation and an externally applied load or force. An electric field serves as the driving force for electrical characteristics including electrical conductivity and dielectric constant. Specific heat capacity and thermal conductivity are two factors that define the thermal properties of a solid body. Magnetic properties can be determined by how a material behaves under an applied magnetic field. When it comes to optical qualities, light or also called electromagnetic radiation serves as the stimulus. Specific optical properties include reflectivity and index of refraction (Callister, 1997). Apart from structure and characteristics, science and engineering of materials also include important factors of performance as well as processing. The processing method of a material with reference to these which composed of four critical parts, defines sample configuration. In addition, the properties of a material define the material.

4.1 Mechanical Properties:

Failure is common with many materials during operation; for instance, the aluminum alloys used in airplane wings and the steel used in automobile axels. It is therefore paramount for one to recognize the various qualities of the material and design their parts in order to avert excessive deformation and fractures. Mechanical design exclusively depends on the characteristics of this material and its capabilities manifested in terms of stiffness, strength, hardness, ductility, and toughness (Pelleg, 2013). These properties also indicate how a material behaves when subjected to loads or pressures that are exerted on it. Comprehensively organized laboratory tests, which mimic service conditions, are performed to accomplish ascertain the mechanical properties of a material. External conditions and the nature and time for which the load is applied should also be taken into account. The load can be either shear, compressive, or tensile, and can either be variable at any time or fixed at any given time. Its duration can range from several seconds to several years depending on the sort of application being made. The service temperature may be the key factor.

4.1.1 Understanding Strength in Metals

Strength is one of the main mechanical characteristics that define how well metals can handle laid on them forces. It is a major aspect of determining whether a given metal is suitable for a certain structural or technical application. Four mechanical properties of strength commonly utilized include tensile strength, compressive strength, yield strength and ultimate strength. All these categories play a role in explaining how a particular metal will behave under certain loads and conditions.

There are various measures of strength; however, the most common one is tensile strength. Tensile strength on the other hand means the amount of stress that can be applied on a material particularly a metal in cases of tension force before it breaks. Tensile test is one in which a material is deliberately placed under fixed tensile stress to its failure in order to obtain its tensile strength. This property is very vital in materials that are likely to come under tension or in such applications as cables, bridges, and beams which are normally under pulling forces. Some of the frequently used units of pressure measurement include Megapascal (MPa) and Pounds Force per square inch (psi). Tensile strength is reportedly the most commonly used value for expressing strength. Tensile strength refers to the maximum stress that is usually placed on any such metal before it fractures. Tensile test refers to the stretching of a sample to the point of failure under a specific load in order to establish tensile strength. This feature is rather significant for the materials used in various structures such as cables, bridges, and beams as they are exposed to tensile stresses. Typically, pressure is expressed in term of pound force per square inch (psi) or in megapascal (MPa).

Compressive Strength: It is the ability of a metal to withstand loads that tends to reduce its cross-sectional area by compressing it. This is especially necessary in structures where weight or layers of the metal are likely to buckle when pressed with pressure such as in columns, support systems, and foundations. While some ductile materials have similar tensile and compressive strength values, brittle materials may drastically differ in these values where the latter is usually higher as compared to the former. When stress is applied it can be seen that many metals display certain elastic and flexible behavior. Metals must have the characteristic of the ability to deform at the elastic area and then regain their initial form after the stress has been released. The slope of the curve in the specific region is recognized as the modulus of elasticity or Young's modulus, which characterizes the stiffness of a material. In this region the metals get its permanent set and deformed irreversibly since the imposed load is beyond the yield limit. Ductility is the capacity of a metal to deform in the flexible state without breaking and is part of mechanical properties.

The Ultimate Tensile Strength (UTS) on the other hand is the maximum tensile stress that a material can withstand in tension associated with other materials such as metals when exposed to tension forces. Beyond this point another process referred to as necking occurs whereby the metal flow reduces in cross sectional area until it reaches the point where it fractures. The ultimate strength of a metal is necessary to understand the limits of using the particular metal if it is exposed to the maximum load application. Forces such as composition, microstructure, and production methods are the main determinants of metals strength. The process of adding alloying elements also helps to enhance the overall strength of the primary metals. For instances when carbon is added into iron it gets combine to form steel which has a much higher strength than that of iron heat treatments like quenching and tempering have the ability to modify the microstructure of metals, resulting in improved strength and hardness.

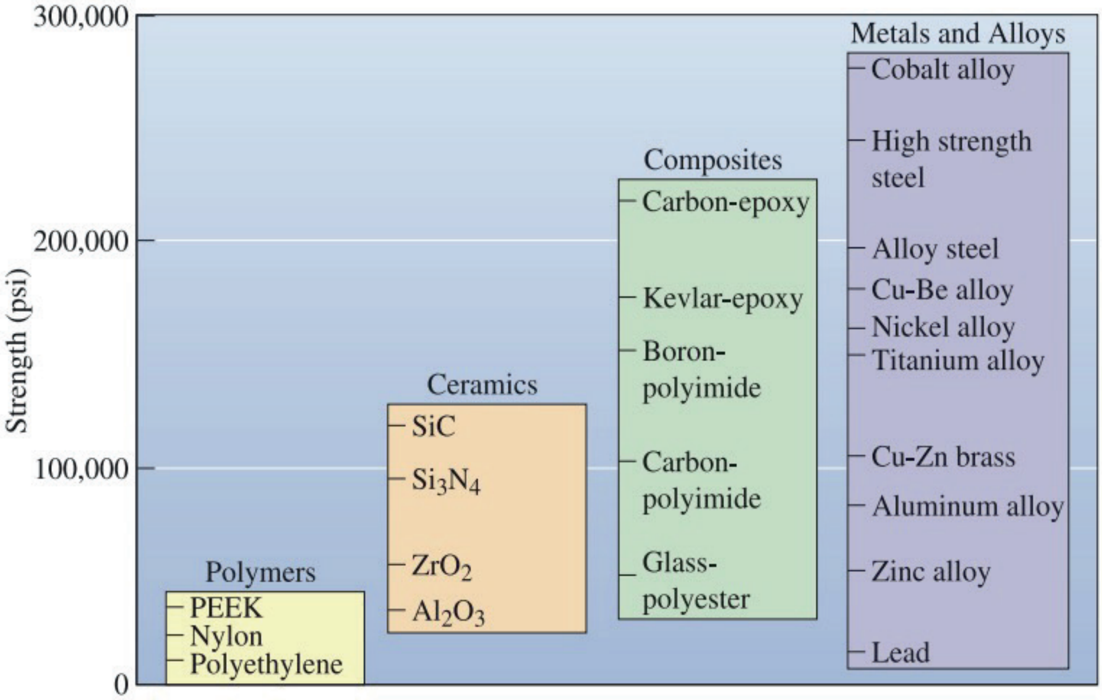


Figure 2. Strengths of materials

The practical use of metals is based on their inherent strength, which allows structures to endure and sustain both load-bearing and operational loads without experiencing any catastrophic failure. The strength of metals is a fundamental aspect of modern engineering and design, whether it be in the construction of skyscrapers, the manufacturing of machinery, or the fabrication of common consumer products. Gaining knowledge and enhancing the effectiveness of metals enables the creation of products and buildings that are safer, more efficient, and have a longer lifespan.

4.1.2 Hardness

Hardness is one of the essential mechanical properties that reflect the ability of the material to bear deformation, indentation, or scratching. It is an important property which is very important in the determination of the ability of a material to perform under conditions of friction and erosion. By defining hardness, engineers and designers can then choose the right materials for specific applications, thereby guaranteeing the longevity of products and structures. Hardness can be scientifically described as the material characteristic to withstand the formation in relation to permanent indentations at a very localized scale and can therefore be viewed as a gauge of the extent of ease regarding the materials surface is capable of being altered permanently. This attribute is most important especially where the material may be used in applications that might involve physical contact such as cutting tools, bearings, gears and surface coatings.

There are many approaches to the determination of the hardness of material with each method being applicable to specific classes of materials and purposes. Some of the common techniques used in hardness testing are Brinell, Rockwell, Vickers, Knoop, and Mohs hardness. A Brinell test is a technique that involves pressing a hard steel or carbide ball against a material's surface with a certain force. They assert that this test is particularly ideal when it comes to assessing the hardness of material that has a rough or an irregular surface. The Rockwell test is employed to determine the depth of the indentation made by a considerable load, then a smaller load, and is applicable for various materials (Pintaude, 2023). The Vickers test uses a diamond pyramid indenter to obtain accurate results for delicate materials and tiny parts. The Knoop hardness test, which is similar to the Vickers test, employs a pyramidal diamond indenter that is more extended and ideal for measuring the hardness of ceramic materials and thin layers. Mohs test is a qualitative procedure to rank materials by the way they scratch which helps in identification of minerals.

The material hardness of a substance depends on its composition, microstructure, heat treatments and work hardening. From the viewpoint of material chemistry, the hardness of a material depends significantly on its composition which defines the kinds as well as the proportions of the components used in making the material. The process of strengthening steel is achieved by adding carbon to iron since carbides limit the flow of dislocations and thus increases the toughness of the metal. Grain size and the organization aspect influences the hardness of materials and thus the microstructure. Normally, a material with fine grains is harder than the material with coarse grains, mainly because of grain refining mechanism at grain boundaries. Quenching and tempering are some of the heat treatments that affect the hardness of a metal through the alteration of its microstructure. Tempered steel is stronger than annealed steel because it forms martensite. Similarly, the formation of plastic deformation during the operations like machining and forming improves the hardness of a material through the process of work hardening, particularly in metals like copper and aluminum.

Various industrial processes rely on the understanding and control of hardness. For instance, when using steel to produce cutting tools, it is desirable that hardness is high in order to reduce wear rate by cutting through materials. Ceramic-matrix composite parts used in automotive industries and aerospace applications have a high degree of wear resistance and maintain their strength under pressure. Besides the wear, hardness is often connected with other mechanical properties such as tensile strength and fatigue strength. Hard material has a higher ability to withstand cracks and bending moment when force is applied on it hence it is ideal for use in high performance (Dhanasekar et al., 2022).

Hardness determines how much a material can stand to deform and to be abraded. Various hardness testing techniques provide crucial information that enables determination of materials suitable for certain applications, reliability, endurance, and dependability. Engineering experts can enhance the quality and endurance of the products they create through understanding the facets of hardness and the material chemistry behind it and calculating it accurately.

4.1.3 Elasticity

Elasticity refers to a material capacity that allows the component to return to its pre-deformation state after being deformed in a force-dominated regime. Knowing how materials behave under load and containing the force that will put it under stress is critical in engineering structures and components that will not deform permanently under load. E modulus is obtained by stress (σ) and strain (ε) relationship within the elastic limit of material. This relationship is in most cases described by Hooke’s law which postulates that

$$\sigma = E\varepsilon$$

where E represents the Young's modulus of the material.

Young’s modulus (E) measures the stiffness of a material in terms of stress and strain on the stress-strain graph and is relevant to the linear portion of the curve. High Young’s modulus materials like steel as well as diamond are quite rigid and can resist deformation thereby being suitable for uses where firmness and strength of structure is desirable. On the other hand, those that have low Young’s modulus like elastomers and polymers among others are more flexible and can even deform significantly when stressed. This characteristic is useful in situations where flexibility and the ability to accommodate energy are desirable.

However, it is important to note that there are several elastic moduli that can be used to describe how a material reacts to different forms of stress. Shear modulus (G) describes the behavior of a material subjected to shear stress that defines the ability of the material to resist changes in shape without changing volume. The bulk modulus (K) indicates a material’s response to equal pressure, proving its effectiveness in maintaining or changing compression. These moduli are related and dependent on the Poisson's ratio (v) of the material: this is the ratio of lateral strain to axial strain when a rod of the material is subjected to uniaxial stress (Kim & Chen, 2004).

The nature and organization of the atoms and molecules in the material determine its elastic properties. Metals have metallic structure that allows the atomic planes in the metal lattice to slide past one another, which makes metals possess highly desirable elastic properties. This is because polymers elongated chains of molecules are capable of stretching to regain their original forms. Ceramics and glasses composed of ionic or covalent bonds hold less elasticity and higher levels of brittleness due to the restricted freedom of atoms (Basu & Balani, 2011). The yield point is also referred to as the elastic limit is the maximum limit up to which stress can be applied before experiencing some amount of elastic deformation. Beyond this limit, the material moves to the plastic deformation regime where the stress strain relationship becomes nonlinear, and the deformation is not fully recoverable. The elastic limit is one of the most significant design factors which ensure that materials perform at their elastic limit under service loads and conditions in order to prevent failure (Reiner, 1948). In various engineering applications, elasticity is a significant consideration. Any steel and concrete that is used in civil engineering applications must be able to have some level of elasticity so as to be capable of absorbing and releasing energy from loads and vibrations thereby increasing the structural durability and safety. In automotive engineering, elasticity of tires and suspension is essential in improving automobile comfort and maneuverability. This is done by smooth and efficient isolation of road vibrations and maintaining constant contact with the road surface. Biomedical engineering applies elastic materials such as in prosthetics and implants to mimic the biomechanical movement of tissues so as to provide not only utility but also quality comfort to the user (Egbo, 2021).

The aim of emergence in material science is to increase the flexibility of structure by incorporating molecular design modifications and seeking composites. Scientists can also manipulate the elastic properties of the materials through altering the size, shape, and even the nature of the structure. This enables them to meet the exact performance standards wherever they are and in whatever circumstances. By understanding and managing flexibility at the molecular level, it is possible to create elaborate materials with high mechanical performance and reliability.

Elasticity is one of the critical properties with regard to the ability of the material to bear force which influences their functionality and durability in various applications. Elasticity is a measure of shape memory of a material and is described by factors such as Young 's modulus, Shear modulus, and Bulk modulus. Engineers and scientists are then able to use our understanding of elasticity to design materials or structures to achieve the optimal level of performance and reliability in a variety of harsh or challenging environments.

4.1.4 Toughness

Toughness is crucial material property that refers to the capacity of a material to deform plastically in an elastic manner without cracking. This represents the capacity of a materials resistance to crack initiation as well as propagation, especially in cases of shock and impact loadings. Toughness is a synergy of strength and ductility, which is the total amount of energy that a material can withstand before fracture (Kobayashi, 2004) . It is defined as the area under the stress-strain curve derived from a tensile test where the properties of both elastic and plastic deformation are incorporated.

In this regard, materials with high toughness are those which can bear high amount of stress and strain before getting damaged. Some of the metals that possess high toughness include steel commonly used for construction and car manufacturing since they have both high strength and ductility. This is why steel is preferred for use in areas that require hardness and elasticity like the construction of bridges, buildings, and vehicles bodies (Callister, 1997). On the other hand, materials such as ceramics and glass are normally very rigid and have low amounts of toughness as they have high stress levels but low plastics deformation capacity causing them to break. In general, the strength of materials depends on microstructure, chemical content, and temperature. In metals, features that can improve this property are fine grained structure and/or presence of alloying elements that create high toughness, such as nickel and chromium in steel. Other heat treatment procedures like tempering can also improve the toughness by altering the microstructure and placing internal stresses in order. Toughness in the case of polymers and composites depends highly on the molecular structure and the reinforcing phases. Said deformation in polymers like increasing the toughness by using cross-linking to avoid the extension of cracks.

Temperature has a significant influence in terms of toughness. Most materials have improved toughness at increased temperatures due to higher atomic diffusion that enables more deformation before failure. At low temperatures however, many materials become loss their toughness and a material that is very important in cold environments becomes brittle. This shift from ductile to brittle behavior with decreasing temperature is an important factor that needs to be taken into account when selecting material and designing parts (Feng et al., 2017).

Toughness is usually conducted by impact tests like Charpy or Izod test that estimate the amount of energy required to fracture the material (Handbook, 2000). These tests involve use of a hammer to strike a notched sample and determining the energy needed to fracture the material. The results give the relative ranking in terms of hardness and are effective in the assessment of materials used in impact applications. For safety and reliability of structures and components in engineering practice it is crucial to achieve sufficient level of toughness. For instance, the aerospace industry requires high toughness of materials as they experience dynamic loads in the process of flight. Likewise, in construction, the measure of strength indicates a material's capability to dissipate energy from an earthquake or impact without failure.

Overall, the toughness is an all-encompassing parameter that describes a material's ability to accommodate energy and plastically deform before failure or cracking due to crack propagation. It is dependent on microstructure, composition, temperature, as well as loading conditions. High-toughness materials are useful in areas where there is a need for durable and robust structures that can resist impacts and shock loads for safe and reliable functioning of various engineering systems (Billinton & Allan, 1992). Toughness and its control through material choices and processing methods are basic to improving the performance and durability of numerous applied technologies today.

4.1.5 Plasticity

Plasticity is a physical property that describes the ability of a given material to undergo permanent deformation without breaking. This particular characteristic varies significantly depending on the type of materials under consideration; these include metals, ceramics, polymers and semiconductors (Askeland et al., 2003). This variation can be attributed to the fact that atomic characteristics of the materials and how they bond are provoked by natural material chemistry.

Due to the nature of metallic bonding and forming of crystals, flexibility of metals is evident. Since metallic connections are inherently delocalized, atoms can only glide over one another in a smooth fashion when stressed, and this reduces the possibilities of breakages. It is possible to deform a crystal plastically through the movement of dislocations as line defect within the crystal. Metallic materials are highly sensitive to their microstructure in terms of the characteristics of the grain size distribution and the type of alloying constituents (Becker, 2004). Mechanical properties like increasing the density of dislocations and promoting grain formation by means of an annealing process can promote plasticity. Copper and aluminum are relatively ductile metals that require less effort in terms of creating various forms and shapes in various assignments (Chakrabarty, 2012).

This is attributed to the fact that ceramics are ionic and covalent bonded materials, which limits atomic mobility. Such connections are known to have high directional strength and cannot easily allow the movement of dislocations. Therefore, they are susceptible to brittle fracture during deformation as opposed to plastic deformation. The flexibility of ceramics is further restricted by their features of the crystal structure, which consists of rigid and tightly packed atoms (Basu & Balani, 2011). The advancement in material chemistry, the abilities to dope and make composite ceramics tries to enhance the mechanical properties associated with ceramics. However, the fragility of these materials remains a considerable challenge to date because of their intrinsic nature. Ceramics have relatively low plasticity and are valuable due to their high hardness, high melting temperatures and chemical inertness which make them suitable for applications where they would be subjected to high heat or friction.

The elasticity of polymers depends on the molecular structure of the polymer and types of linkages that are available in it. Thermoplastics do entail elongated polymer chains that are wound together and hence linked by van der Waals forces, and this gives them considerable flexibility (Howe, 1993). With the application of heat, these polymers become ductile, and the movement of individual chains becomes random and undergoes irreparable deformation. Thermosetting polymers go through a process of curing where their molecules solidify and then form a rigid series of bonds. This network reduces their versatility and capability to modify their shape and form and thus makes them more fragile. One can be able to change the degree of flexibility of polymers through using copolymers including the use of plasticizers and also the extent or level of crystalline formations. Certain thermoplastics including polyethylene and polyvinyl chloride (PVC) are commonly used where flexibility and molding capability is required like packaging and pipe sections (Oberoi & Malik, 2022).

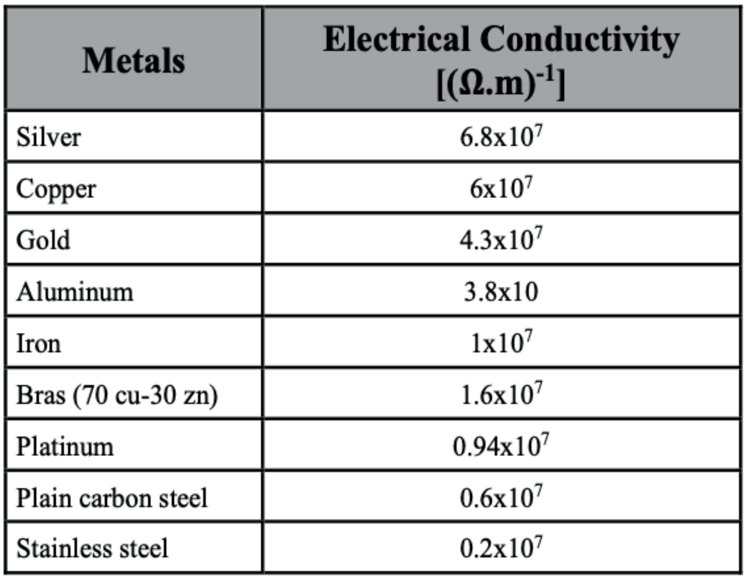
Materials like silicon and germanium for instance, have restricted mobility because of their covalent frameworks and crystal structures. Under namely, low temperatures, semiconductors are known to be very brittle and easily crack under pressure (Pirouz et al., 1999). However, when these substances are subjected to high temperatures, then a certain amount of the deformation is possible due to the movement of dislocations, which bear a passing similarity to what may be observed with metals; though these materials are not as prone to this sort of deformation as metals are. New approach in material chemistry and nanotechnology in recent years is looking at how to make semiconductors more flexible (Sun & Rogers, 2007). This includes using dopants as well as developing structured materials to increase mechanical properties specifically to electrical and opto-electron applications.

In a way, the ability of a material to change shape is determined largely by how atoms are connected together and the characteristics of the microstructure of a material which is in turn dictated by the chemistry of the given material. Metals are of a higher rank when it comes to metals, because they have specific metallic bonds that cause great free movement of electrons, and thus a great ability to take plastic deformation. whereas ceramics, restricted by strong ionic and covalent interactions, have a minimal ability to undergo plastic deformation. Polymers exhibit a wide range of flexibility depending on their molecular structure and bonding, while semiconductors typically have limited plasticity, which can be improved through chemical and structural alterations (Q. Zhang et al., 2022). Comprehending and controlling these characteristics is essential for enhancing materials for certain purposes, ranging from structural elements to electrical gadgets.

4.2 Electrical Properties

Now we will examine the electrical behavior of materials focusing on their trait under an extrinsic electric field, or how they interact to an imposed electric field. We embark on an exploration of the electrical conduction phenomenon, including its expression characteristics, the material's conductivity is dictated by its electron energy level daigram, and the mechanism of electron conduction (Solymar et al., 2014). These ideas also apply to semiconductors, insulators, and metals. First, the properties of semiconductors are discussed in detail, followed by semiconductor devices. Additionally, included are the dielectric properties of insulating materials.

Table 1-Electrical conductivities of some common metals



Metals	Electrical Conductivity [(Ω.m)$^{-1}$]
Silver	$6.8x10^{7}$
Copper	$6x10^{7}$
Gold	$4.3x10^{7}$
Aluminum	$3.8x10$
Iron	$1x10^{7}$
Bras (70 cu-30 zn)	$1.6x10^{7}$
Platinum	$0.94x10^{7}$
Plain carbon steel	$0.6x10^{7}$
Stainless steel	$0.2x10^{7}$

Ferroelectricity and piezoelectricity are the subjects of the latter sections.

4.2.1 Electrical conduction:

Ohm's Law

A solid substance's capacity to efficiently conduct electric current is a vital electrical property. According to Ohm's law, the applied voltage (V) and current (I) are related by the fundamental relation:

$$V=IR$$

where R denotes the material's resistance to electric charge flow. Electric potential difference(V), electric current (I), and electrical resistance(R) are quantified using unit i volts (J/C), amperes (C/s), and ohms (V/A). The electrical resistance is impacted by its geometric organization and is current-independence across diverse materials. The electrical resistivity r is unaffected by its physical dimension but correlated to R in accordance with the relation.

$$\rho=RA/l$$

The voltage is measured at two distinct point, separated by a defined distance e, and A represent the orthogonal cross-sectional area with respect to the current alignment. The units for Rare ohmmeters (Ω-m). derived from Ohm's law.

4.2.2 Electrical Conductivity

Electrical conductivity and resistivity are inversely connected, and it specifies the electrical behavior of materials. Mathematically,

$$\sigma=1/\rho$$

It indicates the degree to which a substance can conduct an electric current easily. Reciprocal ohmmeters (Ω.m)-1 are the units used for σ. The descriptions of electrical qualities that follow make use of both conductivity and resistivity.

Moreover, Equation 18.1, Ohm's law may be exemplified by

$$J=\sigma E$$

The current density J, is defined as—the current per unit of specimen area I/A—an E symbolizes the electric field strength, or the voltage gradient between two points, divided by the distance between them.

No other physical attribute varies as much as the electrical conductivities of solid materials, which can vary by more than 27 orders of magnitude. There are three categories in this categorization scheme for solid materials: conductors, semiconductors, and insulators. This classification scheme is based on how easily a material conducts an electric current. Metals have conductivities of 107 (Ω.m)-1, making them good conductors. Electrical insulators are materials that exhibit remarkably low level of conductivities, which fall amongst 10-10 and 10-20 (Ω.m)-1 (Callister, 1997). These materials are at the other extremity of the spectrum. Semiconductors are materials having intermediate conductivities, usually between 10-6 and 104 (Ω.m)-1.

4.2.3 Energy band structures in solids

Electronic conduction is the only type of conduction allowed in all materials, including conductors, semiconductors, and insulators. The quantity of mobile electrons that are participate in the conduction process solely determines the degree of electronic conduction. However, it is important to note that a selected group of electrons within an atom experience acceleration under influence of an electric field. Each material determines the concentration of electrons accessible for conducting electricity based on the configuration of electron energy levels and the electrons' filling of these states. Conducting a comprehensive examination of these topics is challenging and necessitates a deep understanding of quantum mechanical principles (Bassani & Celli, 1961). As a result, the subsequent advancements may exclude certain concepts and streamline others. The lecture explored the concepts of electron energy levels, their occupancies, and the resulting electron configurations for atoms in isolation. Electrons can occupy unique energy levels in each atom, which we group into shells and subshells. We use integers like 1, 2, 3, etc. to represent shells, and alphabetical notation s, p, d, and f to represent subshells. Each subshell, namely s, p, d, and f, has one, three, five, and seven states, respectively. The Pauli exclusion principle dictates that electrons in the majority of atoms occupy the state alone with the minimal energies. Specifically, each state can accommodate two electrons with opposite spins. An isolated atom's electron configuration depicts the organization of electrons within the permitted energy level. This enables us to apply some of these concepts to tangible substances. A solid is a collection of atoms, denoted as N, first isolated, then assembled and connected to create the organized atomic structure observed in a crystal lattice material. At significant distances, individual atom operates independently from the others. Furthermore, they possess identical energy state of an atom and electron configurations, as if they were separate entities. However, the nuclei of adjacent atoms influence or disrupt the electrons as they approach each other. This phenomenon results in the fragmentation of a solid material into a sequence of electron energy states with a high degree of proximity and derived from distinct atomic states, thus forming an electron energy band (Callister, 1997). The atoms primarily affect the electron shells on the outermost layer as they come together, defining the initial level of splitting. The energy levels within each band are discrete, but the differences between adjacent states are minimal. Band creation is unlikely to occur for the electron subshells located closest to the nucleus when the band gap separation is at equilibrium. Furthermore, as depicted in the illustration, there might be spaces between neighboring bands. Generally, energies within these gaps are unavailable for electron occupation.

Each band contains an equal number of states, representing the combined contribution of all N atom states. For example, a p band encompasses 3N states, whereas a s band spans N states. Each energy level can accommodate a maximum of two electrons, each with opposite spins. Bands in solids consist of electrons that formerly held similar energy levels in individual atoms. For instance, electrons from the 4s orbitals of isolated atoms make up the 4s energy band in a solid. It is worth mentioning that bands may only be partially occupied in some situations, while in other cases they may not be occupied at all. The layout of an object's outermost electron bands and their electron filling, known as its electron band structure, determine its electrical characteristics. We observe four different and unique forms of band topologies at a temperature of absolute zero (0 K) (Siu, 2022). In the initial situation, the outermost layer contains electrons only to a certain extent; the Fermi energy Ef represents the energy level associated with the highest occupied state. Certain metals, specifically monovalent metals like copper, exhibit the described band structure. A single 4s electron is denoted by each copper atom. Despite this, in a solid with N atoms and the 4s energy band can only accommodate a maximum of 2N electrons. Consequently, solid occupies only half of its electron sites. In metallic solid, a second band structure is observed, featuring an overlap between an unoccupied band and an occupied band. In terms of magnesium's energy band diagram, each atom's 3s subshell contains two electrons. On the other hand, solidification causes the 3s, 3p energy level to coincide or intersect. The Fermi energy, at absolute zero temperature (0 K), represents the energy level where two electrons occupy N atoms in each of their N states. The last two band structures are indistinguishable in that they both exhibit an energy band gap that divides the valence band, which is completely filled with electrons, from the conduction band, which is empty. Within this gap, electrons in highly pure materials may lack energy. Electrons in highly purified materials may lack energy within this specific range. The magnitude of the energy gap determines the disparity between the two band structures. In semiconductors, the band gap is narrow (Figure 18.4d), while in insulators, it is significantly wider (Figure 18.4c). Both of these band topologies possess Fermi energy, that exist in the band gap, close to its midpoint.

4.2.3.1 Metals

In order for an electron to be liberated, it must be stimulated or elevated to one of the unoccupied and accessible energy levels beyond the Fermi energy Ef. In metals, which exhibit either of the band structures, there exist unoccupied energy levels next to the maximum occupied state at Ef. Consequently, a relatively low energy is sufficient to elevate electrons to the vacant states that are situated at a lower energy level, as depicted in Figure 3 Usually, the electric field provides enough energy to stimulate a significant electron occupancy excited to conducting states.

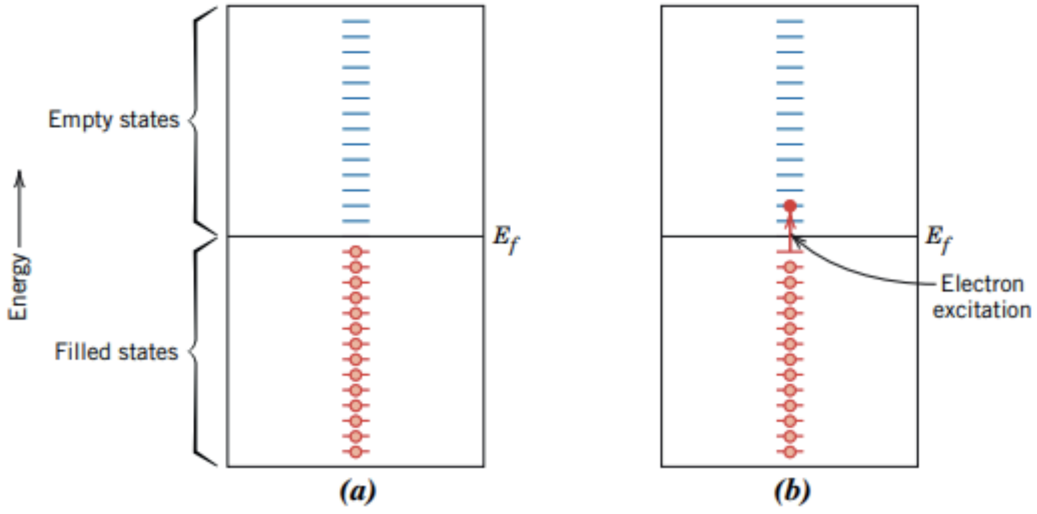


Figure.3. For a metal, occupancy of electron states (a) before and (b) after an electron excitation.

The metallic bonding model assumes that all valence electrons are free to move and create a homogeneous electron gas/cloud throughout the ion core lattice. Although these electrons are not specifically attached to any individual atom, they still need to be stimulated in order to become fully unrestricted conducting electrons (Papaconstantopoulos, 1986). Thus, despite only a small proportion of electrons being stimulated, this nevertheless yields a considerable quantity of unbound electrons, resulting in elevated electrical conductivity.

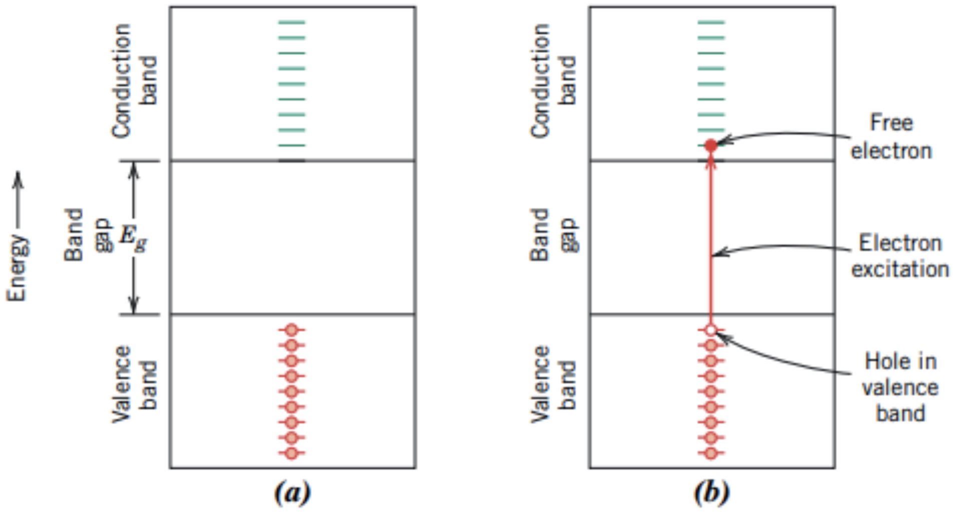


Figure 4. electron state occupation in non-conducting and semiconductor (a) before and (b) after an electron transition from the valence to the conduction band, creating a pair of free electron and hole

4.2.3.2 Insulators and semiconductors

These are two types of materials that have different electrical conductivity properties. In insulators and semiconductors, there is a lack of accessible unoccupied states around the upper limit of the occupied valence band. Hence, in order for electrons to attain freedom, is compelled to be elevated above the energy band gap and occupy vacant positions at the lowermost level of the conduction band. To do this, it is necessary to provide an electron with the precise amount of energy that corresponds to the difference across these two energy level, is roughly/ equivalent to the energy of the band gap Ef.

For numerous materials, the band gap has a width of several electron volts. Usually, the excitation energy is derived from a non-electrical source, such as heat or light, with heat being the more common source. The quantity of electrons that are thermally stimulated to go into the conduction band is contingent upon the width of the energy band gap and the temperature. At a specific temperature, a higher value of Ef leads to a decreased likelihood of a valence electron being elevated to an energy level in the conduction band, resulting in a reduced number of conduction electrons. Put simply, a greater band gap results in less electrical conductivity at a specific temperature. Hence, the differentiation between semiconductors and insulators is in the magnitude of the band gap: it is narrow for semiconductors and comparatively broad for insulators. As temperature elevate in a semiconductor or an insulator augments the thermal energy accessible for electron excitation, which stimulates a greater number of electrons to move into the conduction band, consequently, conductivity is improved

Atomic bonding models play a key role in understanding the electrical properties of insulator and semiconductors. Electrically insulating materials exhibit either ionic or highly covalent interatomic bonding, where peripheral electrons are firmly attached to or jointly held by specific atoms. The electrons in the crystal are strongly confined to specific regions and are not able to move freely. In the context of semiconductors, the bonding is primarily covalent and possesses a relatively low strength, resulting in valence electrons being less tightly linked to the atoms. As a result, these electrons can be more readily expelled through thermal excitation compared to insulators.

4.2.4 Electron mobility

Free electron experiences a force when subjected to an electric field, causing them to accelerate in the opposite direction of the field due to their negative charge. Quantum mechanics states that within a flawless crystal structure, electron in motion do not interact with atomic nuclei. Under these circumstances, the existence of an incident field will cause the free electron to accelerate, resulting in a continuously growing electric current. Nevertheless, it is understood that when a field is applied, a current reaches a steady value immediately, indicating the presence of frictional forces that oppose the acceleration caused by the external field. The scattering of electrons by crystal imperfection's, resulting a force that oppose their motion. such as foreign atoms, missing atom(vacant sites), extra atom, dislocations, and even the atoms thermal motion (Askeland et al., 2003). Every instance of scattering results in the electron losing its kinetic energy and altering its travel direction. Nevertheless, there is a certain amount of electron movement in the opposite direction of the field, and this movement of electric charge is what constitutes the electric current.

The scattering phenomenon is observed as an impediment to the flow of an electric current. The extent of this scattering is described by several parameters, such as the mean electron velocity and the electron transport efficiency. The drift velocity, denoted as υ_d, is the mean velocity of electrons aligned with the applied field of direction .

The relationship between it and the electric field is one of direct proportionality, expressed as follow,

$$\upsilon_d=\mu_e E$$

The electron mobility, denoted as me, is a constant that represents the frequency of scattering events. It is measured in square meters per volt-second (m^2/V. s).

The conductivity of most materials can be represented by the equation.

$$\sigma=n \mid e \mid \mu_e$$

where n is the density of electron available for conduction per unit volume (e.g., per cubic meter) and |e| is the absolute charge of an electron ($1.6 * 10^{-19}$ C). Therefore, the conductance of material is directly related to either the quantity of unbound electrons and the ability of electrons to move.

4.2.5 Electrical Resistivity

The electrical resistivity of materials is an inherent property that shows significant variance among different types of materials, including metals, ceramics, polymers, and semiconductors, due to their distinct atomic and electronic structures. Free electrons in metals, not bound to any specific atom, form a "sea" of delocalized electrons, leading to their low electrical resistivity.

The metallic bonding model allows for the unimpeded passage of electrons throughout the lattice, thereby facilitating efficient electrical conduction. However, lattice defects like dislocations, impurities, and thermal vibrations (phonons) cause electron scattering, which significantly increases the resistivity of metals. With an increase in temperature, the phononic interactions become more prominent, resulting in a rise in resistance (J. Chen et al., 2022). Copper and silver possess remarkably low resistivities, making them extremely effective conductors (Cho et al., 2010). On the other hand, ceramics typically exhibit high electrical resistivity due to their ionic or covalent bonding, which restricts the movement of electrons and impedes their free flow. These strong connections create a rigid and orderly structure, firmly binding electrons to their respective atoms or ions, significantly hindering electrical conduction. While some ceramics, like zinc oxide, can display conductivity at high temperatures under particular conditions (Moezzi et al., 2012), they generally act as insulators. Their high resistance is advantageous in situations that require electrical insulation and stability at high temperatures.

Polymers generally display a significant degree of electrical resistance (Hummel & Hummel, 2001). Covalent bonding in the carbon-hydrogen backbone of most polymers creates a structure that limits the mobility of electrons, inhibiting their free movement. Consequently, polymers generally demonstrate insulating characteristics. Conjugated double bonds, when incorporated into the polymer structure, create conductive polymers that significantly reduce resistance (Bidan, 1992). To increase the number of charge carriers in electrical and optoelectronic applications, substances that donate or take electrons impregnate conductive polymers.

Semiconductors have an electrical resistance that falls between metal resistance and insulator resistance (Rahman, 2014). They show a high level of sensitivity to temperature changes and are highly susceptible to pollutants. A slight disparity in energy levels between the valence band and the conduction band dictates their electrical properties. At low temperatures, semiconductors have a high resistivity because there is a lack of electrons that have enough thermal energy to cross the band gap. With an increase in temperature, more electrons get sufficient energy to move from the valence band to the conduction band, leading to a reduction in resistivity. Specific impurities (n-type or p-type doping) inject additional charge carriers into semiconductors, significantly altering their electrical properties and enabling precise resistivity changes. It is crucial to have the capability to alter or adapt the properties of semiconductor devices, such as diodes, transistors, and integrated circuits, in order for them to function correctly.

4.2.6 Electrical Characteristics of Commercial Alloy

Copper is the most common metal conductor because it is so good at moving electricity. Oxygen-free high-conductivity (OFHC) copper is copper that possessing a limited concentration of oxygen and other impurities. Well-suited for various electrical purpose. Electrical conduction is also achieved with aluminium, even though it is only about half as good at conducting electricity as copper. Even though silver is a better conductor than both copper and aluminum, it is too expensive to be widely used (Pino et al., 2014).

Increasing the mechanical strength of a metal combination without making it much less conductive to electricity is sometimes needed. When doing this, conductivity and hardness are often traded off. This is especially true when solid-solution alloying or cold working is used. g a second phase that does not affect conductivity as much is a familiar way to boost strength with a small degree of influence on conductive behavior. For instance, Precipitation hardening treatment enhances the strength of copper-beryllium alloys, but they are only about five times as good at conducting electricity as pure copper (Lomakin et al., 2019).

When used in places like furnace heating parts, high electrical resistance is a good thing. The spreading of electrons makes it easier for energy to be lost as heat. For these kinds of uses, the materials need to have high melting points, high resistivities, and the ability to stay solid at high temperatures. Because of these qualities, nichrome, which is a combination of nickel and chromium, is often used for heating elements.

4.2.7 Dielectric Behavior

A dielectric material is an insulating substance that cannot conduct electricity and has the ability to form an electric dipole structure. This means that it may create a separation of positive and negative charges at the molecular or atomic level. Dielectric materials are utilized in capacitors due to their interaction with electric fields, which is a result of dipole interactions.

When a capacitor is subjected to a voltage, one plate acquires a positive charge while the other plate acquires a negative charge. This results in an electric field that is directed from the positive plate to the negative plate. The capacitance C is directly proportional to the quantity of charge stored on each plate Q and is inversely proportional to the voltage V applied across the capacitor.

$$C=Q/V$$

The units of capacitance are expressed as the ratio of coulombs to volts, or in farads (F).

Analyze a parallel-plate capacitor with a vacuum-filled space between its plates (as shown in Figure 5).

$$C=\varepsilon_o A/L$$

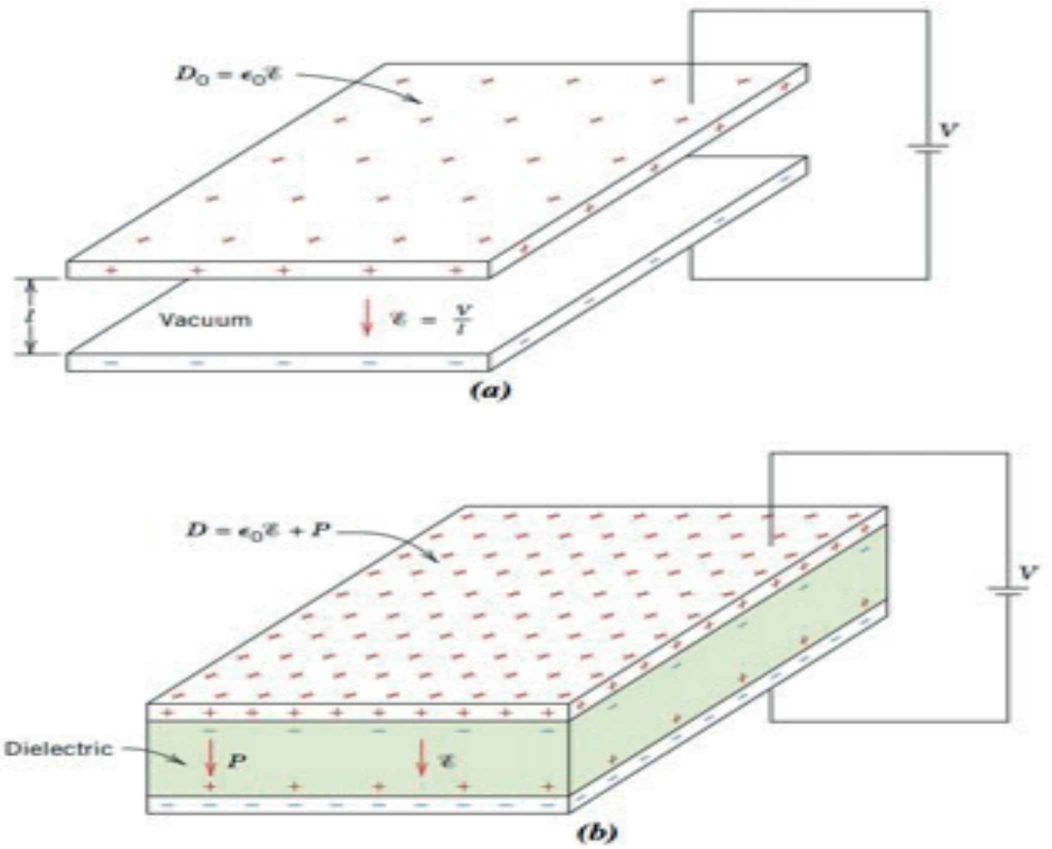


Figure 5. A parallel-plate capacitor (a) under vacuum conditions and (b) with a dielectric substrate. (From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering.)

The capacitance can be calculated using the equation where A is a parameter representing the surface area of the plates and l is the gap width between the plate. The constant ε_o, known as the vacuum permittivity, equal to 8.85 x 1012 F/m, applicable everywhere.

When a dielectric material is placed between the plates in Figure 5,

$$C=\varepsilon A/L$$

The permittivity of this dielectric media, denoted as ε, has a higher value than εo. The relative permittivity (εr), also known as the dielectric constant, is defined as the ratio.

$$\varepsilon_r=\varepsilon/\varepsilon_o$$

The dielectric constant is a value greater than one that quantifies the increase in charge storage capacity when a dielectric medium is inserted within the plates spacing. When designing capacitors, the dielectric constant is a key material property to consider. The table provides the ε_r values for several dielectric materials.

Table 2 Typical Room-Temperature Electrical Conductivities

Material	Dielectric Constant		Dielectric Strength (V/mil)
	60 Hz	1 MHz	
	Ceramics		
Titanate ceramics		15-10,000	50-300
Mica		5.4-8.7	1000-2000
Steatite (MgO-Si02)		5.5-7.5	200-350
Soda—lime glass	6.9	6.9	250
Porcelain	6	6	40—400
Fused silica	4	3.8	250
	Polymers		
Phenol-formaldehyde	5.3	4.8	300-400
Nylon 6,6	4	3.6	400
Polystyrene	2.6	2.6	500-700
Polyethylene	2.3	2.3	450-500
Polytetrafluoroethylene	2.1	2.1	400-500

4.2.8 Other Electrical Characteristics of Materials

Two additional groundbreaking and innovative electrical attributes can be observed in subset of material, are worth mentioning briefly—ferroelectricity and piezoelectricity.

4.2.8.1 Ferroelectricity

An example of a dielectric material is ferroelectric materials, which can become polarized even when there isn't an electric field acting on them. They are like ferromagnetic materials, which can have magnetic qualities that last a long time. The structure of barium titanate, a typical ferroelectric material, shows that ferroelectric materials have permanent electric dipoles. Barium titanate spontaneously polarizes because of the way the Ti+4, O-2   Ba+2 ions are arranged in a repeating unit cell (Chakrabarti, 2011), As demonstrated in Figure 6. The unit cell has tetragonal symmetry, which means that the Ba ions are anchored at the corner points. This results in a cell shape that is a slightly longer cube.

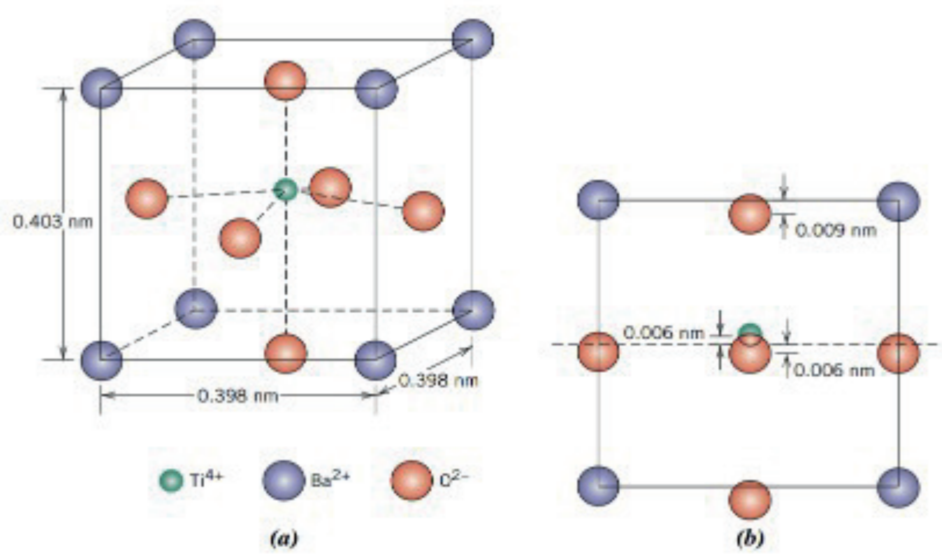


Figure 6. A Barium titanate (BaTiO3) unit cell (a) in an isometric projection, and (b) looking at one face, which shows the displacements of Ti_4 and O_2 ions from the center of the face

The dipole moment in barium titanate is caused by the O^{-2} and Ti^{+4} ions moving out of their balanced places, as depicted in the unit cell's side view. The O^{-2} ions are close to the middles of all six faces, but a little below them. The Ti+4 ions, on the other hand, are farther away from the unit cell's center and higher up. Because of this, each unit cell has a constant ionic dipole moment, which can be seen in Figure 6b. If you heat barium titanate beyond its ferroelectric Curie temperature of 120°C (250°F), the repeating unit cell shapes up into a cube and the ions line up evenly. This change creates a perovskite crystal structure, which takes away the ferroelectric qualities of the material.

In ferroelectric materials, spontaneous polarization happens when permanent dipoles that are close to each other interact and line up in the same way (Krohns & Lunkenheimer, 2019). In barium titanate, the oxide ion O^{-2} and tetravalent titanium ion, Ti^{+4} ions having the same orientation throughout all unit cells that are in a certain volume of the material. Rochelle salt ($NaKCl_4H_4O_6$) is another mineral that shows ferroelectricity (Kandpal et al., 2023). Potassium niobate $KnbO^{-3}$, potassium dihydrogen phosphate (KH_2PO_4), and lead zirconate–titanate (Pb [ZrO_3]) are some of the chemicals that are used (F. Li, 2013). When applied electric fields with relatively low frequencies, ferroelectric materials have very high dielectric constants. At room temperature, the dielectric constant of barium titanate can reach up to 5000. This means that capacitors fabricated from this material can have a significantly reduced size compared to those made from traditional dielectric materials.

4.2.8.2 Piezo magneticity

Piezoelectricity, which is a term that translates to "pressure electricity," is a peculiar phenomenon that is demonstrated by specific ceramic materials and certain polymers. Electric polarization (an electric field or voltage) in the piezoelectric crystal is induced by mechanical strain (dimensional change) from an applied external force (F. Li et al., 2020) (Figure 8). Reversal of the force lead to reversal of the electrical field direction, such as from tension to compression. These materials also exhibit the piezoelectric converse effect, marked via the generation of a mechanical strain in response to an electrical field.

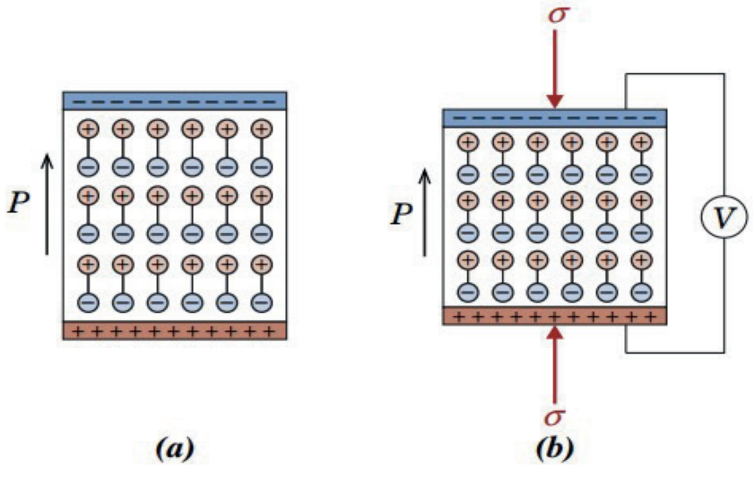


Figure 7-(a) Dipoles within a piezoelectric material. **(b)** A voltage is generated when the material is subjected to a compressive stress.

Additionally, piezoelectric materials can function as transducers, facilitating the conversion of mechanical and electrical energies. In sonar systems, an underwater detection system that utilizes ultrasonic emission and reception to identify and localize submerged objects, including submarine's, piezoelectric ceramics were one of the early applications (Manbachi & Cobbold, 2011). The oscillation of a piezoelectric crystal in response to a high-frequency electrical signal excites a transducer, generates mechanical vibrations that propagate as a pressure waves through the water. These signals are reflected back when they encounter an object. The reflected vibrational energy is then received by another piezoelectric material, which further converts it into an electrical impulse. The range to the reflecting object is calculated based on the time delay between signal transmission and reception.

A recent increase in the utilization of piezoelectric devices has been attributed to the growing interest of consumers in sophisticated devices and the advancements in automation. These components are employed in a variety of contemporary applications, include automotive (wheel electronic balances, seat-belt buzzers, tire tread depth sensor, keyless entry, and crash detection for airbag sensors), computer accessories (microphones, micro actuators for hard disks, speaker and notebook transformers), commercial/consumer (smoke detection system, strain gauges, ultrasonic welding equipment, and precise ink-jet printer heads), and medical (compact insulin pumps, ultrasonic therapy for pain, and ultrasonic phacoemulsification cataract-removal devices) (Yan et al., 2020). Ceramic materials that are piezoelectric entail potassium niobate (KNbO3), lead zirconate (PbZrO3), lead zirconate-titanate (PZT) [Pb(Zr,Ti)O3], and barium titanate (BaTiO3). This characteristic is found in materials with low symmetry and complex crystal structures (Sahu, 2011). Heating above Curie temperature augmented piezoelectric features of polycrystalline specimen's and subsequently reducing it to ambient temperature in a electric field with high field strength.

4.3. Thermal Properties

Thermal property pertains to how a material reacts when exposed to heat. When a solid absorbs heat energy, its temperature increases, and its size expands. If there are temperature differences inside the specimen, the energy can be transferred to colder areas, perhaps causing the experimental material become molten (Ventura & Perfetti, 2014). Specific heat capacity, thermal expansion, and thermal conductivity/heat transfer coefficient are essential qualities that play a crucial role in the practical use of solid material.

4.3.1 Heat Capacity

Heating a solid material, its temperature goes up, signifying that it has absorbed thermal energy. Heat capacity is a measure of how well a material can gain heat from its nearby medium. It quantifies the amount of energy needed to increase the temperature of the substance by one unit. The heat capacity C is mathematically defined by the following expression:

$$C=dQ/dT$$

where a dT temperature change requires energy dQ to create. Heat capacity is normally stated in units of J/mol. K or cal/mol. K per mole of substance. Sometimes used, specific heat (typically indicated by a lowercase c) is the heat capacity per unit mass expressed in a variety of units (J/kg. K, cal/g. K, Btu/lb_m. F).

Depending on the surroundings that accompany heat transmission (Rohsenow et al., 1998), this attribute can be quantified in two ways; one aspect is the capacity for heat at the fixed specimen volume, $C\upsilon$; the other scenario involved uniformed external pressure, C_p. for the majority of solid materials at moderate temperature and lower, the difference is extremely little, C_p is consistently higher than or equal to $C\upsilon$ in magnitude.

4.3.2 Vibrational Heat Capacity

The principle means for thermal energy uptake in most solids is through the amplification of atomic oscillation energy in the atoms. Atoms in rigid materials exhibit continuous, rapid oscillations at exceptionally high frequencies and with comparatively small magnitudes. The vibrations of nearby atoms are connected due to atomic bonding, instead of being independent of each other. The synchronized vibration generates traveling waves in the lattice, as depicted in

Figure 7. These can be considered as elastic waves or sound waves, characterized by extremely high frequencies and small wavelength, that travel through the crystal at sonic velocities. The thermal vibrational energy of a material is comprised of a sequence of elastic waves that exhibit a variety of frequencies and spatial distribution. The energy is quantized, meaning that only specific energy values are permitted. A phonon represents a discrete packet of vibrational energy. A phonon is similar to a photon, which is a quantum of electromagnetic energy. Phonons are sometimes used to refer to vibrational waves. The thermal randomization of delocalized electrons during electrical conduction is caused by the interaction with vibrational waves. Additionally, these elastic waves facilitate energy transfer during heat conduction.

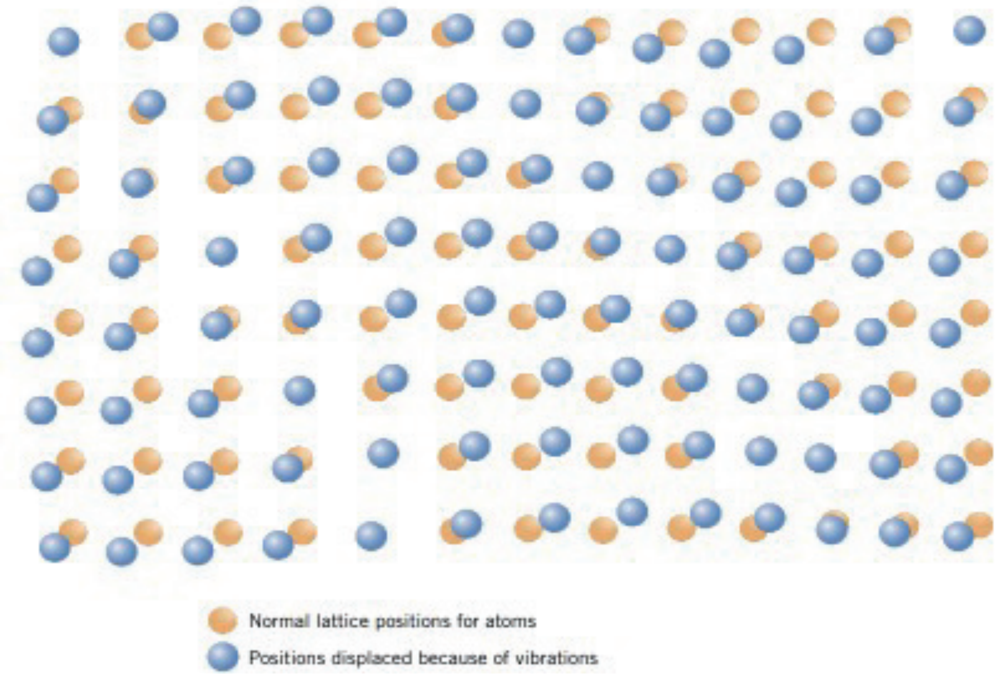


Figure 8 Schematic illustrating the creation of lattice waves within a crystal through atomic vibrations. (Hummel, 1998)

Thermal expansion

Most solid substances undergo expansion when they are heated and contraction when they are cooled. The thermal expansion coefficient of a solid substance represents the length variation with temperature.

$$(l_f - l_o)/l_o = \alpha_l(T_f - T_o)$$

where l_o and l_f represent, respectively, initial and final lengths with the temperature

change from T_o to T_f. The parameter al is called the linear coefficient of thermal expansion.

Thermal expansion occurs because of the uneven curvature of the potential energy through, not because of the higher amplitudes of atomic vibrations as temperature increases (Mittal et al., 2018). If the potential energy curve exhibited symmetry, as shown in Figure8, there would be an absence of any overall alteration in interatomic separation, resulting in the absence of thermal expansion.

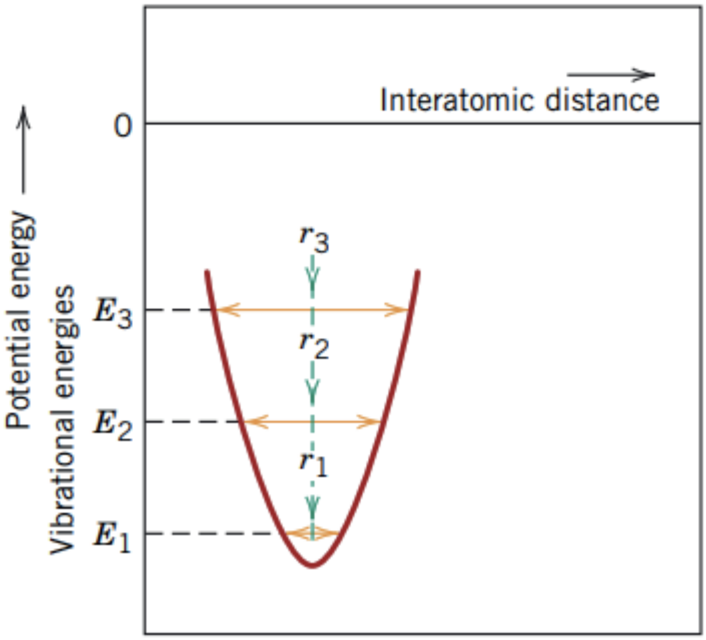


Figure 9 For a symmetric potential energy–versus–interatomic distance curve, there is no increase in interatomic separation with rising temperature (i.e., r1 = r2 = r3). (Adapted from R. M. Rose, L. A. Shepard, and J. Wulff, The Structure and Properties of Materials, Vol. 4, Electronic Properties

The depth and narrowness of the potential energy trough increases as the atomic bonding energy increases for each type of material, including metals, ceramics, and polymers. Consequently, the rise in temperature leads to a smaller increase in interatomic separation, resulting in a reduced value of l. Regarding temperature dependency, the coefficient of expansion becomes more as the temperature increases. For a more extensive compilation of coefficients of thermal expansion.

The linear coefficients of thermal expansion for typical metals vary from approximately 5 x 10^{-6} to 25 x 10^{-6} °C^{-1} (Grimvall, 1999). These values fall within a range of magnitudes of the coefficients for material such as ceramic and polymer. Outlined in the essential information box, various metal alloys with reduced-expansion and managed-expansion properties were created. These alloys are utilized in situations where dimensional stability is necessary despite changes in temperature.

Ceramic materials exhibit high interatomic bonding forces, resulting a reduced thermal expansion coefficient. The reading for thermal expansion habitually vary from approximately 0.5 x 10^{-6} to 15 x 10^{-6} °C^{-1} (Kompan et al., 2008). Non-crystalline ceramics and ceramics with cubic crystal formations exhibit isotropy. Alternatively, when heated, certain ceramic materials exhibit anisotropic behavior, meaning they contract along certain crystallographic orientations while expanding along others. The coefficient of expansion in inorganic glasses is composition dependent. Fused silica, which is a type of high-purity SiO2 glass, exhibits a low coefficient of thermal expansion (Moore & Smith, 2022), measuring 0.4x10^{-6} °C^{-1}. This phenomenon can be attributed to a low atomic packing density, which results in only minor changes in macroscopic dimensions when there is interatomic expansion.

Ceramic materials intended for exposure to temperature fluctuations must possess relatively low and isotropic coefficients of thermal expansion. Alternatively, these fragile materials may undergo fracture due to uneven dimensional alterations caused by thermal shock.

Polymers are large molecules composed of repeating subunits called monomers. Certain polymeric materials exhibit significant thermal expansions when heated, with coefficients ranging from around 50 x 10^{-6} to 400 x 10^{-6} °C^{-1}. Linear and branched polymers have the greatest values due to the weak secondary intermolecular connections and minimal crosslinking (Takata & Aoki, 2018). As crosslinking increases, the expansion coefficient drops. Phenol-formaldehyde and similar thermosetting network polymers, have the lowest values due to the predominantly covalent bonding.

4.4 Optical properties

Optical qualities pertain to the manner in which a substance reacts when subjected to electromagnetic radiation, namely visible light. This chapter commences by examining fundamental principles and concepts pertaining to the characteristics of electromagnetic radiation and its potential interactions with solid materials. Subsequently, it analyzes the optical properties of metallic and nonmetallic substances, with specific attention to their absorption, reflection, and transmission traits (Tilley, 2020). The concluding sections address luminescence, photoconductivity, and light amplification by stimulated emission of radiation (laser), along with their practical applications and the utilization of optical fibers in communications.

The behavior of light as it interacts with a substance is strongly influenced by the material's structure and electrical characteristics. Below is an analysis of how several material categories interact with light:

Metals possess a delocalized electron cloud, which results in their high reflectivity across a wide range of wavelengths. The "sea of electrons" easily engages with incoming light waves, resulting in their reflection. Nevertheless, certain metals have the ability to absorb particular wavelengths, resulting in the manifestation of their distinctive colors. Gold exhibits the property of selectively absorbing blue light, which leads to its characteristic warm yellow color (Guo et al., 2023). The optical characteristics of ceramics differ based on their unique composition and crystal lattice. Certain ceramics, such as alumina (aluminum oxide), seem white and non-transparent because of the phenomenon of light scattering occurring within its microstructure (Sharma, 2013). Furthermore, certain ceramics have the ability to be transparent within specified ranges of wavelengths. Yttrium aluminum garnet (YAG) is transparent to infrared radiation, which makes it valuable for laser applications (X. Li, 2009). The addition of particular elements to ceramics can further alter their light absorption and emission characteristics.

Semiconductors occupy an attractive position between conductors and insulators in terms of their interaction with light. Their electrical conductivity and interaction with light are significantly affected by their band gap, which is the energy difference between the valence and conduction bands. Semiconductors with narrower band gaps have the ability to capture photons with lower energy levels, such as visible light (Klein, 1968). On the other hand, semiconductors with wider band gaps allow visible light to pass through them but can absorb photons with higher energy levels, such as ultraviolet (UV) radiation. The flexibility to adjust their properties makes them suitable for many purposes such as solar cells (which absorb sunlight) or light-emitting diodes (LEDs) that produce distinct hues of light when stimulated by electricity.

Polymers are substances that consist of large molecules made up of repeating subunits called monomers. The optical characteristics of polymers are greatly influenced by their chemical composition and the existence of functional groups. Polymers with transparency, such as polystyrene (often found in throwaway cups), have a molecular structure that is relatively simple and weak intermolecular connections, which enables most light to flow through (Carraher Jr, 2017). In contrast, polymers containing conjugated double bonds, such as those found in certain types of plastics, have the ability to absorb particular wavelengths of light, which causes them to exhibit a colorful look. By incorporating light-absorbing or light-emitting molecules into polymers, their optical capabilities are enhanced, rendering them highly useful in various applications such as optical fibers or organic light-emitting diodes (OLEDs) (Carlos et al., 2007).

Comprehending these connections between the structure and properties enables us to create materials tailored for particular optical uses. By manipulating the structures of materials, such as metallic mirrors and LEDs, a wide range of opportunities in the field of optics can be explored.

4.5 Chemical properties and reactivity

The atomic and molecular structures of materials such as metals, ceramics, polymers, and semiconductors dictate their chemical characteristics and reactivity, ultimately shaping their behavior in different chemical surroundings. These features are essential for their utilization in various sectors and technologies.

Metals have the property of electron loss, which enables them to readily create positive ions. The reason for this characteristic is the low ionization energy and the existence of delocalized electrons in a metallic link. Metals readily engage in oxidation-reduction reactions, as demonstrated by their corrosion behavior (F. Li et al., 2022). Iron undergoes a chemical reaction with oxygen and water to create rust, which is iron oxide. In contrast, highly reactive metals such as sodium react vigorously with water, resulting in the production of hydrogen gas and a hydroxide compound. Metals like platinum and gold have reduced reactivity, which makes them well-suited for applications in jewelry and electronic contacts because of their resistance to oxidation and corrosion. Alloying can alter the reactivity of metals, leading to increased resistance against chemical assault and improved mechanical qualities (Davis, 2001).

Ceramics typically demonstrate exceptional chemical stability as a result of their robust ionic and covalent interactions. Due to their inherent stability, these materials exhibit resistance to the majority of chemical reactions occurring at normal room temperature, hence making them highly appropriate for use in hostile chemical environments. For example, alumina (Al_2O_3) and zirconia (ZrO2) exhibit exceptional resistance to both acids and alkalis (Sequeira et al., 2017). Nevertheless, ceramics exhibit a reaction when exposed to high temperatures. For instance, silicon carbide (SiC) undergoes oxidation at extreme temperatures, leading to the creation of a protective film of silicon dioxide (SiO2) that effectively halts further oxidation (Gupta & Akhtar, 2011). Ceramics are highly valuable in applications such as chemical processing equipment, refractory materials, and biomedical implants due to their inertness, which is essential for withstanding chemical attack.

Polymers exhibit a diverse array of chemical characteristics and reactivities that are contingent upon their molecular structure (Sperling, 2005). Polymers primarily consist of carbon atoms, which can create different functional groups that impact their reactivity. For instance, polyethylene exhibits chemical inertness and resistance to numerous chemicals owing to its uncomplicated hydrocarbon structure, but polyvinyl chloride (PVC) has chlorine atoms, rendering it more chemically reactive (Khanam & AlMaadeed, 2015). Polymers can undergo deterioration through mechanisms such as hydrolysis, oxidation, and photodegradation. For example, polyesters can undergo hydrolytic breakdown when exposed to water (Hosseini et al., 2007). Polymers can have their resistance to chemicals improved by either cross-linking or by adding stabilizers and antioxidants. These additives provide protection against breakdown caused by heat and oxidation (Sperling, 2005).

Semiconductors have distinctive chemical properties as a result of their moderate electrical conductivity and band gap structure (Landsberg, 2016). Silicon, the predominant semiconductor, is unreactive at ambient temperature but can undergo oxidation at elevated temperatures to create a safeguarding layer of silicon dioxide (SiO_2), which is crucial in the manufacturing of semiconductor devices. Doping is a method used to modify the electrical properties of semiconductors without affecting their chemical stability. It involves introducing small amounts of impurities to alter their reactivity. Semiconductors such as gallium arsenide (GaAs) display distinct reactivity in comparison to silicon (Fang et al., 1990). GaAs has the ability to undergo oxidation, resulting in the formation of gallium oxide (Ga_2O_3) and arsenic oxides. These oxides have the potential to impact the performance of electronic devices. The chemical characteristics of semiconductors play a critical role in their functionality within electronic devices, where the chemistry of their surfaces and the stability of their interfaces are essential for ensuring device dependability and performance.

The atomic and molecular structures of metals, ceramics, polymers, and semiconductors have a significant impact on their chemical characteristics and reactivity. Metals often have a tendency to react and corrode, while ceramics are chemically stable and can withstand high temperatures. Polymers have varying levels of reactivity depending on their composition, and semiconductors have controlled reactivity that is crucial for electronic applications. Comprehending these characteristics is crucial for choosing and designing materials for particular chemical surroundings and uses.

5 Structure-Property Relationship

5.1 Influence of material structure on its properties

The interesting dance between structure and characteristics governs the universe of materials. A material's macroscopic behavior is determined by the arrangement of its constituent atoms, including its crystal structure, bonding types, and defect existence. For example, metals are excellent at electrical conduction because of their easily movable electron cloud, which is delocalized (Newnham, 2012). On the other hand, despite their remarkable strength and thermal durability, ceramics—which are frequently bound together by strong ionic or covalent bonds—have poor electrical conductivity. Similar to this, the structure of polymers allows for customization of their strength, flexibility, or certain capabilities due to their chain architecture and intermolecular interactions. Through the understanding of these structure-property correlations, material scientists can create novel materials with characteristics that are ideal for our constantly changing technological requirements.

Structure-property interactions in materials science concern to understanding how the intrinsic structure of a material at different scales (atomic, molecular, micro, and macro) impacts its qualities and behavior under diverse circumstances. The relationship described is essential in various categories of materials, such as metals, ceramics, polymers, and composites (Y. Q. Cheng & Ma, 2011). It plays a critical role in customizing materials for specific purposes. In this analysis, we will explore the connections between the structure and qualities of different material classes, emphasizing the complex relationship between their structural characteristics and their specific attributes.

5.2 Structure-property relationships in different classes of materials:

5.2.1 Metals

Metals are distinguished by their crystalline structures, which are commonly organized in a face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal close-packed (HCP) lattice (Askeland et al., 2003). The mechanical, thermal, and electrical properties of these structures are greatly influenced by the atomic arrangement within them.

The crystal structure and existence of flaws primarily determine the mechanical properties of metals, including strength, ductility, and hardness. Metals such as aluminum and copper, which have a face-centered cubic (FCC) structure, typically demonstrate a notable capacity for plastic deformation and high ductility, allowing them to endure large deformation before breakdown. The reason for this is the abundance of slip systems (planes that allow for dislocation movement) in FCC metals, which makes deformation easier (Wood, 1940).

Unlike FCC metals, BCC metals such as iron and chromium possess a smaller number of slip systems, resulting in greater strength and hardness but reduced ductility (Weinberger et al., 2013). Dislocations, grain boundaries, and other imperfections significantly influence the mechanical characteristics. Work hardening, also known as the increase in strength, caused by plastic deformation, occurs as a consequence of the multiplication and interaction of dislocations within the structure of the metal (Pant et al., 2003).

Metals possess exceptional conductivity for both heat and electricity, which is a result of the presence of their unbound electrons. The density and mobility of these electrons are influenced by the crystal structure. Within pure metals, the crystal lattice possesses a high degree of symmetry, which facilitates the unrestricted movement of electrons. This, in turn, leads to elevated levels of electrical and thermal conductivity. Nevertheless, the presence of impurities and alloying elements can disperse these unbound electrons, resulting in a decrease in conductivity. For instance, the addition of carbon to iron in order to create steel greatly diminishes its electrical conductivity in comparison to pure iron.

Ceramics are commonly made up of ionic or covalent bonding, leading to a structure that is either crystalline or partly crystalline. Ceramics possess distinctive mechanical, thermal, and electrical capabilities due to their robust bonding and intricate crystal structures. They are renowned for their exceptional hardness and inherent brittleness. The presence of ionic or covalent connections results in the formation of a rigid and stable lattice structure, which contributes to their exceptional compressive strength. Nevertheless, the inherent bonding characteristics impede the mobility of dislocations, leading to reduced ductility and increased brittleness. Flaws and microcracks in ceramics can greatly affect their mechanical strength, often resulting in complete failure when subjected to tensile stress (Munz & Fett, 2013).

Ceramics typically have exceptional thermal stability and great temperature tolerance. This phenomenon can be attributed to the robust intermolecular connections within their crystalline arrangement, necessitating a substantial amount of energy for disintegration. In addition, ceramics exhibit lower heat conductivity in comparison to metals, making them advantageous for applications that necessitate thermal insulation. For instance, the application of ceramic tiles on space shuttles serves to shield them from the severe temperatures encountered during re-entry into the Earth's atmosphere.

The electrical characteristics of ceramics exhibit significant variability based on their structure and composition. Certain ceramics, like alumina, possess exceptional electrical insulating properties because they lack free electrons and have bonding that is confined in nature (Sequeira et al., 2017). On the other hand, ceramics such as zinc oxide and barium titanate display semiconducting and dielectric characteristics, respectively. The electrical behavior of these materials is influenced by their crystal structure, which governs the mobility and interaction of charges inside the lattice.

5.2.2 Polymers

Polymers consist of elongated sequences of recurring molecular units known as monomers, and their characteristics are greatly influenced by the organization and interplay of these sequences.

Factors such as chain length, cross-linking, and crystallinity have an impact on the mechanical properties of polymers, including elasticity, tensile strength, and toughness. Amorphous polymers, characterized by their disordered and intertwined chains, typically demonstrate a high degree of elasticity and are capable of experiencing substantial deformation. Cross-linked polymers, characterized by interconnecting chains, exhibit increased rigidity and enhanced tensile strength. Crystalline polymers, which contain organized sections within the material, demonstrate greater strength and resistance to deformation in comparison to their amorphous counterparts.

The structure of polymers also determines their thermal characteristics. Crystalline polymers generally exhibit higher melting points and glass transition temperatures in comparison to amorphous polymers (Takata & Aoki, 2018). Cross-links can increase thermal stability by necessitating a greater amount of energy to disrupt the interconnected chain network. Thermosetting polymers, characterized by their extensive cross-linking, do not undergo melting when heated. Instead, they undergo decomposition, rendering them ideal for use in high-temperature scenarios.

Polymers typically exhibit electrical insulating properties as a result of their limited availability of free electrons. Conjugated double bonds introduced into the polymer chain facilitate electron mobility, leading to the formation of conductive polymers (Ates et al., 2012). The electrical conductivity of the polymer is substantially influenced by its structural characteristics, such as the level of conjugation and the presence of dopants. Conductive polymers, such as polyaniline and polythiophene, find application in a range of electrical devices, including flexible screens and organic solar cells.

Composites are substances created through the amalgamation of two or more distinct elements in order to get qualities that surpass those of the individual constituents. The links between the structure and properties of composites are influenced by the characteristics of the matrix and reinforcement materials, as well as the interface between them.

The distribution, orientation, and interaction of the reinforcing material inside the matrix make a substantial impact on the mechanical response of composites, including strength, stiffness, and toughness. Carbon fiber-reinforced polymers (CFRPs) demonstrate exceptional strength and rigidity as a result of the arrangement of robust carbon fibers within a polymer matrix (Hegde et al., 2019). The interface between the fibers and the matrix is crucial for the transfer of loads and the overall mechanical performance. Inadequate adhesion at the interface can result in detachment and structural failure when subjected to stress.

The thermal characteristics of composites are determined by the thermal conductivities of both the matrix and the reinforcement, as well as the proportions in which they are present. For instance, the incorporation of ceramic particles into a polymer matrix can augment the thermal stability and heat resistance of the composite. The composition of the structure, including the arrangement of various materials, can also generate thermal barriers or channels that are specifically designed for thermal management purposes.

By integrating conductive fillers into an insulating matrix, the electrical characteristics of composites can be deliberately manipulated. For example, the incorporation of carbon nanotubes or metallic particles into a polymer matrix can result in a composite material that exhibits improved electrical conductivity. The percolation threshold, also known as the critical concentration of conductive fillers, required to establish a continuous conducting network, plays a crucial role in determining the electrical characteristics of the composite material. Composites can be produced for specific applications, such as electromagnetic interference shielding and flexible electronics (M. Chen et al., 2014), by precisely regulating the filler content and distribution to achieve desired electrical characteristics.

Gaining insight into the connections between the structure and qualities of materials is essential for the purpose of designing and creating materials that possess the needed characteristics for certain uses. The mechanical and thermal properties of metals are greatly influenced by the arrangement of atoms in the crystal lattice and the occurrence of defects (Pelleg, 2013). Ceramics possess distinctive characteristics as a result of their robust bonding and intricate crystal structures, rendering them well-suited for applications requiring high temperatures and insulation. The molecular structure, chain length, and degree of crystal order of polymers hold a critical impact on their charcteristics properties, allowing for a diverse spectrum of mechanical, thermal, and electrical characteristics. Composites leverage the benefits of many materials to attain exceptional qualities, with the interplay between the matrix and reinforcement being a crucial determinant.

By utilizing the understanding of structure-property correlations, materials scientists and engineers have the ability to customize materials to fulfill the specific requirements of many industries, including aerospace, automotive, electronics, and healthcare. A profound comprehension of this subject matter is crucial for the ongoing progress of material technologies and the creation of inventive resolutions to intricate engineering problems.

The behavior of materials is closely connected to their internal structures, which encompass flaws, microstructure, and phase transitions. These characteristics have significant impacts in different categories of materials, including metals, ceramics, polymers, and semiconductors. Realizing the impact of these factors on the properties of materials is essential in the realm of materials chemistry and engineering.

5.3 Role of defects, microstructure and phase transitions in determining material behavior

5.3.1 Material Imperfections

Defects refer to the presence of flaws or irregularities in the atomic or molecular arrangement of materials. The defects can be categorized as point defects, line defects, and planar defects.

5.3.1.1 Defects at the atomic level

Point defects include vacancies (absence of atoms), interstitials (additional atoms located between regular lattice sites), and substitutional atoms (foreign atoms substituting host atoms). Point flaws in metals have a substantial influence on qualities such as electrical conductivity and strength. For example, the existence of empty spaces can increase the spread of substances, which is crucial for processes such as combining metals and compacting. Point defects in ceramics can impact the ionic conductivity observed in materials utilized for solid oxide fuel cells. Specifically, the presence of oxygen vacancies enables the facilitation of ionic transport (Yasui, 2023).

5.3.1.2 Line Imperfections

Line defects, also known as dislocations, refer to disturbances in the orderly pattern of atoms along a certain line within the crystal lattice. Dislocations play a critical role in influencing the mechanical characteristics of metals (Vitek & Paidar, 2008). They facilitate plastic deformation by facilitating slip, which is the movement of atomic planes past one another. Dislocations' density and mobility have a direct impact on a metal's yield strength and ductility. Methods such as work hardening, which involves raising the density of dislocations, and annealing, which involves reducing the density of dislocations, are used to alter these characteristics.

5.3.1.3 Planar Defects

Planar flaws encompass grain boundaries, twinning boundaries/interfaces, and stacking sequence faults. Grain boundaries, acting as interfaces amidst distinct crystal orientations in polycrystalline materials, have a substantial impact on mechanical behavior (Salvadori & Giacomini, 2013). Metallic materials that have a high concentration of grain boundaries, known as fine-grained metals, generally demonstrate increased strength as a result of the grain boundary strengthening process. In this mechanism, the borders serve as obstacles to the passage of dislocations. Nevertheless, grain boundaries can also serve as locations for corrosion and various types of deterioration (Gertsman & Bruemmer, 2001).

5.3.2 Microstructure

Microstructure refers to the arrangement and characteristics of the small-scale components or features within a material or substance. Microstructure pertains to the arrangement and characteristics of a material at the micrometer to millimeter scale, including properties such as grain size, phase distribution, and the organization of distinct phases (Phillips, 2001).

5.3.2.1 Metals

Thermal and mechanical treatments are used to regulate the microstructure of metals. Steels undergo processes such as quenching and tempering, which result in the formation of distinct microstructures (martensite, bainite, pearlite) that exhibit varying levels of hardness and toughness. By customizing the microstructure, it becomes possible to enhance the qualities of materials to suit certain uses, such as developing high-strength low-alloy steels for building or durable, wearresistant tool steels (Alavi Zaree, 2009).

5.3.2.2 Ceramics

In ceramics, the microstructure is commonly defined by the dimensions and arrangement of grains, as well as the existence of porosity. Sintering methods are employed to manipulate the microstructure, minimizing porosity and augmenting density, hence improving mechanical strength and thermal conductivity. Engineered microstructures in advanced ceramics are utilized in applications that demand exceptional thermal stability and resistance to wear, such as turbine blades and cutting tools (Basu & Balani, 2011).

5.3.2.3 Polymers

The microstructure in polymers pertains to the organization and interplay of polymer chains. Crystallinity, cross-linking, and the use of chemicals are significant factors. Polymers with a high degree of crystallinity, such as polyethylene, exhibit enhanced tensile strength and resistance to chemicals. On the other hand, amorphous polymers like polystyrene provide better transparency and resistance to impact. Cross-linking, as observed in vulcanized rubber, improves the material's elasticity and thermal stability, rendering it appropriate for demanding applications such as tires.

5.3.3 Phase transitions

Phase transitions are changes in the physical state of matter, such as from solid to liquid or from liquid to gas. It refers to alterations in the state or structure of a substance, which frequently result in notable modifications in its properties. Phase transitions play a vital role in alloying and heat treatment processes in metals. For instance, the conversion of austenite to martensite in steel leads to the production of a rigid and fragile state that can be tempered to enhance its resilience. Metallurgists can create materials with precise qualities by studying phase diagrams and the impacts of various alloying elements.

5.3.3.1 Phase transitions in ceramics

Ceramics can undergo phase transitions that result in alterations to their crystal structure and mechanical properties. At high temperatures, zirconia experiences a phase shift from tetragonal to monoclinic, resulting in an increase in volume. This characteristic is employed in hardened zirconia ceramics, where the transition caused by stress can improve the resistance to breaking (Patil & Subbarao, 1970).

5.3.3.2 Phase transitions in polymers

Polymers experience phase changes, such as the shift from a glassy state to a more fluid state and the transition from a solid to a liquid state (S. Z. D. Cheng, 2008). The glass transition point (Tg) signifies the shift from fragile, solid state to more flexible, elastic one. This transition is essential for applications that necessitate adaptability and durability under varying temperatures. The melting temperature (Tm) is crucial for processing methods like extrusion and injection molding, as it ensures that the polymer can flow smoothly without undergoing degradation.

Phase transitions in semiconductors

Phase transitions in semiconductors can impact electrical characteristics. For example, the change from a disordered state to an ordered state of silicon greatly enhances its ability to conduct electricity, making crystalline silicon the preferred material for solar cells and electronic devices. Researchers are investigating phase transitions in materials such as VO2, which have the ability to transition from being an insulator to a metal (Whittaker et al., 2011). These transitions are being studied for potential use in smart windows and electrical switches.

Defects, microstructure, and phase transitions tremendous alter the behavior of materials.

These parameters play a crucial role in influencing the mechanical, thermal, electrical, and optical characteristics of metals, ceramics, polymers, and semiconductors. Materials scientists and engineers can create materials with specific qualities for different uses by modifying their internal structures using different processing processes. Having this knowledge is crucial for the progress of technology and the enhancement of the efficiency and resilience of materials in real-world uses.

6 Applications

Materials science plays a crucial role in various fields by providing essential innovations that enhance functionality and performance. Applications of materials span across numerous industries, driving advancements in technology, healthcare, energy, and environmental solutions as shown in Fig 10. These materials are tailored to meet specific requirements, offering unique properties and benefits.

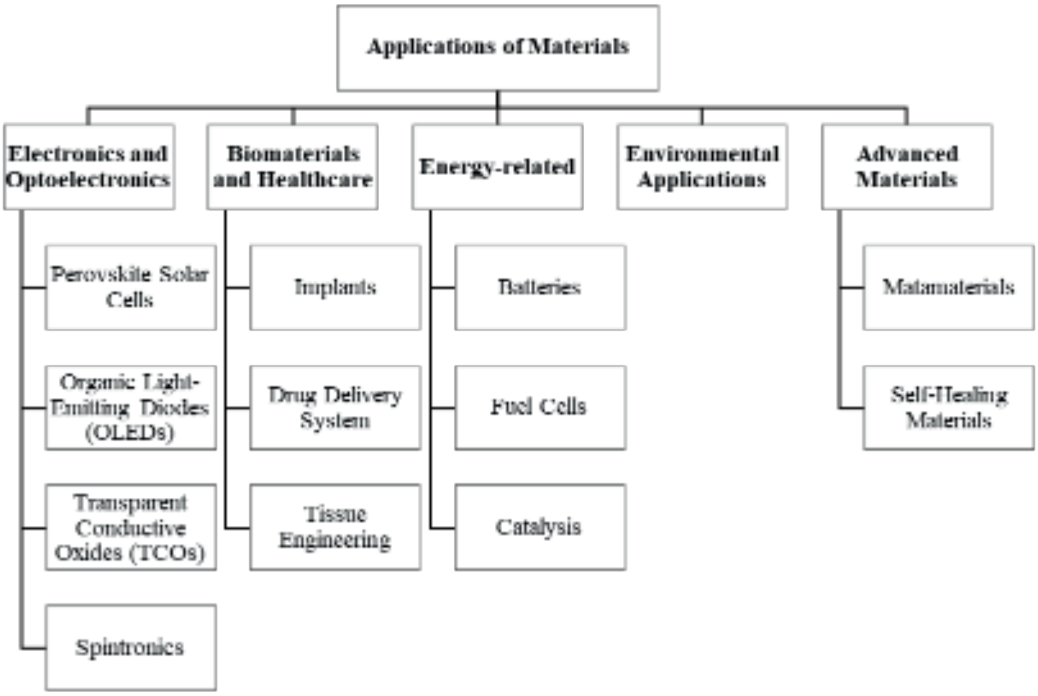


Figure 10 Schematic depicting applications of materials in different fields.

6.1. Electronics and Optoelectronics Applications:

6.1.1 Perovskite solar cells:

The photovoltaic performance of perovskite solar cells, driven by materials chemistry, is largely attributed to their intrinsic properties such as a high absorption coefficient, tunable band gap, large carrier diffusion length, ambipolar carrier-transport ability, and carrier mobility. Organic-inorganic hybrid perovskite (OHIP) materials, with the chemical formula ABX_3 as shown in figure 11, where A is an organic cation, B is an inorganic cation, and X is a halide ion, stand out as efficient and cost-effective candidates for solar cell applications. These materials display exceptional optical and electrical features, including a substantial Bohr radius, feeble binding energy, enhanced dielectric constant, and superior light-absorbing capacity. Typically, a perovskite solar cell consists of an absorber layer, such as $CH_3NH_3PbX_3$, positioned between electron-transport and hole-transport layers. Upon light exposure, the absorber layer generates free charge carriers that traverse through the carrier-transport materials to produce current, with the efficiency of this process depending on the material's thickness. These advanced properties, stemming from meticulous materials chemistry, make OHIP materials pivotal for the development of highly efficient and affordable solar cells

(Suresh Kumar & Chandra Babu Naidu, 2021).

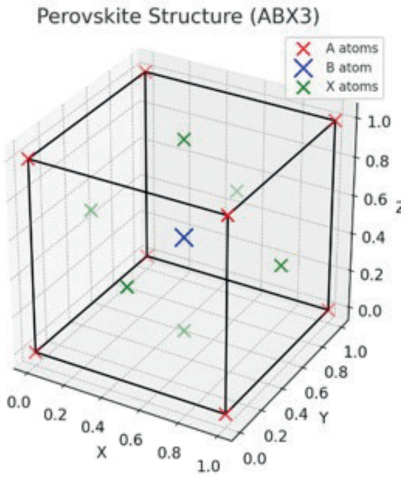


Figure 11 Perovskite Structure.

Miyasaka et al. first showed the application of perovskite materials in solar cells in 2009, using $CH_3NH_3PbX_3$ as a sensitizer in dye-sensitized solar cells (DSSCs), achieving a power conversion efficiency (PCE) of 3.81% (Miyasaka, 2011). Further research has highlighted the potential of organic-inorganic hybrid perovskite (OHIP) materials for solar cell development on account of their favorable inherent properties and the simplicity of their preparation techniques, such as vacuum deposition and atmospheric solution processing. Over a short period, significant advancements have been made, with PCEs improving to as high as 23.3%. The electron-transport layer (ETL) is crucial in perovskite solar cells, traditionally utilizing colloidal thin films of SnO_2, TiO_2, ZnO, or their mesoporous systems. However, these materials often suffer from natural defects and recombination at interfaces. To address these issues, researchers have explored single-atomic layer transition metal dichalcogenides, like MoS_2 and WS_2, as ETL materials due to their virtually defect-free nature and rapid charge carrier transportation capabilities.

The hole-transport layer (HTL) are essential for boosting the efficiency of photovoltaic devices. Extensive research has been conducted on to improving the conductance of HTLs and reducing charge carrier loss at the HTL-perovskite boundary through doping modifications. Among various HTMs, spiro-OMeTAD has been prominent, though its raw form exhibits poor PCE due to insufficient oxidation states. To enhance its performance, dopants such as cobalt complexes and FeCl3, as well as acid additives, have been employed to accelerate the oxidation process and increase hole concentration. Recent innovations include the development of low-cost, dopant-free HTLs, such as fluorinated spiro-OMeTAD-2,7-diamine, which have demonstrated impressive stability and efficiency in CsPbI2Br perovskite solar cells. Additionally, the introduction of CuSeCN films for HTL applications in p-i-n perovskite solar cells has shown promising results, with negligible hysteresis and excellent long-term stability, marking significant progress in the field of high-performance photovoltaic materials (Shi et al., 2020).

To date, most flexible perovskite solar cells have been produced with small surface areas. It is well-documented that as the size of these devices increases, their power conversion efficiency (PCE) tends to decrease due to inevitable film inhomogeneity. Thus, the method used to deposit thin films on a larger scale significantly impacts the performance of these large-area flexible perovskite solar cells. Therefore, it is crucial to develop large-scale deposition techniques for fabricating all layers of flexible perovskite solar cells. Additionally, adopting alternative technologies could further reduce fabrication costs and advance the practical application of these solar cells (F. Chen, 2019).

6.1.2 Organic Light-Emitting Diodes (OLEDs):

The basic structure of an OLED includes a thin organic material layer between two electrodes. The transparent anode is usually indium tin oxide (ITO), while the reflective cathode is metal. When voltage is applied, holes and electrons are injected from the anode and cathode, respectively, into the organic layer (100-150 nm thick). These charges move and recombine to form excitons, emitting photons. The colour of the light depends on the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the organic material. Efficient hole injection requires a low barrier relative to the HOMO level, and effective electron injection requires a low barrier relative to the LUMO level. To enhance performance, low work function metals or stable combinations such as Mg/Ag alloys or LiF with aluminium are used for the cathode (Geffroy et al., 2006). Organic light-emitting diodes (OLEDs) have garnered significant interest due to their potential to revolutionize flat-panel displays by replacing traditional cathode ray tubes (CRTs) and liquid crystal displays (LCDs). The primary advantages of OLEDs in display applications include their self-emissive nature, high luminous efficiency, vibrant full-color capability, wide viewing angles, and high contrast. Additionally, OLEDs offer low power consumption, lightweight designs, large-area display capabilities, and flexibility, making them ideal for diverse mounting options. OLEDs do not require backlighting, polarizers, or diffusers, unlike LCDs, which further enhances their versatility. They are well-suited for various applications such as heads-up instrumentation in aircraft and automobiles, small displays for handheld devices like mobile phones and PDAs, in-car electronics, high-resolution personal communicators, and potentially large flat-panel screens and wall-hanging television display (Wei et al., 2018).

Looking to the future, OLED technology is poised for significant advancements driven by the development of new luminescent materials and innovative fabrication techniques. Researchers are continuously discovering more efficient materials with tunable optical and electronic properties, which promise to surpass the performance of existing options. From a technological perspective, new device configurations and manufacturing methods, such as roll-to-roll processing, are expected to play a crucial role in creating stretchable and biocompatible optoelectronic devices. The efficiency of cutting-edge OLED devices already exceeds that of traditional fluorescent lamps, suggesting that OLEDs will soon replace conventional lighting systems with more efficient alternatives. As research and development progress, we can anticipate even greater advancements in OLED technology, leading to more efficient and versatile lighting and display solutions (Park et al., 2011).

6.1.3 Transparent Conductive Oxides (TCOs):

Transparent conducting oxides (TCOs), a distinctive category of wide bandgap semiconductors, are renowned for their exceptional combination of high conductivity and transparency within the visible spectrum, making them indispensable in photoelectronic. TCOs, such as SnO_2, In_2O_3, ZnO, and CdO, are typically doped with elements like F, In, Ga, Al, Ti, and Cu to enhance their electrical properties. Common n-type TCOs include AZO (Al: ZnO), ITO (Sn: In2O3), and GZO (Ga: ZnO), which are extensively utilized due to their high carrier densities. In contrast, p-type TCOs, such as $CuAlO_2$, $SrCu_2O_3$, and NiOx, have yet to achieve widespread application primarily because of their comparatively lower carrier densities (Z. Wang et al., 2019b). The material chemistry of TCOs also reveals their intriguing permittivity behavior, particularly in the near-infrared (NIR) region where epsilon-near-zero (ENZ) phenomena can induce unique physical effects such as superluminal speeds and large nonlinearities. Moreover, TCOs can excite surface plasmon (SP) modes at interfaces with matched permittivities, enabling the design and fabrication of ultra-compact NIR devices that could potentially replace noble metals in these applications. This versatility underscores the significant role of TCOs in advancing modern optoelectronic and photonic technologies.

Indium tin oxide (ITO), fluorine-doped tin oxide (FTO), aluminum-doped zinc oxide (AZO), and gallium-doped zinc oxide (GZO) are among the widely utilized transparent conducting oxides (TCOs) due to their exceptional combination of high transparency (>95% in the visible range) and low resistivity (as low as 10^{-4} Ωcm). These TCOs find extensive application in various fields, ranging from optoelectronics to metamaterials and ultrafast switches. For instance, ITO, known for its outstanding performance as a TCO, is employed in metamaterials and hyperbolic metamaterials owing to its ultrafast response and low infrared losses. However, to meet specific application requirements, researchers have developed alternative materials based on indium oxide and cerium oxide, such as ICO:H (indium cerium oxide with 1.3% hydrogen doping). Additionally, Al-doped ZnO (AZO) exhibits relatively low infrared losses compared to other TCOs, making it suitable for plasmonic applications in the communication band. Furthermore, beyond cationic doping, oxygen can also be substituted by other anions, as seen in the case of fluorine-doped tin oxide (FTO), which has been widely used in low-emissivity windows since the 1970s (Visaveliya et al., 2022). Recent advancements have explored the surface plasmon properties of FTO, particularly in the mid-infrared region, showcasing its potential for various applications such as optical resonators and electro-optic modulators.

Moreover, emerging materials like graphene and spinel-type oxides are gaining attention for their unique properties in transparent conductivity. Graphene, a two-dimensional material with ultra-fast carrier mobility, is utilized in transparent electrodes due to its metal-like behavior and ability to support surface plasmons. Its applications extend to optical switches, resonators, and metamaterials in the mid-infrared and terahertz ranges. Similarly, spinel-type oxides exhibit high carrier densities and tunability, making them crucial in photonics applications where few p-type semiconductors can excite surface plasmons in the near-infrared region. For instance, Ga2FeO4 (GFO) nanocrystals demonstrate localized surface plasmon resonance (LSPR) around 1000 nm, with carrier densities that can be tuned to support both p-type and n-type behavior, further highlighting the versatility of spinel-type oxides in photonics and related fields. These advancements in material chemistry pave the way for the development of innovative TCOs with enhanced properties and diverse applications in optoelectronic devices and beyond (Z. Wang et al., 2019a).

6.1.4 Spintronics:

Spintronics stands as a burgeoning domain poised to shape the landscape of future nanoelectronics devices, aiming to curtail power consumption while amplifying memory and processing capabilities. These innovative devices harness the spin degree of freedom inherent in electrons and/or holes, which may also engage with their orbital moments. Through the deployment of magnetic layers acting as spin-polarizers or analysers, or through spin-orbit coupling mechanisms, control over spin polarization is achieved in these systems. Additionally, spin waves emerge as viable conduits for transporting spin current within these devices (Ohno et al., 2016). Spintronics holds promise for diverse applications, extending into energy harvesting, bioinspired computing, and quantum technologies. From nanoscale spintronics sensors that enhance hard disk drive density to magneto resistive random-access memories (MRAMs) poised to replace flash memories, static random-access memories (SRAM), and dynamic random-access memories (DRAM), spintronics offers multifaceted solutions for memory and processing enhancements (Ohno et al., 2016). Moreover, spin current utilization and torque enable the development of oscillators and information transmission sans current, further expanding the scope of spintronic applications.

The advent of non-local spin-valves has enabled the detection of spin Hall and inverse spin Hall effects, demonstrating lateral device configuration advantages. Additionally, materials exhibiting a large anomalous Hall effect, such as non-collinear antiferromagnetic (AF) materials like Mn5Si3 and Mn3Sn, open avenues for innovative spintronic devices. The continuous exploration of novel materials, efficient charge-to-spin and spin-to-charge current conversion mechanisms and controlled magnetic property manipulation through voltage application hold significant promise for future spintronic advancements, offering potential breakthroughs in fields like IoT, ultralow-power electronics, and high-performance computing (HPC).

In the next decade, the success of magneto resistive random-access memories (MRAM) is expected to influence the widespread adoption of spintronics across various technologies. Ongoing research on innovative materials, efficient current conversion mechanisms, and precise spin manipulation in semiconductors is crucial for furthering spintronic applications. Moreover, the exploration of oxide materials, characterized by their crystallinity akin to semiconductors, may offer new avenues for future spintronic devices, potentially capitalizing on the advantages conferred by crystalline structures. As such, material research remains pivotal in shaping the trajectory of spintronics over the next 13 years (Hirohata et al., 2020).

6.2 Biomaterials and Healthcare Application:

6.2.1 Implants:

Advances in medical sciences and engineering have led to the development and widespread use of implants in the human body, with research dating back to the 1890s resulting in innovations such as pacemakers and defibrillators. Bioimplants are specialized devices designed to replace, support, or enhance natural organs. Their development has focused on biocompatibility and the ability to replicate the functions of natural body parts. Today, bioimplants are utilized in a wide array of applications, including brain and neural implants, sensory implants, spinal implants, organ stimulation implants, subcutaneous implants, dental implants, cosmetic implants, and other structural implants such as stents, braces, rods, heart valves, bones, pins, hip prostheses, and knee replacements (Prakasam et al., 2017).

Bioimplants can be categorized based on their material type, which includes bioceramics, polymers, and metallic biomaterials. Bioceramics, particularly those based on calcium phosphates, are well-regarded for their similarity to natural bone and are used extensively in tissue engineering applications. These materials are available in various forms such as dense, porous, bimodal, and amorphous states. Recent advancements have focused on bioresorbable bioceramics, which degrade over time and are replaced by natural tissue. Ideal bioactive ceramics are biocompatible, osteoconductive, osteoinductive, enable angiogenesis, and are biodegradable. Common applications of bioceramics include dental, periodontal, cochlear, maxillofacial, and spinal disc implants (Prakasam et al., 2017).

Polymers are also widely used as bioresorbable materials for clinical applications such as bone implants, sutures, and drug delivery devices. Polymers like PGA, PLA, and PLGA are preferred for their non-corrosive properties and ability to be molded into various shapes. However, they may experience a loss of mechanical strength over time due to degradation. Magnesium-based implants are another emerging area, offering potential benefits in orthopedic and cardiovascular applications. Titanium alloys are known for their excellent integration with bone tissue and are used in pacemaker cases, implantable drug pumps, screws, and dental implants (Meffert et al., 1992). The development of metallic-polymer composites continues to evolve, with materials like Mg/PCL showing promise due to their compressive strength and biocompatibility. Despite these advances, there remains a need for further research to optimize the performance and safety of biodegradable and bioresorbable implants in medical applications.

6.2.2 Drug Delivery Systems:

Biodegradable polymeric biomaterials have significantly advanced drug delivery applications and continue to refine pharmaceutical and biomedical fields. Polymers, derived from the Greek words "poly" (many) and "mers" (parts or units), play a crucial role in colloidal drug carrier systems due to their compatibility with body tissues and controlled release kinetics. These systems, which include small particles, optimize drug loading and release properties. Non-toxic, biodegradable, and biocompatible polymers are highly advantageous, especially those capable of crossing the blood-brain barrier and providing protection against chemical degradation. Smart polymers, which respond to environmental stimuli like temperature, pressure, and pH changes, are particularly beneficial for targeted drug delivery, enhancing the precision and efficacy of treatments (Bae, 2002).

Polysaccharides, composed of monosaccharide units joined by O-glycosidic linkages, are stable, hydrophilic, non-toxic, and biocompatible, making them ideal for drug delivery and targeting. Commonly used polysaccharides include hyaluronic acid, chitosan, glycol chitosan, pullulan, dextrin, and alginate. Chitosan and its derivatives, like glycol chitosan, self-assemble into nanoparticles under certain conditions, facilitating multifunctional drug delivery systems. Additionally, polymers such as poly (lactic-co-glycolic acid) (PLGA) have gained popularity due to their biocompatibility, biodegradability, and tunable mechanical properties. These polymers are used in various drug delivery systems, including hydrogels, liposomes, and nanoparticle-based carriers, offering controlled and sustained release of therapeutic agents (Prajapati et al., 2019).

Synthetic biodegradable polymers, such as polyurethanes, polycarbonates, and polyanhydrides, have garnered attention for their biocompatibility and mechanical properties, making them suitable for medical devices and drug delivery systems. Polyurethane-based materials, known for their flexibility and biodegradability, are used in tissue repair and drug delivery applications. Polycarbonates, like poly (trimethyl carbonates) (PTC), exhibit slow degradation and high flexibility, ideal for controlled drug release. Biodegradable polymeric nanocarriers are particularly promising for improving the efficacy of drug, protein, peptide, DNA, or RNA delivery. These nanocarriers offer potential for various drug delivery routes, including oral, parenteral, nasal, and transdermal, as well as for gene delivery and cancer therapy. The development of biodegradable polymers continues to evolve, aiming to enhance their degradation patterns and minimize toxicity, thereby advancing biomedical applications and improving therapeutic outcomes (Zahin et al., 2020).

6.2.3 Tissue Engineering:

Tissue engineering and regenerative medicine is a dynamic field that merges expertise of materials sciences, life sciences, and engineering to create tissue-engineered grafts that can restore and replaced missing or severely damaged tissues and organs. These grafts, composed of scaffolds and biochemical cues from support cells and growth factors, are promising substitutes for donor organs. A biomaterial-based scaffold is crucial in tissue engineering, providing mechanical support, a conducive environment that encourages cell survival, expansion, and maturation, and facilitating tissue repair and regeneration. Ideal scaffolds possess specific architectural, mechanical, physicochemical, and biological properties. They must be porous architecture to support cell attachment and migration, have shape stability and mechanical properties similar to the defect tissues, be biocompatible and biodegradable, and exhibit low immunogenicity (Yi et al., 2017).

The development of tissue-engineered scaffolds that can produce viable artificial tissues and organs is a critical goal of tissue engineering and regenerative medicine. These scaffolds provide mechanical stability for regenerating tissue, integrates biochemical signals, guidance and cellular direction and tissue remodeling, and create an optimal microenvironment for tissue repair and regeneration. Ideal scaffolds must execute various stipulations, including biomechanical properties, surface topology, biodegradability, biocompatibility, and diffusion capacity. At this juncture, tissue-engineered scaffolds molded from synthetic biopolymers and naturally derived biomaterials are frequently employed, as these materials can be tuned to optimize physicochemical performances (Y. Zhang et al., 2020). One of the key benefit of extracellular matrix (ECM) scaffolds is their reduced immunogenicity, reducing the risk of adverse immune responses and chronic inflammation, which can limit the clinical application of allotransplantation and xenotransplantation.

Numerous ECM analogues have been developed to support cellular function, including synthetic scaffolds derived from polymeric substrates, hydrogels synthesized from crosslinked hydrophilic polymers, ceramic-based scaffolds, and natural biopolymers. These analogues mimic physiological 3D microenvironments but often lack the complex biochemical properties and 3D ultrastructure of native mammalian ECM. Advances in proteomic and bioinformatics techniques have improved the understanding of ECM components, facilitating the design and fabrication of biomaterials that meet the anatomical and physiological needs of native tissues. Decellularization of native tissues and organs has enhanced the application of ECM biomaterials, promoting in situ tissue remodelling and serving as templates for whole-organ engineering. Ongoing improvements in decellularization techniques and recellularization strategies will further advance the biocompatibility, endothelialisation, and functional integration of ECM scaffolds, highlighting the promising future of ECM biomaterials in tissue engineering and regenerative medicine (Jammalamadaka & Tappa, 2018).

6.3 Energy-related Applications:

6.3.1 Batteries:

Materials chemistry plays a crucial role in the production and optimization of electrode materials for energy storage devices, such as lithium-ion batteries and supercapacitors. These devices rely on the conversion of chemical energy into electrical energy, with the energy stored in the chemical bonds of electrode materials. Key performance indicators for these devices include energy density, power density, and safety, all of which are heavily influenced by the electroactivity, electron/ion conductivity, and structural stability of the electrode materials. Critical issues that need to be addressed in electrode materials include energy density, the kinetics of ion and electron transport, storage and reaction, and structural stability during electrochemical reactions (K. Chen & Xue, 2016).

Electrode materials are the fundamental components that determine the performance of batteries and supercapacitors. High-energy electrode materials, capable of multiple-electron transfers per metal cation, have driven the evolution from lead-acid, nickel-cadmium, and nickel metal hydride batteries to modern lithium-ion batteries. The high energy density of lithium-ion batteries has revolutionized portable electronics and the electrification of transport. Among emerging technologies, lithium-sulfur (Li-S) batteries are gaining attention due to their high theoretical energy density and the abundance and low cost of sulfur. However, challenges such as the insulating nature of sulfur and lithium sulfide, the dissolution of intermediate lithium polysulfides, volume changes during cycling, and the formation of a non-uniform solid electrolyte interface must be addressed.

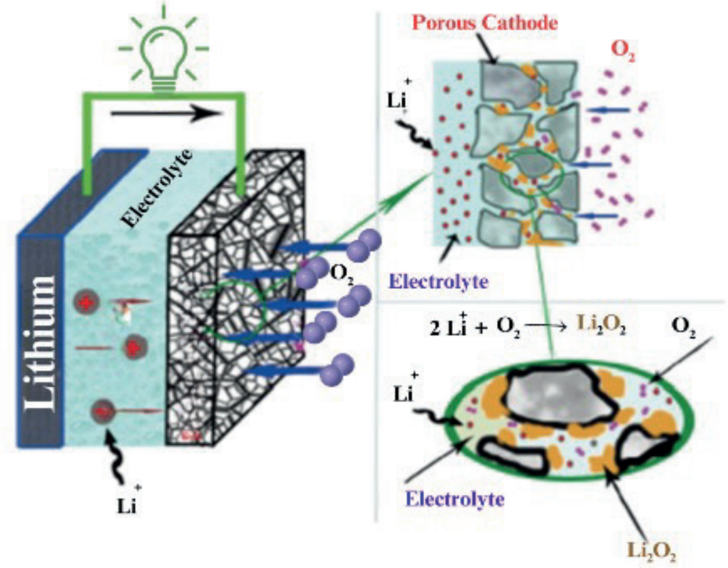


Figure 12 Schematics of aprotic lithium-oxygen battery and the cathode electron structure

Electrolytes in Li-S and Li-O2 batteries play a critical role in ion transport and overall battery performance. In Li-S batteries, the dissolution of polysulfides and the shuttle effect significantly impact performance, necessitating the development of advanced electrolyte systems. Additionally, carbon-based electrode materials, such as graphite and graphene, are extensively used in lithium-ion batteries as shown in figure. 12 and supercapacitors due to their favorable properties and environmental benefits. Advances in materials chemistry have facilitated the design of electrode materials with enhanced electroactivity and stability, combining experimental and computational approaches to optimize their structure and function. The emergence of hybrid devices like supercapatteries, which combine the properties of batteries and supercapacitors, highlights the ongoing innovation in the field driven by materials chemistry (L. Li et al., 2017).

6.3.2 Fuel Cells:

The escalating interest in efficient yet reasonably priced renewable energy has driven widespread attention in the commercial advancement of fuel cell technology, particularly as a mock-up for combustion-based energy origins. Among the various fuel cell technologies, direct methanol fuel cells (DMFCs) have gained prominence due to their ability to utilize methanol, an abundant and easily stored liquid fuel. Methanol can be readily produced predominantly from natural gas and, to a lesser degree, sustainable energy sources such as biomass, and it boasts a high power density of 6000 Wh/kg. Additionally, DMFCs operate at relatively low temperatures (40-80°C), making them suitable for implementation in the automotive, consumer electronics, and portable power generation (Koenigsmann & Wong, 2011).

DMFCs are uniquely advantageous compared to hydrogen-based fuel cells because of their use of liquid methanol, which simplifies storage and transportation. However, despite these advantages, the commercialization of DMFCs has been hindered by their suboptimal efficiency rating and the sky-high cost of precious metal catalysts, such as platinum. Efforts to reduce platinum loading and improve utilization without compromising electrochemical activity have led to the exploration of alloying platinum with transition metals and using non-noble metal-based electrocatalysts like tungsten trioxide and tungsten carbide. These materials have shown promise due to their high electrical conductivity and stability in acidic media, but further development is necessary to enhance their catalytic performance for widespread use (Koenigsmann & Wong, 2011).

Recent advancements have focused on the potential of one-dimensional (1D) nanostructured electrocatalysts to address the inherent limitations of traditional nanostructured catalysts. The unique structural and electronic properties of 1D nanomaterials, such as preferential disclousure of smooth, impeccable, reduced-energy crystal facets, can enhance both the methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR). Additionally, these nanostructures exhibit improved stability against annulment and ripening, modifying to suit for long-term use. However, there remains a need for scalable, environmentally friendly synthesis techniques and further investigation into the structure-property correlations of these materials to fully realize their potential in upgrading the cost-efficiency and execution of DMFC technology (Maslova et al., 2023).

6.3.3 Catalysis:

Nano-catalysts and catalytic enzyme hold significant aptitude in bioenergy output, an area that bridges biotechnology and renewable energy. These process catalysts are crucial for synthesizing bioenergy by enhancing selectivity, caliber, and yield potential. Nanoparticles, both inorganic and organic, employed to boost biofuel production, proving to be consistent and cost-effective for enzyme immobilization. This immobilization amplify biofuel harvesting in microorganisms. Integrating enzymes with nanotechnology enhances the resilience, functionality, efficiency, and agility of enzymes in bioprocessing. In biodiesel fabrication, nano-catalysts serve as process reactants and catalysts, improving turnover rate, mass transfer, and thermal and physical traits (Cui et al., 2018). The synergistic response of nano- and enzymatic catalysts offers innovative solutions for bioenergy production, addressing environmental issues such as greenhouse gas emissions and climate change. Nano-catalysts, with their high surface area-to-volume ratios, significantly enhance catalyzed transformation, optimizing biodiesel production and improving product quality. Enzymatic catalysts, empowered by nature's efficiency and targetedness, enable the efficient conversion of biomass feedstocks into bioethanol and biodiesel. This combination of catalysts reduces waste and energy consumption in biofuel production, driving sustainable energy innovation for homes, automobiles, and industries. The ongoing development of extremely dynamic, meticulous, and tailored nano-catalysts is crucial to address the need of industrial-scale biofuel manufacturing, thereby facilitating a shift toward sustainable energy landscape (K. Chen & Xue, 2016) (Wong, 1989).

6.4 Environmental Applications:

Water is a fundamental necessity for all living organisms. However, historical cultivation, globalization, and industrialization have led to significant water contamination, negatively impacting environmental health, particularly aquatic ecosystems. Various pollutants, such as dyes, heavy metals, and microplastics, contribute to water pollution. Dyes, widely used in textiles, food, cosmetics, and medicine, are a major concern as approximately 50% of these dyes are lost in the effluent stream, which is often used for activities like washing and bathing or discarded into rivers, lakes, and canals. Even a small concentration of dye, as low as 1 mg/L, can cause undesirable coloration, making the water unfit for consumption. Heavy metals from industrial processes and microplastics from discarded plastic products also pose significant threats. Microplastics enter the ocean through rain and river movements, leading to seawater pollution and causing digestive blockages, metabolic disorders, and reproductive issues in aquatic organisms. The complex nature of these pollutants disrupts ecological systems, emphasizing the need for effective remediation and treatment methods (Maheshwari et al., 2021).

Biomaterials have emerged as environmentally friendly alternatives for water purification due to their cost-effectiveness, availability, non-toxicity, and excellent performance. Nowadays, the use of biomaterials like chitosan, Luffa, sisal, and hydroxyapatite is highly effective in water and wastewater technology for removing dyes, heavy metals, and pharmaceuticals. Hydroxyapatite, a phosphate material found in bones and teeth, has proven useful in bone tissue engineering, biological delivery systems, and bioactive coatings. Its excellent properties have also made it valuable in environmental pollution control. Hydroxyapatite can be sourced from materials like seashells, sea corals, and various bones, offering versatile applications in removing pollutants (Mamba et al., 2021). Chitosan, a biopolymer known for its biodegradability, non-toxicity, and outstanding chelation behavior, has been extensively studied for dye and heavy metal ion removal. Its ability to be shaped into various forms, such as flakes, powders, beads, gels, films, and porous particles, enhances its practical applicability. The chemical structure of chitosan makes it highly relevant for dye removal applications. Hydrogels, with their porous three-dimensional network structure, offer a high specific surface area and contain many polar functional groups, providing active sites for heavy metal adsorption. Hydrogels can swell significantly in aqueous solutions, increasing their contact area with contaminants and improving adsorption efficiency (Yang et al., 2021). Microplastics, a byproduct of discarded plastic products, pose a significant threat to the water environment. These small plastic fragments enter the ocean through rain and river movements, leading to seawater pollution. Microplastics are ingested by aquatic organisms, causing digestive blockages, metabolic disorders, and reproductive issues. The trend of plastic emissions suggests that, if unmitigated, the amount of plastic in the ocean could surpass that of fish. Technologies to treat microplastics in rivers are urgently needed to prevent further marine ecosystem pollution. Additionally, microplastics can adsorb and enrich discharged drugs like antibiotics, exacerbating their environmental hazards (Hale et al., 2020).

Various techniques, including adsorption, filtration, membrane technology, and advanced oxidation methods like ozonation and photocatalysis, have been developed for wastewater treatment. Membranes are preferred over conventional water treatment processes due to their effectiveness and limited environmental hazard. They act as barriers, selectively allowing water molecules to pass through while preventing impurities. However, most commercial membranes are made from non-biodegradable polymers, which are susceptible to fouling. To address this, innovative designs like self-cleaning ultrafiltration membranes incorporating TiO2 nanoparticles and polyvinyl alcohol hydrogels have been developed. These membranes offer improved hydrophilicity, self-healing properties, and enhanced performance, making them promising materials for sustainable wastewater treatment (Yang et al., 2021).

6.5 Metamaterials and Self-healing Materials:

Artificially structured metamaterials have revolutionized the manipulation of electromagnetic waves, enabling functionalities such as the cloak of invisibility based on coordinate transformation. Unlike other cloaking methods, which are typically limited to subwavelength objects, the transformation method allows the design of devices that render macroscopic objects invisible. This approach is not sensitive to the object being cloaked, and significant strides have been made in designing non-magnetic cloaks operating at optical frequencies. These metamaterials and plasmonic media have garnered significant attention due to their potential applications in various fields, including cloaking. They enable sub-wavelength focusing and "perfect lensing," opening exciting possibilities in camouflaging, low-noise measurements, and non-invasive sensing and probing in medicine, biology, and optics (Monticone & Alu, 2017). At optical frequencies, the combination of metamaterials with plasmonics and nanophotonics has advanced the control of light propagation, radiation, localization, and scattering. Metamaterials enable unprecedented wave manipulation, such as creating artificial plasmas at microwaves, artificial magnetism in optics, and negative refraction. These capabilities are not only paving the way for fascinating research directions but also have direct applications in electromagnetic and optical technology. For instance, directive scatterers and nanoantennas driven by localized nanosources can be used in point-to-point wireless communication at the nanoscale, nano-sensing, nanoscale spectroscopy, and the realization of directive and efficient single-photon emitters (Cai et al., 2007) (Alu & Engheta, 2008).

Product commercialization in industries typically follows key milestones: idea generation, laboratory implementation, pilot line upscaling, and industrial applications. Currently, self-healing materials are mostly in the early stages of development, either at the preliminary or product level, with their broader applications yet to be realized. However, their future potential spans nearly all industries. Presently, the automotive, aerospace, and construction industries are leading the way in applying these materials. For instance, Nissan has commercialized a self-healing clear coat for car surfaces, known as "Scratch Guard Coat," which repairs minor scratches autonomously. Similarly, Bayer Material Science has developed self-healing polyurethane clear coats for aesthetic maintenance. The aviation industry anticipates the use of self-healing composites for aircraft, while the construction industry looks forward to self-healing concrete and corrosion-resistant coatings for long-term structural integrity. Additionally, biocompatible self-healing materials are poised to extend the service life of medical implants like artificial bones and teeth. These advancements demonstrate the broad and transformative potential of self-healing materials across various sectors (Ma et al., 2020).

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ADVANCES IN CATALYSIS

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The ability to speed up chemical processes without consuming itself is known as catalysis, and it is essential to many scientific and industrial uses. This chapter presents an in-depth analysis of catalysis, starting with an overview of its basic concepts and workings. It highlights significant discoveries and technical developments while examining the historical viewpoints and significant turning points that have defined the field. The principles of catalysis are explained, including surface chemistry, reaction kinetics, and the function of catalysts in increasing the rate of reaction and selectivity. The latest advancements in the study of materials, nanostructures, and customized surface functions that maximize catalytic performance are the main topics of discussion while examining recent advances in catalyst design. Computational method advances are investigated as essential instruments for catalyst design and discovery, utilizing quantum physics and simulations of molecules to forecast. Zeolites, metallic-organic frameworks (MOFs), and catalysts with one atom are examples of novel catalytic structures and materials that are explored for their special qualities and potential uses in a variety of sectors. The chapter explores catalysis for environmentally friendly chemistry, with a focus on ecologically friendly techniques, renewable feedstocks, and green catalytic processes. Applications of catalysts in energy conversion, such as fuel cells, photocatalysis, and hydrogen production, demonstrate how important catalysts are to the development of sustainable energy solutions. To address new areas like bio catalysis, artificial based on intelligence catalyst development, and dynamic catalytic systems, recent trends and potential futures in catalysis are examined. This comprehensive evaluation of catalysis's prospects and challenges—such as deactivation of catalysts, scalability, and economic viability—offers ideas on removing obstacles and promoting innovation in the sector.

1- Introduction to Catalysis

A chemical reaction can be accelerated by a catalyst (Cuccu et al., 2023). It accomplishes this by bonding with the molecules undergoing the reaction and letting them react to produce a product that separates from the catalyst and remains unchanged, making it ready for the subsequent reaction (Zaera, 2021). The catalytic reaction can be thought of as a periodic event in which a catalyst takes part and, at the end of the cycle, returns in its original form (Shetty et al., 2020). Let's look at the catalytic reaction that produces product P when two molecules, A and B, come together (see Fig. 1.1). The binding of molecules both A and B to a catalyst initiates the cycle. Then, within this complex, A and B react to produce a product P that is likewise linked to catalyst. Product P detaches from the catalyst in the last stage, returning the reaction cycle to its initial condition (Zaera, 2021).

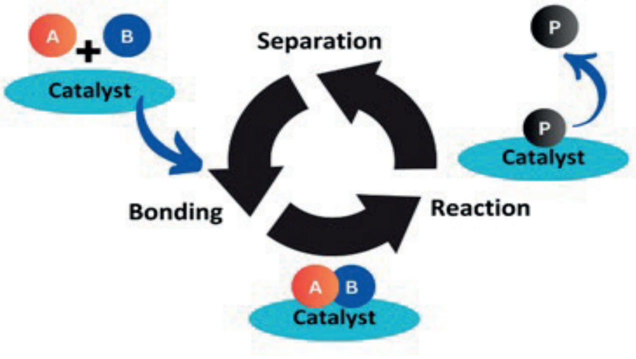


Figure 1.1. Reactant molecules attach to a catalyst, where they undergo a reaction. Afterward, the product separates from the catalyst, freeing it for use in the subsequent cycle. This is the basic process of every catalytic reaction (Zaera, 2021).

We must examine the possible energy graph in Fig. 1.2, which contrasts the catalytic and non-catalytic reactions, to understand how the catalyst quickens the reaction (Takigawa et al., 2018). The picture represents the well-known method of visualizing the Arrhenius equation for the non-catalytic reaction (Subramanian & Ragula, 2020), which happens when A and B meet with enough energy to cross the activating barrier in Fig. 1.2. Between the two reactants, A and B, and the product, P, there is a variation in Gibbs free energy of DG. The spontaneous bonding of reacting agents both A and B to a catalyst initiates the catalytic process (Takigawa et al., 2018). As a result, the complex forms in an exothermic manner, lowering free energy. The reaction between both A and B as they are attached to the catalyst then happens. Although there is an activation energy for this phase, it is far less than the activation energy for the uncatalyzed process. In the final step, an endothermic separation of product P from the catalyst occurs (Takigawa et al., 2018).

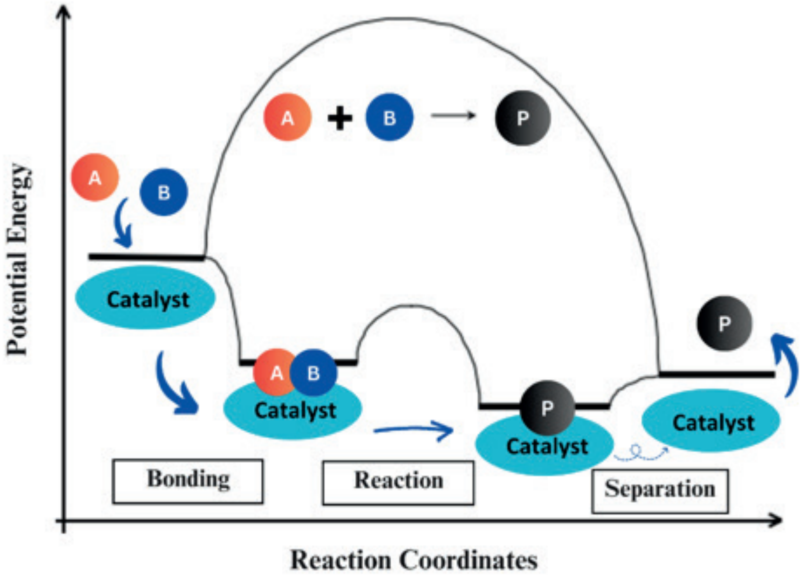


Figure 1.2. Diagram showing the potential energy generated by a heterogeneous catalytic process with a solid catalyst, gaseous reactants, and products. It should be noted that while the obstacles in the catalytic approach are significantly smaller, an uncatalyzed reaction must overcome a significant energy barrier (Takigawa et al., 2018).

Several significant points are illustrated by the energy diagram in Figure 1.2:

- The catalyst provides the reaction with a different, clearly more difficult, but energetically far more advantageous path (Chintawar et al., 2021).

- The catalytic reaction has a much higher rate because its activation energy is substantially lower than that in the uncatalyzed process (Etim et al., 2023).
- The catalytic reaction's total change in free energy is equal to that that occurs in the uncatalyzed reaction. Therefore, an equilibrium constant of the total reaction from A + B to P is unaffected by the catalyst. A catalyst cannot therefore reverse the thermodynamic unfavourability of a process. Catalysts alter the thermodynamics but not the kinetics (Aprahamian & Goldup, 2023).
- The catalyst has the same amount of acceleration effect on the forward and reverse reactions. Put another way, a catalyst that speeds up the process of forming P from both A and B will also speed up P's breakdown into A as well as B (Noor et al., 2022).

It is currently readily apparent that there are certain situations in which using a catalyst in conjunction with reactants or products would not work:

- In contrast, if the bond between the catalyst and one of the reactants, say A, is too strong, the catalyst will be mostly occupied with species A, and B will not be available to form the product (Loenders et al., 2023). If both A and B form powerful bonds with the catalyst, the intermediate situation with A or B on the catalyst may be so stable that reaction becomes unlikely. If the bonding between reactants and catalyst is too weak, there will be very little conversion of A and B into products (Takigawa et al., 2018).
- According to Fig. 1.2, the following level is buried so deeply that the catalyst's activation energy for P formation is too high. It is believed that the reactants poisoned the catalyst (Takigawa et al., 2018).
- Similarly, it's possible that product P is too tightly bonded to the catalyst to allow for separation. Here, the catalyst gets poisoned by the product.

1.1 Solid surfaces, molecules, atoms, and enzymes can all act as catalysts

There are many different types of catalysts, ranging from molecules and atoms to big structures like enzymes or zeolites (H. Zhang et al., 2021). They can also be used in a variety of environments, such as liquids, gases, or surfaces of solids. An essential specialization that we will discuss in later chapters is the preparation of a catalyst in the ideal form and the precise examination of its composition and shape (Hughes et al., 2021). The three subdisciplines of catalysis that are typically distinguished are homogeneous, heterogeneous, and biocatalysis. We provide an example for each.

1.2 Homogeneous Catalysis

Both catalytic agent and the products of reaction are in the same phase during homogeneous catalysis, meaning that all the molecules are either in the liquid phase or, more frequently, the gas phase (Kumar et al., 2022). The study of atmospheric chemistry provides one of the most basic examples. Among other things, ozone in the environment breaks down through an interaction with atoms of chlorine (Langdon Ward, 2020).

$Cl + O_3 \rightarrow ClO_3$

$ClO_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

or overall

$O_3 + O \rightarrow 2O_2$

Although ozone can break down naturally and in response to light, a Cl atom greatly speeds up the process. The Cl atom functions as a catalyst since it exits the chemical cycle unchanged (Langdon Ward, 2020). This reaction cycle is an illustration of homogeneous catalysis since the catalyst and reactant both exist in the same phase, which is the gas phase. To create chemicals, industry employs a wide range of homogeneous catalysts in many types of processes. The carbonylation of methanol to acetic acid under catalysis by $[Rh(CO)_2I_2]^-$ complexes solutions are only one of numerous instances (Langdon Ward, 2020).

$CH_3OH + CO \rightarrow CH_3COOH$

Organometallic complexes are created using techniques that use molecular control in homogeneous catalysis, which is frequently used to produce delicate medications (Farina, 2023). This ensures that the reacting molecules are directed towards the desired products by the careful selection of ligands (Farina, 2023).

1.3 Heterogeneous Catalysis

Solids catalyze reactions between molecules in a gas or solution in heterogeneous catalysis. Catalytic reactions take place at the surface of solids because, unless they are porous, they are often impermeable (Rigby, 2023). Catalysts are typically nanoscale particles placed on an inactive, porous structure to make economical use of the frequently costly materials (such as $CuFe_2O_4/MgFe_2O_4$) (Fig. 1.3) (Z. Zhang et al., 2022).

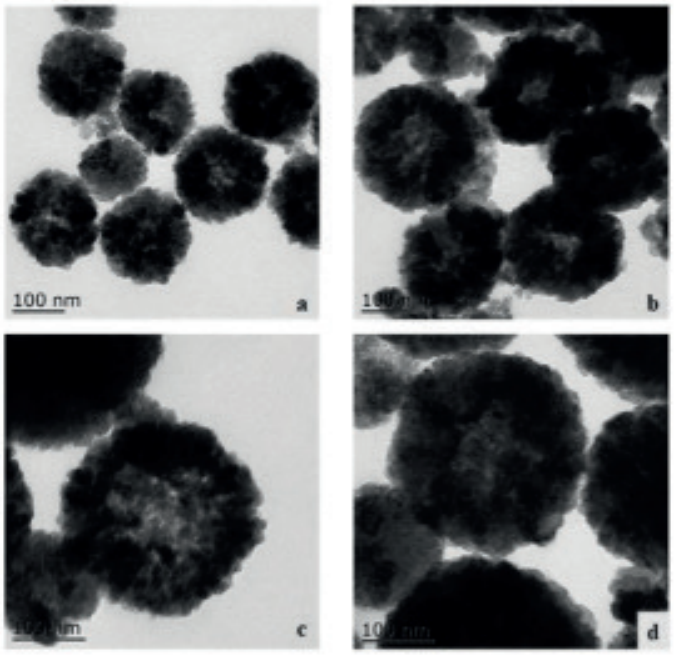


Figure 1.3. TEM images of $CuFe_2O_4/MgFe_2O_4$: (a) Cu:Mg = 1:0.5; (b) Cu:Mg = 1:1; (c) Cu:Mg = 1:2; (d) Cu:Mg = 1:3 (Z. Zhang et al., 2022).

Figure 1.3 displays the TEM images of CuFe2O4/MgFe2O4 with various Cu/Mg ratios in the precursors. It's evident that every sample created wormholes among the fine grains and hollow, spherical objects with rough surfaces. In the application process, this type of structure may help the photocatalytic reaction have a greater surface area, more active sites, simpler mass dispersion and transport, lighter penetration, and a higher quantum efficiency (Z. Zhang et al., 2022). The microspheres had a diameter of 200–300 nm, and their magnetic properties are what caused the hollow spherical formations to aggregate (Z. Zhang et al., 2022). Catalysis is nanotechnology, and catalysts are nanomaterials (Bilal et al., 2023). In the field of catalysis, nanoparticles have been used commercially for nearly a century, if we consider nanotechnology as a field of materials science that aims to regulate material characteristics on the nanoscale scale (Lopez-Cantu et al., 2022). For heterogeneous catalysts, a variety of synthetic methods can be used to create tiny particles and maintain their stability under the frequently challenging circumstances of an industrial reactor (Abbas et al., 2024). Nanotechnology is at the forefront of modern catalysis (Noreen et al., 2022).

One of the primary processes in exhaust cleaning for cars is the catalytic breakdown of carbon monoxide (CO) on the outer layer of noble metals like rhodium, palladium, and platinum (Feng et al., 2023). This serves as an introductory example. We shall suppose that the top layer of metal has active sites, indicated by the letter "*," to explain the process. Later, we give them a proper definition (Bahtilla & Hui, 2020). The adsorption of CO and O2 on the platinum surface initiates the catalytic reaction cycle, causing the O_2 molecule to split into two O atoms (X* denotes that the molecule or atom is adsorbed on the surface, i.e. attached to the site *) (Feng et al., 2023):

$O2 + 2^* \rightleftharpoons 2O^*$

$CO +^* \rightleftharpoons CO^*$

Following their surface reaction, the adsorption O atom and CO molecule combine to create CO2, which interacts on the platinum surface extremely weakly and desorbs nearly instantly since it is very stable and very unreactive (Matsui et al., 2006):

$CO^* + O^* \rightleftharpoons CO_2 + 2^*$

It should be noted that the catalyst's adsorption sites are freed in the latter stage, making them accessible for more reaction cycles. The chemical cycle and a potential energy diagram are displayed in Figure 1.4.

Where is the catalyst's critical influence in this cycle? Assume that the reaction occurs in a gas state without the use of a catalyst. If the temperature is raised to the point where the O2 molecule splits into 2 O atoms (radicals), the process will continue (Bakhtchadjian, 2023). When these radicals are present, the CO to CO2 conversion happens right away. About 500 kJ mol–1, or the energy needed for splitting the powerful O–O bond in O2, will be the energy needed for activation of the gas stage of the process (Bakhtchadjian, 2023). On the catalyst's surface, nevertheless, the molecule of oxygen dissociates readily during the catalytic reaction—in fact, it does so without the need for an activation energy (Etim et al., 2023). The reaction that occurs among deposited CO and O molecules, which has an energy of 50–100 kJ mol–1, is linked to the activation energy (Bakhtchadjian, 2023).

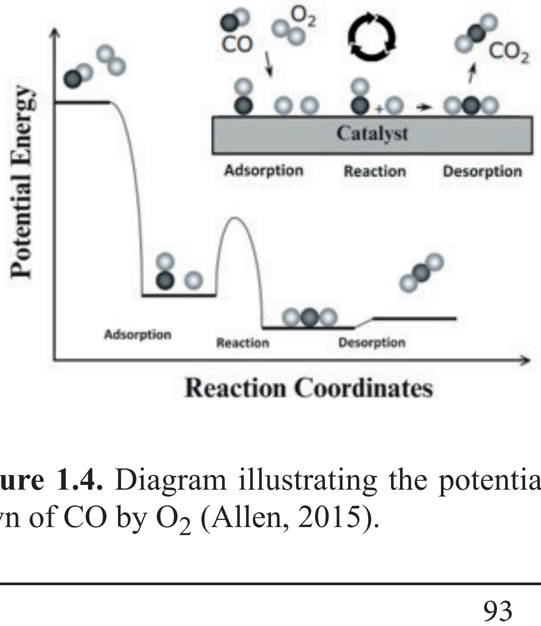


Figure 1.4. Diagram illustrating the potential energy and reaction cycle for the catalytic breakdown of CO by O_2 (Allen, 2015).

1.4 Biocatalysis

The catalysts of nature are enzymes. For the time being, it is adequate to think of an enzyme as a big protein whose structure produces an active site that is highly shape-specific (Fig. 1.5) (Palomo, 2021). Enzymes are very selective and effective catalysts because of their ideal structures, which direct reactant molecules (also known as substrates) into the best configuration for the process (González-Granda et al., 2023). Catalase, for instance, is an enzyme that catalase the breakdown of H2O2 into oxygen and water at a startlingly fast pace of up to 107 molecules of hydrogen peroxide each second (Singh et al., 2023).

$2H_2O_2 \rightarrow H_2O + O_2$ (catalase)

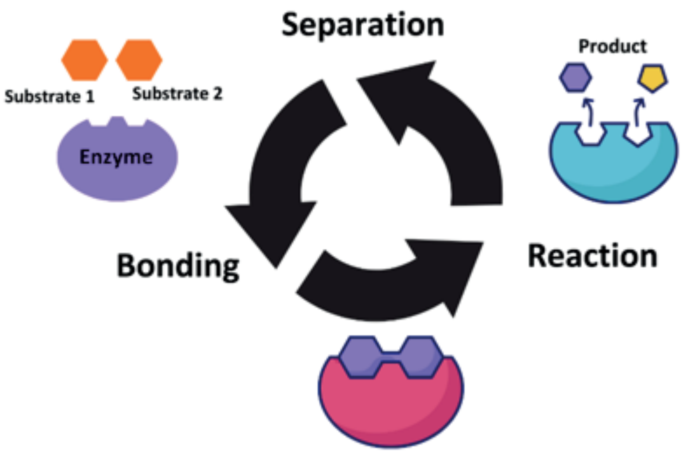


Figure 1.5. Diagram showing the reaction that is catalyzed by an enzyme. The form of the substrates that enzymes bind to or the change in phase of the reaction that they catalyze are frequently complementary. Since they are very effective catalysts, enzymes can be used as an excellent source of motivation for creating technical catalysts (Palomo, 2021).

Enzymes facilitate biological reactions at the speeds required to sustain life, such as the synthesis of proteins and DNA, the disintegration of molecules, and the energy storage in sugars (Wozniak & Brzezinski, 2023). One example that can be very interesting to students is how the body uses the enzyme alcohol dehydrogenase to convert alcohol to acetaldehyde (Zhai et al., 2023). Aldehyde hydrogenase then transforms the acetaldehyde into acetate. Some people do not have the correct type of an enzyme that breaking down acetaldehyde, which causes them to flush after even a tiny amount of alcohol (J. C. Liu et al., 2023).

2- Historical Perspectives and Milestones

Berzelius first used the term "catalysis" in 1836 (Filippi & Pizzolitto, 2022). In addition to "Affinity," he concluded that "Catalytic Force" is another force at work (J. Li et al., 2020). Catalytic contact caused the reaction to happen. Originating in Greek, the word "catalysis" means "down" and "loosen" (J. Li et al., 2020)." Catalysis in industry is not a new technique. Wine and beer have long been produced with the aid of catalysts (Uzuner, 2022). A couple of inorganic oxidation processes, such as the Deacon process (which converts HCl into Cl_2) and the synthesis of sulfuric acid, are among the earliest commercial catalytic processes (Jia et al., 2023). These procedures were created prior to the establishment of a scientific foundation for chemical reactivity. A structure for catalyst development wasn't available until Van't Hoff developed the concept of chemical equilibria (Mihara et al., 2024). This had a significant influence on the creation of a method for ammonia synthesis at the start of the 20th century, enabling a methodical, empirically supported hunt for an effective catalyst (Emmanuel, 2024). It also marked the beginning of chemical engineering advancement that life could not exist without catalysis. All living things in the natural world, including humans, rely on enzymes, or biocatalysts, to guide the chemical reactions necessary for their survival and reproduction (X. Zhang et al., 2023). Clearly, the use of catalysis by humans to produce a product date back for further than the birth of life. However, that was a long time ago, and catalysis was not even a concept at the time ("Introduction to Heterogeneous Catalysis," 2022). For about 8000 years, yeast's enzymes have been utilized to transform sugars into goods like bread, beer, and wine (Uzuner, 2022).

Thus, catalysis—more especially, biocatalysis—has made it possible for humans to establish civilizations and lead civilized lives (Rozendal et al., 2006). Safe water and food supplies, as well as their storage, were crucial after humans began to dwell in close quarters in big numbers (Mishra, 2023). Relatively safe drinking supplies were guaranteed using yeast to generate alcoholic beverages while also inhibiting all other pathogenic microbes. Similarly, yeast-based bread produced products that could be stored (Cabello-Olmo et al., 2023). Another frequent use of catalysis is the growth of Lactobacillus and related organisms that overpower pathogens while producing acidic media and thereby suppressing all other microbes (Balakumaran et al., 2021). The process of catalytic creation of lactic acid is utilized in the production of yoghurt, cheese, and numerous other dairy-based goods to preserve milk, as well as in the production of salami and numerous other kinds of food (Dahiya & Nigam, 2023). By wrapping the meat in papaya leaves, the meat was softened and rendered more palatable for human ingestion thanks to the proteases found in the leaves (Obajuluwa et al., 2020).

Catalysis as a concept began to take shape in the second half of the nineteenth century (Loenders et al., 2023). Depending on whatever solid was added, it was found that ethanol might either break down into ethylene or acetaldehyde, which has a strong odor (Fustier et al., 2011). We now understand that while oxides with acid activity cause dehydration, metals catalyze dehydrogenation (Cabello-Olmo et al., 2023). The sensor that can identify explosive gases was the first application that was created by humans, but at the time they were unaware of the notion. With the help of a teenage Michael Faraday, Davy discovered in 1817 that H_2, CO, and CH_4 in the air could be detected by a heated Pt wire because the oxidation of the gases would cause the wire to light up with heat (Balakumaran et al., 2021). This made it possible to identify dangerous gases in mines for coal before their concentrations rose to the point where an explosion was possible. Based on this, the Miner's lamp—a crucial safety tool in mines for coal at the time—was created. Inspired by the Greek word for "loosen," JJ Berzelius originally coined the term catalysis in 1835 and explained the underlying mechanism (Dahiya & Nigam, 2023). It was suggested that the catalyst could cause organic materials, such as the elements in mine gas, to decompose (Obajuluwa et al., 2020). The idea was not fundamentally dissimilar from the idea of dissociation adsorption in surfaces today.

3- Fundamentals of Catalytic Processes

Relevant economic limitations exist for catalyst expenses, catalytic efficiency, and process selection (Fustier et al., 2011). Enhancing the catalyst does not always result in a system that is useful in real-world scenarios. It's interesting to note that new possibilities for catalyst choice are directly correlated with our grasp of molecular prediction, as the catalyst choice issue will demonstrate (Elphick, 2021). Mass and heat exchange play a major role in extrinsic kinetics, which also influences reactor selection and catalytic performance. The relationship between the energy content of the final product and the raw material plays a major role in the energy conversion technology process selection (Ren et al., 2020).

3.1 Selection of Catalyst

The creation of a computer method for assessing and forecasting the catalytic activities of heterogeneous catalytic systems is a significant contribution of computational catalysis (J. Xu et al., 2021). This approach makes use of the relationship between a calculated reactivity descriptor and a measured rate of a reaction. This approach takes advantage of the physical-chemical interpretation of the behaviour like a volcano (Mañosa et al., 2023). The Sabatier principle has led to this. The maximum in the volcano curve happens when the rate of reactant activity and the rate of product desorption are equal, if one utilizes the interaction intensity of the reactant with the catalyst as a reactive parameter (Figure 3.1) (Králik, 2014). The rate of reaction rises as you increase interaction energy to the left side of the volcano and reduces with rising reaction energy to the right. The total catalytic rate exhibits a maximum rate at the reactivity descriptor's optimal value (Mañosa et al., 2023).

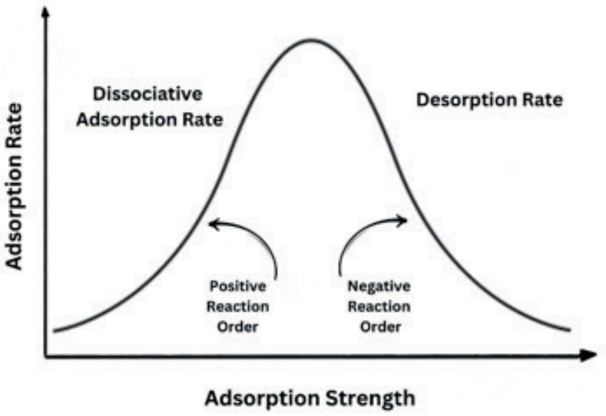


Figure 3.1 According to Sabatier's concept of catalytic reactivity, the rate of reaction peaks when the reagent and catalyst have the best possible relationship (Králik, 2014).

Using a linear activated energy–reactivity descriptor connection of the Brønsted type for elementary reactions on the surface is the second component of the extrapolative rate prediction (J. Xu et al., 2021). A thermodynamic quantity such as the chemical reaction energy of a crucial fundamental reaction step is employed as a reactivity descriptor. This is known as the Brønsted–Evans–Polanyi relation (BEP) for surface reactions (Chun et al., 2020).

In Figure 3.2a, one such relationship is depicted. Plotting the calculated energy of activation for CO dissociation, or C–O bond cleavage, versus the total of the adsorbed C and O adsorption energies is done (Andersson et al., 2006). There are corrugations on the surface. The BEP proportional constant, or the curve's slope, is almost one. It shows that the C–O bond is extremely weak in the phase transition state and that the framework of the dissociated state and transition state are extremely comparable. When there is a substantial amount of available experimental data, the appropriate descriptor can be utilized to create a volcano curve once the reliability of the BEP relation for an important reaction stage in a catalytic reactions step has been confirmed (Stratton et al., 2023). Such information can also be computationally generated through the application of micro kinetic methods for modelling of the innate catalytic rate.

Figure 3.2b displays a plot of the catalytic reaction's experimentally determined rate constants:

$CO + 3H_2 \rightarrow CH_4 + H_2O$

as opposition to a reactivity descriptor defined as the total of the breakdown products Ediss adsorption energies. The Sabatier concept is followed in finding a volcano-type response rate dependence. The reactivity descriptor's optimal value is nearest to 0 (Andersson et al., 2006).

The ability to access a volcanic curve like the one shown in Figure 3.2b makes it possible to computationally test many metal combinations. The total of C and O's adsorption energies (Ediss) for various metal compositions must then be determined. This allows for the computational analysis of the reaction kinetics for a wide variety of metal combinations. Using this technique, substitutes for the pricy Co and Ru metals that exhibit peak methane reforming reaction performance have been identified (Andersson et al., 2006).

The application of these variables to determine the preferred material from an economic standpoint is demonstrated in Figure 3.3 (Védrine, 2017). An example of an Ediss Pareto plot of a specific metal combination vs its price is displayed. The material performs at its best when Ediss is zero (Magnuson & Ma, 2022). This will never match the best deal unless very rare circumstances arise. A trade-off between the best performance and the lowest process can be made using the Pareto plot. The alloy FeNi3 has the lowest price and near-maximum performance, according to the Pareto plot (Magnuson & Ma, 2022).

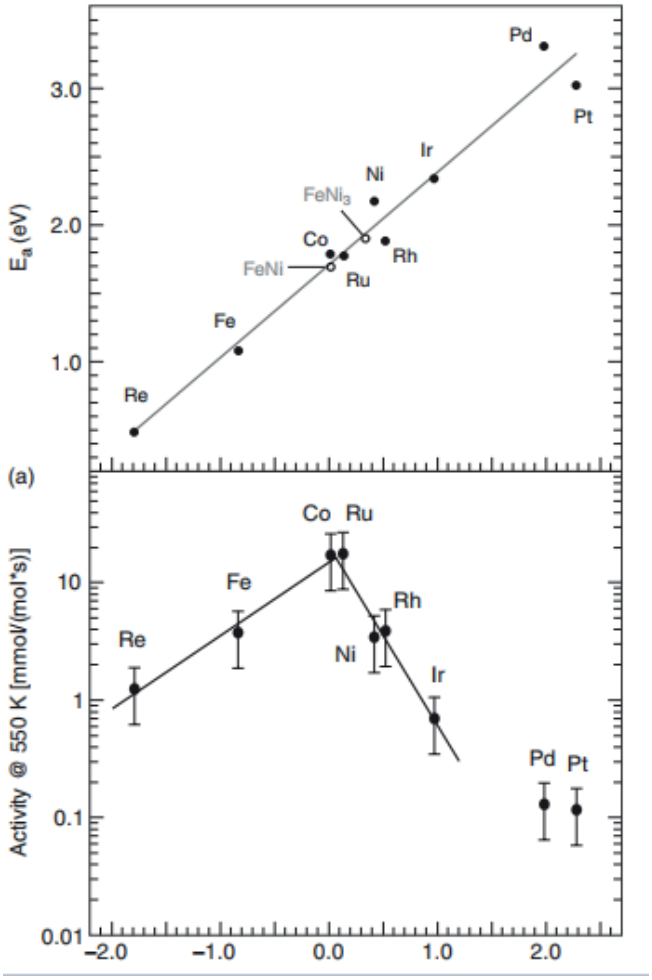


Figure 3.2 (a) BEP connection between the CO dissociation energy and the activating energy for CO dissociation, Ediss. **(b)** Catalytic activity measurements for supporting metal catalysts are displayed against Ediss. The RPBE exchange correlation was utilized in the computations on stepped fcc (211) metal slabs that were periodically repeated and had 12 layers in the (211) direction (Andersson et al., 2006).

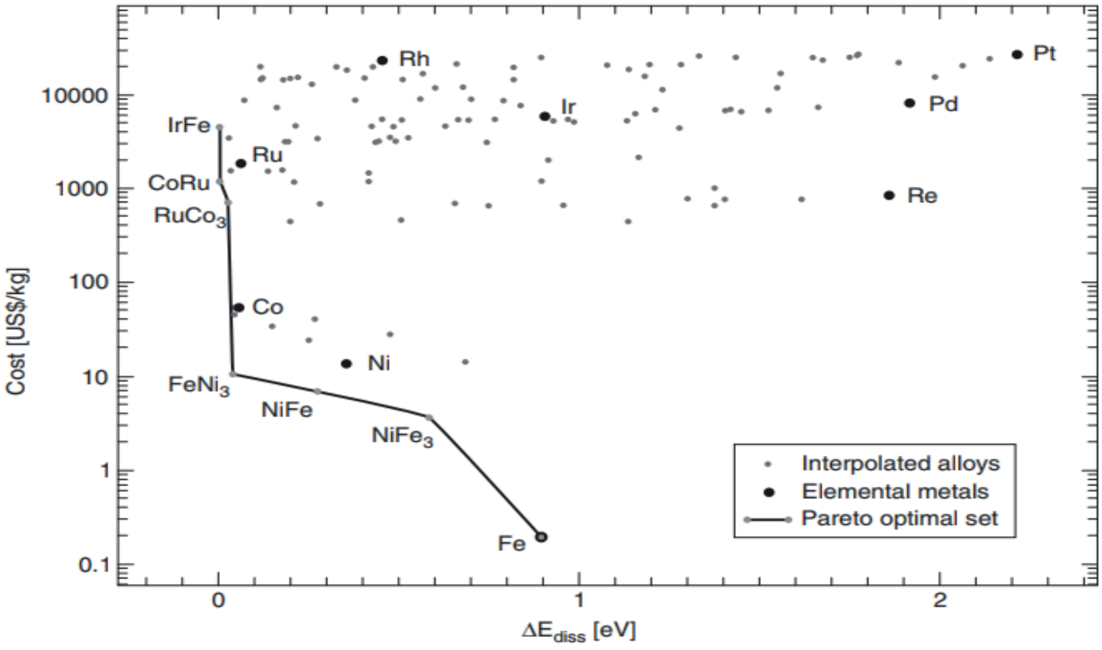


Figure 3.3 The activity measure's Pareto plot ΔEdiss = |E′diss − Eoptdiss | and the price of 117 bimetallic alloys and elemental metals (Védrine, 2017).

3.2 Choice of Reactor

It's not always the case that the catalyst with the highest activity is also the most practical. Extrinsic kinetic characteristics like mass and heat exchange rates also influence the total rate of a catalyzed reaction. Reactivity regimes for three processes are contrasted in Figure 3.4 (Ountaksinkul et al., 2022). The reservoirs for gas and oil are produced by petroleum geochemical processes. These processes have an extremely low space-time yield. Additionally, a comparison between the ideal operating window for commercial catalysis and the biochemical processes involved in fermentation is presented (Moulijn et al., 2011). Take note of the three order of magnitude disparity between biological and industrial catalysis. The trade-off between two factors accounts for the industrial process' optimal window. One is a catalyst's intrinsic rate, which should ideally be maximum (Mbatha et al., 2021). The rate at which mass may be transferred from or into the catalyst or the quantity of heat that needs to be added or removed, however, might become limiting variables when a reaction reaches extremely high rates. These restrictions are imposed by reactor design. Usually, the process is run at its best when production rate is constrained by mass and heat transmission (Mbatha et al., 2021). Then, the allowable limitation values are determined by intrinsic kinetics. It seems obvious that production increases with improved control and augmentation of the extrinsic kinetic parameters (Moulijn et al., 2011).

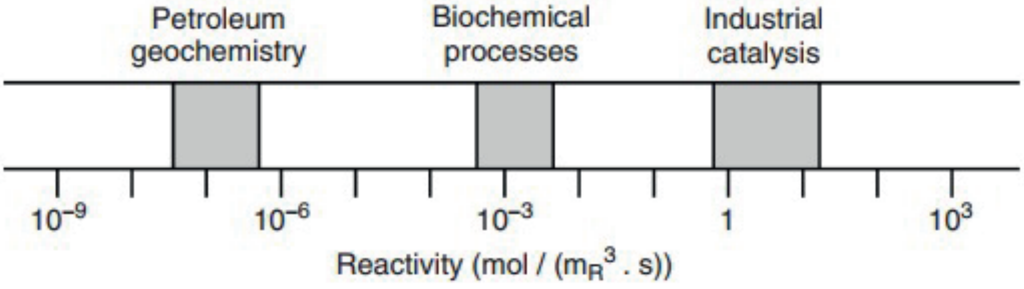


Figure 3.4 Reactivity thresholds for many chemical reactions (Moulijn et al., 2011).

3.3 Choice of Process

When choosing a process, thermodynamics and material efficiency are crucial factors. Sheldon et al., 2022, established the idea of Atom utilization to gauge material efficiency (Sheldon, 2022). The main concept is to count the total amount of atoms in the starting materials divided by the number of atoms in the product to determine how much waste material is produced. To assess effectiveness on a weight basis, it is helpful to translate the Atom utilization number into a ratio of weight for practical reasons (Sheldon, 2022).

The choice of reactor and catalyst can affect the effective Atom utilization. It is dependent upon a reaction's selectivity (Y. Zhang et al., 2022). We show this in Figure 3.5 for epoxidation reactions to ethylene (Pilli & de Assis, 2018). Using Cl2 and Ca(OH)2 as reactants, the traditional pathway passes through the intermediate chlorohydrin. 25% of atoms are used, and the waste product is CaCl2 (L. Wang et al., 2023). Ethylene epoxide is optimally produced with 100% selectivity using the Ag-based catalytic method. There is 100% atom utilization. When the reaction is conducted with 90% selectivity in practice, 77% of the atoms are effectively utilized. It serves to highlight the significance of catalytic processes. This figure remains notably greater compared to that of the chlorohydrin pathway (L. Wang et al., 2023; Y. Zhang et al., 2022).

Thermal efficiency is crucial when handling transformation operations like turning petrol or coal into liquid fuels for transportation. This is calculated by dividing the product's combustion heat by the total amount of feedstock consumed (Y. Zhang et al., 2022). For example, oil refineries usually have a 90% thermal efficiency. In comparison, the heating efficiency of producing a non-fuel product like methanol, which has an energy efficiency of only 67%, should be considered (L. Wang et al., 2023).

De Jong et al., 2022, cited two crucial guidelines for effective processes (de Jong et al., 2022):

- Reducing the amount of process stages
- Variation in the hydrogen content between the feed and the final product

The transformation of coal or natural gas into liquid carriers of energy serves as an example of the significance of hydrogen content (Tashie-Lewis & Nnabuife, 2021). The transformation of natural gas to hydrogen-rich paraffinic compounds has a significantly better heating efficiency than the transformation of coal, as shown in Figure 3.6 (Boretti & Banik, 2021; Tashie-Lewis & Nnabuife, 2021).

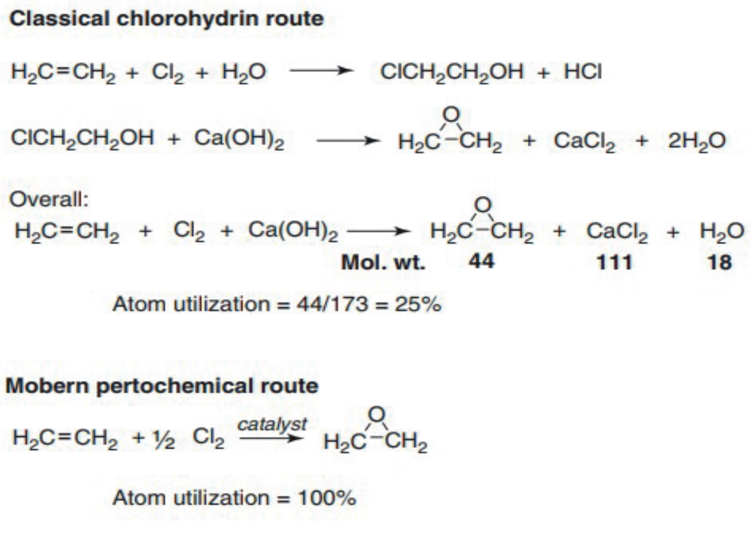


Figure 3.5 The contemporary petrochemical approach uses 100% atom utilization, while the traditional chlorohydrin route uses 25% (Pilli & de Assis, 2018).

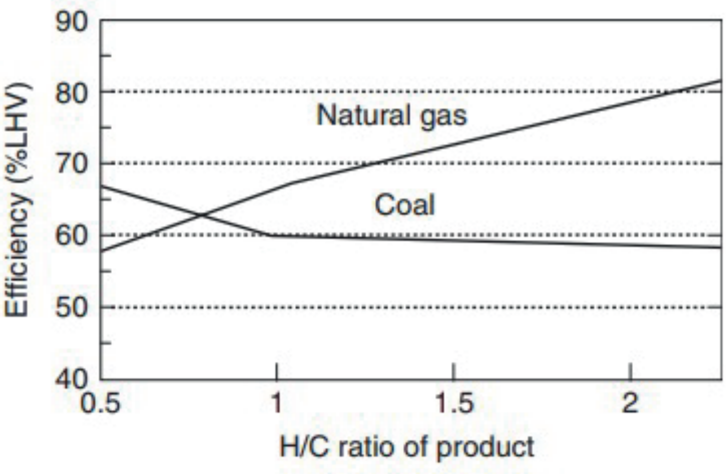
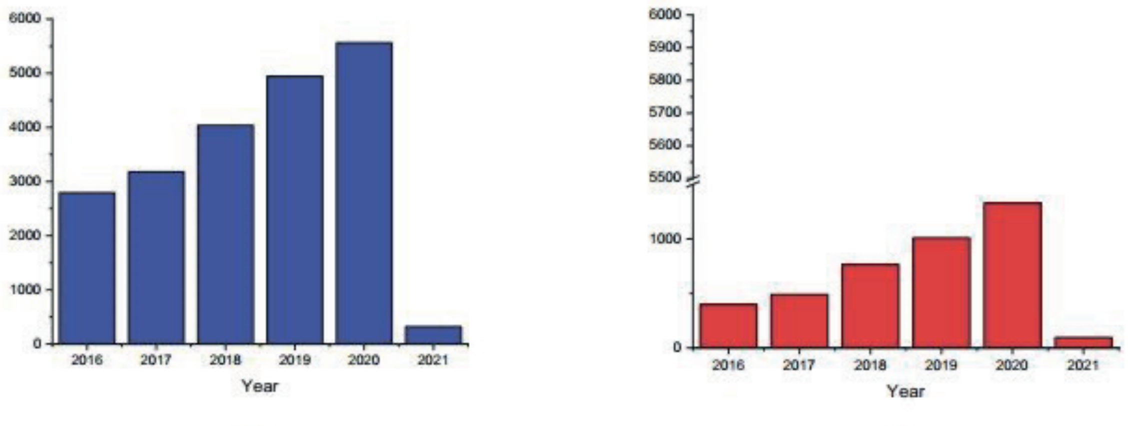


Figure 3.6 Maximum thermal efficiency of the synthesis gas into hydrocarbon in synthetic fuels (Boretti & Banik, 2021; Tashie-Lewis & Nnabuife, 2021).

4- Recent Developments in Catalyst Design

Every chemist is aware of how important it is to have an effective catalyst to maximize stereo- and regioselectivity and increase reaction rate (Cuccu et al., 2023). A variety of techniques, including the simulation of various catalyzed processes, trial and error methods, screening of preexisting catalyst libraries, and, lastly, sound chemical intuition and understanding, are used in the search for new catalysts (Zhuang et al., 2024). Most of the time, a mix of these strategies is used, and serendipity also plays a significant part. Either way, controlling chemical reactions using precisely engineered catalysts—that is, molecules or material that are both effective and may meet other crucial needs like cheap cost and minimal environmental impact—is the very ambitious goal (Bollini et al., 2023).

A search of the Scopus database was conducted to determine the significance of rationally tailored catalysts. The search yielded 43,897 entries related to the string “Catalyst AND Design” for the years 1928 to 2021; of these, 20,838 entries are from the years 2016 to 2021, indicating a sharp rise in interest in and work on catalyst design over the previous five years (Figure 4.1a) (Kobayashi & Sunada, 2020; Ma et al., 2019). When the full term "Catalyst AND Design AND Strategy" is entered into the search, 4087 results covering the years 2016–2021 are identified when strategy is included (Figure 4.1b) (Kobayashi & Sunada, 2020; Ma et al., 2019). Significantly, both graphs show that the number of works is rising annually, a sign of the scientific community's interest in the methodical and directed hunt for new catalytic systems. Computational approaches are a valid assistance in this case for various reasons. First, precise quantum chemistry methods have produced quantitative energy and kinetic understanding by revealing mechanistic insights of both simple and complex events within the past 20 years (Ta et al., 2021). These days, (super) computers can be used to study chemical reactions involving complicated systems, thanks to the remarkable advancements in silicon technology. In conclusion, the use of machine learning to screen vast collections of chemical substances is regarded as a standard best practice for investigating possible activities in silico or extracting key properties for designing functional molecules (Zhuang et al., 2024). With the help of all these data, we can predict that chemists will soon be able to design effective catalysts and create them in the laboratory with the least amount of expense and work.



(a)

(b)

Figure 4.1 Outcomes of a Scopus database search restricted to the years 2016–2021: The search terms "catalyst AND design" in (a) and "catalyst AND design AND strategy" in (b) (Ma et al., 2019).

A method for shielding palladium catalysts from Sulphur species has been described by Betti et al. (Betti et al., 2021) and used in the catalytic oxidation process of methane. Different researchers have explored and analyzed in detail the issue of asymmetric olefin epoxidation using salenMn immobilized on graphene oxide as a catalyst ("Advanced Strategies for Catalyst Design," 2021; Orian, 2021). Inspired by the silicon analogue, Kobayashi and Sunada have reported the production of a four coordinated Fe(II) digermyl complex that is used as a catalyst in the dehydrogenation of ammonia borane (Kobayashi & Sunada, 2023). According to Hernández et al., introducing Pt to the Ag/Al_2O_3-WO_x catalyst improves the elimination of NO_x utilizing C3H8 and H2 (González Hernández et al., 2020). Muangmora et al.'s study uses Mn/Ti nanorods to remove fundamental mercury in the form of SO2, demonstrating how the TiO_2-coated Mn is protected from SO_2, an undesired deactivation (Muangmora et al., 2021). WU et al.'s review paper focuses on the difficulty of developing a nontoxic catalyst for acetylene hydrochlorination, which is catalyzed by $HgCl_2$ supported on activated carbon (WU et al., 2021). Alternative options are evaluated, and benefits and problems are critically discussed, for noble as well as non-noble metallic and nonmetal catalysts. The research on alternatives to petroleum products derived from fossil fuels was documented in the article by WU et al. The authors have demonstrated the production of 22-carbon tricarboxylic acid and its ester using the Diels-Alder reaction, commencing with polyunsaturated fats (PUFAs) and their corresponding esters, fumaric acid and fumarate. A catalyst has been employed with iodine (WU et al., 2021). Carlucci et al. have worked on developing methods to turn waste cooking oil into biofuels, and they have been successful in maximizing the conditions of the reaction (acid catalysis) to achieve high yields of up to 99% (Carlucci, 2021). In their investigation into the removal of chemical waste from wastewaters, Rottach et al. suggested the contact glow discharge electrolysis (CGDE) method, which has the potential to be a low-cost solution (Rottach et al., 2023). Lastly, two theoretical investigations have been given by Kim et al. and Orian et al. The first one involves the asymmetric cyanation of olefins using ethyl cyanoformate, which is catalyzed by Ti(IV). The second one involves the cycloaddition of acetylene [2+2+2] to benzene, which is catalyzed by Rh/Cr indenyl fragments. It is clear from the precise explanation of the reaction processes and the activating strain model that the time is right for an exacting and quantitative in silico catalyst design (Rottach et al., 2023).

5- Computational Approaches in Catalysis

In addition to offering a flexible toolkit for researching the mechanistic specifics of catalytic reactions, computational chemistry has the potential to produce useful approaches that will facilitate the logical in silico design of catalysts (Kee, 2023). The system's ubiquitous activity and complex electronic structural affects. Traditionally, chemical intuition and professional advice of the researcher have been crucial to computational investigations on catalytic reactions (Lledós, 2021). The human-bias from computational catalysis investigations may be eliminated thanks to recent advancements in sophisticated automated reaction path analysis techniques. All initiatives for the construction of sustainable chemical technologies that are atom- and energy-efficient rely heavily on catalysis. Today, nearly all consumer goods, from fertilizers and transportation fuels to fabrics and medications, are produced using inexpensive oil, gas and coal feedstocks, which are vital to civilization (Iroegbu & Ray, 2021). Dependence on these renewable feedstocks raises the risk of political and economic instability on a worldwide scale and is linked to significant greenhouse gas emissions, raising concerns about climate change. It is obvious that this scenario leads to an unsustainable future. To make it possible to directly use alternative renewable raw materials and to improve the efficiency and environmental friendliness of currently in use technologies, new ones must be invented and developed quickly (Mariotti et al., 2020). The move to more robust and effective catalytic systems, ideally composed of elements that are abundant in the earth, is implied by attempts to make catalyst utilization more sustainable (Kumar et al., 2022). These endeavors should be performed in tandem with work towards the feasible use of chemical feedstocks.

Computational chemistry has emerged over the past 20 years as a major component of catalysis research and has made a name for itself alongside common laboratory methods like infrared spectroscopy (IR), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD) in the catalysis toolbox (Rivera-Torrente et al., 2020). The advancement of our basic comprehension of catalytic events has been greatly aided by computational modelling and molecular simulations (Lledós, 2021; Ta et al., 2021). To provide an atomic structure for the analysis of spectroscopic data and the clarification of catalytic mechanisms, computations have become essential. The study of chemical reactivity, the analysis of intricate reaction pathways, and the modelling of catalytic reaction kinetics are all best served by state-of-the-art quantum chemical methodologies, especially the density functional theory (DFT) approaches (Ugwu et al., 2022). Important instructions for the creation of novel and enhanced catalytic systems are provided by theoretical research. The availability of easy quantum chemical and molecular modelling software, which makes it possible to practice quantum chemistry without the need for extensive programming skills or specialized theoretical expertise, has made computational chemistry more widely applied (Mazzola, 2024).

These days, atomistic DFT modelling results are widely used not only by theorists but also by a wide spectrum of experimental catalysis groups, who use the data in support of mechanistic proposals gained from the experiments (Morales-García et al., 2021). The enormous achievement of near-chemical precision that can be reached with the current computational methodologies has made a direct relationship between the outcomes of molecular modelling and experimental data a standard practice (Kee, 2023). In computational chemistry, accuracy is typically defined as the ability of a given approach to compute certain fundamental chemical properties in relation to experimental or extremely precise theoretical conclusions(L. Wang et al., 2023). The total accuracy of practical calculations involving catalytic systems is also highly dependent on the model's quality, or how well it captures the crucial chemical characteristics of the reaction or feature under consideration (J. Xu et al., 2021). The approach (degree of theoretical approach) and model accuracies (amount of chemical information incorporated in the model) naturally trade off with one another.

5.1 Competition in computational catalysis between model and method accuracies

Since electronic structure theory is the only one that can explain the fundamental process of catalysis, which is the breaking and creation of chemical bonds, it plays a crucial role in the understanding of intricate reaction mechanisms (Rocchigiani & Bochmann, 2021). The discussion of computational chemistry's correctness in relation to research on catalytic structures based on three-dimensional transition metals is the main objective of this section. Within this framework, the issue of computational accuracy can be perceived as consisting of two primary elements: (a) the precision of the technique utilized to ascertain the electrical composition of the chemical system, and

(b) the precision or caliber of the chemical model utilized to explain the fundamental phenomena that underlie the feature significance of the chemical system (Keith et al., 2021). Achieving the optimal levels of models and method accuracy at the same time is frequently unattainable due to the intricate chemistry and electrical structure of these catalytic systems (Rey et al., 2024). As a result, several apologies and simplifications must be made to define the model system and describe the electronic structure. The selection of a density functional, the degree of correlation applied in post-Hartree-Fock techniques, or the dimensions and kind of the basis set are a few examples of these methodological approximations (Determan & Wilson, 2024). Crucially, the selection of the concept level dictates how comprehensive the set of basic physical occurrences is that one may dependably use to explain the computing itself. This highlights the need of accurately calibrating these methods and estimating the errors incorporated into the computational study in real computational catalysis research (Jung et al., 2022). As a result, we will offer suggestions for using electrical structure theory techniques to produce (semi)quantitative results in this section. To make the system tractable and achieve the required computational accuracy, the model approximations are mostly connected to the necessity of reducing the model's size in a general way (i.e., the number of atoms, size of the configurational or reactive space probed in the simulation, etc.) (Bürkner et al., 2023).

5.2 Accuracy of Quantum Chemical Methods - Density Functional Theory (DFT)

Since density functional theory (DFT) has a wide range of applications in computational catalysis, it will be covered first. DFT has become quite popular because of its simplicity and application, even though historically it was brought to chemically relevant problems considerably later than the other key family of quantum chemical approaches, the wave function theory (WFT) methods (Butera & Butera, 2024). Since DFT has been thoroughly covered in many great textbooks and review articles, this chapter provides a very brief overview of the method's fundamentals here to lay the groundwork for our discussion of the benefits and drawbacks of related methodologies for researching realistic catalytic systems (Ugwu et al., 2022).

The two Hohenberg-Kohn theorems, which assert that the ground-state energies can be calculated variationally and can only be determined from the electron density, are the basis of density functional theory (DFT) (Determan & Wilson, 2024). According to the second theorem, an energy larger than or equivalent to the true potential can be estimated if the exact definition of the density is known. Kohn and Sham developed a method that served as the foundation for the current Kohn Sham DFT (KS-DFT), which is akin to the self-consistent field (SCF) method used to solve the Hartree-Fock (HF) equations (Belleflamme et al., 2023).

The majority of practical DFT approaches now use KS-DFT, which assumes that there are no interacting electrons in the system (Belleflamme et al., 2023). The electrons that have an electron-to-electron correlation create the genuine (full) ground-state density. Then, the Eigen function is a conventional Slater determinant created by individual one-electron operations, the eigenvalue is a sum of one-electron eigenvalues, and the Kohn−Sham operator, the DFT counterpart of the Fock operator, is written as the total of one-electron operators (Izsák et al., 2023). The density, or electron density, is an expression of three-dimensional spatial coordinates, and the function that sums the potential and kinetic energy operators is a density functional (Kocák et al., 2023).

Utilizing machine learning to expedite the chemical space exploration is an alternate strategy that has begun to get a lot of traction (Keith et al., 2021). It is anticipated that data-driven approaches would hasten the process of identifying important characteristics that can serve as catalytic descriptors and aid in computational catalyst design (H. Li et al., 2023). To create a thorough theoretical foundation for computational catalysis, those methods can be integrated with the subjects (new electronic framework theory methods, complicated modelling, computing of many reaction paths, and reaction network analysis) (Bernales et al., 2018).

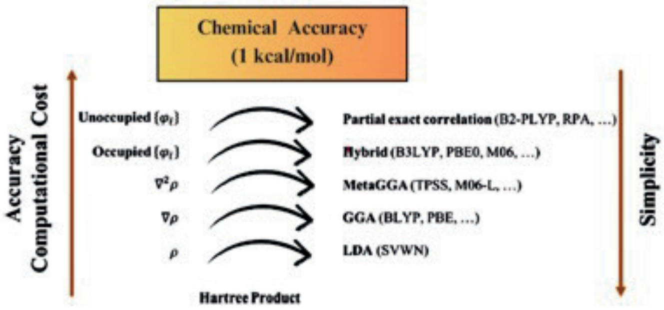


Figure 5.1 Diagrammatic representation of the different DFT approximations sorted by decreasing simplicity, increasing accuracy, and increasing processing expense. For every rung, a few popular and representative functional are provided (Olatomiwa et al., 2023).

6- Novel Catalytic Materials and Structures

In heterogeneous catalytic reactions involving the transformation of chemicals produced from biomass, the breakdown of metal catalyst is a frequent occurrence that can have a direct impact on the pace, conversion, and selectivity of the reaction (Mo et al., 2023). To avoid deactivation, improve catalytic performance, and increase selectivity towards the intended product, catalyst design is crucial (Tafete & Habtu, 2023). The design of supported metal catalysts, with an emphasis on alloy, micro-structure, or hybrid composites, which are functionalized supports with appropriate microstructure or strong interaction, and quite a few other novel structural catalytic materials, has been aided by the development of synthesis techniques and characterization technologies (Song et al., 2024). In this chapter, we primarily focus on newly developed structural catalytic substances with exact crystalline structures. These materials include metal nanoclusters and porous materials like zeolites, MOFs, and COFs.

6.1 Porous materials

(I) Zeolite

One type of naturally occurring alum inosilicate with evenly spaced pores is called zeolite. Another name for synthetic zeolite is molecular sieve (Kianfar, 2020). Ax/n (SiO_2) (AlO_2) x·mH_2O (A = cation) is the general formula for a molecular sieve. Its four-junction framework is TO_4 (T = Si, Al, etc.) (Carreon, 2008). Numerous configuration types result from the various TO_4 connection modes. 235 varieties of both natural and synthetic zeolites have been identified thus far, with each kind given a three-letter designation by the International Zeolite Association (Z. Wang et al., 2012). Figure 6.1 depicts the architecture of a few widely used zeolites (D. Yang et al., 2021). The frameworks of these rings are made up of varying diameters, which match the pore windows. Zeolites are classified into four groups based on the biggest pore size: small-pore (≤8-ring), medium-pore (10-ring), large-pore (12-ring), and extra-large pore zeolites (>12-ring) (Meier, 1986). Zeolites with diverse shapes are capable of selectively producing certain products by catalysis, thanks to the unique spatial constriction of their pores and the distinct Brønsted (B)/ Lewis (L) acid active sites in their structures (Kianfar, 2020). As a result, zeolites are frequently employed as heterogeneous catalysts, playing a significant role in both traditional petrochemical industries and cutting-edge sustainable processes including the conversion of biomass, purification of water, C1 molecule conversion, and others (Carreon, 2008). Zeolites can also be used as supports to create multifunctional composites with superior catalytic capabilities (Z. Wang et al., 2012).

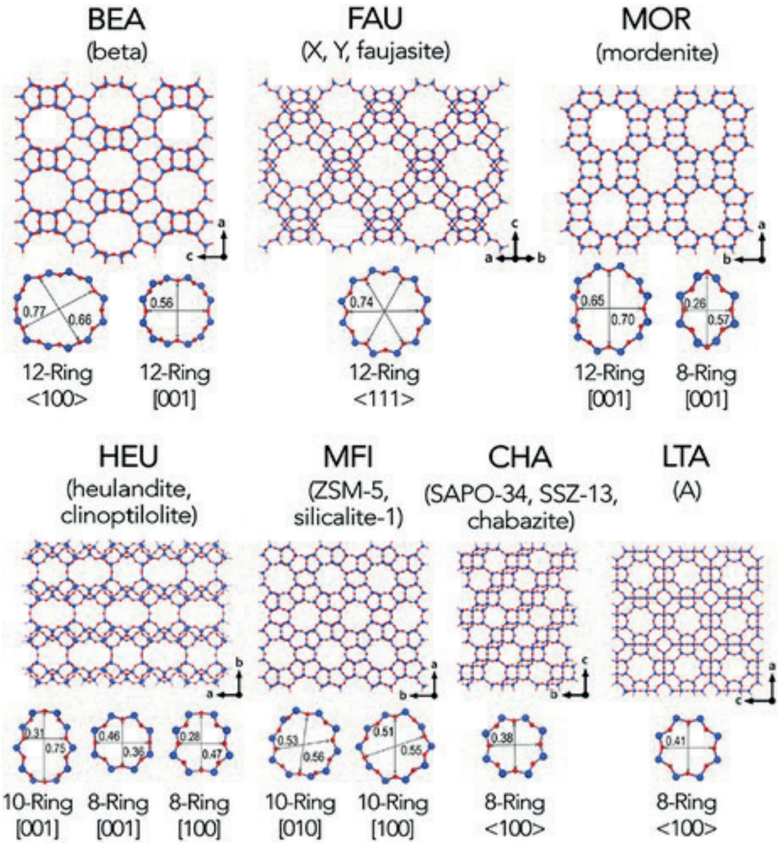


Figure 6.1 Zeolite framework varieties. Red represents O atoms, blue = Si and Al atoms (D. Yang et al., 2021).

(II) Organic framework materials

For a long time, scientists have been interested in studying covalent chemistry (Hassan et al., 2020). Covalent bonds enable MOFs and COFs to form the joint of molecular building pieces, contributing to the accuracy and versatility of covalent science from molecules to more complex organized structures (Hassan et al., 2020) (D. Yang et al., 2021)(Figure 6.2B). Due to varying chemical binding energies between molecular building blocks, these two possibilities exhibit distinct stability and crystallization (J. Liu et al., 2021). They are both crystalline substances with atomically precise porosity framework architectures. Strong covalent linkages give rise to ongoing porosity (Figure 6.2A) in MOFs and COFs structures, making them more robust than some of earlier-developed metal-bipyridine structures made of metal-L base bonds (Kianfar, 2020; D. Yang et al., 2021). This gives MOFs and COFs properties that are comparable to those of conventional porous materials like zeolites. Like their many special qualities, MOFs and COFs have lately been used with remarkable results to catalyze the transformation of biomass platform molecules (Weng et al., 2024).

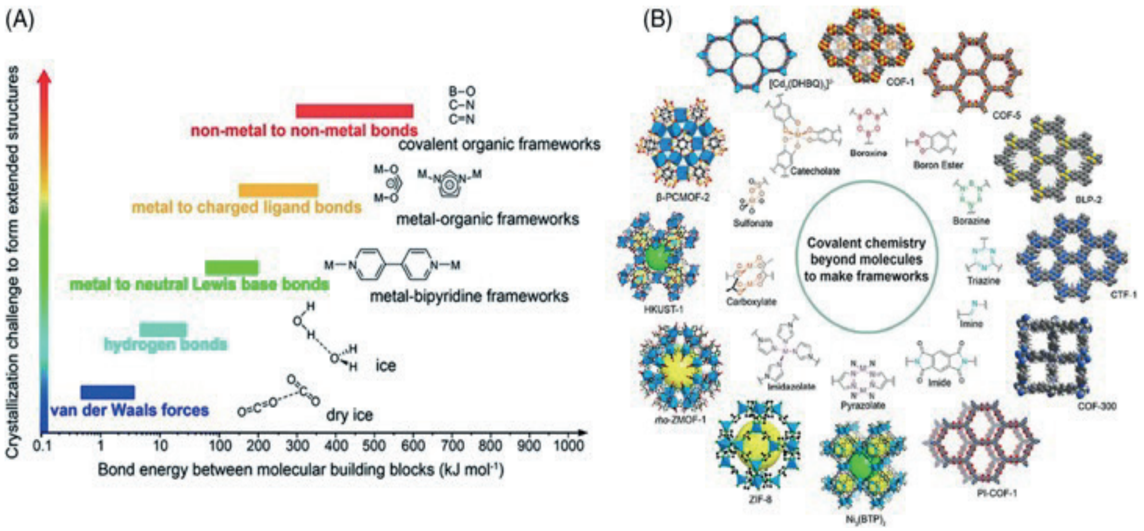


Figure 6.2 (A) The bond energy of the connections between molecule building blocks and the stability and crystallization of crystalline expanded structures are correlated. **(B)** Common COF and MOF kinds with various covalent connections (D. Yang et al., 2021).

(a) Metal–organic framework

Since its initial report by Yaghi's group, MOF—which consists of porous structures formed by metal (nodes) plus organic ligands (linkers) through coordination bonds—has attracted a lot of attention (Du et al., 2022). MOF has customizable morphologies, structures, and physical properties since most transition alloys, post-transition metals, and lanthanides may serve as nodes, and bi- and tri-carboxylate-involved benzene rings and N-involved cycloalkane can be linkers (Iniyan et al., 2023). Over 20,000 different varieties of MOFs have been recorded to far, including ZIF-8, MIL-53, UiO-66, MOF-808, HKUST-1, and others (Al Obeidli et al., 2022). Figure 6.3 displays a few common MOF structures. Furthermore, via ligand exchange and heating post-treatment, MOFs can serve as designs or indicators to form carbons that are porous (PCs), metal-encapsulated PCs, and permeable metal oxide (Chu et al., 2021). This process produces a rapidly growing number of hybrid MOFs and makes it easier for MOFs to be used in a wide range of applications (Chu et al., 2021).

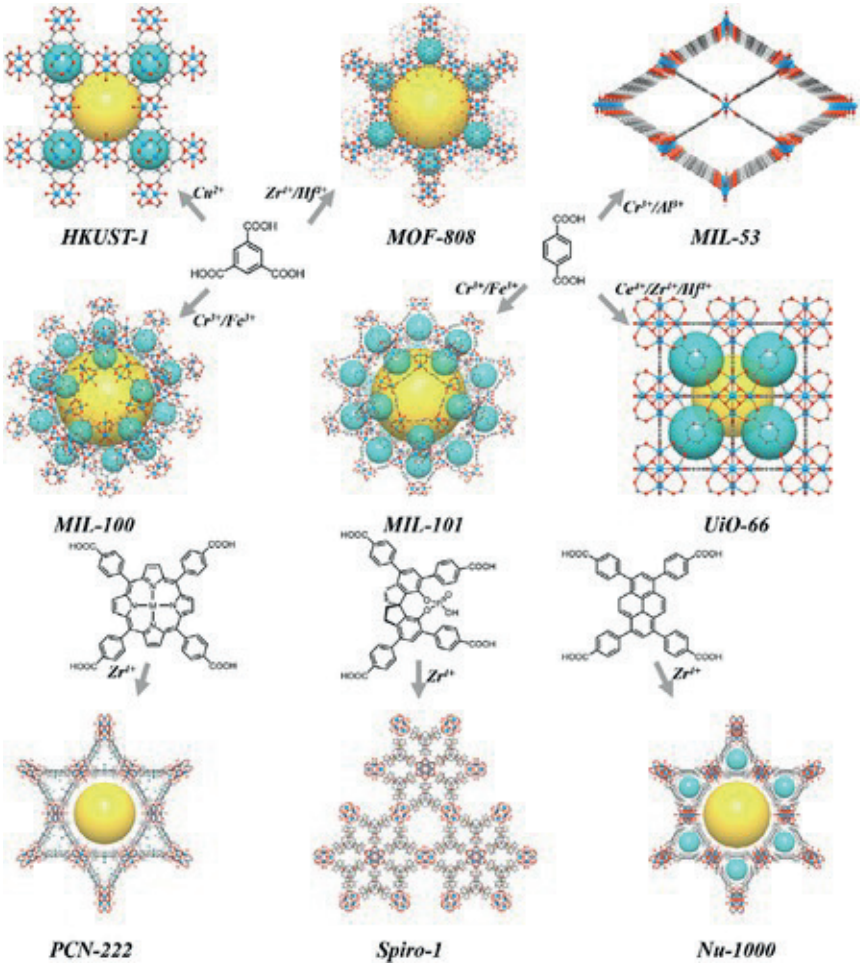


Figure 6.3 Common MOF kinds with various active sites (D. Yang et al., 2021).

(b) Covalent organic framework

Several organic linkers are polymerized to create COF, a natural polymeric component (Figure 6.4). In this instance, COF's crystallinity is reduced because of its more stable structure compared to MOF, which has metal-oxide linkages and a framework connected by strong covalent connections (Gong et al., 2023). Furthermore, the pre-made linker monomers can regulate the spatial architectures of COFs. It has been claimed that a variety of chemical linkers, including sp2-carbon, boroxine, imine, boronic ester, hydrazone, triazine, and phenazine, can produce COFs (Gong et al., 2023). Like MOFs, COFs can also be an excellent platform for modifying materials using a variety of techniques, including chemical conversion, metalation, functionalization, and monomer truncation, to produce a variety of multifunctional materials (Bukhari et al., 2023).

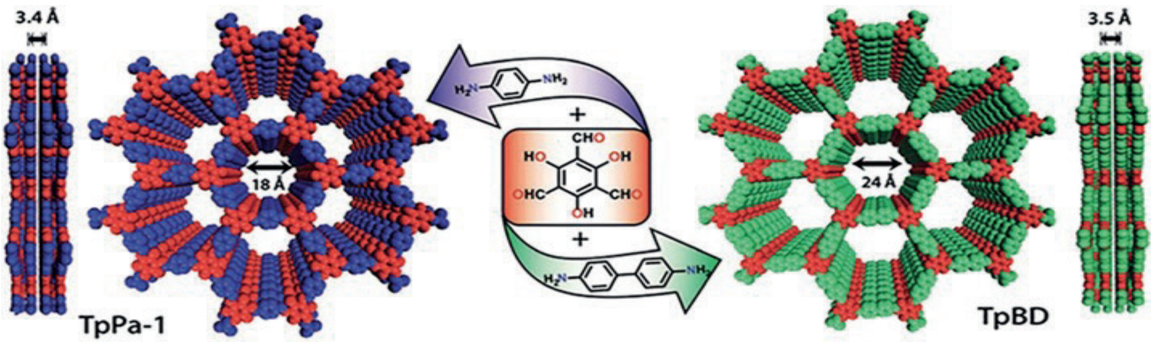


Figure 6.4 Diagrams that show the porous apertures and stacking lengths for the COFs and the packing models during synthesis (D. Yang et al., 2021).

Cluster materials

(I) Polyoxometalate

Polyoxometalate (POM) is a particular type of anionic poly-nuclei metal-oxygen cluster (Lockey et al., 2022). POM generally falls into two categories: heteropolyoxometalates ([XxMyOz]n-, X = Si, P), where negative electrical charge is balanced by counter cations, and isopolyoxometalates ([MxOy]n-, M = V, Mo, W, Nb, Ta, and Ti) (D. Yang et al., 2021). MO6 octahedra, MO5 pentahedra, or MO4 tetrahedra make up most common POM formations (Lockey et al., 2022). Figure 6.5B lists ten types of documented structures, including Lindqvist, Keggin, Anderson, Dawson, and others (D. Yang et al., 2021). Different counter cations, heterometals, ligands, and coordination polyhedral thereby provide POM with varying L/B acid and redox characteristics (Lin, 2021). POM can serve as a great starting point to create a variety of permeable crystal structure materials (Figure 6.5A) (Lin, 2021). Furthermore, POM can be added to specific structural crystalline porous materials, such COF, MOF, and so on, to create novel materials with improved performances in addition to preventing POM from aggregating and deactivating during the catalytic process (Cui & Hu, 2021).

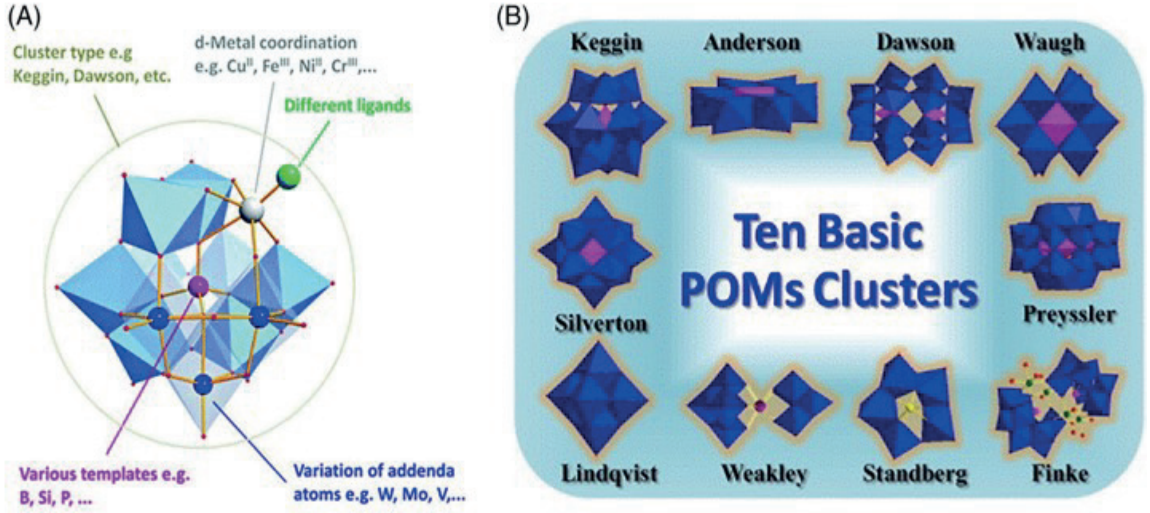


Figure 6.5 (A) Modification sites in polyoxometalate, such as the template, addenda, heterometal, ligand, and counterions; and **(B)** the ten fundamental POM cluster structures (D. Yang et al., 2021).

(II) Metal nanoclusters

Several or even hundreds of metal atoms make up a metal nanocluster, a novel "small" (1 ~ 3 nm) ligand-protected metal nanomaterial that differs from traditional big nanoparticles in that each atom has a distinct energy level (Zhu, 2023) (Maqbool et al., 2023). With surface "staple" structures and kernel structures made up of metal atoms, nanoclusters have their own unique atomic structures. Keep in mind that maintaining the stability of the nanocluster structure depends on the surface structure (Zhu, 2023). Numerous metal nanoclusters have been described up to this point, including mono-metallic Au, Cu, Ag, Ni, Pd, and bi-metallic nanoclusters (Figure 6.6A) (Kang et al., 2020; D. Yang et al., 2021). As an illustration, the gold nanocluster (Figure 6.6B) features a variety of kernel configurations, including face-centered cubic (fcc), body-centered cubic (bcc), hexagonal close-packed (hcp), and icosahedral and biicosahedral structures. Aux (SR)x+1 "staple," such as monomeric staple M-SR-M, dimeric staple SR—AU—SR—AU—SR, pentameric Au5(SR)6, and so on, serve as the main defense for the surface structure (Zou et al., 2023). As a result, metal nanoclusters with clearly defined active sites and high molecular purity can occasionally outperform nanoparticle catalysts, providing platforms for deciphering the atomic-level catalytic mechanism and the structure-catalytic property link (Pei et al., 2024).

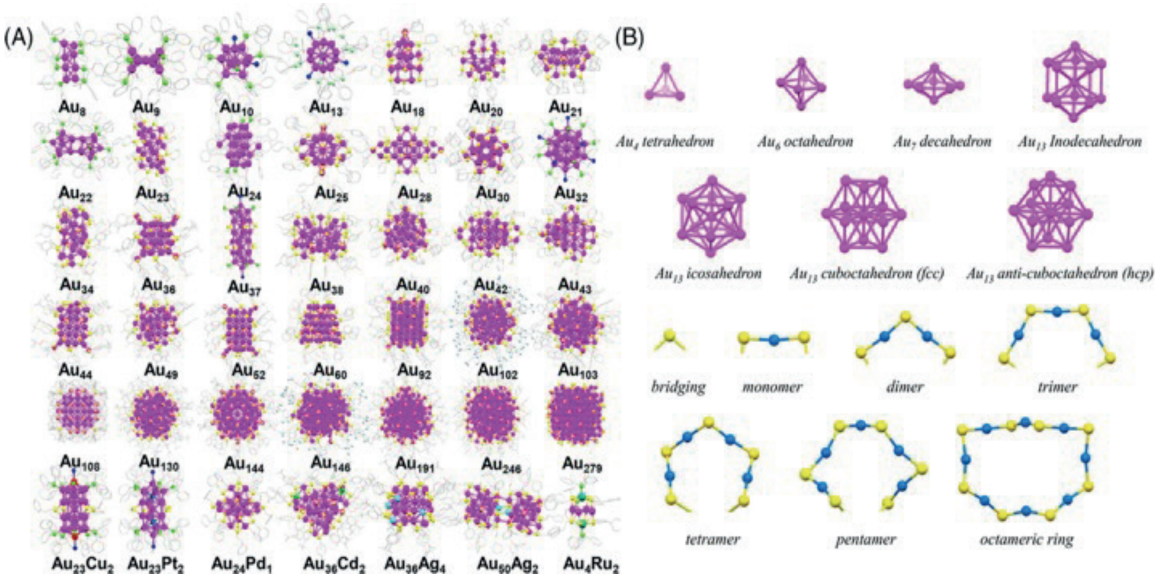


Figure 6.6 (A) Crystal structures of typical Au nanoclusters. **(B)** Au nanoclusters' fundamental kernel architectures and surface-protecting motifs (D. Yang et al., 2021).

7- Catalysis for Sustainable and green Chemistry

Creating catalytic chemical reactions for an environmentally friendly future is an ongoing task spanning several fields of study. Multidisciplinary approaches involving the environment, industry, society, and economic sectors are needed (Cámara et al., 2022). Additionally, to attain increased sustainability, catalytic chemical processes need to be continuously assessed, particularly when used in enterprises or on a household level. Indeed, creating a sustainable future requires chemical catalysis (Sheldon, 2022). Since chemical reactions are used in so many diverse processes, including the production of fuels, food, medicine, and energy, they are inextricably linked to our topic (Lynd et al., 2022).

Here, we incorporate scientific knowledge to assist make these procedures more environmentally friendly. As a result, it lessens the adverse effects on the environment. Reducing the energy required for the processes is essential for chemical catalysis (Lopez et al., 2023). This helps make these systems possible by lowering the usage of energy sources that cause pollution, including fuels sourced from petroleum (Sharma & Shrestha, 2023). Moreover, the increased requirement for high pressure and temperature settings leads to higher energy consumption and, as a result, the generation of waste that contaminates the environment (Kumar et al., 2022). Therefore, the goal of chemical catalysis must be to lower the energy needed for these procedures, such as in the creation of strong catalysts. The development of durable catalysts for use in industry can take various forms, including solid, liquid, or gaseous (Sharma & Shrestha, 2023). The production of desired products must be a part of the catalysts' sustainable working principle. A stabilization power, or the catalyst's ability to be reused in the same process again, reduce the creation of polluting species, and be economically feasible, is another important consideration in the creation of sustainable catalysts (Centi & Perathoner, 2023). Catalytic systems are thus realized on a broad scale through the establishment of sustainable reaction processes. It is possible to lower the amount of energy and environmentally harmful trash produced by using this method. This fact supports green chemical methods and suggests a reduction in the amount of energy derived from oil (Grilli et al., 2023).

Thus, catalysis plays a distinct role in the development of clean, renewable, and ultimately sustainable technology. In this sense, catalysis plays a key role in the creation of fuel cells, which sustainably transform chemical energies into electrical energy (Khademi et al., 2023). Similarly, the process of catalyzing the conversion of biomass—a renewable resource—into biofuels is essential

(Kumar et al., 2022). Today's scientific research enhances the creation of efficient, ecologically friendly, and catalytic chemical processes. Given its attributes, including ease of preparation, low cost, and high catalytic activity, Santos et al. (2023) established prepared WxCeMnOδ/3DOM $ZrTiO_4$ catalysts with usage possibilities for the simultaneous removal of soot particles and oxides of nitrogen from the diesel engine exhaust (Santos et al., 2023). Upon analysis, the produced materials exhibited high levels of structural and catalytic activity. Its flawless structure, plenty of acid sites, sizable area of surface, and the synergistic interaction of the active ingredients all contribute to its high catalytic power. In addition to showing general thermal endurance (250°C–396°C) at the smallest temperature for 90% NO conversion, the produced catalyst W1CeMnOδ/3DOM $ZrTiO_4$ also had an outstanding NO conversion rate (52%) at the soot combustion temperature (Santos et al., 2023).

One ongoing concern is the decrease of greenhouse gas emissions. This information aids in the creation of effective catalytic processors that work together to lessen these impacts. In this regard, Usman et al.'s work offered a suggestion for using catalysts based on Cu, Zn, and Al to catalytically hydrogenate CO2 into useful compounds such methanol (MeOH) and dimethyl ether (DME) (Usman et al., 2023). By using this method, the researchers were able to show how the CO2 and H2 adsorption equilibrium values on the catalysts supplied information on the reaction process. The capacity for adsorption of the reagents was found to relate to the catalytic function, conversion, and yields under investigation. This correlation was confirmed at pressure and temperature that were like those of the hydrogenation reaction. As such, a novel method can be employed to assess and aid in the creation of novel catalysts (Usman et al., 2023). Applications of sustainable catalytic processes can benefit from the use of enzymes (Noor et al., 2022). Because of their distinct catalytic behaviour, enzymes are extensively researched in a variety of catalysis processes. Enzymes can participate in a variety of processes of industrial importance, including alcoholysis, C-C bond formation, transesterification, and esterification (Noor et al., 2022).

Many industrial processes use enzymes, including those in the dairy industry (cheese recovery, flavor improvement, and enzyme-modified cheese (EMC) the manufacturing process), pharmaceutical industry (ibuprofen, naproxen), detergent industry, agricultural industry (pesticides, insects), chemical industry, and oil chemical reactions (fats and oil hydrolysis and bio-detergent synthesis) (Acharya et al., 2022). Because of their unique characteristics, enzymes can be used in place of chemical catalysts in addition to modifying the parameters of the reaction of interest. In this situation, changes to their side chains, domain alterations, and amino acid residues can result in the altering of enzyme activities (Corbella et al., 2023). The function of residue modification on the catalytic function and molecular identification of an alpha-chymotrypsin (CHT) enzyme in the context of a formalin covalent crosslinker was investigated by Biswas et al. in their investigations (Biswas et al., 2022). As the formalin concentration was increased, the results showed a decrease in catalytic activity (Biswas et al.). But the results of (Biswas et al.'s) work might provide insights into drug-target interaction, molecular identification, and macromolecular modification in the future, allowing for the creation of novel binding sites for improved ligand binding via DNA engineering proteins (Biswas et al., 2022).

These days, there is a lot of focus on molecular hydrogen (H2) as the main sustainable fuel for various uses in the future (Ahad et al., 2023). Using catalysts made of precious metals is one method of producing molecular hydrogen (Solakidou et al., 2023). The goal of Kaim et al.'s work was to create substitute non-precious metal catalysts for platinum in the production of hydrogen (Sukackienė et al., 2023). The study employed the enzyme hydrogenase as a model. The variety of elements in a periodic table that are suitable for catalyzing the hydrogen evolution reaction is increased by these investigations with manganese catalysts. Since manganese was included as an extra metal atom that is abundant on Earth in the sequence of mononuclear hydrogen generators, Kaim et al.'s work created a new avenue for research on sustainable hydrogen synthesis. Moreover, manganese is an intriguing option for hydrogen due to its inexpensive cost, wide availability, and benign environmental profile (Sukackienė et al., 2023).

Gaining a thorough grasp of chemical reactions and optimizing systems requires elucidating the role and catalytic features of enzymes (Taylor et al., 2023). To this end, the latest developments quantum mechanics/molecular mechanics (QM/MM MD) simulation of Born-Oppenheimer was employed in the studies of Liu et al. to systematically understand the mechanism of deAMPylation of AMPylated BiP catalyzed by the enzyme FICD (filamentation induced by cAMP domain protein, commonly referred to as HYPE) (M. Liu et al., 2023). Instead of the common theory that refers to a nucleophilic attack of water molecules adding, the investigations were able to demonstrate that the transfer of protons from the protonated histidine (His363) in FICD to the AMPylated threonine (Thr518) in BiP commences the deAMPylation process. Moreover, it was discovered that humans can change the critical AMPylation inhibitor Glu234—which has been shown to be necessary for the bacterial deAMPylation process (M. Liu et al., 2023). Liu et al.'s study clarifies the physiological function of the FICD protein and posttranslational modifications (PTMs).

8- Catalytic Applications in Energy Conversion

A key force in the energy countryside, catalysis affects processes all the way through the energy life cycle (Hosseinzadeh-Bandbafha et al., 2023). Catalytic processes are crucial in determining how energy systems are shaped, from the conventional production of fossil fuels to the emergence of environmentally friendly energy sources like hydrogen energy and artificial photosynthesis. The complexity of catalysis in energy applications is explored in this chapter, which presents studies and reviews that provide insight on the complex interplay between catalytic mechanisms and the changing energy paradigm (Afolabi, 2024). Catalytic processes play a major role in traditional fossil fuel extraction by allowing hydrocarbons to be valuably extracted. In this situation, catalytic reaction optimization is still crucial for efficiency and environmental reasons catalysis plays a key role in enabling greener and more sustainable energy alternatives, such as the generation of biofuel from renewable resources or the removal of CO_2 from the environment from power plants, or industrial sites (S. Li et al., 2023).

The move to sustainable energy brings with it new opportunities and problems, and catalysis turns out to be a major facilitator of this change (Isahak & Al-Amiery, 2024). One major area of focus is hydrogen as a green energy carrier. The creation, storage, and use of hydrogen depend heavily on catalysis, which also affects the feasibility and efficiency of hydrogen as an environmentally friendly fuel (Muhammed et al., 2023). Solar light-harvesting systems have gained significance in the quest for renewable energy (Bouclé et al., 2023). In these efforts, catalysis plays a crucial role, especially in the creation of materials and procedures for artificial photosynthesis. These developments hold potential for sustainable energy generation since they mimic nature's efficiency in absorbing and transforming solar energy into chemical energy.

Anwar et al. presents a novel electrocatalyst made by pyrolyzing Cu-tpa MOF with low Pt loading and exhibits good ORR performance on par with commercial Pt/C (Anwar et al., 2020). It is highlighted that metal-organic frameworks (MOFs) can be used as precursors for nanocomposites because of their stable electrochemical reactions at elevated temperatures and distinct porosity architectures. Using density functional theory (DFT) computations to improve our understanding of ORR catalysis is another important issue (Liao et al., 2022). The effect of CO_2 activation and reduction on faulty FeS surfaces is thoroughly investigated by Dzade et al. Having such mechanistic insights is crucial to creating effective CO_2 conversion catalysts (Dzade & de Leeuw, 2021).

Moreover, the papers devoted to coordination compound-derived and perovskite-based catalysts demonstrate creative methods for overcoming ORR-related difficulties. A highly effective and long-lasting LaMnO3@C-Co_3O_4 composite is introduced in the study by Karuppiah, et al. which shows excellent oxygen electrocatalysis in an alkaline environment (Karuppiah et al., 2021). Expanding on the thoughtful contributions previously mentioned, a variety of further groundbreaking discoveries that push the boundaries of catalysis for uses in energy. A simultaneous electrocatalyst for the oxygen reduction process (ORR) is introduced by Sridharan et al. In alkaline media, the combination of Co-doped CeO2 and N- and S-doped reduced graphene oxide (rGO) showed improved ORR performance. By highlighting the possible uses of the synthesized electrocatalyst beyond conventional fuel cells and metal-air batteries, this study highlights its versatility (Sridharan et al., 2022).

An interesting reversal of the photo galvanic effect caused by doping NiSalen polymers with anionic porphyrins is explored in the article by Petrov et al. This surprising occurrence presents a new facet in the field of photoelectrochemical processes and opens new paths for studying the interaction between conductive polymers and dopants. It was investigated using ultraviolet-visible spectroscopy and cyclic voltammetry (Petrov et al., 2021). In addition, Cross et al. offer a basic knowledge of Ni3N surfaces related to the hydrogen evolution reaction (HER). The study provides knowledge about the durability of Ni3N surfaces, water adsorption, and energies of activation for HER using dispersion-corrected density functional theory (DFT-D3). This thorough theoretical approach provides important insights for designing effective Ni-based HER catalysts (Cross et al., 2021).

Aladeemy et al. discuss the electrooxidation of urea, a vital step in the treatment of wastewater. When nickel hydroxide was electrodeposited onto commercial carbon paper using dimethyl sulphoxide solvent, an extremely stable and active electrocatalyst for the electrooxidation of urea in an alkaline environment was produced. This work presents a viable method using transition metal electrocatalysts to activate commercial carbon paper (Aladeemy et al., 2021). Furthermore, Matienzo et al. assess perovskite materials for alkaline water electrolysis's oxygen revolution reaction (OER). To provide a methodical evaluation of perovskite-based electrocatalysts for sustainable energy production, the study considers industry requirements and criteria (Matienzo et al., 2020).

A novel method is used by Alekseeva et al. to create a bimetallic Cu/Pt catalyst. This product demonstrated exceptional resistance to the existence of methanol in the solution in addition to having significant activity in the ORR. The continuous efforts to create effective catalysts for fuel cell applications are aided by this work. The wide variety of catalysts investigated and the use of sophisticated methods like DFT calculations not only expand our knowledge but also create opportunities for the creation of more sustainable and effective energy conversion systems (Alekseeva et al., 2020).

9- Emerging Trends and Future Directions

In the past, transition metal catalysts have dominated the area of catalysis in chemistry. Precious metals have been essential in creating catalysts for novel processes of chemical bonding activation and creation because of their special set of features (Vieira et al., 2023). However, one significant and inherent disadvantage of precious metals is their scarcity; developing alternate catalysis mechanisms is important factor in modern research to shift chemistry to more environmentally friendly utilization of the world's scarce resources. One of the most important contributions to solving the most pressing global issues is heterogeneous catalysis (Low et al., 2023). The common characterization methods and ideas in the most recent literature represent a trend that the catalysis field has seen in recent years: a blurring of the lines separating traditional thermal catalysis, photocatalysis, and electrocatalysis (Suremann et al., 2023).

Three main topics may be identified in the current state of catalysis research: the creation of novel catalysts, the investigation of reaction mechanisms, and reaction design for specific processes (Zhao et al., 2023). In catalysis research, creating catalysts with novel structures or formulations might always encourage the study of new phenomena. From a fundamental perspective, comprehending the molecular and atomic arrangements of solid catalysts is essential for designing catalytic materials logically and for desired reactions (S. Xu et al., 2024). The manner of contemporary research on catalysis reflects this tendency, typically utilizing numerous advanced characterization techniques to disclose the atomic and molecular structures of the active sites. Practically, advances in materials fabrication and reaction engineering have demonstrated significant promise in tackling global issues like climate change and the switch from fossil fuels to clean energy sources (Kar et al., 2024).

Future catalyst development is anticipated to focus on two primary areas: developing new processes that make use of different raw materials with the help of new catalysts and refining current methods to increase yield and selectivity while saving energy in the production process (Serrano et al., 2024). Homogeneous transition metal catalysis is currently essential to the wide range of catalytic processes and is predicted to become even more important in the future.

In homogeneous catalysis, data-driven knowledge development based on premium databases and machine learning algorithms is revolutionizing the profession (H. Li et al., 2023). Catalytic transformations have traditionally been developed or improved using computational mechanistic studies or trial and error methods. On the other hand, new experimental and digital methods are generating catalytic system data more quickly, which makes it easier to train predictive machine learning models for catalyst discovery (Mace et al., 2024). Notwithstanding the encouraging developments in the subject, several problems, including a lack of data and code transparency, are impeding the industry's advancement. For that reason, we believe that to fully utilize ML approaches, an open access philosophy about methods and data will be essential (Casacuberta et al., 2024). Furthermore, we believe that easily navigable interfaces like ROBERT and public repositories like the ioChem-BD database will be critical in facilitating the wider chemistry community's adoption of machine learning (ML) tools and bringing them closer to organic/organometallic laboratories in near future (Tom et al., 2024).

10- Challenges and Opportunities in Catalysis

Catalyst innovation has led to numerous advancements in industrial chemistry, and it is possible that catalysts will hold the key to solving today's problems. Scholars have discovered new applications for catalysts to address issues in business, health, and the environment. These investigations could grow into large-scale applications in the upcoming years.

10.1 Machine Learning

Since novel catalysts are often extremely complicated structures with a wide range of features, designing them has consistently been a trial-and-error process. Because of this intricacy, researchers find it very challenging to forecast the effects of minute modifications to the structure on performance. They must instead rely on real-world trials of every variant, which adds cost and time to the research process by creating, testing, and then discarding many potential outcomes.

However, a fresh method for designing catalysts is provided by developments in machine learning (Zhuang et al., 2024). Catalysis research is only one of several sectors using artificial intelligence (AI) to tackle problems as machine learning advances. In ways that humans could never notice, specially trained programmers are able to use extra data to make predictions and identify patterns and correlations. Machine learning can save time and money by reducing the number of possible designs without the need for real-world testing in the catalysis process (Çıtmacı et al., 2022).

Recently, Chinese researchers showed how machine learning could be applied to catalysis research (Lee et al., 2024). The group's goal was to create a perovskite oxide catalyst that would accelerate oxide reduction in solid-oxide fuel cells through their research on these fuel cells. They might utilize the AI to discover relationships between specific important characteristics and catalyst performance after training it with a carefully chosen data set. By using this approach, the researchers expect to expedite the production of catalysts soon for similar initiatives (Lee et al., 2024).

10.2 Enzyme Engineering

Enzyme engineering has also made use of machine learning. Since enzymes are biological catalysts, businesses have been designing enzymes through genetic engineering. Microorganisms can create enzymes that catalyze processes by modifying amino acids (Porras-Dominguez et al., 2024). Enzyme engineering is a relatively new technique but is already used in industrial and medical operations. Enzyme engineering is not without restrictions, though (J. Yang et al., 2024). Gene manipulation can be an uncertain procedure, and naturally occurring enzymes are typically less robust than modified enzymes. Although some enzyme compositions have eluded scientists, machine learning may be able to change this. Recently, Moderna has created a technique that uses machine learning to improve medicinal enzyme engineering. This method might be modified for industrial application, opening new possibilities for biological catalysis (Feng et al., 2024).

10.3 Alternatives to Precious Metals

Precious metals are catalysts in numerous chemical reactions. Platinum is used in catalytic converters, which is a clear example, but precious metals are also needed in numerous manufacturing processes to catalyze reactions (Willner, 2024). This is obviously a concern because as the supply of these metals decreases and new applications are discovered, the demand will only rise, making them more expensive and difficult to find. In the future, this will pose a significant obstacle to catalysis, so scientists are already looking for a substitute. Though progress is sluggish, some strides have been made.

Photocatalysis has been found to be an effective substitute for precious metal catalysts in some reactions, according to research conducted in conjunction with Princeton University, Rice University, and Syzygy Plasmonic Inc. (H. Li et al., 2024). Light can accelerate catalysts known as photocatalysts because photon energy excites electrons and produces free radicals (Jiang et al., 2023). Though photocatalysts have been theoretically proposed for almost a century, commercial applications have not yet been realized.

In this project, ammonia was converted to hydrogen for use in fuel cells using a photocatalyst based on iron (G. Li et al., 2023). Previously, ruthenium—much harder to get than iron—was employed in this reaction. The accomplishments of this group are noteworthy for precious metal catalysis in general as well as for this particular technique. It moves the industry closer to creating photo catalysis and displacing precious metals. In this project, ammonia was converted to hydrogen for use in fuel cells using a photocatalyst based on iron. Previously, ruthenium—much harder to get than iron—was employed in this reaction. The accomplishments of this group are noteworthy for precious metal catalysis in general as well as for this particular technique. It moves the industry closer to creating photo catalysis and displacing precious metals (G. Li et al., 2023).

10.4 Electro catalysis

Catalysts employed in electrochemical reactions—those brought on by an electric current—are known as electrocatalysts (Toan et al., 2023). Electrocatalysts are already used in a lot of electrochemical processes, but scientists are working to make them more robust and effective. Fuel cells made of hydrogen are one application for them. Fuel cells aren't a reliable source of energy since the electrochemical process of separating hydrogen and oxygen molecules takes too much energy now (Christopher & Dimitrios, 2012). Electrocatalysts with higher efficiencies have been researched for decades with the goal of developing fuel cell technology. Because it would address the problem of energy storage, this would be a huge advancement for green energy (G. Zhang et al., 2024).

10. 5 Catalytic Waste Management

Catalysts may be the answer to tackling another environmental problem, namely plastic waste. It is commonly known that plastic is difficult to dispose of due to its extraordinarily extended breakdown time (Dey et al., 2024). Existing techniques, like mechanical recycling, incineration, and landfills, all have serious disadvantages, and attempts to cut back on plastic use have failed because garbage output keeps rising. Some researchers are using catalysis to stop this epidemic of plastic trash (Yim et al., 2024). Several investigations have discovered catalysis-based techniques for handling different types of polymers (Naumann, 2023). These techniques not only reduce waste but also yield useful goods like chemicals or fuel that can be put back to use in other industrial processes. This warrants funding for such technologies from an economic and from an environmental perspective.

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MEDICINAL CHEMISTRY, DRUG DESIGN AND DEVELOPMENT

Oladoja A. AWOFISAYO

Ibuotenang Nnamso DOMINIC

This chapter includes the medicinal chemistry is an aspect of science that is directly related to the art and technicalities involved in the chemistry of drugs and their biological activity. It is a composite of various fields like chemistry biology and the relationship of structure to the activity of drug molecules. It is a dynamic field that involves synthetic engineering, chemical synthesis, natural product chemistry, drug metabolism and the action of drugs on the body and vice-versa. It also involves the study of various classes of drugs like l anti-infective agents, anticonvulsants, anti-cancer, hypoglycemic agents, anxiolytic agents, and adrenergic and cholinergic agents. It also relates to biological profiling of natural products, total synthesis, in vivo, in vitro animal study evaluation of potential drug candidates, and drug-receptor interaction drug design using computational chemistry. Nature is a chemist with a reservoir of varying lead compounds which can serve as a starting point for further investigation. Traditional methods involved the characterization of active phytocompounds from medicinal plants, in vitro animal studies, and clinical trial stages. Lead search from natural products is capital intensive, involves a long period and there's no guarantee that the drug derived will perform excellently in the clinical trial stage. The lead compounds are generated from natural products, natural product derivatives, and synthesized small molecules. A shift from this earlier method is what is known as rational drug design this method is based on an understanding of drug in Bracket ligand and receptor interaction. Receptors are small molecules like cellular proteins and DNA that serve different functions and are involved in physiological mechanisms or disease prevention of disease progression in humans or microorganisms. Identification of Lead compounds that interact with the cellular proteins and receptors can result in the modulation of the physiological process. They regulate the disease state and can be optimized in silico such that the efficacy is improved at reduced toxicity and side effects due to off-target binding.

1. Introduction

Medicinal chemistry is that aspect of chemistry that deals with the various methods used to source for drugs, the way the drug is handled by the body, the effect of the drug on the body, the interaction of the drug with the target biomolecule (protein/DNA) and the navigation of the drug for its entire course through the body (Boström et al., 2018; Wood, 2005). The drug in the ideal situation after performing its task and being a foreign entity must be eliminated from the body. The entire process of the drug from inception (drug design and development), its entire course through the body (pharmacokinetics), what the body does to the drug (pharmacodynamics), the interaction with the target, toxic effects through binding with off-target, the conversion to a polar molecule and it’s exit from the body forms major aspects of medicinal chemistry. The study of the way the diseased state and how the drugs reverse this are all integral parts of medicinal chemistry (Andrade et al., 2016).

The plant has been used right from the time of existence of man to treat various ailments and diseases (Raj et al., 2018). The medicinal chemist strives to determine the components responsible for the activity when used for the treatment of various ailments. In doing this, the part of the plant he is interested in (leave, stem, root, fruit, or back) is passed through various processes to obtain the active component responsible for a particular effect and in the treatment of an ailment (Nelson et al., 2017).

Nature therefore offers the medicinal chemist a variety of active scaffolds that can be modified to provide optimized scaffolds that can provide therapy for human disease (Boström et al., 2018). The process of obtaining viable scaffolds from nature is laborious and takes approximately 12 years

(Hiesinger et al., 2021). Computer Aided Drug design offers a novel approach to the laborious methods of obtaining the active components of a plant utilizing screening methods for example High Throughput screening (HTS). This novel approach is feasible through the knowledge of the molecular basis of disease genomics and proteomics of both humans and pathogens as made feasible a drug design modality that allows drugs to be designed and subsequently developed based on the knowledge of the structure of the target function and mechanism of action.

Fields of studies incorporated as associated with Computer Aided Drug Design include chemistry, biophysics, molecular biology, bioinformatics, biotechnology, genomics, proteomics, mathematics, and statistics (Poduri, 2021). Information science computer science computation computational about medicine neurology biomedical engineering proteogenomic, system biology, and network pharmacology

This method CADD the Experimental method of isolating drug molecules can therefore be compared with in silico CAD approach (Gupta et al., 2021). Methods like molecular docking fragment-based drug Discovery don't have novel design as well as structure pharmacophore modeling which is dependent on ligand properties. The link compound can therefore be formulated based on nanotechnology. Application of quantitative structure-activity relationship QSAR. Affinity relationship it can be applied to why can't be based on drug design. This method generates a lot of molecules in the drug design pipelines that can be screened.

Medicinal chemistry includes the essential field of drug design and development, which seeks to find new tiny molecules to use as late compounds in the treatment of many maladies and infections. (Ghosh & Brindisi, 2015)

The branch of research that deals directly with the chemistry of pharmaceuticals has been called medicinal chemistry. It is a combination of biology and biochemistry, among other related sciences. Bows are also taught in the curriculum. artificial engineering the synthesis of chemicals drug testing in vivo, vivo, and in vitro, as well as natural product chemistry and biological profiling

Drug classes such as anticancer, hypoglycemic, and anticonvulsants are studied, as well as adrenergic, anti-addinagic, cholinergic, and anticholinergics holytics.

2. The art of obtaining novel drugs

Currently, drugs in use may have toxicity problems on the right desirable side effects solubility issues and in the case of anti-infectives antimicrobial resistance multidrug resistance and extensive drug resistance have become major factors which make available drugs to be effective against the microorganisms’ drug design, therefore, play a pivotal room in the discovery and development of new compounds that are safe and if effective to combat disease (Choudhary et al., 2017).

Recently, CADD simplified the drug discovery process through the mix fields it is possible to generate multiple targets and decipher other means of inhibition of metabolic pathways of metabolic pathways to obtain unique targets that can serve as receptors of novel drug molecules (Ebhohimen et al., 2019).

The modulation of physiological processes that regulate biological activities in disease progression has also been explored. Vaccine development is another area the immunology. The paradigm shift from the traditional method to CADD is a complementary method to experimental methods and not a total replacement. Screening is a vital aspect and is called high throughput screening (HTS). Virtual screening is a method that has been applied indeed the from the 80s and improved with higher computational technology and performance (Ma et al., 2015)

3. Quantitative Structure-Activity Relationship (QSAR)

Quantitative Structure-Activity Relationship is an advanced powerful computing tool used in drug design and development (Batool et al., 2019; Usha et al., 2018b). Quantitative Structure-Activity Relationship (QSAR) is a computational approach within ligand-based virtual screening (LBVS) that establishes mathematical connections between chemical, structural, statistical, and physical properties of small molecules and their biological activities (Asirvatham et al., 2019). Rather than being limited to an academic tool for data rationalization, QSAR serves to derive meaningful relationships between molecular structure, chemistry, and biology. These relationships facilitate the development of predictive models, which, when combined with sound judgment and expertise, can be applied to numerous practical scenarios. QSAR techniques are extensively utilized across various fields due to their versatility and practical applications as shown in the Figure 1. A mathematical model is generated as a training set and this is used to predict the bioactivities of novel compounds. There is also the quantitative structure-property relationship (QSPR) in which the response variable is a particular property, quantitative structure-reactivity relationship (QSRR), quantitative structure-toxicity relationship, Quantitative structure-electrochemistry relationship, and quantitative biodegradability relationship (Treifeldt et al., 2020).

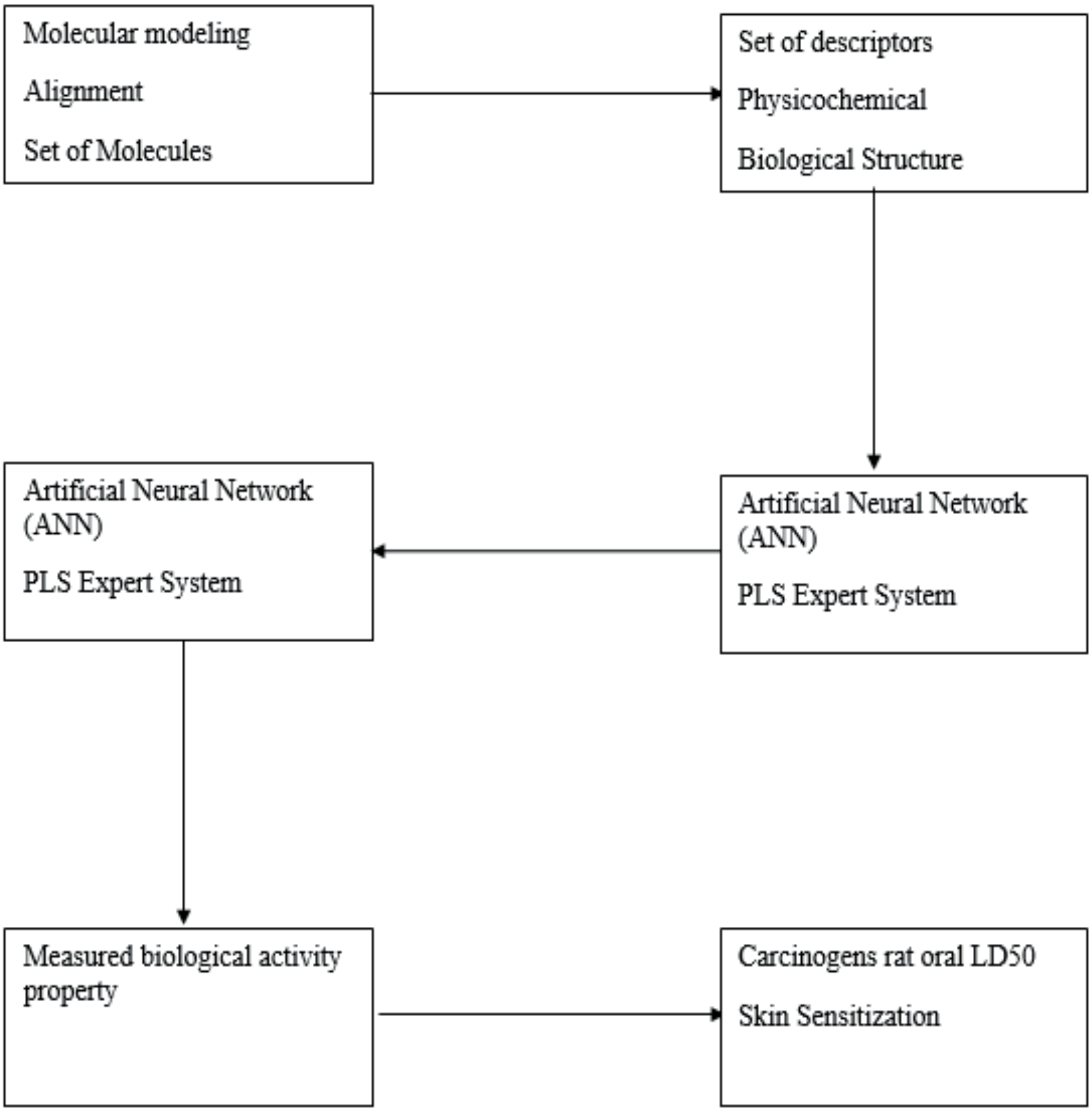

Figure 1 QSAR Techniques

QSAR uses regression analytical models where the "descriptors" are identified for the training set of molecules, for example, 3D properties in space etc (Danishuddin & Khan, 2016). On the other hand, "Predictors" variables are the biological activities of the training set e.g. inhibitory concentration and measure of the effectiveness of a substance in inhibiting a specific biological receptor or biochemical function (IC50), the concentration of an inhibitor that will induce a response halfway between the baseline and the maximum (EC50). Others are median Lethal dose (LD50), LC50 (median lethal concentration) (Hodyna et al., 2016; Shiri & Ghasemi, 2013).

In the past, correlation of biological activity has been done with physicochemical properties like molecular weight, lipophylicility, acidity, boiling point or melting point). This is referred to as 1D-QSAR. Subsequently, there is 2D QSAR, 3D QSAR, 4D QSAR, 5D and 6D QSAR (Bahia et al., 2023). The quantification of the chemical structure remains a challenge. Statistical methods are used to develop the QSAR model and different methods like clustering, partial least squares, principal component Analysis.

4. Applications of QSAR

1) The QSAR models are used to predict the biological activity of novel molecules on a specific target before synthesis and ultimately in vitro, and in vivo testing.

2) Ligand-based virtual screening of compound libraries can be performed using QSAR models so as to select the best compounds with predicted biological activity against the specific target (see Figure 2).

3) QSAR-guided lead optimization paves the way for screening a large database of molecules, comparing molecules with suitable features, and selecting the best molecules to fit the target.

4) QSAR models help to filter molecules so as to optimize the ADME-tox properties (Abdel-Ilah et al., 2017; Jeremić, 2017).

Chimenti et al. (2006) and Asirvatham et al. (2019) both reported that 2D descriptors, including thermodynamic, spatial, electronic, and topological parameters, were calculated for QSAR analysis using Vlife MDS software. These parameters have specific functions: thermodynamic parameters represent the free energy change during drug-receptor complex formation, spatial parameters quantify the steric features of drug molecules necessary for complementary receptor fit, and electronic parameters describe the weak non-covalent bonding between drug molecules and receptors.

During QSAR analysis, regression was performed using IC50 values as dependent variables and the calculated parameters as independent variables, as illustrated in Figure 3. This approach aids in understanding the relationship between the molecular properties of drug candidates and their inhibitory effects on specific biological targets, ultimately facilitating drug discovery and optimization.

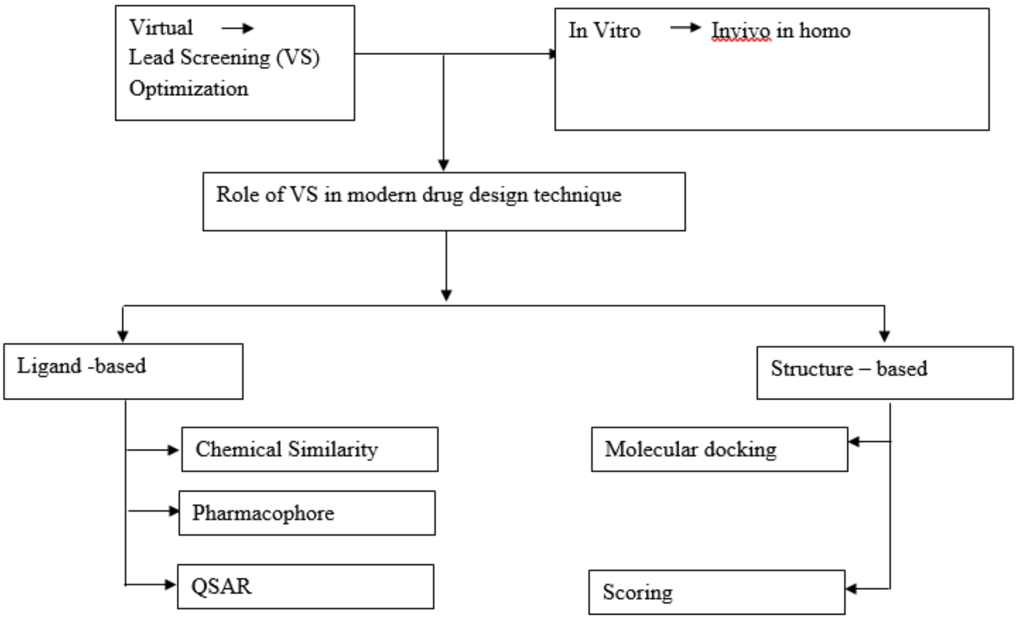

Figure 2: Virtual Screening Methods

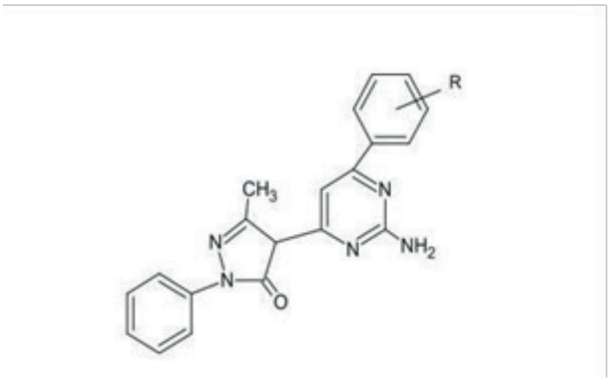

Figure 3: Derivatives of substituted pyrazolones (Asirvatham et al., 2019).

In addition, Neves et al., (2018) emphasize the importance of QSAR modeling in drug discovery as shown in Figure 4 due to its cost-effectiveness and efficiency compared to high-throughput screening (HTS) platforms. QSAR plays a significant role in prioritizing compounds for synthesis and biological evaluation, aiding both hit identification and hit-to-lead optimization.

During the hit-to-lead optimization process, QSAR models can be utilized to achieve a balance between potency, selectivity, and pharmacokinetic and toxicological parameters, which is crucial for the development of safe and effective drugs. This optimization can be accomplished through several iterative cycles without the need for compound synthesis or testing before computational evaluation. Consequently, QSAR represents a labor-, time-, and cost-effective method for obtaining compounds with desired biological properties, accelerating the drug discovery process as shown in Figure 5. The process begins with the curation and integration of data sets obtained from external sources to eliminate or rectify inconsistent data. Following this step, QSAR models are developed and validated in accordance with OECD guidelines and established modeling best practices. Once validated, these models are employed to identify chemical compounds that are predicted to exhibit activity against selected endpoints within extensive chemical libraries.

By following this approach, researchers can efficiently leverage QSAR models to screen large numbers of compounds and prioritize those with the highest likelihood of desired biological activity, streamlining the drug discovery process and facilitating the identification of promising drug candidates.

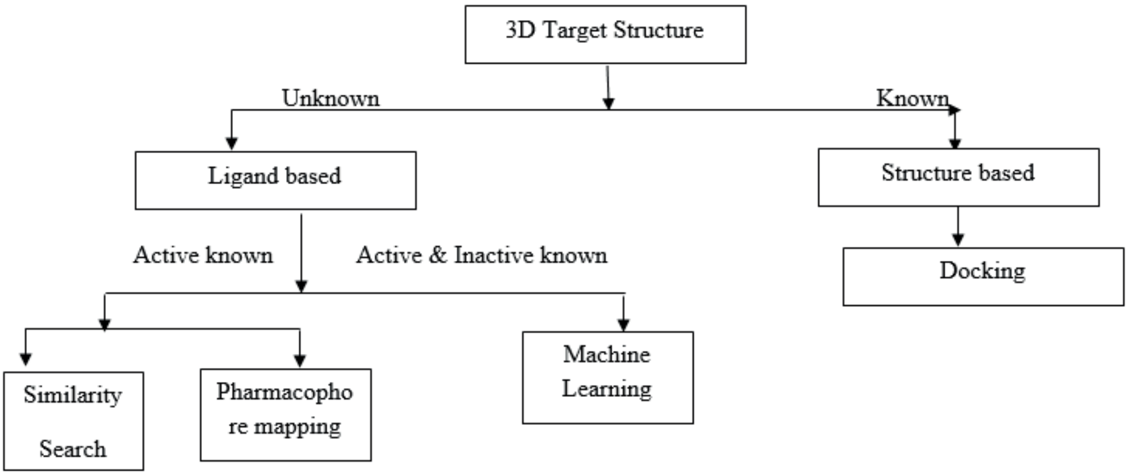

Figure 4: Drug discovery diagram

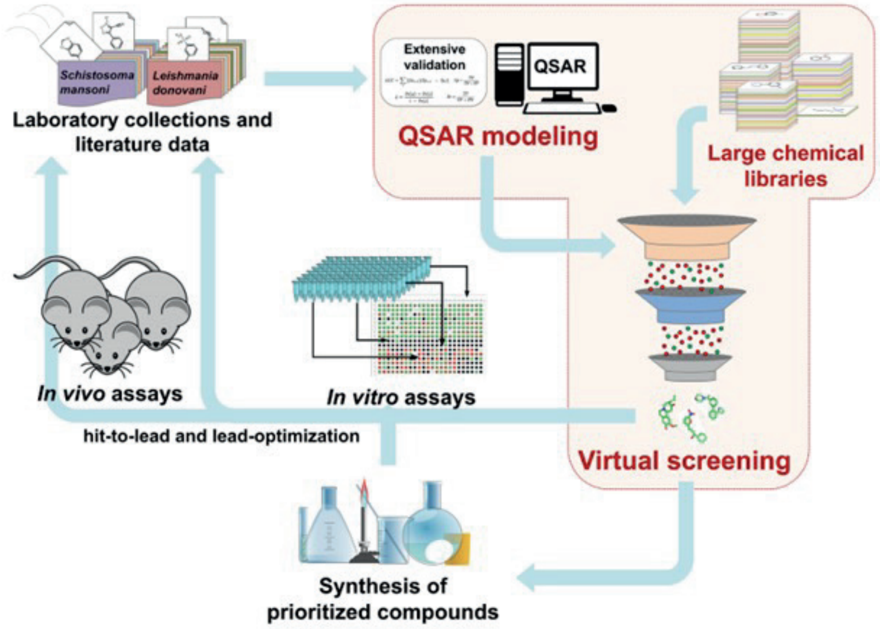

Figure. 5: Virtual screening workflow based on QSAR (Neves et al., 2018).

Jagiello et al., (2016) discussed the growing relevance of computational studies in understanding the activity and toxicity of nanoparticles, particularly fullerene derivatives. These studies are primarily guided by the fundamental chemistry principle that structurally similar compounds tend to exhibit similar biological properties.

Among these computational techniques, Quantitative Structure-Activity Relationships (QSAR) modeling stands out as the most prominent approach. Over the years, there has been a substantial rise in the application of both classic and 3D QSAR methods in nano-QSAR studies to explore the biological activity of nanoparticles. While these techniques have their advantages, it is also essential to consider their limitations when employing them for predictive modeling in nanomaterial research (Jagiello et al., 2016; Mikolajczyk et al., 2015).

The classical QSAR approach, also known as Hansch Analysis (Jagiello et al., 2016), operates on the premise that the biological activity of chemicals can be associated with their physicochemical properties and structural descriptors (Puzyn, Mostrag-Szlichtyng, et al., 2011). These descriptors represent specific structural attributes, encompassing aspects such as polarizability, electronic properties, and steric parameters (Puzyn, Rasulev, et al., 2011).

In this approach, a model is developed by selecting statistically significant variables (descriptors) that offer valuable insights into the mode of interaction being investigated. However, a major limitation of the classical QSAR approach is its inability to consider the 3D geometric features of molecules, which can result in challenges when attempting to accurately describe ligand-receptor interactions. This drawback has led to the exploration and development of alternative methods, such as 3D QSAR techniques, to address these limitations and improve the predictive capabilities of QSAR models (Jagiello et al., 2016).

To better understand and model interactions that involve 3D geometric features, the application of 3D QSAR methodology can yield more accurate results. The pioneering technique in this area, Comparative Molecular Field Analysis (CoMFA), was first introduced by Cramer et al., (1988). CoMFA operates on the assumption that variations in biological activity correspond to modifications in the shapes and strengths of non-covalent interaction fields surrounding the molecules (Cramer et al., 1988).

Building on the foundation of CoMFA, several other techniques have been developed to quantitatively describe 3D interactions. These include Comparative Molecular Similarity Indices Analysis (CoMSIA), proposed by (Klebe et al., 1994), and the GRID/GOLPE program, developed by Reynolds et al., (1989). Both CoMSIA and GRID/GOLPE can be considered extensions of the original CoMFA method, aiming to broaden its applicability. In numerous instances, these approaches are employed as alternatives to CoMFA, thus contributing to the advancement of 3D QSAR techniques.

When considering the importance of bioactive conformation in understanding ligand-receptor interactions, 3D QSAR techniques have been found to be more suitable than classical QSAR approaches (Jagiello et al., 2016). Both classical QSAR and 3D QSAR methodologies are currently being extensively applied to study the biological activity of nanoparticles. However, the question arises: How can one select the most appropriate approach for accurately and reliably describing the biological activity of nanomaterials?

To address this query, a comparison of the efficiency and applicability of both nano-QSAR (the classic Hansch approach) and 3D nano-QSAR (CoMFA/CoMSIA approach) is necessary. By evaluating these techniques, researchers can provide valuable recommendations for QSAR modelers and model users, guiding them towards the most suitable methodology for effectively investigating the biological activity of nanoparticles. Such comparisons can ultimately help determine the best approach for obtaining accurate insights into the behavior and properties of nanomaterials (Jagiello et al., 2016).

5. Limitations

1) QSAR models are largely dependent on the quality and diversity of the training data as well as the choice of molecular descriptors and statistical methods.

2) A QSAR model may perform well on the training data but poorly with the novel molecules.

3) QSAR models may be difficult to interpret if there are multiple targets which the molecules interact with.

6. Molecular Docking (MD)

The elucidation of the 3D structure of protein via proteomics, proteogenomic, high protein purification as well as instrumental methods like Nuclear Magnetic Resonance (NMR) and X-ray crystallography has helped to advance structural details of protein and protein-ligand complex (Singh et al., 2021; Jeremić, 2017). It has been widely used in Structure-Based Drug Design (SBDD) since the 80s. The prediction of the mechanics of interaction of the small molecule ligand (SML) at the binding site (BS) of the receptor can be visualized and analyzed. The BS in the receptor is that portion that has a cavity C or sub-pocket and atoms or the functional groups that form bonds with the ligand (Ahamad et al., 2019; Singh et al., 2021).

MD allows a vigorous study of protein molecular behavior and the characterization of ligand interaction at the atomic level as it occurs at the target site of the protein so that complex biochemical pathways and networks can be explained (Shahbaaz et al., 2018). There are two paths to MD namely the pose which tells about the position of the ligand, its conformation, and orientation. Imagine that you have taken various shots (pictures) of yourself and you select the best shot out of the whole lot- that is the best pose and perfect fit of the ligand into the binding site.

7. HOW DO I KNOW THE BS

The accurate determination of the BS increases the efficiency of the docking process and this can be obtained from a literature search of a ligand to the same protein or proteins belonging to the same family. Various programs can be used for this CHECK, GRID, POCKET, SurfNet, PASS, and MMC.

Types of docking include

Rigid-Ligand-Rigid-Receptor bas proposed by Fischer on the key and Lock theory Flexible-Ligand-and Rigid-Receptor This method was used due to computer limitation Flexible-Ligand-and Flexible-Receptor as described by the induced fit theory of Koshland,

(1994). The molecular events can be captured the intermolecular interactions can be determined that stabilize the small molecule ligand-protein complex (SMLPC).

SAMPLING ALGORITHM

In the 3D space, there are degrees of freedom on the X, Y and Z axis which give translational, rotational and conformational freedom.

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ADVANCES IN ORGANOMETALLIC CHEMISTRY

Zobia ARIF

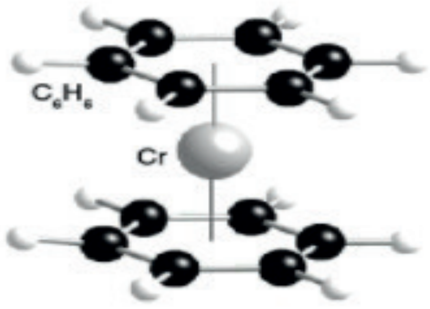
Organometallic chemistry deals with the study of organic compounds having metal-carbon bonds and in recent decades it has undergone remarkable transformation and significant progress. This field has evolved from early discovery of organometallic compounds to modern science with various advances in material science, medicine and medicinal chemistry, polymeric chemistry, bio-organometallic chemistry, catalysis and optoelectronics. New and recent advancement is in the realm of catalysis in which older simpler and expensive compounds are converted into more economical, commercially beneficial, less toxic and less expensive, complex organometallic compounds with variety of applications. The gap between inorganic chemistry and organic chemistry is bridged due to the exploration of biocatalysts, bio-organometallic enzymes, bio- organometallic co-factors, bio-organometallic co enzymes and metalloenzymes that offers novel pathways for catalytic transformations. This field has broad applications in material science where polymeric organometallic compounds are used for the synthesis of coatings, films, and semiconductor and also finds its applications in the manufacturing of LEDs, diodes, organometallic framework (OMFs) and metalloorganic framework (MOFs) shows unique optical, electronic and mechanical properties. Organometallic compounds such as organolithium compounds, organoplatinum complexes, organorhenium etc. also find its applications in sensing technologies, preparation of biosensors and also used in drug delivery. These organic polymeric organometallic compounds are used in cancer treatment, shows antimicrobial activities and peptide synthesis.

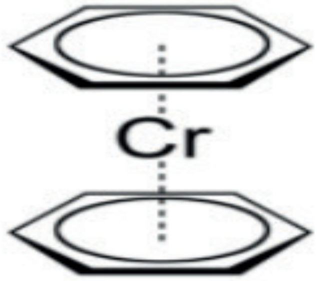
1. Introduction

Organometallic chemistry is the branch of chemistry that deals with the study of organometallic compounds and organometallic compounds are those compounds that contains organic part, metallic part that is actually inorganic part. Organometallic compounds are those chemical compounds which consist of at least one bond that is present between inorganic portion of compound which is metallic element and organic portion of compound which is carbon atom. In some industrial chemical reactions, some metalloids like tin, selenium, boron and silicon are also used in organometallic compounds where these compounds can behave as catalysts to speed up the industrial chemical reactions having polymers as their target molecules. These organometallic compounds can also use in pharmaceutical related chemical reactions in which these compounds can behave as agents which can increase the rate of reaction.

The bond between the carbon atom of organic portion and metallic element of inorganic portion is basically of covalent nature. In some organometallic compounds, the carbon atom has the tendency to show negative character and present in carbanion form if the metal is highly electropositive like lithium, aluminum and sodium and bond becomes polarized covalent bond in which electron pair is shared but not equally shared. The organic portion in organometallic compounds is also called 'ligand' (Crabtree, 2009).

Examples of such organometallic compounds are tetracarbonyl nickel, dimethyl magnesium, Grignard reagents containing magnesium atom as metal, Gilman reagents that contain specifically copper and lithium, polyphophazene and ferrocene that is a highly stable compound containing two hydrocarbon rings in which iron atom is sandwiched etc. An example of organometallic compound is shown below in which carbon atom of benzene ring bond with chromium (Mehrotra, 2007).





1.1 Classification of organometallic compounds

The broad classification of organometallic compounds is based on the type of metal and also on the basis of type or nature of bond present between metal and carbon atom. Following are the main types of organometallic compound on the basis of type of metal:

- **Compound containing normal metal:** Such organometallic compounds mainly consist of metal of s-block (group 1 and 2) which are normal metal or representative elements belongs to A-subgroup of periodic table and present on the left corner of the periodic table. For example, methyl lithium, methyl potassium etc.
- **Compounds containing transition metals:** Such organic compounds mainly consist of metals of d and f- blocks which are transition metals as outer transition metals and inner transition metals (lanthanides and actinides), respectively, belongs to B-subgroup of periodic table and present in the center of the periodic table. For example, dimethyl mercury, tetramethyl lead etc.
- **Compounds containing metalloids:** Such organic compounds mainly consist of metalloids like silicon, tin, boron and selenium etc. belongs to A-subgroup of periodic table as these are also present in p-block of periodic table. For example, tetramethyl silicon etc. (Tyagi et al., 2023).

The following classification is on the basis of type of bond:

- sigma bonded compounds
- pi- bonded compounds
- combination of sigma and pi bonded compounds

1.2 Properties of organometallic compounds:

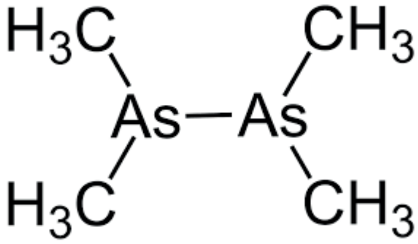
As organometallic compounds belong to diverse class of compounds in which metal is connected to mono-ligand and also poly-ligands to form polymeric compounds showing variety of properties but some are listed below:

- The structure and formation of organometallic compound is based on 18-electron rule.
- The stability and reactivity of organometallic compounds is based on nature and strength of bond between organic part and metallic part of compounds.
- The main cause of reactivity of organometallic compounds is the ‘polarity of bond’ that also is the main reason of the application of these compounds in organic synthesis.

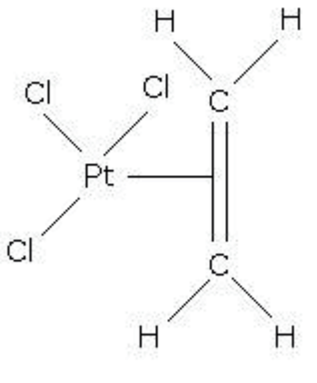
- Organometallic compounds can also act as reducing agents due to the presence of metal.
- These compounds can also be very toxic in nature for human if highly electropositive metal like sodium and lithium etc. is present in them which is volatile and also help in spontaneous combustion.
- Organometallic compounds, consist of aromatic ligand or ring structure in their organic part, mainly exist in the form of solids.
- Some organometallic compounds have ordinary covalent bond in which electrons are shared. Some compounds have bonding that involve two atoms show multicenter covalent bond. Very few compounds can also have bond that is ionic in nature as if lead is present as metal in any compound. The extent of polarization of bond depends on strength with which the metal atom binds electron.
- Their heat and oxidation ability vary from compound to compound (Allardyce & Dyson, 2006).

1.3 Historical development

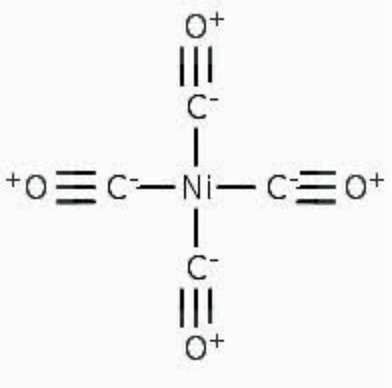
First organometallic compound that is 'tetramethyl diarsine' commonly named as cacodyl abbreviated as TMA or TMAs, (CH3)4As2, was isolated accidently by a French chemist named Louis Claude Cadet de Gassicourt in 1757. He was doing an experiment with invisible inks by the combination of potassium acetate and cobalt ore having arsenic. This was considered an organometallic compound although arsenic is not a true metal but a metalloid. Structure of cacodyl is:



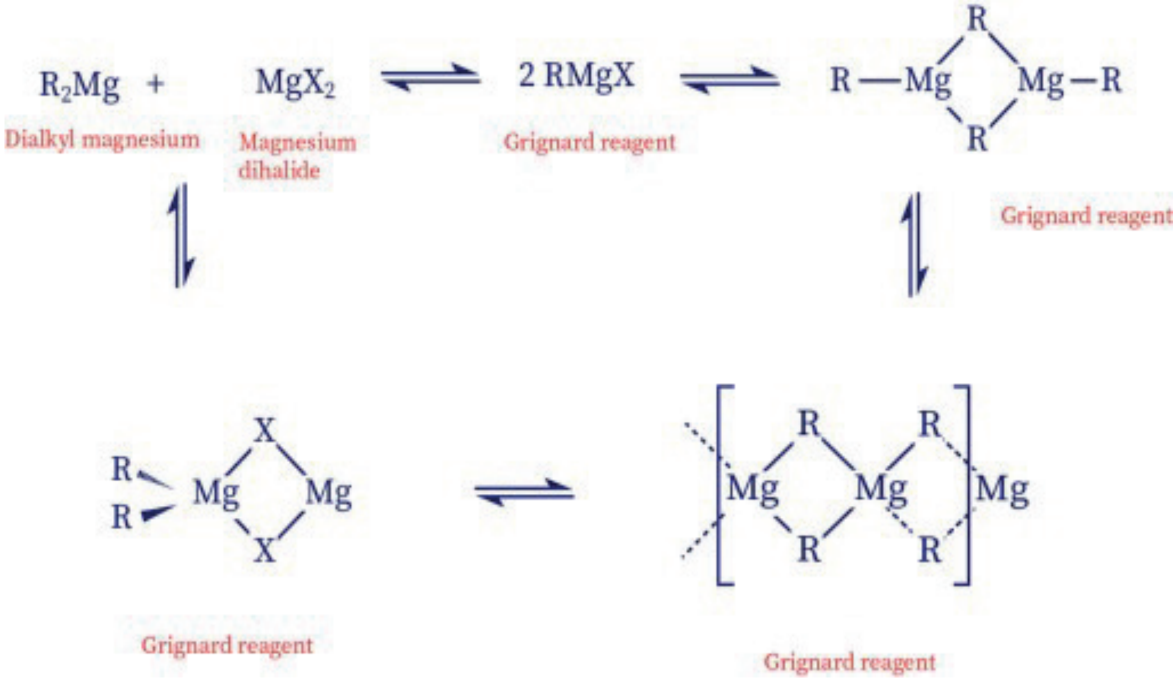
67 years later, a Danish organic chemist William Christopher Zeise discovered first organometallic compound containing a transition metal by placing platinum tetrachloride in boiling ethanol. Trichloro-ethene-platinate (II) anion is formed as a resulting anion, then Zeise salt can be formed when this anion is combined with a potassium counter ion. Structure of Zeise salt is given:



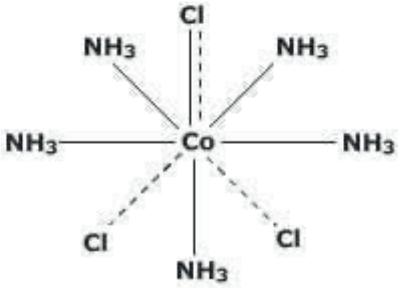
In later 19th century, a British chemist Ludwig Mond synthesized compounds such as diethyl zinc and very toxic nickel tetracarbonyl that initiated an entirely new class of compounds called metal carbonyls. Following is the structure of nickel tetracarbonyl:



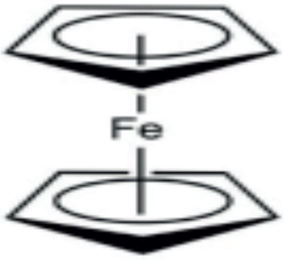
In 20th century, a new method of coupling carbon to the carbon of carbonyl group of aldehyde or ketone that is carbonyl compound by coupling of magnesium metal with alkyl or aryl halide with the help of nucleophilic addition reaction was discovered by French Chemist Victor Grignard and because of his tremendous discovery, he was awarded with Nobel prize of Chemistry in addition with Paul Sabatier. Even 100 years later this Grignard reagent is used in variety of carbonyl derivative as coupling reagent (Bandini, 2009).



In 1913, a Swiss inorganic Chemist named Alfred Werner was awarded with Nobel Prize as his work involved the coordination chemistry of ligands to metals, specifically the structure of hexamine cobalt (III) chloride. His work was important key step in understanding of chemical reactions of compounds, organometallic coordination and greatly contributed in the opening of independent organometallic discipline. Following is the structure of hexamine cobalt (III) chloride (Coates, 2012):



In 1951, American Chemist Peter Pauson and Tom Kealy created orange powdered ferrocene by the reaction of ferric chloride and cyclopentadiene magnesium bromide. They didn't deduce the real structure of organometallic salts and proposed that between the first carbons of two cyclopentadiene molecules, the iron acted as bridge and also presented sandwich model to explain the structure of ferrocene. Later, an English Chemist Sir Geoffrey Wilkerson in collaboration with American Chemist Robert Woodward explained the detail structure of ferrocene in which iron metal was sandwiched between two cyclopentadiene molecules that behave as ligand. Fischer also expanded the study of metallocene by using other metals. In 1973, Fischer and Wilkerson shared Nobel Prize because of their contribution in the expand study of metallocene compounds. Following is the structure of ferrocene:



In 1963, two chemists were awarded with Nobel Prize, Chemist named Karl Ziegler and Giulio Natta created a catalytic organometallic compound named dicyclopentadiene zircon (IV) dichloride by the polymerization of terminal olefins and they led to two entire classes of catalysts which are organometallic named as Ziegler-Natta catalysts.

In late 20th century, chemists introduced new methods to couple carbons together and these include sharpless epoxidation which earned Nobel Prize in 2001, famed Heck reaction that earned Nobel Prize in 2010 and Grubbs olefin metathesis which earned Nobel Prize in 2005 (Adamson, 1993).

2. Catalytic applications of organometallic complexes

The organometallic compounds have their applications as catalyst in different industrial organic reactions. As the process in which catalyst is used called catalysis and it is of two types that is homogenous catalysis and heterogeneous catalysis but the organometallic compounds found its application in homogenous catalysis that is discussed as following.

2.1 Homogenous catalysis

Homogenous catalysis is a process in which the phase of catalyst and reactants is same as both can be in solid, liquid or gas phase. As the organometallic compounds used in homogenous catalysis and its example is 'alkene metathesis' (Herrmann & Cornils, 1997).

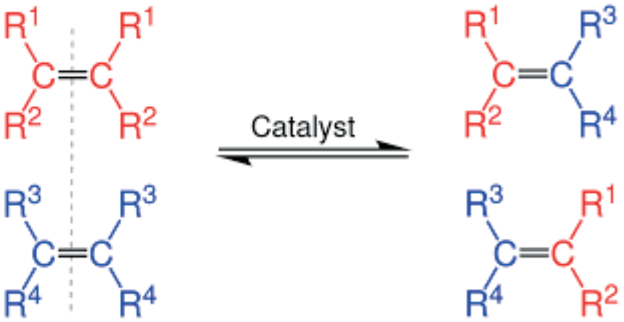
2.1.1 Application and mechanism:

One of the best applications of homogenous catalysis in which organometallic compounds are used is alkene metathesis whose mechanism is also given below.

Alkene metathesis:

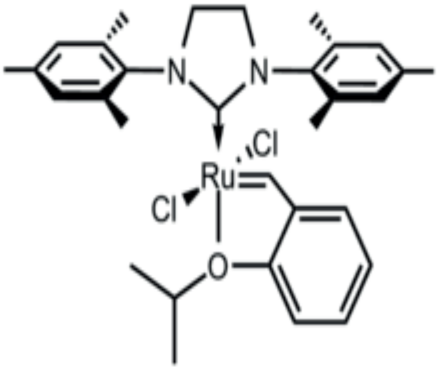
Alkene metathesis reaction is a reaction that is used to synthesize unsaturated polymeric counterparts and olefinic compounds which are unsaturated in nature. The metathesis reaction is famous for a family of reactions in which

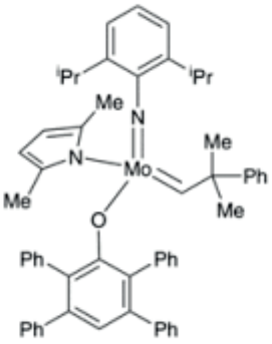
"Cutting and stitching" of olefinic bond involves in order to synthesize different unsaturated compounds. Olefinic compounds and other olefinic polymers are formed by the reaction of olefins with a metal carbene intermediate by varying the reaction conditions of metathesis reaction. Metathesis is an unusual process in which new olefins that are unsaturated in nature can be generated by this catalysis in which C=C is broken and then formed also.



During this metathesis process, metal carbene catalysts are used but many are developed but all of them don't work because all catalysts are not functional group tolerant. Utility of metathesis reaction can be broadened by developing functional group tolerant catalysts.

Schrock's Mo catalyst is effective for metathesis reaction because of display of high activity and Grubb's Ru catalyst is also used because it's easy to handle. Grubb's Ru catalyst is given on the left corner and Schrock's Mo is given below on the right corner.





Further extension of metathesis process is ring closing metathesis (RCM) for conjugated dienes in systems where the final product has no high ring strain. Ring opening metathesis (ROM) is the reverse of ring closing metathesis which occur in the presence of ethene (olefin).

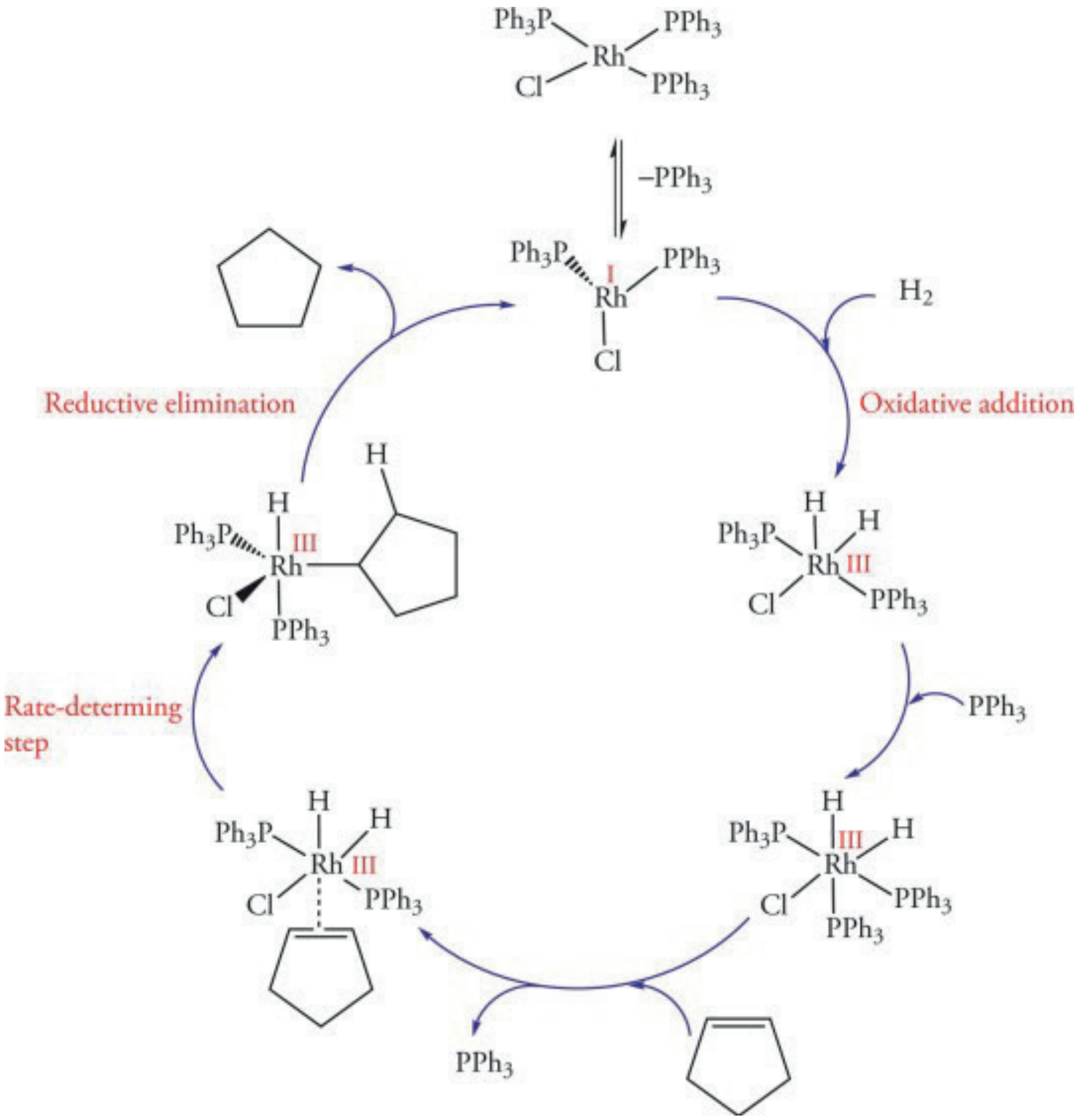
Polymerization reaction can be forwarded by relieving the ring stain of cycloalkenes by using the variants of metathesis like the acyclic diene metathesis (ADMET) and the ring opening metathesis polymerization (ROMP) for producing polymers. These reactions also have their applications in the production of block copolymers (Marciniec & Pietraszuk, 2003).

2.1.2 Industrial organic applications of organometallic catalytic process

1. Hydrogenation catalysis:

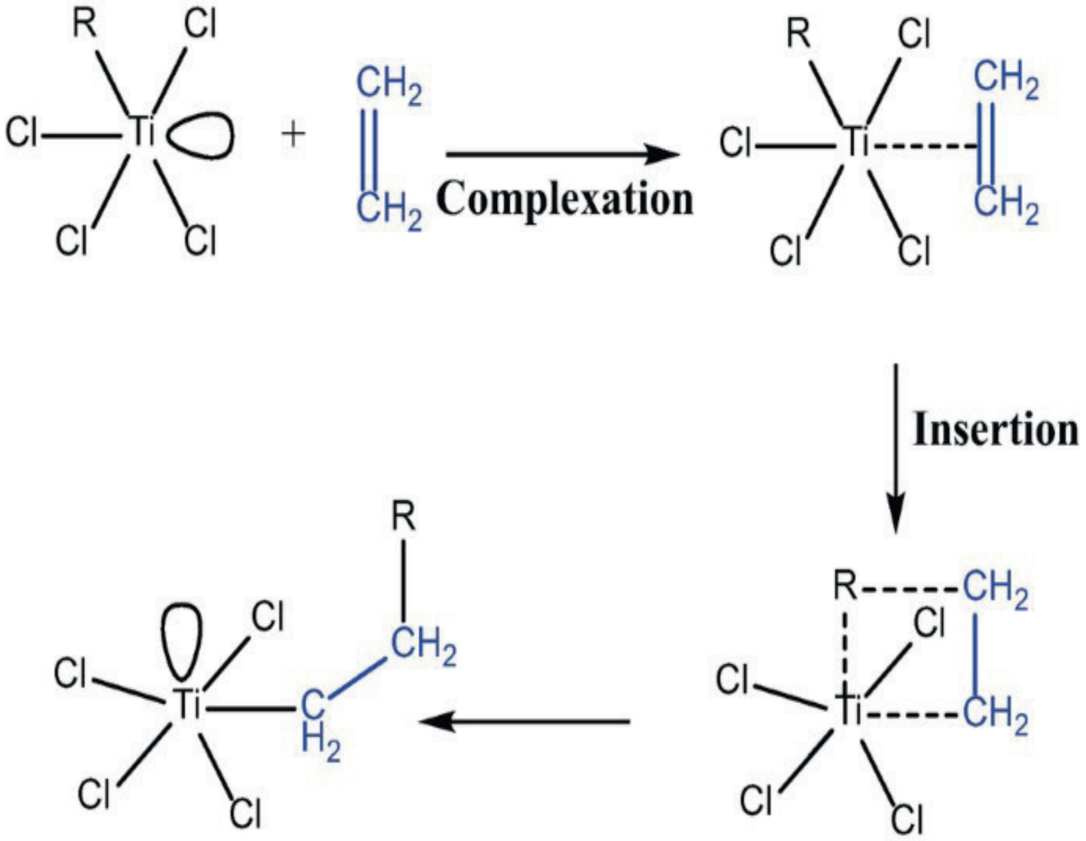
Wilkinson catalyst that is a Rh-catalyst is used for the hydrogenation of olefins. Wilkinson catalyst is a complex that is chlorotris (triphenylphosphine) rhodium (I) complex having a square planar geometry. Chlorobis (triphenylphosphine)rhodium (I) is formed by the loss of triphenylphosphine ligand from Rh-complex and it becomes a real catalyst otherwise firstly it's a pre-catalyst. The catalyst is in equilibrium with the pre-catalyst as the loss of triphenylphosphine ligand is a reversible process. After undergoing a series of events during this equilibrium, a specie named trigonal bipyramidal is formed that has the ability to add an olefin that binds side-on to Rh-complex. Olefin insertion can be done because olefin is in cis-position to hydride ligand.

A branched alkyl complex is formed by the formation of Rh-C bond when the second carbon in the carbon chain of olefin. Linear complex can also be formed by the formation of Rh-C bond with the first carbon in the carbon chain of olefin. The branched alkyl complex has more steric hindrance than the linear alkyl complex so it can regenerate olefin and trigonal bipyramidal Rh-complex by beta-hydride elimination as a side-reaction. The catalytic cycle can be completed when linear alkane and RhCl (PPh3)2 catalyst is formed by reductive elimination of linear alkyl Rh complex and after this a new cycle get starts. Following is the mechanism of hydrogenation catalysis in which an organometallic compound that is Wilkinson catalyst is being used (Jones et al., 2003).



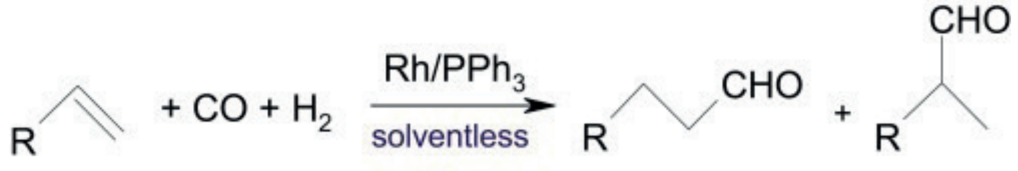
2. Ziegler-Natta polymerization

This reaction has very good reputation and quite important industrially for the synthesis of unsaturated polymeric alkenes like polyethylene. These catalysts are both homogenous and heterogeneous too. ZN catalyst is particularly useful for the polymerization of alpha olefins with high linearity and stereoselectivity. A ZN catalyst consists of two components that is a co-catalyst which is organoaluminium compound and other one is transition metal compound. Homogenous catalyst is metallocene catalysts and their mechanism is well understood than the mechanism of heterogeneous catalyst. Examples of Ziegler-Natta catalyst is TiCl3+ AlEt2Cl, TiCl4 +Et3Cl. A catalyst like mixture of triethyl/methyl aluminum and titanium chloride are added into monomers during Ziegler-Natta polymerization. Performance of catalyst is improved and modification of catalyst is done by the addition of compounds like magnesium chloride then this mixture has the capacity to produce an insoluble solid that is actually a heterogeneous catalyst. Mechanism for Ziegler-Natta polymerization is given below (Eisch, 2012):



3. Hydroformylation:

An aldehyde with and extra carbon atom than the original alkene can be produced by the addition of hydrogen and carbon monoxide to alkene. This catalysis finds its application in petrochemical sector in which radium catalyst and Co2 (CO)8 are used. In this catalytic cycle, catalytic intermediates are used in succession. Hydroformylation results in the production of aldehyde which are further converted into alcohols that have applications as plasticizer, detergents, and solvents and in other products production and these products are produced massively as millions of tons per anum (Pruett, 1979).



4. Cross-coupling reactions:

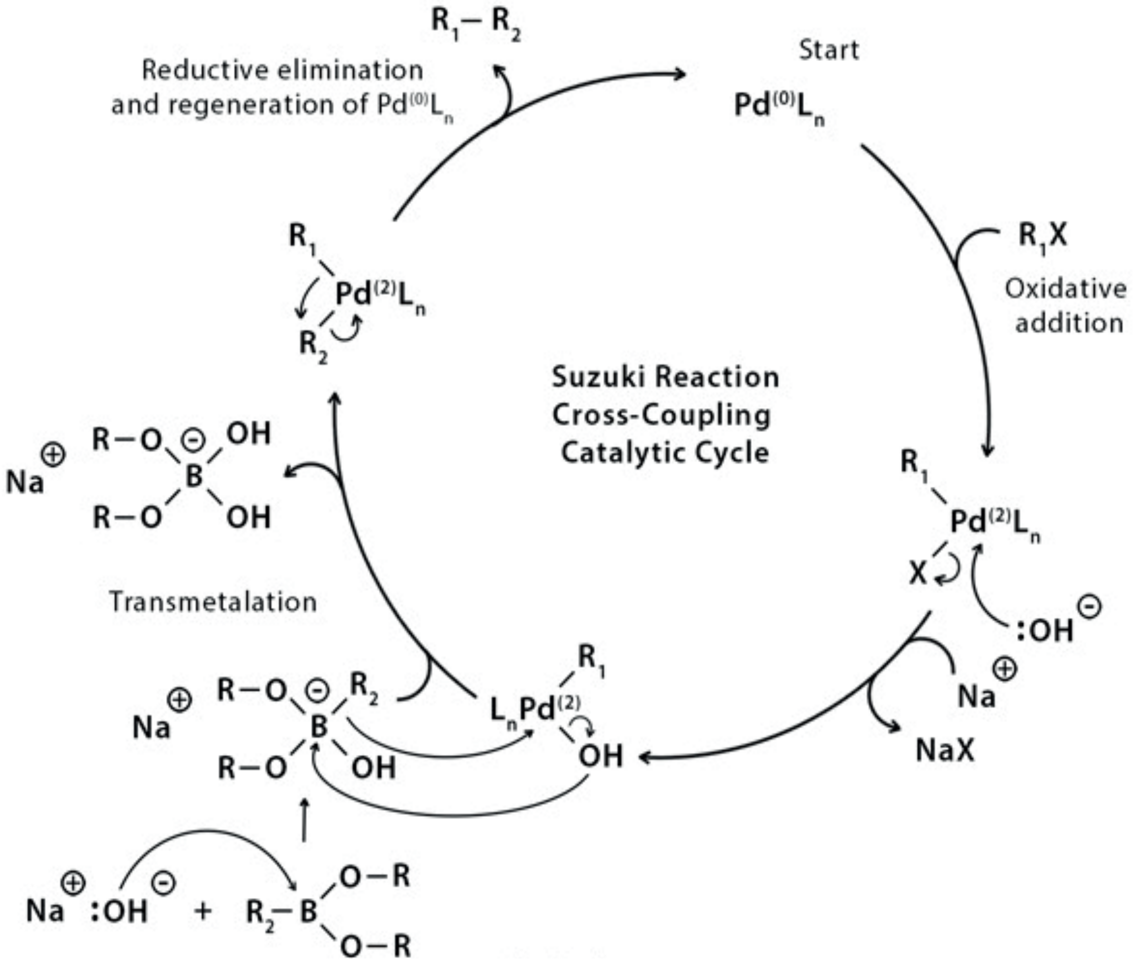
Cross coupling reactions are the reactions in which C-C, C-N, C-H, C-S, C-O, C-M, C-P bond formation take place when an organic electrophile combines with organometallic reagent having metals from A-subgroup of periodic table in the presence of metal catalysts having metals from group VIII to X. Cross coupling reactions are actually a type of synthetic transformations. Many organometallic reagents like organotin, organosilicon, organoboron and organozinc for cross-coupling reactions were prepared in early 1970s by Kumada, Corriu, Murahashi and Kochi. Multiple synthetic methods for molecular assemblies were discovered when metal complexes and different type of electrophiles were employed in these reactions (Campeau & Hazari, 2018).

Preparation of Liquid crystals, polymers, natural products, pharmaceuticals and many other organic synthetic applications are associated with cross-coupling reactions. Some of the examples of cross-coupling reactions are:

- Suzuki reaction
- Heck reaction
- Sonogashira reaction

Suzuki reaction

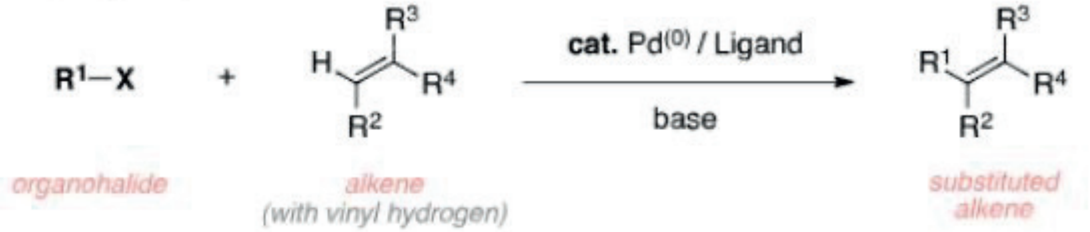
An organohalide and boronic acid are the coupling partners in this organic coupling reaction named Suzuki coupling reaction. In this coupling reaction, palladium (o) complex is used as a catalyst. This reaction is also called ‘Suzuki coupling’ or ‘Suzuki-Miyaura reaction’. A base leads the C-C bond formation by the coupling of halide with organoboron specimen over palladium (o) catalyst. The reaction is illustrated as below:



In Suzuki-Miyaura reaction, organohalide reacts with organoborane in the presence of palladium catalyst, ligands and base to produce coupled product, organoborane and sodium halide (Miyaura & Suzuki, 1995).

Heck coupling reaction

This reaction is also called 'Mizoroki-Heck reaction' after the name of the scientist, Richard Heck, who discovered this and later awarded with a Nobel Prize too in 2010. Palladium (o)/palladium (II) followed by a carbon-carbon bond formation was first time produced by this Heck- reaction. One of the examples of such reaction is given below:



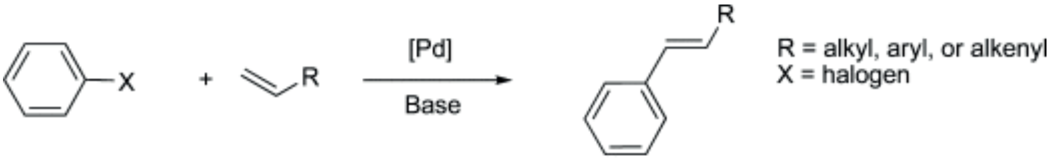
In this reaction, unsaturated halide was added to the palladium by oxidative addition and then palladium has provided a site for the migratory insertion of alkene. Then the starting catalyst is regenerated to end the cycle by the removal of hydride from beta position of alkene and then adding the base to the palladium catalyst.

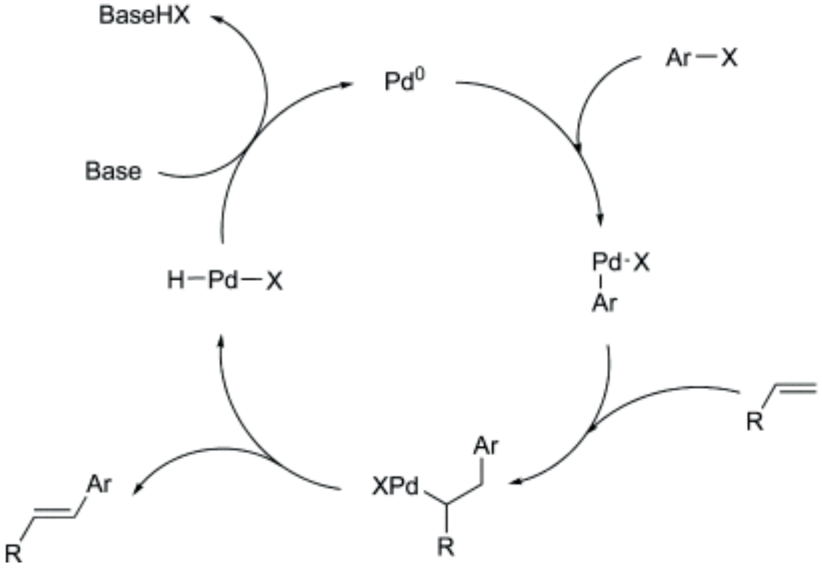
The mechanism of Heck reaction is described in few steps as in 1st step, a palladium pi complex is formed with unsaturated hydrocarbon that is alkene when palladium is added or inserted into the aryl-bromide bond by oxidative addition. In 2nd step, sync addition takes place as in this alkene is incorporated in the palladium-carbon bond on the very same side of double/triple bond. In the 3rd step, another alkene-palladium pi complex is formed by the elimination of hydride from the beta position of alkene. In the 4th step, potassium carbonate is added when the palladium-alkene pi complex is disintegrated that results in the regeneration of palladium (0) complex through the reductive elimination of palladium (II).

Heck reaction can be modified into the following:

- Heck oxyarylation
- Ionic liquid Heck reaction
- Amino-Heck reaction

The mechanism of Heck reaction is given below (McGuinness et al., 1999):

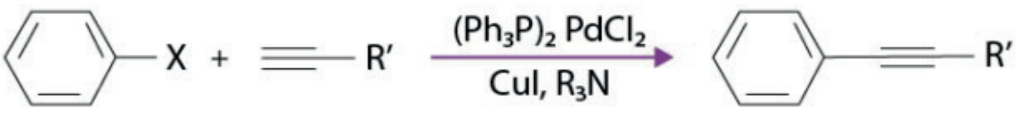




Sonogashira coupling reaction

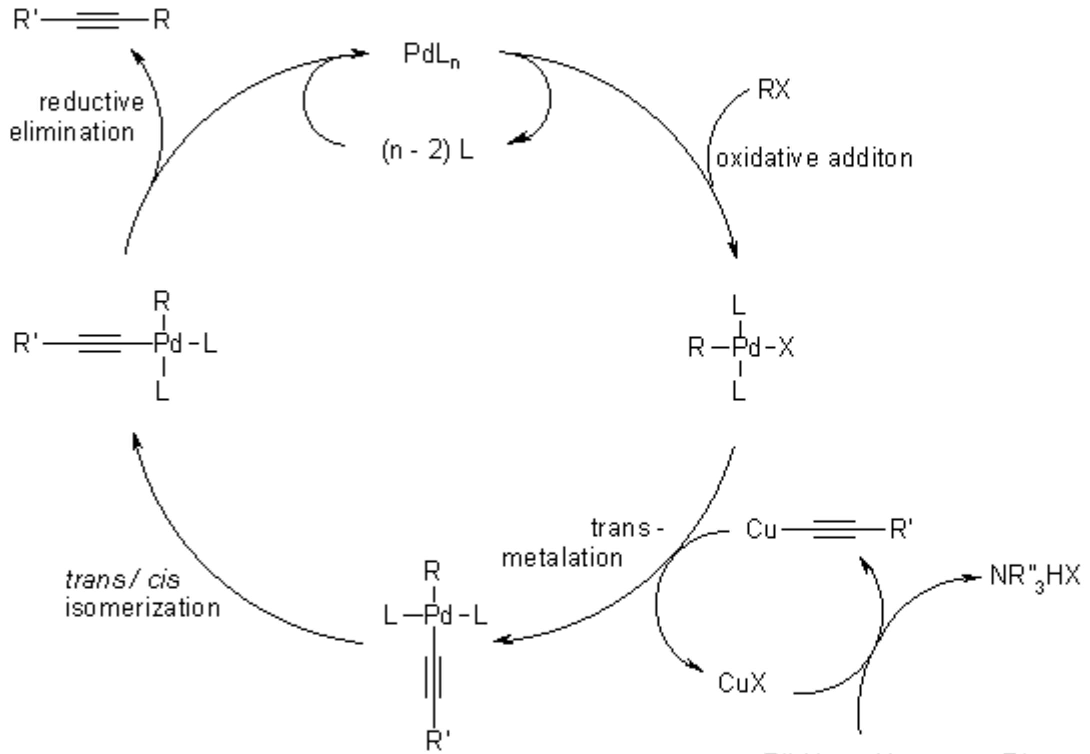
Kenkichi sonogashira, Yasuo tohda and Nobue Hagihara proposed this reaction which is the extension of Heck reaction and Dieck in which palladium was used as a catalyst. But in this sonogashira reaction, palladium as well as copper is used as catalysts. This reaction is very helpful in organic synthesis as it is used to produce C-C bonds. This reaction has found its applications in pharmaceuticals, nanomaterials, natural product chemistry, material science pharmaceuticals. Complex molecules can also be produced by the Sonogashira coupling reaction at room temperature by applying mild conditions.

Altinicline also known as acne and psoriasis can be treated by the synthesis of tazarotene that can be synthesized by the Sonogashira coupling reaction. As given below:



The mechanism of Sonogashira coupling reaction is very hard to understand as organometallic compounds are involved in this reaction which are difficult to isolate and then analyze. Palladium cycle and copper cycle are predicted to be near to be the right mechanism in which organometallic compounds are present as the reaction intermediates.

The presence of base is necessary for the production of complex E and pi-alkyne complex. As the presence of base has the ability to make the proton more acidic which is present in alkyne. The copper halide can be generated by the reaction of palladium with compound F. The mechanism is given below (Chinchilla & Nájera, 2007):



3. Recent advances in transition metal complexes

Very stable range of alkyls containing complexes like alkylcyclopentadienyliron dicarbonyl series RFe (C_5H_5) $(CO)_2$, alkylmanganese pentacarbonyl, RMn $(CO_5$ are prepared by using earlier transition metals like Ti, Mn, Cr, V. These reactions are highly important because these can be used in vivo and vitro catalytic systems. In catalytic processes, these transition metal alkyls behave as main intermediates. As, alkylcobalt carbonyls are involved in the hydroformylation and related carbonylation processes as this cobalt is also present in vitamin B12 as it is a natural organometallic system in which this metal is connected with adenosyl group by carbon. **Titanium alkyls** are also used in Ziegler-Natta olefin polymerization as the chain carriers in which transient intermediates are palladium alkyls.

All these cobalt alkyls and other transition metal alkyls act as 'ligands' which has the capacity to provide stabilizing effects to the whole compound and reaction medium.

3.1 Novel ligand design and its impact on reactivity

In most of the cases, the metal center that electropositive center which is Lewis acidic in nature and is surrounded by ligands which are Lewis's base and electronegative in nature has the capacity to donate electrons to the central metal atom to form coordinate covalent bond according to covalent bond theory. There are all different types of ligands like H, cyclopentadienide, alkyl where the central metal atom and ligands have comparable electro negativities. Metal- ligand bond is considered to be covalent in nature when the late highly electropositive transition metals are used. According to covalent bond classification (CBC) method also known as LXZ notation, the interactions between these ligands and central metal atoms and their nature can be used as a basis to classify the ligands as:

- L- ligand
- X- ligand
- Z- ligand

These ligands and their interactions are described briefly so their mechanism and impact on reactivity can easily be understood.

- **L- ligand**

These ligands have the ability to donate two electron means one electron pair to the central metal atom and act as Lewis bases. These electrons which are donated can be sigma donors, pi donors and lone pairs. Coordinate covalent bonds also known as dative bonds are formed between central metal atom and L- type ligands. Examples of these ligands are PR3, H2O, NH3, alkenes, carbenes and CO.

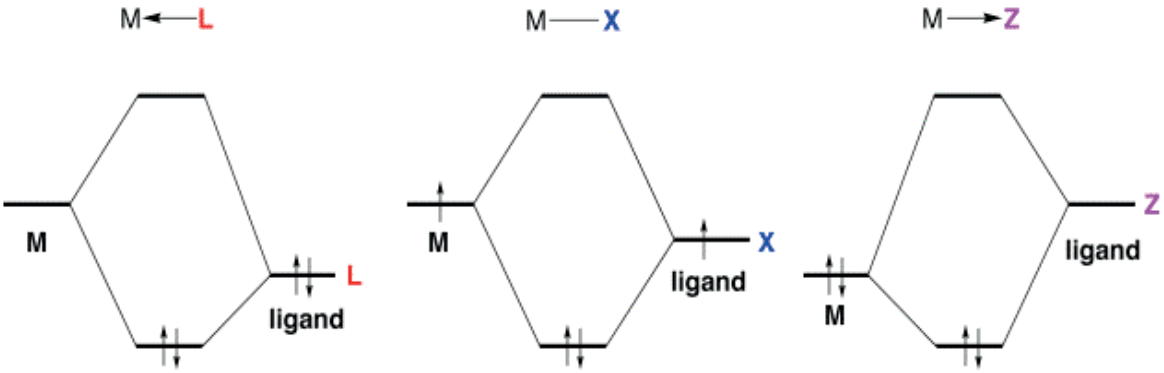
- **Z- type ligand**

These ligands have the ability to gain the two electrons means one electron pair from the central metal atom. Like the L- type ligands, these ligands also have the capacity to form dative or coordinate covalent bond with the central metal atoms. These are the least used ligands because of least reactivity due to nature to behave as acceptors. Examples of these ligands are mostly Lewis's acids like BR3.

- **X- type ligand**

These are the ligands that have the ability to undergo mutual sharing of electrons as one electron is donated to the ligand and the other electron is accepted from the central metal atom when neutral ligand method of electron counting is used. These ligands also have the capacity to donate two one electron pair means two electrons to the central metal atom when donor pair method of electron counting is used. These ligands are the most used ligands because of their reactivity and ability to lose and gain and share electrons. Normal covalent bonds are formed between central metal atom and these ligands either these ligands are anionic or neutral in its nature. Some of the examples of these ligands are halogens, hydrogen, methyl and NO (bent) (Mendoza-Ferri et al., 2009).

Following is an illustration of these ligands:



L ligand	X ligand	Z ligand
both electrons provided by ligand	one electron provided by ligand and by metal	both electrons provided by metal
e.g. PR_3, CO, C_2H_4	*e.g.* H, Cl, R	*e.g.* BF_3
(neutral molecules)	(radicals)	(Lewis acids)
Dative Covalent Bond	**Normal Covalent Bond**	**Dative Covalent Bond**

An **L**–function orbital is occupied by a **pair** of electrons.

An **X**–function orbital is filled by a **single** electron.

A **Z**–function orbital is **empty**.

An example of these ligands and their reactivity is discussed in the following paragraph. In modern organometallic chemistry, the C-C double bond formation is established by olefin metathesis. Stable and adjustable Grubbs, indenylidene type second generation catalysts having N-type heterocyclic carbenes (NHC) and Hoveyda-Grubbs are well-defined ruthenium complexes which play vital role in these reactions. Catalyst can be anchored both covalently and non-covalently. Covalently linked catalysts are used during these processes but still they can be moderately re-used and also their activity get decreased immensely. Non-covalently linked catalyst is dependent on the reversible pi interactions, electrostatic interactions, physio-sorption on porous materials like charcoal, wool, filter paper, cellulose, dendrimers etc. Synthesis of covalently bound analogues are quite difficult and complicated as compared to the production of non-covalently immobilized catalysts that is more straightforward and simpler. Non-tagged catalyst preparation is easy as compared to tagged catalyst according to synthetic point of view, for example, the preparation of Ru3 and Ru4 which are quaternary ammonium tagged catalysts is complicated because it involves the additional three to four steps.

Benzolyation that is ester formation is the main method for the synthesis of N-heterocyclic ligands (NHC) having Bronsted base tags. Olefin metathesis ruthenium catalysts are synthesized by using these tagged NHC ligands having 4-(dimethylamino) benzoic acids and isonicotinic agents. Basicity of these tagged fragments helps to provide a site for the non-covalent immobilization of these catalysts and the non-ionic nature helps to remove the problems that's been faced during the synthesis of quaternary ammonium-based catalysts on the basis of carbene.

Other types of ligands whose reactivity also depends on the type of bond and their structure, on the basis of their structure, are as following:

- Simple alkyl ligand
- Alkylidene ligand

- Alkylidyne ligand
- Alkene and alkyne ligands
- Polyene ligand
- Cyclic polyene ligands
- Aromatic ligands (Green, 2012).

3.2 Advances in metal catalyzed C-H activation

C-H bond activation is a process in which the whole series of mechanism takes place by which the cleavage of stable C-H bonds present in any organic compound takes place. C-O, C-N and C-C bonds are produced or synthesized which are present in more complex intermediates and product compound which is the main application of this process. This process is also used to prepare commercially beneficial complex molecules from the cheap and less toxic feedstock molecules under milder conditions by the cleavage of C-H bonds. The more commercially important compounds produced by this method are used in pharmaceuticals and also have fine chemical applications.

Different mechanisms are used for C-H activation like sigma bond metathesis, electrophilic substitution, oxidative addition, biocatalytic, photocatalytic reactions, electrocatalytic reactions and hybrid methods like photoelectrocatalysis, photobiocatalysis and all these methods are catalytic mechanisms. For more sustainable and accurate approaches to chemical synthesis, many of these techniques are used to activate C-H bonds by using metal catalysts which are abundant in earth and milder conditions are used. Transition metals like Rh, Pt, Ir etc. are used for C-H activation by catalytic oxidative addition. In this mechanism, intermediate organometallic specie is produced when transition metal coordinates with the proton attached to carbon atom present on the hydrocarbon that acts as substrate. Functionalized or active carbon atom is formed when this intermediate reacts with other species. Cleavage of C-H bond and activation of carbon atoms are done stoichiometrically. For example, transition metals are beneficial for the production of C-B bonds by borylation/ C-H activation. Electrophilic aromatic substitution is used for Friedal-Craft chemistry. Organoboron compounds are used for the formation of C-C bonds by cross-coupling reactions.

In C-H activation reactions, electron rich metals who are low valent in nature like Rh(I) and Ir(I) undergo the process of oxidative addition and high valent metals like Rh (III), Ru (II), Ir (III), Pd (II) undergo the reaction by electrophilic pathway. Functional group positional selectivity is driven by the central metal atom which is either coordinated or chelated. In ortho metalation and functionalization of aromatic hydrocarbons specific C-H bonds are targeted by directed C-H activation.

Functionalization of C-H bonds can be done as a result of Friedal- Craft's reaction which is either Friedal- Craft's acylation or Friedal- Craft's alkylation. C-M bonds are formed by the C-H activation in metalation reaction. In lithiation reactions, C-Li bond formation takes place by C-H activation/ metalation reactions.

There are multitude of variables which can affect the expected outcome in these catalytic reactions. The factors on which these catalytic reactions depend are ligands, reagents, reactants, catalytic metals, pressure, temperature, mixing, dosing rates, catalysts etc. that's why these reactions need great care in proceeding and careful control over variables during the reaction to get desired results (Raţ et al., 2018).

4. Organometallic complexes in material sciences

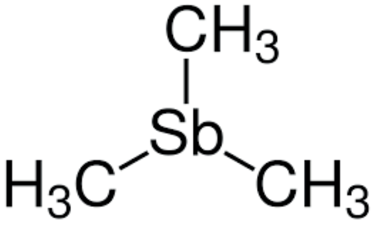
Polymers like homopolymers, copolymers, complexes, blends of small molecules, alloys, composites are used in microelectronics, electronics, nanoelectronic systems instead of regular metals and ceramics. These polymers are preferred because of many properties like attractive optical properties, chemical properties, physical properties, electrical and electronic properties, mechanical properties and also because of their complex mechanical properties.

Organometallic polymers are used to achieve multiple attributes and requirements in electronic systems as to get short lead time, reduced weight, can be molded into complex shapes and low cost. These above attributes are hard to get in nanoelectronics and microelectronics which is based on flexible polymeric substrates which are bendable and stretchable, 3D- PCBs that is three-dimensional printed circuit boards, MID that is molded integrated devices, integrated electronic systems like integrated circuits ICs and many other electronic components working at high temperature. Developed generations of nanoelectromechanical systems NEMS, microelectromechanical systems MEMS are the further examples in which silicone Q polymers are used in integrated circuits (Schwartz & Bernasek, 2001).

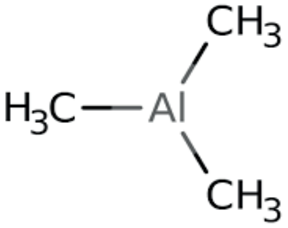
4.1 Role of organometallics in semiconductor materials

For structuring of electronic systems, organometallic compounds which are here specifically called electronic organometallics also known as hybrid organometallic polymers are used which contains organic component and also inorganic component. Ideal organometallics used for the actuators due to high piezoelectric coefficient are silicon rubber that is polydimethylsiloxane PMDS, dendrimers which are highly branched dendritic polymers, polydiphenylsilane. Organometallic polymers are also the representative of best class of stretchable electrically conductive polymers based on silicones which are used in the form of adhesives.

Electronic polymeric organometallics are used in research oriented and industrial methods as stoichiometric reagents. These organometallics are used in the manufacturing of some semiconductors and these reagents are trimethylaluminium, trimethylindium, trimethylgallium and trimethylantimony. Trimethystibine also called as trimethylantimony is an organometallic compound which is used for synthesis of semiconductor and it is synthesized by the reaction of methyl Grignard reagent along with antimony trichloride. It is a weaker Lewis base which is used for the synthesis of III-V semiconductors.



Trimethyl aluminium is also an organometallic compound having Al in the center and is tetrahedral which is surrounded by methyl groups surrounded by five neighbors. Polyethylene, polypropylene and other polyolefins are produced by using organoaluminium compounds by Ziegler-Natta catalysis. An activator of many transitions metal catalyst is methylaluminoxane synthesized from TMA. The fabrication of semiconductor is done by using trimethylaluminium which is used to deposit thin film. Atomic layer deposition or chemical vapor deposition is used for deposition of high-k dielectrics like Al2O3. For metalorganic vapor phase epitaxy (MOVPE) of aluminum containing compound semiconductors like AIN, AIAs, AISb, AllnGaN, AllnGaP, AllnGaNP, AIP, AlGaN etc use trimethylaluminium as a precursor (Weibel & Oliver, 1974).



4.2 Applications in molecular electronics and optoelectronics

The variety of organometallic polymers are used for the development of fibers, coatings, fiber matrix composites, infiltrated media, ceramic bulk parts and near net shaped manufactured ceramic components and all these are precursor- driven. Techniques and methods from polymer process engineering are used for the production of green parts. These organometallic polymers are used in the manufacturing of electronic components, polymeric electronic components, nanoelectronics and optoelectronics because of electrical conductivity of some polymers. Electronic polymers are prepared from organic polymeric electronic components.

Organic light emitting diodes OLEDs, displays in nanoelectronics and microelectronics and development of novel electronics are developed by the field of material science which helps in the development and production of small molecules, complexes and electrical conducting polymers which are actually called electronic polymers, electrically active polymers EAPs, organic electronic compounds which have inherent electrical conductivity.

Production of light emitting diode (LEDs) and other semiconductors is done by metalorganic vapor phase epitaxy (MOVPE) in which volatile compounds which are organometallics like trimethylgallium, trimethyl aluminum, trimethyl gallium and trimethylindium are degenerated or decomposed along with ammonia, arsine, phosphine and some other related hydrides on a heated substrate. Dimethylzinc is also an organometallic compound that is used for the synthesis of semiconducting films and it is a volatile pyrophoric liquid (Popczyk et al., 2019).

5. Bio- organometallic chemistry

Bio-organometallic chemistry is a branch of Chemistry which deals with the study of biomolecules, compounds containing minimum of one carbon atom which is attached to the metal and these compounds are biologically active compounds which are lying at the interface of organometallic compounds.

This new branch of Chemistry extends the study of organometallic chemistry to medicine, life, living organisms, biology and bioanalytics.

5.1 Bio-organometallic interactions and their relevance

There are many enzymes and cofactors are present in our body which are organometallic in nature and having at least one direct carbon metal bond. The naturally occurring vitamin B12 family also known as cobalamines which are actually vitamin B12 co-enzyme are actually organometallic compounds as these have dimethyl mercury that is produced by bacteria to eliminate and remove toxic metal mercury and cobalt carbon bond (Co-C).

The naturally occurring hydrogenases which helps in undergoing heterolytic splitting mechanism to catalyze the reversible conversion of molecular hydrogens to protons and electrons. CO ligand and CN- ligands are present in the center of dinuclear Ni-Fe which itself is present in the active site of (NiFe) hydrogenase. During the catalytic or activation process, ligand sphere can be changed by the catalytic activity and active site structure of hydrogenase.

The naturally occurring bio-organometallic is the acetyl CoA synthetase (ACSs) is a vital enzyme in the anaerobic carbon dioxide fixation that is Wood- Ljungdahl pathway which is operated by a mechanism having a series of protein bound intermediates like Ni-CO, acetyl- Ni and methyl- Ni.

One of the naturally occurring organometallic compound which is CO dehydrogenase (CODH) which act as catalyst in the reversible oxidation of carbon monoxide to carbon dioxide. This bio-organometallic compound helps in the utilization of carbon monoxide as a source of energy and carbon by global carbon cycle. There are two types of CODH exists:

- Ni-CODH
- Molybdopterin/Cu/Fe-S cluster

The nickle containing enzyme (Ni-CODH) is used in anaerobes and present as a component of large complex with acetyl- coenzyme or can exist as an independent enzyme. The molybdopterin/ Cu/Fe-S cluster is found in aerobic microorganisms.

Methyl coenzyme M reductase (MCR, F430 cofactor) is also a bio-organometallic compound is used in the terminal step of methanogenesis as a catalyst by using co enzyme B (CoBSH). Heterodisulphide, methane and CoBS-SCoM are produced when methyl coenzyme M (methyl-SCoM) is reduced when two electrons are donated by CoBSH. Many catalytic mechanisms are proposed to understand the method of production of methane which are different from each other because of the unclear understanding of production of either methyl radical or methyl- Ni (II) as the first catalytic intermediate. Hemolysis of methyl-Ni (II) can produce methyl radical which is suggested by the most recent proposal (Jaouen & Metzler-Nolte, 2010).

5.2 Medicinal applications of organometallic complexes

- Following are the few medicinal applications of organometallic compounds:
- Technetium sestamibi is used to image the heart muscle in nuclear medicine.
- Several crucial enzymatic reactions take place in human body in which an organometallic compound is used that can act as a cofactor named Adenosylcobalamin which is found rarely in the body as it’s a metal (cobalt) and alkyl.
- Industrial production of alcohols is done by using an organometallic compound which is trimethylaluminium having a bridging methyl group.
- Before the invention of modern antibiotics, organometallic compounds containing mercury like thiomersal was used as an antibiotic.
- A nonselective antimicrobial organometallic is used in medicine that contains arsenic like salvarsan.
- Anti-cancer activity is displayed by an organometallic compound named Titanocene dichloride.
- Current anticancer medicine is also an organometallic compound which is dichloridobis [(p- methoxybenzyl) cyclopentadienyl] titanium.
- For the design of new radiopharmaceuticals, arene and cyclopentadienyl complexes provide kinetically inert platform.
- As carbon monoxide is gasotransmitter so many organometallic compounds have been used and studied which has the ability to release carbon monoxide.

- Incentive salience and habituation are efficiently increased by using dopamine transporter which are actually created by using semi-synthetic ligands namely with the phenyltropane compound named as [n6- (2beta-carbomethoxy-3beta-phenyl) tropane] tricarbonylchromium.
- Organometallic compounds are used as biosensors.
- Organometallic compounds are used in the peptide synthesis (Martins et al., 2014).

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Advances In Organic Chemistry

Ghashia AMEEN

This chapter includes organic chemistry, which serves as the basis for a wide variety of commonplace products such as clothing and medicine, is continuously undergoing development. Organic chemists are pioneering new solutions that are environmentally friendly since they are aware of the influence that outdated technologies have on the environment. These fascinating developments are discussed in depth in this chapter, with an emphasis on environmentally friendly synthesis methods that are beneficial to both the scientific community and the environment. A more environmentally friendly toolbox for organic synthesis is currently being developed by researchers. This toolbox includes enzyme-powered and photo-catalysed reactions, as well as asymmetric catalysis for complex compounds. Finding a way to achieve precise control over reaction sites and molecular configurations (regio and stereoselectivity) is very important, particularly when it comes to the production of complicated chiral compounds. Innovative tactics such as protecting groups and even computer simulations are being utilized to build environmentally friendly synthesis routes. Green chemistry promotes sustainability by designing environmentally friendly chemical processes is another important aspect of organic chemistry.

1. Introduction

The historical understanding of "organic" and "synthesis" evolved significantly. In contrast to non-organic bodies, which were unorganized, the phrase "organic chemistry" originated from organic or organized bodies, or living organisms (corps organisés). Though their etymological roots in Aristotle's work hinted at their future roles (instrumental and putting together, respectively), the 17th century iatrochemists lacked the concept of organic chemistry despite their work with pharmaceuticals. While Buffon, Bergman, and Gren in the 18th century defined organic materials as those derived from living things, these discrete compounds remained elusive. The late 18th and early 19th centuries saw the isolation of natural organic products by Scheele and Chevreul's separation of carboxylic acids from fats, marking the dawn of organic chemistry. Lavoisier's invention and Berzelius' refinement of combustion analysis provided crucial characterization tools. Building on Descartes' principle of synthesis validating analysis, Bergman and others laid the groundwork for a paradigm shift. The prevailing belief, championed by Berzelius and Chevreul, was that a "vital force" was necessary for life and anything derived from it, including organic chemicals. This rendered the synthesis of organic compounds from inorganic materials seemingly impossible. Thus, Wöhler's 1828 synthesis of urea from ammonium cyanate and Kolbe's later synthesis of acetic acid from elements (1845) revolutionized the field. Wöhler's work, achieved by treating silver oxycyanate with ammonium chloride or lead oxycyanate with ammonia, unexpectedly yielded the organic compound urea. Finally, Berthelot's 1853 syntheses of non-natural fats solidified the modern definition of organic chemistry as the study of carbon compounds, irrespective of their natural origin. The collective efforts of Chevreuil, Lavoisier, Wöhler, Liebig, Kolbe, and Berthelot significantly undermined the Vital Force theory. While some continued to adhere to this notion, their work paved the way for the foundation of modern organic chemistry as we recognize it today: the study of carbon-based compounds, irrespective of their natural origin (Wentrup, 2022).

Undoubtedly, organic chemistry significantly influences our quality of life. However, the economic, environmental, and social issues in our society continue to demand that chemistry improves synthetic methods to be more efficient, readily scaled, and cost-effective. Chemical goods should ideally be both accessible and inexpensive to all individuals, while also being manufactured in a way that maintains or enhances the existing status of the environment. This is closely related to and is a component of the 12 principles of "Green Chemistry".

Within the chemical industry, achieving highly selective reactions that generate specific, valuable products is paramount. To accomplish this, catalyst development hinges on a deep understanding of selectivity control. Computational chemistry has emerged as a powerful complement to traditional methods, offering insights into the structure, properties, and reaction mechanisms of compounds. This computational validation provides crucial evidence of key reaction features. The increasing collaboration between computational and experimental chemists is propelling research forward, particularly in the realm of reliable mechanistic studies of chemical reactions, ultimately leading to more accurate molecular geometry determinations (Nakliang et al., 2021).

2. New Reaction Methodologies

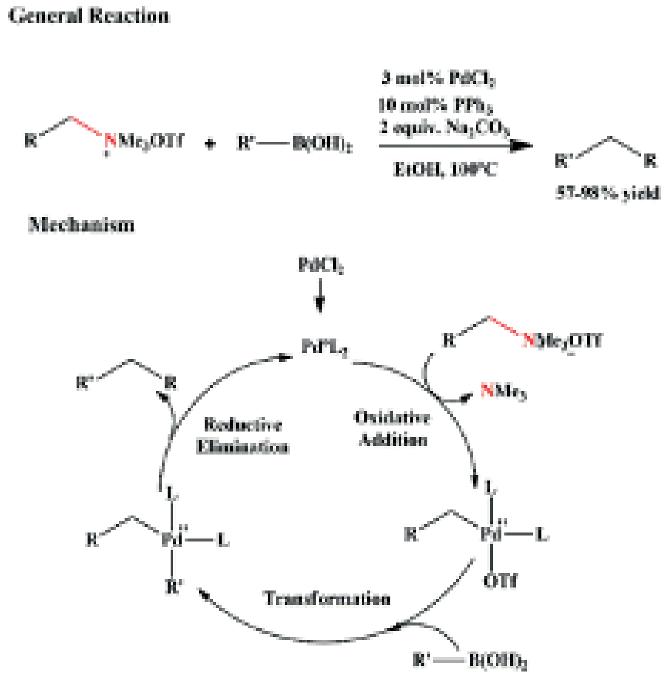
Following are some recent advancements in organic synthesis.

2.1. Transition metal-catalyzed reactions for diverse transformations

Catalysis, regarded as the core of modern science, has revolutionized the approach to creating intricate molecular structures with exceptional selectivity and efficiency. Transition-metal catalysis and organocatalysis have mostly driven the advancement of catalysis in synthetic organic chemistry. Transition metals may accomplish remarkable and unconventional transformations because of their capacity to switch between several oxidation states while building complexes with the reagents in a catalytic cycle. Furthermore, these metal complexes' reactivity and selectivity may be adjusted to meet the demands of the catalytic process with the help of a variety of elements, including the steric and electronic properties of metal-coordinated ligands and counterions (Yorimitsu et al., 2021).

Radical reactions are powerful tools for organic synthesis, but radicals are hard to control due to their short lifespan. Combining them with transition metal catalysts offers a solution: the metal stabilizes the radicals, allowing for selective reactions and preventing unwanted side reactions (Huang et al., 2020).

Nitrogen atoms are often found in several organic compounds and biomacromolecules. Hence, the creation and alteration of C–N bonds are very captivating subjects in the field of organic synthetic chemistry. The breakage of C–N single bonds using transition metal catalysts was first observed in 1980. The breakage of C–N single bonds by transition metal catalysts offers a new approach to form C–C bonds, C–N bonds, and N-containing compounds. Transition-metal-catalyzed selective cleavage of C-N bonds can efficiently synthesize a range of valuable organic molecules, such as alkanes, alkenes, alkynes, biaryls, ketones, carboxylic acid esters, amines, alcohols, organosilanes, phosphine oxides, organoboronates, and N-containing heterocycles (Liu et al., 2021). C-N bonds in amines are tough to break due to their strong bond energy. Chemists therefore target "activated" C-N bonds for cleavage, which are more reactive. Quaternary ammonium salts, a common example, are useful substrates for such transformations in organic synthesis. A study even showed palladium-catalyzed Suzuki cross-coupling using benzyltrimethylammonium salts (Wang et al., 2017).



Scheme 1. Pd-catalyzed Suzuki cross-coupling

2.2. Asymmetric catalysis for creating chiral molecules

Modern organic synthesis hinges on the development of novel chiral ligands for superior stereocontrol in metal-catalyzed reactions. Producing bioactive molecules as pure enantiomers is increasingly vital, and asymmetric catalysis using metal complexes offers one of the most efficient routes to optically active compounds. Homogeneous metal complexes with novel chiral ligands are particularly powerful for achieving highly enantioselective transformations. The remarkable progress in this field is driven by the creation of these ligands, designed to deliver high enantiocontrol and efficiency across diverse reaction systems through architectural modifications. Established examples include TADDOL, BOX, BINAP, BINOL, and SALEN, which coordinate metals via heteroatoms. However, complementary carbon-coordinating neutral N-heterocyclic carbenes (NHCs) and cyclopentadienyl anions (CpX) have also emerged as effective chiral ligands for asymmetric metal catalysis.

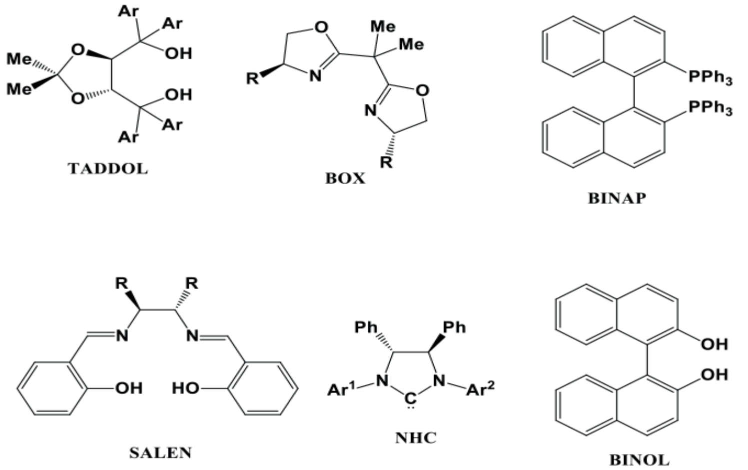
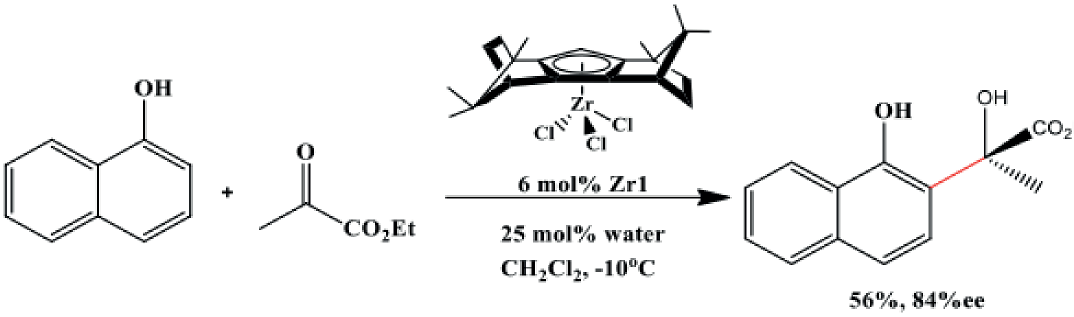


Figure 1 Some chiral ligand for achira synthesis

Following the discovery of ferrocene in 1951, the cyclopentadienyl anion (Cp) has emerged as a prevalent class of ancillary ligands for various transition metals. This stability stems from Cp's aromatic nature with its 6π-electrons, making it an effective σ- and π-donor ligand. Typically binding to transition metals in the η5-hapticity mode, Cp contributes to the remarkable stability observed in Cp metal complexes (CpM). A 1990 study by Erker et al. reported the Lewis acid-mediated hydroxyalkylation of 1-naphthol with ethyl pyruvate using a (+)-camphor-derived Cp^xZr^{IV} complex (Zr1) as the catalyst. This Friedel–Crafts-like reaction highlights the potential of Zr1 as a chiral Lewis acid catalyst (Mas-Roselló et al., 2021).



Scheme 2. Zr1-catalyzed Ethyl Pyruvate Hydroxyalkylation of 1-Naphthol

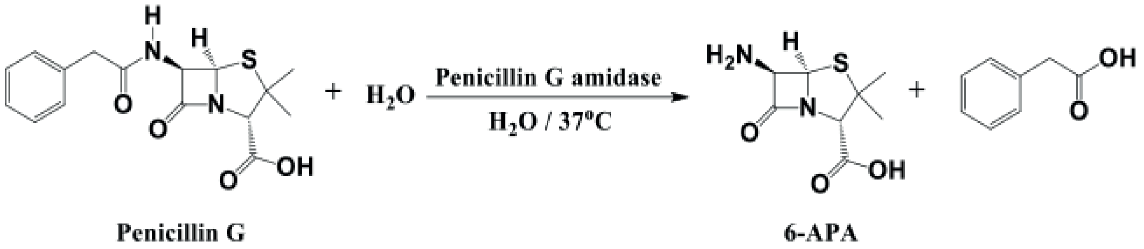
Research into Cp^X ligands has yielded a diverse range of chiral architectures, including central, axial, planar, and even macromolecular chirality. The most prominent of these are undoubtedly the atropochiral binaphthyl-derived scaffolds, which have been successfully complexed with both transition metals (Rh, Ir, Ru, Co) and rare-earth metals (Sc, Y, La, Sm, Gd, etc.) (Shaaban et al., 2020).

L-proline, a naturally occurring amino acid, exhibits remarkable bifunctional catalytic activity due to its combined secondary amine and carboxylic acid functionalities. The amine group acts as a Lewis base, while the carboxylic acid behaves as a Brønsted acid. This unique combination enables L-proline to effectively catalyze a broad range of asymmetric syntheses, including established reactions like Aldol condensations, Mannich reactions, and Michael additions. Furthermore, L-proline demonstrates proficiency in catalyzing the formation of diverse heterocyclic skeletons, including coumarins, spiro-oxindoles, imidazoles, and many others (Thorat et al., 2023).

2.3. Organocatalysis using enzymes or enzyme mimics

Biocatalysis, leveraging the power of specific enzymes for precise chemical reactions, has emerged as a prominent and versatile tool in organic synthesis, finding widespread application in industry. This technique owes its success to the exquisite control enzymes exert within their active sites, leading to remarkable activity, selectivity (stereo-, regio-, and chemo-), and a vast library of available biocatalysts suitable for diverse processes. Furthermore, enzyme engineering allows for customization of these biocatalysts, while the possibility of utilizing multiple enzymes in a single reaction vessel further amplifies the efficiency of biocatalysis (Nestl et al., 2014).

Enzymatic reactions offer a compelling alternative to traditional organic syntheses. They typically occur under mild conditions of near-ambient temperature and atmospheric pressure in water using standard reactors. This eliminates the need for harsh chemicals like Me3SiCl, PCl5, and PhNMe2, and also avoids the complex protection and deprotection steps often required in organic synthesis. This translates to shorter reaction times, less waste generation, and more sustainable processes. A prime example is the biocatalytic production of 6-APA, a key precursor for antibiotic production, achieved by penicillin G amidase. This enzymatic method, developed in the 1980s, replaced the previous approach utilizing stoichiometric amounts of the aforementioned harsh chemicals in organic solvents at high temperatures (40-80°C). The biocatalytic route operates in water at 37°C, requiring only a small amount of ammonia (0.09 kg/kg 6-APA) for pH control, showcasing the significant environmental benefits of enzymatic reactions (Sheldon & Brady, 2019).



Scheme 3. Enzymatic synthesis of 6-APA from Penicillin G

For over a century, a stereoselective benzoin condensation involving baker's yeast has been the cornerstone of industrial (–)-ephedrine production, generating (R)-phenylacetyl carbinol as a key intermediate. Similarly, a regio- and stereoselective C-H oxidation mediated by a fungus plays a vital role in the large-scale synthesis of the anti-inflammatory drug hydrocortisone. These examples highlight the power of biocatalysis in organic synthesis. The Protein Data Bank (PDB), a constantly expanding resource with over 160,000 protein structures, provides invaluable insights into enzyme mechanisms. Techniques like cocrystallization allow us to visualize substrate/product binding within the enzyme's active site, offering crucial information rarely obtainable with traditional catalysts. Furthermore, computational modeling tools complement these structural studies, aiding in the elucidation of enzymatic mechanisms and understanding the remarkable reactivity and selectivity exhibited by biocatalysts (Winkler et al., 2021).

The past two decades have seen a revolutionary transformation in the field of biocatalysis, driven largely by breakthroughs in molecular biology. This progress is exemplified by four key advancements: (i) the discovery of novel enzymes through a combination of genome sequencing, gene synthesis, and bioinformatics tools(Chavali & Rhee, 2018); (ii) the optimization of existing enzymes through directed evolution and computational analysis; (iii) the improvement of enzyme stability and reusability via immobilization techniques; and (iv) the development of multi-step cascade reactions to achieve complex biotransformations (Hwang & Lee, 2019; Sheldon & Brady, 2019). These advancements have significantly expanded the industrial potential and scope of biocatalysis.

2.4. Photocatalysis and its applications in organic synthesis.

Catalysts are crucial for making chemicals and drugs. While easier to separate, solid catalysts (heterogeneous) are often less effective than liquid ones (homogeneous). Scientists are trying to combine the benefits of both, but it's challenging and often makes the catalysts worse. Regular catalysis speeds up reactions by lowering the energy hurdle. Visible-light photocatalysis works differently. Instead, it uses light to directly create reactive molecules for the reaction, bypassing the need for energy reduction. Light irradiation of homogeneous ruthenium or iridium polypyridyl complexes (PCs) generates excited states capable of single-electron transfer (SET) for photoredox catalysis (PRC) through oxidative or reductive quenching cycles. Alternatively, the excited PC can transfer its energy (EnT) to a substrate or reagent to directly trigger chemical transformations(Strieth-Kalthoff et al., 2018). Unlike conventional catalysts, heterogeneous photocatalysts like semiconductors mimic homogeneous catalysis through light-induced electron transfer. Upon absorbing light, these semiconductors excite electrons, creating both oxidizing and reducing species on a single particle for efficient single-electron redox reactions. Titanium dioxide, a naturally occurring mineral with diverse applications, functions as both a white pigment in products like paints and cosmetics and a photocatalyst activated by UV light for water purification, energy conversion, and even organic synthesis due to its semiconducting properties (Gisbertz & Pieber, 2020).

Metallaphotocatalysis, combining photocatalysis with transition metal catalysis, offers a powerful tool for selective carbon-carbon and carbon-heteroatom bond formation under mild conditions. This approach addresses limitations of traditional palladium-catalyzed cross-couplings, particularly for Csp3-Csp2 bond formation. While efficient for Csp2-Csp2 couplings, palladium struggles with slower reaction steps and competing pathways for Csp3-Csp2 bonds. The breakthrough came in 2014 with the demonstration of efficient Csp3-Csp2 couplings using dual photo/nickel catalysis. This approach leverages photocatalysis to generate reactive alkyl radicals from readily available starting materials like carboxylic acids or potassium trifluoroborates, facilitating efficient Csp3-Csp2 bond formation by the nickel catalyst (Reischauer & Pieber, 2021). Visible light photocatalysis has several benefits, leading to its use in different areas of medicinal chemistry such as drug discovery, bioconjugation, late-stage C–H functionalization, and isotopic labeling.

Researchers developed a new approach for metallaphotocatalytic cross-coupling reactions by immobilizing a chromophore and a nickel complex onto titanium dioxide (TiO2). This single-component catalyst, called a dye-sensitized metallaphotocatalyst (DSMP), eliminates the need for pre-formed complexes. The DSMPs are easily prepared in a reaction mixture containing the substrates, a base, and TiO2 alongside a dye and nickel complex, each containing a binding group for TiO2. This method offers operational simplicity and flexibility, allowing researchers to directly evaluate different dyes and ligands for various cross-coupling reactions (C-O, C-S, C-N, C-C) under different light sources (blue, green, red) (Reischauer et al., 2020).

2.5.Electrocatalysis for sustainable and efficient reactions

Electrochemistry is emerging as a powerful tool in synthetic organic chemistry due to its ability to precisely generate reactive radical and radical ion intermediates under mild conditions. This has led to the development of innovative electrocatalytic methods for the selective formation of valuable complex molecules (Cembellín & Batanero, 2021).

Electrochemistry grants organic chemists exceptional control over reactions by offering a tunable "dial-in" redox potential, precise regulation of current, and the generation of reactive intermediates for strategic bond formation. Electrochemical activation, while powerful, offers limited control over reaction selectivity in complex systems due to the absence of molecular recognition at the electrode surface and its inability to influence subsequent chemical steps. In direct electrolysis, substrate engineering and the strategic use of electrocatalysts are crucial for controlling reactivity and selectivity. Two main types of electrocatalysts exist: Type I, which facilitates hindered electron transfer, and Type II, which shuttles both electrons and chemical information to enhance reaction rates and product specificity. Electrocatalysts of Type II have been created specifically for use in the power sector, particularly for the purpose of catalyzing water splitting and reducing CO2 (Siu et al., 2020).

The origins of electroorganic synthesis may be attributed to the 19th century experiments conducted by Faraday, who demonstrated the hydrolysis of acetic acid into hydrocarbons, and Kolbe, who achieved electrochemical decarboxylative dimerization. Indirect electrolysis utilizes redox mediators to achieve electron transfer between electrodes and substrates, offering improved reaction efficiency, better chemoselectivity, and targeted product formation through homogeneous mediator processes. This approach has been particularly successful in facilitating challenging reactions like the selective anodic oxidation of C-H bonds, as exemplified by the N-hydroxyphthalimide (NHPI) mediated allylic C-H oxidation (Zhu et al., 2021).

Conventional methods for creating organic molecules are environmentally harmful due to high energy consumption and CO2 emissions. However, CO2 itself presents an abundant and cheap carbon source. Researchers are exploring nanostructured materials as catalysts for the electrochemical reduction of CO2 (CO2RR), a promising technique to produce C1–C2+ fuels and carbonaceous products, including carbon monoxide, oxygenates and hydrocarbons (Mancuso et al., 2024).

2.6.Use of microwaves in organic synthesis

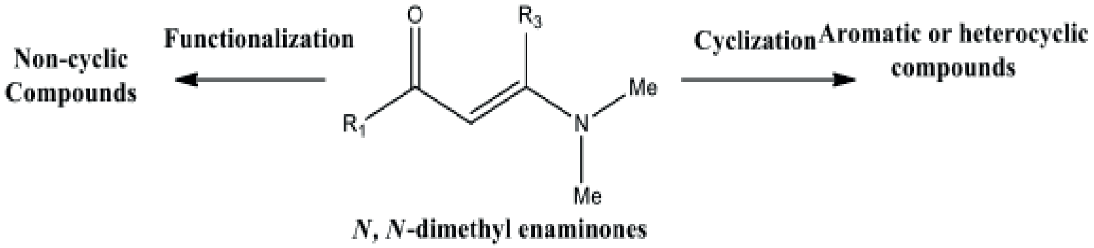
Microwave-assisted synthesis, a green chemistry approach proving successful in organic reactions, including metal-catalyzed ones, is underutilized in inorganic complex synthesis. This technique's time-saving efficiency and ability to facilitate challenging transformations offer significant advantages for inorganic chemists. Microwave-assisted synthesis (MW) significantly accelerates the reaction times for creating palladium(II) complexes containing N-heterocyclic carbenes (NHC) compared to conventional heating methods. This advantage extends to the synthesis of Pd(II) and Pt(II) complexes with specific ligands, achieving faster reaction times (minutes versus hours), reduced solvent usage, and typically higher yields when compared to conventional heating methods (Gabano & Ravera, 2022).

Schiff bases, known for their importance in various fields, were efficiently synthesized via microwave irradiation by reacting salicylaldehyde/o-hydroxyacetophenone, various amino acids (glycine, alanine, etc.), and VOSO4 in a water/ethanol mixture at pH 5.5-5.8. This method yielded high-quality crystals (56-87%) directly under ambient summer conditions, likely due to the slow natural cooling promoting crystallization during microwave irradiation (Wazalwar & Bhave, 2012).

3.Strategies for Selective Synthesis

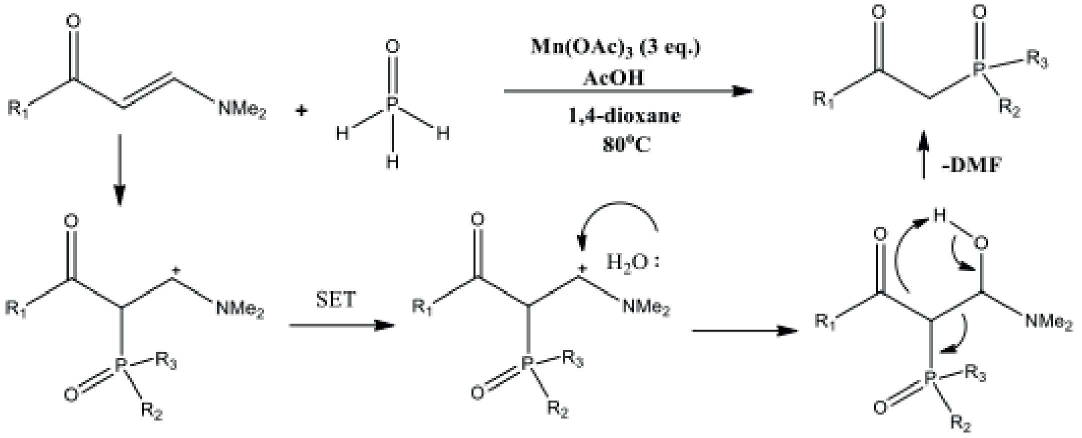
Driven by societal challenges and high-tech industries, organic synthesis is entering a new era. Cutting-edge methods aim to introduce functional groups and complex structures with precise control over reactions. Emerging trends involve achieving absolute selectivity in creating organic molecules, pharmaceuticals, and smart materials. Future advancements point towards "atomic precision" in chemical reactions. The field of selective organic synthesis is witnessing a surge in methodologies for transforming complex, functionalized molecules under mild conditions. This progress is driven by several key trends: the development of efficient methods for incorporating fluorine atoms, a valuable element in pharmaceuticals and functional materials; various catalytic coupling reactions that elegantly forge new carbon-carbon bonds; and atom-economical addition reactions that minimize waste. Additionally, advancements in metathesis processes (rearranging molecular frameworks), oxidation and reduction reactions (controlling functional group states), and heterocyclic compound synthesis (building complex ring structures) are expanding the synthetic toolbox. Further propelling this field are the design of novel catalysts, the utilization of light-activated (photocatalytic) transformations, and the adaptation of these methods for large-scale production. Alongside these advancements, the development of sophisticated techniques to investigate reaction mechanisms is providing crucial insights for further refinement and discovery (Ananikov et al., 2014). Biocatalysis, utilizing defined enzymes for organic transformations, has gained prominence in both academic and industrial organic synthesis due to their exceptional activity and selectivity. This arises from the precise control exerted within the enzyme's active site, leading to high stereo-, regio-, and chemoselectivity in the desired reactions.

Enaminones, particularly N,N-dimethyl enaminones, are attracting significant attention in organic synthesis due to their unique properties. These versatile building blocks possess a highly polarized C=C double bond thanks to the electron-withdrawing carbonyl group and electron-donating amino groups in conjugation. This results in higher electron density at the α-carbon compared to the amino groups. Notably, the N,N-dimethyl group not only serves as a common structural element with multiple reactive sites, but also functions as a superior leaving group compared to other enaminones. This improved leaving group ability allows for further elaboration through a wide range of straightforward chemical transformations.



Scheme 4. Applications of N, N-dimethyl enaminones

A recent study demonstrated the use of N,N-dimethyl enaminones in an innovative oxidative phosphonylation reaction with H-phosphonates, catalyzed by manganese. This reaction selectively cleaves both the C=C double bond and the P-H bond of the H-phosphonate, leading to functionalized beta-keto phosphonates. This approach represents the first example using N,N-dimethyl enaminones for selective C=C bond cleavage to form a C(sp3)-X bond and the first manganese-catalyzed synthesis of beta-ketophosphonates. Interestingly, the reaction can be adapted to synthesize delta-ketophosphonates when starting with 1,3-dicarbonyl compounds.



Scheme 5. Synthesis of β-ketophosphonates

4. Sustainable Organic Chemistry

The ideal organic synthesis is a streamlined process characterized by minimal steps, high selectivity to avoid unwanted byproducts, and efficient use of atoms to minimize waste. Additionally, it prioritizes readily available and inexpensive starting materials for cost-effectiveness. Green chemistry principles further elevate these goals by targeting reactions that produce minimal waste, utilize non-hazardous reagents and solvents, prioritize safety, and responsibly manage energy consumption and natural resources (Cembellín & Batanero, 2021).

Mechanochemistry, the use of mechanical force to drive chemical reactions, has a long history with the mortar and pestle being a prime example. Modern advancements have led to various automated grinding equipment, including high-speed ball mills, planetary mills, and screw mills, for efficient and scalable mechanochemical processes in both research labs and industrial settings (Avila-Ortiz & Juaristi, 2020).

Water has surged in popularity as a solvent for organic reactions in recent decades. Its advantages go beyond low cost and non-toxicity – it's a safe and environmentally friendly alternative to traditional organic solvents. Reactions "in water" offer benefits like easier product isolation, inherent safety, high polarity, and sometimes even faster and more selective reactions.

The concept of "on water" reactions, introduced by Sharpless, further expanded water's utility. This approach allows reactions of insoluble organic compounds to occur in aqueous suspensions, often at significantly faster rates than in organic solvents. As a result, research on water-based chemical reactions has seen tremendous progress (Chatgilialoglu et al., 2024).

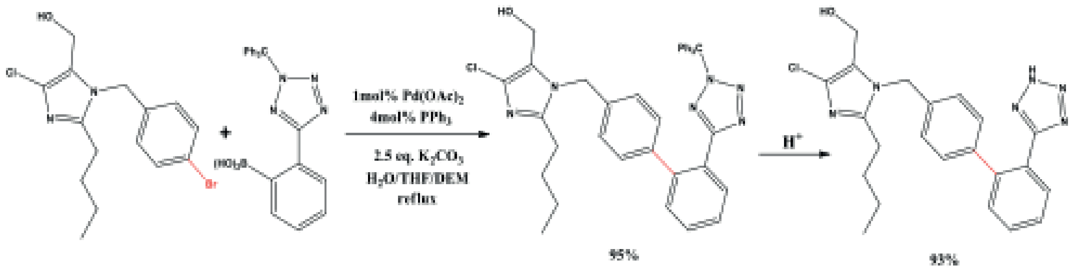
Bioelectrocatalysis emerges as a game-changer in sustainable manufacturing. This technique merges the strengths of biocatalysis (using enzymes) and electrocatalysis (using electrodes) to efficiently produce valuable chemicals, clean biofuels, and degradable materials directly from electricity, offering a green alternative to traditional biomanufacturing processes (Chen et al., 2020).

Electrochemical reactions involving water and nitrogen are a promising avenue for clean energy storage and conversion due to their reliance on abundant and sustainable resources. This technology can be integrated with renewable electricity sources to produce carbon-neutral fuels like hydrogen and ammonia, which can then be used in fuel cells to generate electricity again, creating a closed-loop clean energy system (Li et al., 2021).

5. Applications of Advanced Organic Chemistry

Cross-coupling reactions, particularly Suzuki-Miyaura and Buchwald-Hartwig methods, have become a cornerstone in drug discovery due to their versatility. These reactions efficiently generate carbon-carbon and carbon-heteroatom bonds, enabling rapid exploration of structure-activity relationships (SAR) for lead identification and optimization. This flexibility extends beyond traditional small molecules, facilitating the development of novel modalities like DNA-encoded libraries, new peptides and cyclopeptides, allosteric modulators, and PROTAC degraders.

Losartan, a widely prescribed antihypertensive drug, is presented as an example where a key cross-coupling step was optimized for large-scale synthesis. This involved replacing air-sensitive tetrakis(triphenylphosphine) palladium with a more cost-effective catalyst generated by heating Pd(OAc)2 and triphenylphosphine in a 1:4 THF/DEM mixture, along with identifying a solvent system compatible with the aqueous reaction medium for high-yield (95%) coupling (Buskes & Blanco, 2020).



Scheme 6. Synthesis of Losartan

Advancements in protein engineering and directed evolution are revolutionizing pharmaceutical synthesis through enzyme catalysis. Bioengineered enzymes offer exceptional regioselectivity, chemoselectivity, and stereoselectivity for complex molecule synthesis. This biocatalytic approach, facilitated by low-cost DNA synthesis and progress in protein engineering, bioinformatics, and analytical sciences, tackles major synthetic challenges. Notably, the adoption of oxidoreductases like monooxygenases and oxidases is on the rise due to their ability to perform sustainable redox reactions under mild, environmentally friendly conditions, eliminating the need for toxic reagents and heavy metals. Enzymes are playing an increasingly important role in drug discovery and development. They act as powerful tools by offering access to valuable intermediates, the building blocks needed to create new drugs. Additionally, enzymes like galactose oxidases show promise in selectively modifying DNA-carbohydrate conjugates. This targeted manipulation opens doors for the development of novel carbohydrate-based DNA-encoded libraries, which can be instrumental in the drug discovery process. These libraries essentially function as collections of potential drug candidates, allowing for efficient screening and identification of promising therapeutic leads (Fryszkowska & Devine, 2020).

Porous organic polymers (POPs) have surged in popularity due to their exceptional surface area and customizable design. The ability to precisely incorporate functionalities makes them ideal for applications like adsorption, separation, and catalysis. Researchers are actively designing and synthesizing diverse POPs with tailored structures and properties. Recently, supramolecular macrocycles with strong host-guest interactions have emerged as promising crosslinkers for POP development. These macrocycle-based POPs exhibit hierarchical structures and potentially superior performance due to their well-organized multi-scale organization. This approach offers exciting possibilities for POPs with unique porous, adsorptive, and optical properties, while providing valuable insights into the impact of skeletal complexity on material function.

Recently, supramolecular macrocycles with strong host-guest interactions are being explored as powerful crosslinkers for POPs. These macrocycles can create hierarchical structures with improved performance, offering well-organized organization across different scales. Macrocycle-based POPs exhibit unique porous, adsorptive, and optical properties compared to traditional POPs. This approach provides valuable insights into the intricate relationship between skeletal complexity and material diversity.

The convergence of reticular and macrocyclic chemistry brings significant advantages to porous organic polymers (POPs). Macrocycles, cyclic molecules with well-defined cavities, endow POPs with guest-responsive properties, meaning their structure can adapt in response to captured molecules. Additionally, macrocycles enable precise topological design, allowing for the creation of POPs with specific network arrangements. This, combined with the ease of functionalization inherent to POPs, facilitates the incorporation of desired functionalities. Moreover, macrocycles can contribute to enhanced mechanical strength in the resulting POP structures. By integrating macrocycles into POPs, researchers gain access to a broader range of advanced materials with the potential for exhibiting entirely new properties.

Organic synthesis plays a crucial role in this field. Nucleophilic aromatic substitution (SNAr) is a prominent method for creating highly porous macrocycle-based POPs. For instance, highly porous β-cyclodextrin polymers (TFN-CDP) were synthesized through direct polymerization of β-cyclodextrin's hydroxyl groups with tetrafluoroterephthalonitrile (TFN) as a rigid linker via SNAr reaction. This approach highlights the importance of organic synthesis in crafting POPs with tailored properties for specific applications like removing pollutants from water. In summary, the strategic incorporation of macrocycles and the power of organic synthesis are pushing the boundaries of POP development, leading to a new generation of materials with exceptional properties and functionalities. This field holds immense potential for advancements in various areas of science and technology (Li & Yang, 2022).

Despite the precise control achievable in organic molecule synthesis, constructing crystalline frameworks in 3D is challenging due to competition from uncontrolled polymerization. While progress has been made with crystalline materials like zeolites and metal organic frameworks, the field of crystalline porous organic polymers saw a significant breakthrough with the discovery of covalent organic frameworks (COFs). COFs offer a versatile platform for designing materials with diverse properties due to the ease of incorporating functionalities and utilizing various building blocks. However, the choice of linkage chemistry significantly impacts solid-state emission in 2D COFs. Studies show that imine linkages often quench luminescence, while boron-based linkages like boroxine and boronate promote efficient emission by restricting intramolecular rotation. This approach, particularly with aggregation-induced emission moieties, has yielded highly emissive 2D COFs with potential applications in optoelectronics, sensing, and biomedicine due to their degradability and biocompatibility (Li et al., 2020).

6. Conclusion

Organic chemistry is constantly evolving to address sustainability concerns. Catalysis, particularly transition metal catalysis, plays a key role in accelerating reactions, improving selectivity, and increasing yields. This is especially valuable for synthesizing complex chiral natural products. Additionally, emerging techniques like electrochemistry and microwave-assisted synthesis offer mild reaction conditions and efficiency for organic and even inorganic synthesis. Sustainable practices are a major focus with the use of water as a solvent gaining traction. Bioelectrocatalysis and water/nitrogen based electrochemical reactions are promising avenues for clean energy and chemical production. Furthermore, cross-coupling reactions accelerate drug discovery by facilitating exploration of structure-activity relationships. Bioengineered enzymes offer unparalleled regioselectivity and stereoselectivity for complex molecule synthesis, impacting fields like drug development. Overall, organic synthesis is a dynamic field continuously seeking new methods for efficient, sustainable, and selective creation of valuable molecules.

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Advances In Spectroscopy Techniques

Ghashia AMEEN

Spectroscopy is a powerful technique that investigates the unseen world of atoms and molecules. This approach reveals the underlying concepts and its significant importance in many scientific fields such as chemistry, biology, environmental science, and materials research. Complexities associated with mass spectrometry, nuclear magnetic resonance (NMR), infrared (IR), ultraviolet-visible (UV-Vis), Raman, and X-ray spectroscopies, with a focus on current developments in technology and data interpretation will be discussed in this chapter. Mass spectrometry has made significant advancements in analyzers and ionization techniques, resulting in its widespread use in proteomics, metabolomics, and drug development. NMR spectroscopy is of significant importance in the field of structural characterisation, and recent improvements have facilitated the investigation of solid-state materials. Moreover, the progress in equipment and data processing has significantly enhanced the efficacy of FTIR, UV-visible, and X-ray spectroscopy. Surface-enhanced Raman spectroscopy, characterized by its heightened sensitivity, is a noteworthy advancement that is propelling the frontiers of scientific investigation across various fields. The vast array of applications of spectroscopy in many fields serves as a driving force for researchers to consistently enhance these methodologies and address the challenges they face, so assuring their ongoing reliability and broadening their scope in scientific exploration.

1. Introduction to Spectroscopy

Spectroscopy, the study of interactions between materials and electromagnetic radiation, has become a cornerstone for characterizing Earth Science materials. By analyzing the resulting spectra, scientists can identify and quantify specific components based on unique absorption features. This technique has seen significant advancements since the early 1900s, with the development of infrared spectrometers and the creation of spectral libraries by pioneers like Hunt and Salisbury. These libraries, acting as a Rosetta Stone for geological remote sensing, allow researchers to decipher the complex signals from instruments and understand the composition of Earth's materials (Meer, 2018).

The roots of modern spectroscopy can be traced back to early alchemists' use of flame tests for elemental analysis. These early qualitative methods, alongside colorimetry (comparing solution colors), laid the groundwork for the field. The evolution of light sources, dispersion devices, optics, detectors, and modern technology has since fueled continuous advancements in spectroscopic instrumentation. While the underlying principles and engineering of modern ultraviolet, visible, and infrared spectrometers are sophisticated, user-friendly designs often enable accurate analysis with minimal training. This accessibility has made spectroscopy a cornerstone technique in chemical analysis. In spectroscopy, a spectrum depicts how a material absorbs electromagnetic radiation across a range of wavelengths or energies. This absorption is caused by quantized energy level transitions within the sample's atoms or molecules. While these transitions ideally result in sharp lines (line spectra), most observed peaks have a finite width. This broadening can be attributed to the Heisenberg uncertainty principle as shown in equation 1, where the lifetime (τ) of the excited state is inversely proportional to the energy level uncertainty (ΔE) of the transition. In simpler terms, shorter-lived excited states lead to broader spectral peaks.

$$\Delta E = h/2\pi\tau \quad \text{...............(1)}$$

In spectroscopic analysis, a factor influencing spectral line width is Doppler broadening. This arises because the transition energy (ΔE) between molecular states remains constant. However, the observed frequency, and consequently the perceived energy, of the emitted or absorbed radiation is influenced by the motion of the emitting or absorbing molecule relative to the observer. Molecules approaching the observer experience a slight "blueshift," meaning the observed frequency is higher than the rest energy. Conversely, molecules receding from the observer exhibit a "redshift," with a lower observed frequency. This distribution of velocities within a sample contributes to the broadening of spectral lines (Jespersen, 2006).

Spectroscopy techniques, like fingerprints for materials, are crucial across science and industry for identifying substances, analyzing their structure, and monitoring processes, making them vital tools in fields from astronomy and medicine to forensics and materials science.

2. Modern Spectroscopy Techniques

2.1 Mass Spectrometry

Mass spectrometry utilizes an ion source, mass analyzer, and detector to dissect a sample into charged particles, measure their mass-to-charge ratios (m/z), and identify individual molecules. The mass analyzer plays a critical role, especially in analyzing biomolecules, by separating these lightweight, variably-charged entities for precise mass determination, ultimately fulfilling the instrument's core function of biomolecular identification (Haag, 2016).

Advancements

The growing importance of low-abundance molecules in research, from biomarkers to single-cell metabolites, necessitates ever-more sensitive analytical tools. Mass spectrometry (MS), with its unparalleled sensitivity and specificity, has emerged as a cornerstone technique across diverse disciplines. As the demand for precise analysis intensifies, advancements in MS continue to push the boundaries of detection, ensuring its continued relevance in various research fields. Mass spectrometry sensitivity can be enhanced through various approaches. Pretreatment optimization reduces matrix interferences, improving detection of low-abundance analytes. Novel ionization techniques boost signal intensity and remove matrix interferences, while advancements in ion transmission systems like funnels and lenses improve ion movement. Finally, advancements in mass analyzers enhance sensitivity through improved ion transmission, targeted ion enrichment, utilization rate, and signal-to-noise ratio.

Due to their simple design and affordability, quadrupole mass analyzers are prevalent tools for applications like atmospheric monitoring and aerospace exploration. The Curiosity rover on Mars, for instance, utilizes a quadrupole analyzer to detect light isotopes and volatile compounds, confirming the presence of organic molecules like chlorobenzene on the red planet. However, their limitations in mass range and resolution render them less suitable for analyzing complex macromolecules. Pioneered by Wolfgang Paul and colleagues, the 3D ion trap mass analyzer revolutionized mass spectrometry. Its simple design, combining hyperboloid end-cap electrodes with a ring electrode, facilitates miniaturization while enabling ion focusing, selective ion isolation (m/z), and MSn analysis. These features, along with its modest vacuum needs and high sensitivity, make it ideal for qualitative proteomic studies and have significantly contributed to the advancement of this field. Time-of-flight (TOF) mass spectrometry offers a powerful combination of rapid analysis and high mass accuracy, making it an ideal choice for high-throughput applications and the characterization of large biomolecules. For high-resolution mass spectrometry, the Orbitrap analyzer reigns supreme, often working in tandem with other analyzers. Similarly, the C-trap can be incorporated as a collision cell to generate fragment ions, mirroring the function of a quadrupole analyzer (Li et al., 2021).

2.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) offers a powerful technique for studying materials at the atomic level. It relies on the interaction between nuclei and magnetic fields. When placed in a strong, constant magnetic field, certain atomic nuclei with non-zero spin angular momentum will align themselves. The application of a weak, oscillating magnetic field can then perturb this alignment. If the frequency of the oscillating field matches a specific resonant frequency of the nuclei, an electromagnetic signal is emitted. This resonant frequency is influenced by the surrounding chemical environment of the nucleus, providing valuable information about the structure and dynamics of molecules.

Biomacromolecules' functions arise from a delicate interplay between their intricate 3D structures and their inherent dynamic nature. These flexible molecules exhibit a wide range of motions, from picoseconds to seconds. NMR spectroscopy has become the gold standard for investigating both protein structure and dynamics in solution, as it offers sensitivity to both aspects simultaneously. However, despite advancements in experimental techniques and computational analysis, reconciling structural and dynamic information from NMR data remains a challenge. Thankfully, molecular dynamics simulations have become an invaluable tool to bridge this gap and provide a more comprehensive understanding of these biomolecules. NMR spectroscopy offers a powerful technique for determining biomolecule structure. By studying various "relaxation channels" sensitive to both structure and dynamics, it provides a set of distance and angle restraints. These restraints are then used within a molecular modeling algorithm to generate a three-dimensional representation of the biomolecule (Markwick et al., 2008).

Advancements

Advancements in instrumentation and software have propelled NMR spectroscopy to the forefront of analytical methods in biology. While multidimensional pulse sequences continue to be developed, a small set of 2D experiments can rapidly determine the structure of small metabolites. Even more complex 3D and 4D techniques enable the elucidation of protein structures up to 100 kDa, with over 100 plant protein structures established using NMR. Additionally, NMR finds application in the nascent field of metabolomics, offering unbiased metabolite profiling of plant extracts. High-resolution NMR has become a cornerstone technology for deciphering biosynthetic pathways and metabolite flux through the quantification of multiple isotopologues (Eisenreich & Bacher, 2007).

Solid state NMR

The development of metal-organic frameworks (MOFs) represents a significant leap in materials science. However, despite their exciting potential applications, a gap exists in understanding the local structures, molecular details, and guest interactions that govern their functionalities. Solid-state nuclear magnetic resonance (SSNMR) emerges as a complementary technique to X-ray diffraction (XRD), offering crucial insights into these critical aspects of MOFs. Solid-state NMR (SSNMR) spectroscopy has undergone a remarkable transformation in recent decades, becoming a powerful tool for investigating microporous materials. Multinuclear and multidimensional techniques offer a wealth of information on the framework structure of these materials, including the dynamics of guest molecules within their pores. Solid-state nuclear magnetic resonance (SSNMR) studies often utilize deuterium (^2H or D) nuclei instead of protons (^1H) due to the significant broadening of signals caused by strong homonuclear dipolar interactions between protons. Deuterium possesses a quadrupolar moment, which allows researchers to extract information about the mobility of hydrogen molecules (H_2) within Metal-Organic Frameworks (MOFs) by analyzing the lineshape of the ^2H NMR signal. This approach provides valuable insights into the dynamic behavior of H_2 within these porous materials.

Pulsed field gradient (PFG) NMR allows researchers to probe the self-diffusion coefficient and pathway of guest molecules navigating the channels. Hyperpolarized 129Xe NMR provides detailed insights into the cage and channel structure, as well as communication pathways within the material. Variable temperature (VT) SSNMR is a well-established method for studying the flexibility and dynamic behavior of porous functional materials at the molecular level. Furthermore, SSNMR offers significant potential for elucidating host-guest interactions between small molecules and these porous materials. In situ SSNMR techniques are emerging as a powerful tool for unraveling catalytic reaction mechanisms over microporous materials by enabling the observation of reactive intermediates trapped within the material's voids or channels. Recent advancements in instrumentation and techniques are continuously improving the sensitivity of SSNMR for materials analysis, allowing detection of nuclei with low natural abundance, weak magnetic properties (γ), or significant quadrupole interactions (Li et al., 2020; Wong et al., 2019).

2.3 Infrared (IR) Spectroscopy

Infrared (IR) spectroscopy is a cornerstone technique in analytical pharmacy and chemistry. It provides a window into the vibrational motions of atoms within a molecule, hence the term vibrational spectroscopy. An IR spectrum is generated by passing infrared radiation through a sample and measuring the amount of light absorbed at specific frequencies. Fourier transform (FT) infrared (FTIR) spectrometers have revolutionized the field, offering significant advantages in speed and efficiency compared to dispersive instruments. The core of an FTIR spectrometer is the interferometer, which utilizes a beamsplitter to divide the source radiation into two beams. These beams travel down separate paths, reflect off mirrors, and recombine at the beamsplitter. The path length difference between the two beams determines whether they interfere constructively or destructively, resulting in a signal recorded by the detector. This signal, known as an interferogram, is then mathematically transformed (using the Fourier transform) into an IR spectrum. To obtain the sample's specific absorption profile, two interferograms are collected: one with the sample in the beam path and another without. The ratio of these transformed interferograms yields the sample's IR transmission spectrum. In most cases, the sample is positioned between the interferometer and the detector for optimal analysis.

Advancements

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) is a powerful analytical technique employed in pharmaceutical science due to its speed, minimal sample preparation requirements, and non-destructive nature. ATR-FTIR utilizes the principle of total internal reflection, where an infrared beam reflects entirely off an internal surface when the incident angle surpasses a critical value. This allows for the characterization of a material's surface functional groups without complex sample manipulation. In the realm of pharmaceuticals, ATR-FTIR finds applications in structural Analysis (Characterizing the structure and properties of biological systems like the Stratum Corneum), non-invasive Drug Release Studies (Monitoring the release of drugs from semi-solid formulations without disrupting the sample integrity), Drug Diffusion Measurement (Quantifying drug diffusion from pharmaceutical systems such as polymers and films), drug Penetration Assessment (Investigating the penetration of drugs into artificial and biological membranes, aiding in the design of targeted delivery systems) and drug-macromolecule interaction studies (Elucidating interactions between drugs and various macromolecules, including synthetic, semi-synthetic, and native biomolecules). This analytical power, coupled with its ease of use, makes ATR-FTIR a valuable tool for pharmaceutical scientists across various research and development stages (Dole et al., 2011).

Fourier Transform-Infrared (FT-IR) spectroscopy offers a powerful window into the microbial world. Micro-FTIR spectroscopy allows researchers to analyze the molecular composition of specific microorganisms or their components within a sample with high spatial resolution. This technique is particularly valuable for studying microscopic features or isolated microbial structures. Conversely, Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy excels at analyzing bulk samples, including microorganisms in their natural state (e.g., powdered or granulated forms) with minimal preparation. Together, these FT-IR techniques provide invaluable insights into the intricate biochemical processes underlying microbial interactions that shape ecosystems and biogeochemical cycles (Kassem et al., 2023).

Fourier-Transform Infrared Spectroscopy (FTIR) offers a powerful analytical tool for archaeologists due to its versatility. Requiring minimal sample amounts (milligrams or micrograms), it can analyze a wide range of materials, including organic and inorganic, crystalline and amorphous. This allows archaeologists to identify and compare the composition of diverse archaeological finds, from fired clays and bone fragments to fibers and dyes. This broad applicability makes FTIR a valuable asset for any archaeological laboratory (Margaris, 2020).

2.4 UV-Visible Spectroscopy

Due to its inherent advantages, ultraviolet-visible (UV-Vis) spectroscopy has emerged as a powerful tool for pollutant detection in aqueous environments. These advantages include high precision, fast analysis times, minimal sample disruption, environmental friendliness, affordability, and the potential for portable instrumentation. Underpinning the quantitative analysis capabilities of UV-Vis in water quality monitoring is the Lambert-Beer Law. This law dictates the interaction between light and a light-absorbing medium. A monochromatic beam of light strikes the sample, and as it travels through the medium, a portion of the light energy is absorbed. This absorption reduces the intensity of the transmitted light, with the extent of this reduction being directly proportional to the thickness of the absorbing medium (Kot et al., 2021).

Due to its limited range within the electromagnetic spectrum, visible light differs from other forms of radiation in the energy frequency of its photons. However, the ultraviolet-visible (UV-Vis) region, encompassing wavelengths from approximately 180-800 nm, is frequently utilized for the analysis of organic molecules. Absorption within this region primarily involves electronic level transitions, although vibrational transitions can also contribute. Transitions requiring higher energy input, such as $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$, are typically associated with UV absorption, while $\pi \rightarrow \pi^*$ transitions correspond to UV-Vis absorption. The portion of the molecule responsible for these electronic transitions is termed the chromophore.

Advancements

In instances where a molecule exhibits transparency in the UV-Vis region, various derivatization techniques can be employed to enhance detection sensitivity and, in some cases, selectivity. Several analytical strategies are employed to enhance detection sensitivity, including Schiff base formation, complexation reactions, and enzymatic/catalytic transformations. Additionally, techniques like azodye derivatization, charge transfer complexation, ion-pair analysis, and solid-phase derivatization can further improve signal strength. Furthermore, preconcentration/enrichment steps utilizing solvent or sorbent extraction or membrane separation can be implemented to magnify the target analyte for more effective detection. Recent advancements in UV-Vis spectrophotometry focus on improving sensitivity, precision, and accuracy while simultaneously minimizing analysis costs and time.

Advancements in UV-Vis Detection Technology

Ultraviolet-visible (UV-Vis) detection has undergone significant advancements in recent years. The development of novel detectors has focused on enhancing detection sensitivity, minimizing limitations, and improving data acquisition speed.

Traditional Detectors

Photomultiplier tubes (PMTs): Highly sensitive PMTs offer exceptional low-light detection and high wavelength resolution due to their compatibility with narrow slit widths. These detectors have been widely employed for UV and visible region analyses.

Modern Detector Advancements

Photodiode Array (PDA) Detectors: PDAs excel as multichannel detectors due to their ability to monitor the entire UV-Vis spectrum simultaneously. They can rapidly capture complete spectra, making them ideal for applications like HPLC and flow analysis where transient signals are present. Additionally, PDAs offer advantages like high photon flux quantification, high quantum efficiency, and a superior height-to-width aspect ratio. However, limitations include significant dark current and high read noise.

Charged-Coupled Devices (CCDs): CCDs were developed to address the limitations of PDAs. These silicon chip-based detectors convert light into an electrical signal and boast advantages like low dark count rate, low read noise, and high UV-Vis quantum efficiency, making them exceptional spectroscopic detectors.

Emerging Technologies

Light-Emitting Diodes (LEDs): LEDs, featuring p-n junctions that emit narrow light bands under forward bias, offer several advantages. Their low power consumption, reduced size, high sensitivity, and broad wavelength response with a high signal-to-noise ratio make them attractive options. Notably, their direct pulse-duration-modulated output eliminates the need for expensive A/D converters. These benefits extend beyond simple absorbance measurements, making them suitable for flow-through optical sensors in chromatography and flow analysis applications.

NanoDrop Technology: This technology utilizes a proprietary sample-retention system, enabling analysis with minimal sample volumes (approximately 1 μL). These microvolume spectrophotometers employ a unique design where the sample is precisely positioned between two optical surfaces. Surface tension forces create a liquid column with a controllable path length, eliminating the need for sample dilution across a broad concentration range.

These advancements in UV-Vis detection technology have significantly expanded analytical capabilities, offering researchers greater sensitivity, faster data acquisition, and improved performance in various scientific disciplines (Passos & Saraiva, 2019).

Applications

UV-vis spectroscopy offers a valuable toolbox for chemical engineers due to its versatility and affordability. This non-destructive technique analyzes a broad range of organic compounds and select inorganic species by measuring light absorbance or transmittance across a wavelength spectrum. Applications include quantitative analysis, reaction kinetics investigation, and elucidating reaction mechanisms at the molecular level. Furthermore, hyphenated techniques like HPLC-UV-vis and UHPLC-UV-vis enable both identification and quantification of compounds in liquid streams. Coupling UV-vis with mass spectrometry provides comprehensive identification of all present species. Additionally, UV-vis diffuse reflectance spectroscopy extends the analysis to solid and powdered materials (Rocha et al., 2018).

2.5 Raman Spectroscopy

The convergence of biomedical and nanobiotechnological research has opened exciting avenues for exploration. Studies on antioxidant carotenoids, disease-specific molecular markers, and microalgal production for biofuels all require a deep understanding of biological processes at the cellular level. This is where Raman spectroscopy (RS) emerges as a powerful tool. RS offers a unique window into cellular events by exploiting the Raman scattering phenomenon. Unlike Rayleigh scattering, where the light frequency remains unchanged, Raman scattering involves a shift in the scattered photon's frequency, revealing information about the sample's molecular composition. Notably, Stokes shifts, where the scattered photon loses energy (longer wavelengths), are more prevalent.

Several variations of RS exist, each leveraging Raman scattering differently. The choice of technique depends on factors like sample complexity and target molecule concentration. Conventional RS forms the foundation for a diverse "family tree" of advanced techniques, including Surface-enhanced Raman Spectroscopy (SERS), Coherent Anti-Stokes Raman Spectroscopy (CARS), and Spatially Offset Raman Spectroscopy (SORS). While conventional RS utilizes a continuous wave

(CW) laser, techniques like CARS and SRS employ pulsed lasers for nonlinear optical interactions. Notably, CARS microscopy offers high-resolution, label-free imaging of endogenous chemical structures, proving valuable in various biomedical fields.

Advancements

A key limitation of RS is its inherently weak signal. Fortunately, techniques like Resonance-enhanced Raman Scattering (RRS) address this challenge. By matching the laser excitation wavelength to a molecule's absorption peak, RRS significantly enhances the Raman signal of specific bands, leading to more detailed analysis. (Allakhverdiev et al., 2022).

Surface-enhanced Raman spectroscopy (SERS) offers a powerful analytical tool for scientists due to its exceptional sensitivity. This technique amplifies the weak Raman scattering signal of molecules adsorbed on specific nanostructured materials. The amplification arises from a combination of plasmon-mediated enhancement of the local electric field and potential chemical effects between the analyte and the substrate. This dramatic increase in sensitivity allows SERS to act as a fingerprint technique for low-concentration analytes (Han et al., 2021; Stiles et al., 2008).

Application

The continued development and application of these Raman spectroscopy techniques are poised to significantly advance our understanding of biological processes at the cellular level, propelling further breakthroughs in medicine and biotechnology. Consequently, SERS finds applications in a broad range of fields including surface and interface chemistry, catalysis research, nanotechnology developments, biological and biomedical studies, food science analysis, and environmental monitoring

2.6 X-ray Spectroscopy

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) emerges as a cornerstone technique for exploring surface properties, particularly in the crucial first 10 nanometers. This capability extends across various scientific and engineering disciplines. Understanding a material's surface chemistry, structure, and interfacial behavior is paramount when evaluating its corrosion resistance under diverse environmental conditions. Early surface reactions primarily occur within this nanoscale region, highlighting the necessity for tools adept at probing such depths. XPS stands out as a preferred method, delivering detailed chemical compositions of material surfaces within this 10 nm window. Additionally, XPS offers elemental identification and detection sensitivity as low as 0.1-1 atomic percent (except for H and He), solidifying its position as a unique tool for surface characterization, specifically in corrosion studies. Notably, XPS facilitates the investigation of surface reactions under vacuum environments, with the ability to resolve down to a single monolayer.

The technique allows for analysis of compositional variations within thin films (less than 10 nm) by manipulating the take-off angle of ejected electrons or by employing different X-ray excitation energies. This approach avoids film destruction during analysis. XPS further enables the study of surface film passivity, its breakdown in aqueous environments, adhesion properties, mass transport phenomena, and selective oxidation. This technique has proven instrumental in elucidating the critical role of chromium and molybdenum in stainless steels, particularly regarding their passivation mechanisms.

However, XPS analysis encounters limitations when dealing with films exceeding 10 nm in thickness. These limitations can manifest as artifacts, including preferential etching of specific elements, alterations in oxidation states, ion implantation, and atomic mixing during the ion beam sputtering process used for depth profiling. Additionally, insulating specimens can present challenges due to surface charging, leading to peak shifts, broadening, and asymmetry, potentially compromising the accuracy and complexity of the analysis.

The power of XPS and its application

Understanding the interplay between a material's surface chemistry, structure, and interface is critical for predicting its corrosion behavior in various environments. Since initial surface reactions often occur within the top few nanometers, analytical tools with nanoscale sensitivity are essential. X-ray photoelectron spectroscopy (XPS) emerges as a preferred technique due to its exceptional surface sensitivity (within 10 nm). It offers detailed chemical composition information, elemental identification, and detection limits as low as 0.1-1 atomic percent (except for H and He). This unique combination makes XPS an invaluable tool for surface characterization, particularly in corrosion evaluation.

XPS is a powerful technique for investigating surface reactions at the atomic level. Its high surface sensitivity allows for the analysis of changes occurring within the topmost atomic layer (monolayer) under vacuum conditions. By varying the take-off angle of ejected electrons or utilizing different X-ray excitation energies, XPS can analyze the composition variation within a thin film (less than 10 nm) without compromising its integrity. This capability allows for investigations into film passivity, breakdown in aqueous environments, adhesion mechanisms, mass transport phenomena, and selective oxidation processes. XPS has played a crucial role in elucidating the role of chromium and molybdenum in stainless steels and the underlying mechanisms of passivity.

However, XPS has limitations when dealing with films exceeding 10 nm in thickness. Techniques like ion beam sputtering, used to determine film depth, can introduce artifacts such as preferential etching of elements, modification of oxidation states, ion implantation, and atomic mixing. Additionally, analyzing insulating specimens can be challenging due to surface charging, leading to peak shifts, broadening, and asymmetry, potentially hindering accurate analysis.

The following equation describes the fundamental principle of XPS, where EB represents binding energy, EK signifies kinetic energy, h is Planck's constant, ν is the X-ray photon frequency, and φ is the spectrometer's work function (both constant for a specific instrument).

$$EB=h\upsilon-EK-\varphi$$

This equation assumes electron energy levels as "frozen orbitals," implying minimal change between the initial (ground) and final (excited) states. In reality, the measured binding energies deviate slightly from theoretical values by a few electron volts (eV) due to "relaxation energy" (ER). This energy difference arises from the rearrangement of electrons and their energy levels during the photoemission process (Krishna & Philip, 2022).

X-ray absorption spectroscopy (XAS) advancements

X-ray Absorption Spectroscopy (XAS) offers a powerful toolkit for probing the electronic structure and local atomic arrangements (short-range order) in materials. This versatility makes it highly valuable across diverse scientific disciplines, from physics and chemistry to materials science, biology, and medicine. Notably, unlike X-ray Diffraction (XRD) or X-ray Photoelectron Spectroscopy (XPS), XAS measurements traditionally rely on synchrotron radiation sources due to the specific requirements for high-intensity, tunable X-rays. However, recent advancements in laboratory-based XAS spectrometers are transforming accessibility. These instruments enable researchers to analyze samples relevant to contemporary research within practical timeframes. This innovation addresses a major limitation of synchrotron radiation research – the restricted access for many research groups.

The development of laboratory XAS instruments can be categorized into three generations. The second generation, emerging in the 1980s, paved the way for broader application across research fields. These instruments utilized curved crystals in conjunction with high-power X-ray tubes, achieving the required spectral resolution and photon flux for transmission mode measurements.

This development significantly impacted research areas like catalysis.

The newest, third generation of laboratory XAS instruments encompasses two distinct design concepts. One innovation involves the use of spherical crystals in the Johann geometry for monochromatization. The second approach employs the von Hamos geometry for simultaneous spectral measurement, utilizing either a graphite crystal with exceptional integral reflectivity or segmented crystals.

3. Emerging Techniques

3.1 Terahertz Spectroscopy

Terahertz (THz) radiation, occupying the electromagnetic spectrum between microwaves and infrared, presents unique opportunities for various scientific and technological applications. Generating THz radiation necessitates specialized techniques. Traditional methods include Fourier-transform infrared (FTIR) spectrometers, offering versatility with both broadband and narrow-band options. For pulsed THz generation, electron accelerators, air/laser-induced plasmas, and photo-Dember emitters find application. Early contributions came from gas lasers, enabling continuous-wave (CW) operation and high power output. However, limitations in size and cost hampered widespread adoption. Research efforts have since yielded a diverse range of sources, including Gunn diodes, photonic devices utilizing light-matter interactions, superlattice structures, and optical rectification techniques. Broadly, these sources can be classified as accelerator-based or laser-based. While accelerator-based sources provide highly focused THz radiation, laser-based alternatives offer advantages in compactness and efficiency. Current advancements are directed towards developing high-power THz sources through improved electron accelerators and cost-effective approaches employing multimode laser diodes. This ongoing development is crucial for unlocking the full potential of THz technology across various disciplines (Feng & Otani, 2021).

Applications

Terahertz time-domain spectroscopy (THz-TDS) has emerged as a powerful tool for investigating biological molecules. Studies have shown distinct terahertz absorption fingerprints for DNA, proteins like bovine serum albumin, and structural proteins like collagen. This technique offers advantages over existing methods, allowing researchers to probe not only nucleic acids and proteins but also carbohydrates. Notably, THz spectroscopy, when combined with protein folding studies, can unveil reactions occurring at incredibly fast timescales (femtoseconds) during crucial protein conformational changes. While attempts have been made to analyze the secondary structure of peptides (short protein chains) using THz radiation, challenges in interpreting spectra from dried or frozen samples limit its definitive application in this area. Moving forward, THz-TDS holds significant promise for analyzing protein tertiary structure (3D folding) if the collective vibrational modes of the protein fall below 10 THz. This would enable differentiation between various protein bonds based on their unique terahertz frequencies, leading to a deeper understanding of protein structure and function (Falconer & Markelz, 2012).

Unlike X-rays, THz waves can safely penetrate many non-conducting materials like clothing and paper due to their non-ionizing nature and low power levels. This unique property offers significant advantages for security screening applications. THz technology excels in material differentiation. Clothing appears transparent to THz waves, revealing hidden objects beneath. Additionally, THz imaging distinguishes between plastics and ceramics, overcoming the limitations of X-ray's limited contrast. Furthermore, femtosecond THz pulses enable high-resolution 3D imaging, capable of resolving fine details like individual pages within a sealed envelope.

THz security screening boasts another key advantage: spectroscopic analysis. Terahertz waves can detect the unique chemical "fingerprints" of concealed objects, even when they are sealed or hidden beneath clothing. This spectroscopic capability offers unparalleled detection capabilities for security personnel.

In conclusion, terahertz technology presents a revolutionary approach to security screening. Its ability to safely penetrate materials, differentiate materials, and perform 3D imaging with spectroscopic analysis makes it a powerful tool for identifying concealed objects and enhancing security measures (Wietzke et al., 2010).

3.2 Plasmonic Sensing

In recent decades, plasmonic sensing has emerged as a powerful and versatile technique with applications across diverse fields. It plays a crucial role in chemical and biological sensing, industrial process monitoring, environmental engineering, and even pushes the boundaries of imaging with super-resolution capabilities. Notably, its non-invasive nature has made plasmonic sensing a cornerstone of nanobiotechnology and the development of biomedical nanodevices. This technology's impact is evident in the substantial growth of the global smart healthcare market, reaching a value of 293 billion USD.

The performance of plasmonic technologies hinges on two key factors: the meticulously crafted shape of the employed nanostructures and the intricate characteristics of the interface between these nanomaterials and their surrounding environment. Deviations from perfectly spherical nanoparticles, such as sharper corners or non-symmetrical shapes, can significantly amplify the localized electromagnetic fields near the surface. These localized field modifications exhibit exquisite sensitivity, even to minute changes in the surrounding dielectric environment. Consequently, plasmonic nanostructures act as highly sensitive optical probes. They can detect and reveal the presence of trace amounts of active molecules at the interface between the metal and the surrounding dielectric medium.

Surface plasmon resonance (SPR) has become a cornerstone technology for diverse photonic devices, encompassing demultiplexers, splitters, filters, and crucially, sensors. SPR sensors offer compelling advantages over traditional methods, including unrivalled sensitivity, rapid response times, and a compact footprint. Their operation hinges on the principle that the resonance wavelength of surface plasmons – collective electron oscillations at a metal-dielectric interface – shifts upon interaction with the surrounding environment. This shift is exquisitely sensitive to changes in the effective refractive index (RI) of the sensor structure, triggered by the introduction of different materials. The sensitivity of the sensor can then be meticulously calculated based on this measured RI change.

Optimizing the effectiveness of SPR sensors necessitates careful consideration of several key parameters: sensitivity, resolution, and signal-to-noise ratio (SNR). Sensitivity remains paramount in the design process. Recent advancements have witnessed the exploration of various plasmonic RI sensor configurations, including those incorporating slit waveguides coupled with nanodisk resonators, ring resonators, hexagonal cavities, slit cavities, and strategically placed single defects. Furthermore, high dielectric constant materials, such as silver (Ag) and gold (Au), are favored choices due to their ability to support both localized and propagating surface plasmon modes (Divya et al., 2022).

Advancements

Localized surface plasmon resonance (LSPR) describes the collective oscillation of electrons in metallic nanoparticles upon interaction with an electromagnetic field. These LSPR modes exhibit a unique sensitivity to the incident light field due to their highly responsive nature, allowing for direct excitation from free space without the need for critical momentum matching, unlike surface plasmon resonance (SPR) techniques.

Two crucial aspects governing LSPR sensitivity for sensing applications considered are:

Analyte Adsorption: The intricate shapes and surface properties of nanostructures significantly influence how target molecules (analytes) bind to them. This interaction depends heavily on both the surface area and energy of the nanostructure, ultimately impacting the intensity, polarization, and local electromagnetic fields associated with the LSPR peak.

Nanoparticle Properties: The size and geometry of the metallic nanoparticles within the dispersion dictate the wavelength and symmetry of the LSPR peak. These characteristics are highly sensitive to the surrounding environment, making them ideal for sensing applications. Changes in analyte concentration directly modify the surrounding refractive index, consequently impacting the LSPR band (peak position, intensity, or width). By monitoring these changes, plasmonic sensors can effectively detect the presence and concentration of target analytes (Duan et al., 2021).

Application

Localized surface plasmon resonance (LSPR) offers a powerful toolbox for biosensing due to its ability to enhance light-matter interactions. This translates to highly sensitive techniques like SERS, SEIRA, and surface-enhanced fluorescence. Furthermore, LSPRs can be used as miniaturized sensors due to their excitation by simple light sources and shallow penetration depth, making them ideal for real-time multiplex detection in microfluidic devices. Beyond biosensing, plasmonically functionalized thin films are emerging as robust monitoring solutions for harsh industrial environments due to their durability, sensitivity, and all-optical readout capabilities (Mejía-Salazar & Oliveira Jr, 2018; Tittl et al., 2014).

3. Conclusion

Spectroscopic techniques play a critical role in Earth Science research, providing a comprehensive toolbox for material characterization. Mass spectrometry (MS) excels in high-throughput analysis and detection of low-abundance molecules. Nuclear Magnetic Resonance (NMR) offers unparalleled insights into biomolecular structure and dynamics. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and Fourier Transform-Infrared (FT-IR) spectroscopy offer powerful solutions for pharmaceutical science and microbial analysis respectively. Ultraviolet-visible (UV-Vis) spectroscopy with its recent advancements finds continued relevance. Resonance-enhanced Raman Scattering (RRS) and Surface-enhanced Raman spectroscopy (SERS) provide exceptional sensitivity for detailed analysis. X-ray photoelectron spectroscopy (XPS) emerges as a cornerstone for surface characterization, particularly crucial for understanding corrosion behavior. X-ray Absorption Spectroscopy (XAS) offers a powerful tool for probing material properties across diverse disciplines. Terahertz (THz) time-domain spectroscopy (THz-TDS) presents unique opportunities for biological analysis. Finally, plasmonic sensing has emerged as a powerful and versatile technique with widespread applications. In conclusion, the ever-evolving suite of spectroscopic techniques continues to revolutionize our understanding of Earth Science materials.

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ENVIRONMENTAL CHEMISTRY AND POLLUTION CONTROL

Tatheer FATIMA

This chapter provides comprehensive explanation of Environmental Chemistry and Pollution Control, covering a wide range of topics critical for perceptive and addressing environmental challenges. Commencement with an Introduction to Environmental Chemistry, the chapter elucidates the basic principles underlying chemical processes in the environment. Understanding Pollutants and their sources delves into the origins and classifications of pollutants, also explain their different sources, and pathways in environmental system. Atmospheric Chemistry and Air Pollution Control elaborate the interactions between atmospheric constituents and pollutants, along with strategies for mitigating air pollution. Water Chemistry and Remediation Techniques offer insights into the composition of water bodies, pollution sources, and innovative approaches for water quality restoration. Soil Chemistry and Contaminant Management look into soil composition, contamination sources, and remediation methods to maintain soil ecosystems. Chemical aspects of Hazardous Waste Management specify the characteristics of harmful wastes and strategies for their safe handling, treatment, and dumping. Industrial processes and pollution prevention examine the industrial activities and environmental degradation, emphasizing the importance of pollution prevention procedures. Emerging Contaminants and Their Impacts investigate the evolving landscape of environmental contaminants and their potential ramifications on ecosystems and human health. Environmental Monitoring and Analytical Techniques elucidate the tools and methodologies engaged to assess environmental quality and tracking pollutant levels. Regulations and Policy Frameworks for Pollution Control describe the measures and governance structures aimed at enforcing environmental protection principles. Case Studies in Environmental Chemistry and Pollution Control propose real-world examples shows successful interventions and lessons learned in addressing environmental challenges. Finally, Future Directions and Challenges in Environmental Protection present an outlook on emerging issues and the ongoing efforts required to achieve sustainable environmental stewardship. This chapter underscores vital action to preserve the environment for present and future generations.

1. Introduction to Environmental Chemistry

1.1 Establishing Foundational Principles

Environmental chemistry serves as the cornerstone for understanding the complicated interaction between chemical processes and the environment(Khetan & Collins, 2007). It delves into the composition, reactions, and transformations of various substances in natural systems, elucidating their impacts on ecological balance and human health(Edo et al., 2024). At its core, environmental chemistry also explains the dynamic relations between the a-biotic and biotic components of the environment. These interactions are governed by chemical reactions, equilibrium dynamics, and transport phenomena, shaping the distribution and fate of substances in the environment(Brantley et al., 2011). By unraveling these processes, environmental chemists strive to interpret the mechanisms driving environmental phenomena such as nutrient cycling, pollutant fate and transport, and the formation of natural resources(Borch et al., 2010). Central to environmental chemistry is the concept of the environmental compartmentalization, which categorizes the Earth into distinct reservoirs or compartments based on their chemical characteristics and interactions(Chihi et al., 2015). The atmosphere, hydrosphere (water bodies), lithosphere (earth's crust), and biosphere (living organisms) constitute the primary compartments, each with its unique chemical composition and dynamics. Understanding the exchange of matter and energy between these compartments is crucial for elucidating global biogeochemical cycles and assessing the environmental fate of pollutants(Lindgren et al., 2016).

Figure 1 capturing the essence of environmental chemistry: Earth compartmentalization based on chemical characteristics and interactions

Chemical kinetics and thermodynamics play essential roles in environmental chemistry, governing the rates and extents of chemical reactions occurring in natural systems. Kinetic principles elucidate the mechanisms and pathways of chemical transformations, ranging from simple decomposition reactions to complex biochemical processes. Thermodynamic considerations, on the other hand, elaborate the feasibility and spontaneity of reactions based on factors such as energy, entropy, and equilibrium constants, providing insights into the stability and reactivity of environmental components(Stumm & Morgan, 2012).

Moreover, environmental chemistry encompasses the study of pollutants, both natural and anthropogenic, and their interactions with environmental matrices. Pollutants can arise from diverse sources, including industrial activities, agricultural practices, urbanization, and natural processes, posing significant threats to ecosystem integrity and human well-being(Borch et al., 2010). Characterizing the sources, fate, and toxicity of pollutants is essential for developing effective pollution control strategies and safeguarding environmental quality(Furley et al., 2018). In conclusion, the introduction to environmental chemistry serves as a vital primer for understanding the complex interplay between chemical processes and the environment. By elucidating foundational principles such as compartmentalization, chemical kinetics, thermodynamics, and pollutant behavior, environmental chemistry provides a holistic framework for addressing contemporary environmental challenges and promoting sustainable stewardship of our planet(Hanrahan, 2011).

1.2 Key topics in environmental chemistry include:

- Atmospheric Chemistry: Expplains about the atmosphere of Earth, the formation of pollutants and their effects on air quality and climate(Seinfeld & Pandis, 2016).
- Water Chemistry: Investigating the chemical composition of natural waters, processes

such as acidification, eutrophication, and contamination by pollutants, and strategies for water treatment and purification.

- Soil Chemistry: Understanding the chemical properties of soils, including nutrient cycling, soil pollution, and remediation techniques to restore contaminated soils(Khan & Mohammad, 2014).
- Biogeochemical Cycles: Exploring the cycling of various elements including carbon, nitrogen, and phosphorus through the atmosphere, hydrosphere, lithosphere, and biosphere, and their role in ecosystem functioning.
- Pollution Control: Implementing strategies to mitigate pollution through pollution prevention, waste management, environmental regulations, and sustainable practices(Bashkin, 2003).

By studying environmental chemistry, scientists can assess the environmental impact of human activities, develop solutions to environmental challenges, and promote the sustainable management of natural resources. Collaboration between researchers, policymakers, industries, and communities is essential for addressing complex environmental issues and safeguarding the health of the planet for future generations.

1.3 Understanding Pollutants and Their Sources

Pollution is a serious problem which we are facing. It has hazardous impacts on human life and biodiversity. To effectively mitigate pollution, it is essential to identify the various pollutants and understand their sources, pathways, and impacts. This chapter delves into the diverse array of pollutants found in the environment, examining their origins and the mechanisms through which they enter and interact within environmental systems(Ukaogo et al., 2020).

1.4 Types of Pollutants

Pollutants can be categorized into several categories based on their beginning, chemical composition, and environmental effects. Common types of pollutants include:

1.4.1 Primary Pollutants: Pollutants emitted directly from identifiable sources, such as vehicle exhaust emissions, industrial emissions, and smoke from burning fossil fuels.

1.4.2 Secondary Pollutants: By the reaction of primary pollutants, secondary pollutants are posed. These pollutants including acid rain, smog and ozone have direct dangerous impact on life.

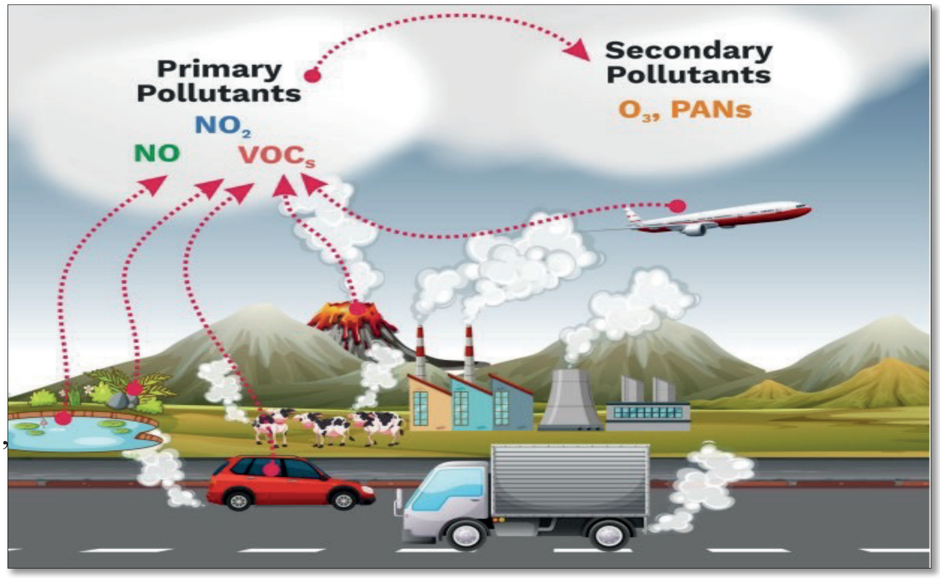


Figure 2 Types of pollutants (Primary and secondary pollutants)

1.4.3 Toxic Pollutants: Heavy metals like Mercury and lead categorized as toxic pollutants.

1.4.4 Nutrient Pollutants: Soil nutrients which are beneficial for plants, if they are excessive in amount may cause drastic effects on plants as well as on human life.

1.4.5 Microplastics: Small plastic particles (<5 mm) that accumulate in the environment, produce threats to marine life and other biodiversity (Xiang et al., 2022).

1.5 Sources of Pollution

Pollution cause in result of man activities, industrial processes, natural events, and atmospheric phenomena. It's major sources are:

1.5.1 Industrial Activities: Factories, power plants, refineries, and manufacturing processes release pollutants such as greenhouse gases, particulate matter, sulfur dioxide (SO2), nitrogen oxides (NOx), and volatile organic compounds (VOCs)(Kwiatkowski et al., 2021).

1.5.2 Transportation: Vehicles, ships, airplanes, and other modes of transportation emit pollutants such as carbon monoxide (CO), nitrogen dioxide (NO2), particulate matter (PM), and hydrocarbons into the atmosphere(Kwiatkowski et al., 2021).

1.5.3 Agricultural Practices: The use of fertilizers, pesticides, and livestock farming contributes to nutrient runoff, soil erosion, and contamination of water bodies with pesticides and nitrates(Kumar et al., 2021).

1.5.4 Waste Management: Improper disposal of solid waste, wastewater, and hazardous materials can contaminate soil, water, and air, posing risks to human health and ecosystems(Kumar et al., 2021).

1.5.5 Natural Sources: Volcanic eruptions, wildfires, dust storms, and biogenic emissions from plants and microbes release natural pollutants such as sulfur dioxide, ash, pollen, and volatile organic compounds(Kumar et al., 2021).

1.6 Pathways and Fate of Pollutants

Once released into the environment, pollutants can undergo various transport and transformation processes, affecting their distribution, concentration, and persistenceetl., (Macdonald et al., 2003). These pathways include:

1.6.1 Deposits of atmosphere: Pollutants can be travel at long distances and deposit there as dry or wet deposits of atmosphere(Jurado et al., 2005).

1.6.2 Waterborne Transport: Pollutants can be carried by surface runoff, rivers, and streams, eventually accumulating in lakes, oceans, and groundwater aquifers(Madhav et al., 2020).

1.6.3 Biological Uptake: Pollutants can be taken up by plants, animals, and microorganisms, leading to bioaccumulation and biomagnification in food webs(Chormare & Kumar, 2022).

1.6.4 Chemical Transformation: Pollutants can undergo physical, chemical, and biological transformations in the environment, altering their chemical properties and toxicity over time. Understanding the sources and behavior of pollutants is essential for developing effective pollution control strategies, implementing regulatory measures, and promoting sustainable practices to safeguard environmental quality and human well-being. Collaboration between scientists, policymakers, industries, and communities is critical for addressing pollution challenges and achieving environmental sustainability(Carpenter et al., 2011).

1.7 Atmospheric Chemistry and Air Pollution Control

The Earth's atmosphere plays a vital role in supporting life and regulating climate, but it is increasingly affected by activities of human that release pollutants into the air. Atmospheric chemistry explores the complex interactions between gases, particles, and radiation in the atmosphere, while air pollution control focuses on mitigating the unfavorable effects of air pollution on health and ecosystems (Ramanathan & Feng, 2009). This chapter examines the key processes driving atmospheric chemistry, the sources and impacts of air pollution, and strategies for air pollution control and management.

1.8 Composition of the Atmosphere: The atmosphere of Earth is composed of a mixture of gases, nitrogen (N2) , oxygen (O2), with other gases such as carbon dioxide (CO2), methane (CH4), ozone (O3), and water vapor (H2O). These gases interact with solar radiation, forming the basis for atmospheric chemistry processes(Kern, 2021).

1.9 Air Pollutants: Air pollutants originate from diverse sources such as industrial facilities, transportation, energy production, and natural events. They include ground-level ozone (O3), particulate matter (PM), sulfur dioxide (SO2), nitrogen oxides (NOx), carbon monoxide (CO), and lead (Pb) (Kern, 2021). Additionally, organic chemicals that evaporate into the atmosphere contribute to ground-level ozone and secondary organic aerosols, posing health risks due to their toxicity. Toxic metals like lead, mercury, arsenic, and cadmium are emitted from industrial processes, fossil fuel combustion, and waste incineration, accumulating in the environment and food chains (Cimboláková et al., 2019). Microscopic particles such as dust, soot, and aerosols can penetrate deeply into the respiratory system, causing respiratory and cardiovascular diseases. Moreover, greenhouse gases such as carbon dioxide (CO2), methane (CH4), and nitrous oxide (N2O) trap heat in the Earth's atmosphere, contributing to global warming and climate change.(Chow & Watson, 2006).

1.9.1 Formation and Transformation of Air Pollutants: Different chemical and physical process occur to transform air pollutants including:

Photochemical Reactions: Chemical processes activated by solar radiation generate ozone, nitrogen dioxide, and other secondary pollutants when precursor gases like volatile organic compounds (VOCs) and nitrogen oxides (NOx) are present.(Rani et al., 2011).

Particle Formation: The nucleation of aerosol particles from precursor gases and subsequent growth through condensation, coagulation, and chemical reactions, influencing air quality, visibility, and climate(Holmes, 2007).

Deposition and Removal: Processes such as dry deposition (settling of particles), wet deposition (removal by precipitation), and scavenging by atmospheric reactions, which remove pollutants from the atmosphere and deposit them onto land and water surfaces(Mariraj Mohan, 2016).

1.9.2 Air Pollution Control Strategies

To reduce air pollution and protect public health and the environment, various control measures and technologies are employed, Implementing cleaner technologies, fuel switching, and pollution control devices (e.g., catalytic converters, scrubbers) to minimize emissions of pollutants from industrial sources, vehicles, and power plants. Enforcing regulations and standards for vehicle emissions, promoting the use of cleaner fuels (e.g., low-sulfur diesel, compressed natural gas), and incentivizing the adoption of electric vehicles and alternative transportation modes. Establishing networks of monitoring stations to measure air pollutant concentrations, track trends over time, and provide early warning systems for high pollution events. Designing cities with efficient transportation systems, green spaces, and zoning regulations to reduce vehicle congestion, promote active transportation, and minimize exposure to air pollution. Collaborating across national borders to address transboundary air pollution issues, such as cross-border transport of pollutants and regional haze, through agreements, protocols, and shared emission reduction targets(Lu et al., 2020).

1.9.3 Challenges and Future Directions: Despite notable advancements in air quality management, persistent challenges in addressing air pollution persist due to factors such as urbanization, population growth, industrial expansion, and climate change. Enhancing air quality and minimizing emissions in the future will necessitate innovative technologies, policy interventions, public awareness initiatives, and international collaboration to meet sustainable development objectives and safeguard the health and well-being of present and future populations. Through a comprehensive grasp of atmospheric chemistry principles and the implementation of robust air pollution control strategies, societies can mitigate the detrimental impacts of air pollution, uphold environmental integrity, and foster healthier and more sustainable communities worldwide.(Wang & Hao, 2012).

1.10 Water Chemistry and Remediation Techniques

Water is a precious resource essential for all forms of life, yet it faces numerous threats from pollution and contamination. Water chemistry explores the composition, properties, and behavior of water molecules and dissolved substances, while remediation techniques aim to restore and protect water quality through various treatment methods(Mishra, 2023). This chapter examines the principles of water chemistry, the sources and types of water pollution, and the diverse array of remediation techniques employed to safeguard freshwater resources.

Water molecules (H2O) possess unique chemical properties, including polarity, hydrogen bonding, and the ability to dissolve a wide range of substances. Dissolved ions such as sodium (Na+), chloride (Cl-), calcium (Ca2+), and bicarbonate (HCO3-) contribute to the chemical composition and pH of water bodies, influencing their suitability for various uses(Abugu et al., 2024). Water pollution arises from a multitude of sources, both anthropogenic and natural, which introduce contaminants into freshwater ecosystems. Common sources of water pollution include: Discrete, identifiable sources of pollution, such as industrial discharge pipes, sewage treatment plants, and waste disposal sites, which release pollutants directly into water bodies. Diffuse sources of pollution, including urban runoff, agricultural runoff, and atmospheric deposition, which transport pollutants from multiple sources over large areas, contributing to water quality degradation(Bashir et al., 2020). Excessive inputs of nutrients such as nitrogen (N) and phosphorus (P) from agricultural fertilizers, sewage effluent, and animal waste, leading to eutrophication, harmful algal blooms, and oxygen depletion in water bodies. Toxic chemicals and heavy metals released from industrial processes, mining activities, urban runoff, and accidental spills, which can persist in the environment and pose risks to aquatic organisms and human health(Khan & Mohammad, 2014). Bacteria, viruses, and parasites from human and animal fecal contamination, inadequate sanitation, and wastewater discharge, which can cause waterborne diseases and outbreaks of waterborne illnesses(Pal et al., 2018). Various physical, chemical, and biological parameters are used to assess water quality and determine the presence and concentration of pollutants. Key water quality parameters include: Temperature: Influences the solubility of gases, rates of chemical reactions, and aquatic habitat suitability. PH: Measures the acidity or alkalinity of water, affecting chemical equilibria and the bioavailability of nutrients and metals. Dissolved Oxygen (DO): Essential for aerobic organisms, DO levels indicate the health of aquatic ecosystems and the potential for oxygen depletion. Turbidity: Measures the clarity or cloudiness of water, influenced by suspended particles, sediments, and organic matter. Nutrient Concentrations: Assess the levels of nitrogen, phosphorus, and other nutrients contributing to eutrophication and algal growth(Sigdel, 2017).

1.10.1 Remediation Techniques

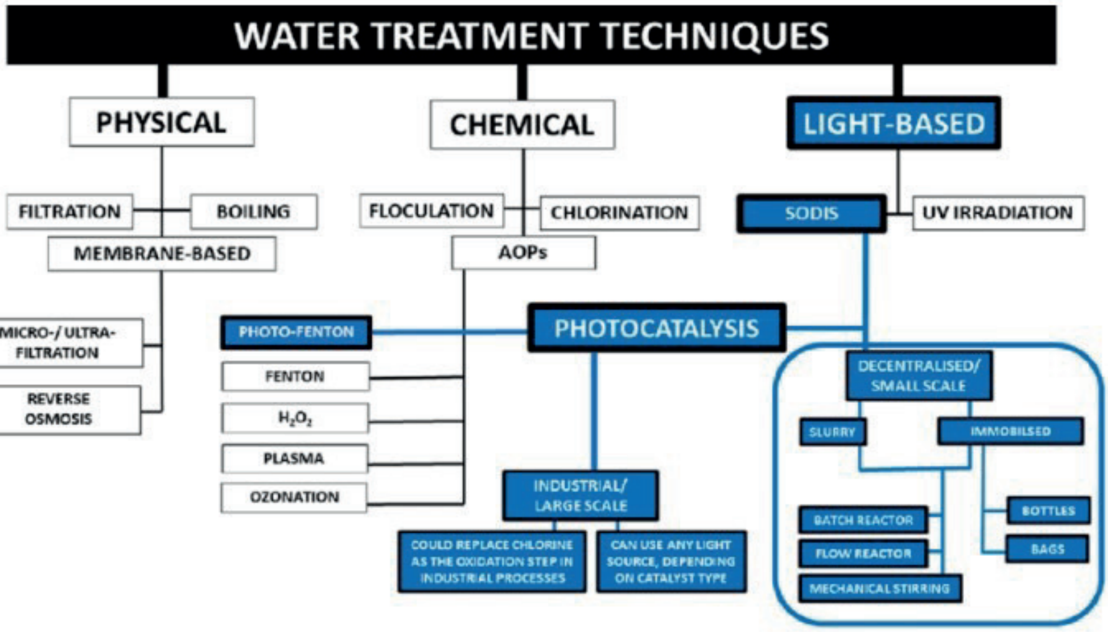
To restore and protect water quality, various remediation techniques and treatment processes are employed, tailored to the specific contaminants and environmental conditions. Remediation techniques include:

Physical Methods: Filtration, sedimentation, and adsorption processes remove suspended solids, particulate matter, and colloidal particles from water through physical separation.

Chemical Methods: Coagulation, flocculation, oxidation-reduction reactions, and precipitation techniques remove dissolved contaminants, metals, and organic pollutants through chemical reactions and precipitation(Au et al., 2011).

Biological Methods: Bioremediation, constructed wetlands, and phytoremediation utilize microorganisms, plants, and natural ecosystems to degrade organic pollutants, metabolize nutrients, and improve water quality(Hussain et al., 2018).

Advanced Treatment Technologies: Membrane filtration, reverse osmosis, ultraviolet (UV) disinfection, and activated carbon adsorption provide high-level treatment for removing pathogens, trace contaminants, and emerging pollutants from water(Kumar et al., 2022).



Integrated Water Management: Achieving sustainable water management requires an integrated approach that combines pollution prevention, source control, treatment, and monitoring strategies at local, regional, and global scales. Collaboration among stakeholders, including governments, industries, communities, and non-governmental organizations, is essential for implementing effective water management practices and ensuring the long-term health and resilience of freshwater ecosystems. By understanding the principles of water chemistry and employing innovative remediation techniques, society can address water pollution challenges, protect freshwater resources, and promote the sustainable use and management of water for current and future generations(Mishra, 2023).

1.11 Soil Chemistry and Contaminant Management

Soil plays a crucial role in the Earth's ecosystem by supporting plant growth, facilitating nutrient cycling, and filtering water. Yet, its quality faces growing threats from contamination originating from industrial activities, agricultural practices, and improper waste disposal. Soil chemistry delves into the composition, characteristics, and natural processes within soil, while efforts in contaminant management aim to reduce the harmful impacts of soil pollution and safeguard soil health.(Smith et al., 2015). This chapter delves into the principles of soil chemistry, the sources and types of soil contaminants, and strategies for soil remediation and contaminant management.

Soil is a complex mixture of mineral particles, organic matter, water, air, and living organisms, each contributing to its chemical, physical, and biological properties. Key components of soil include: Inorganic materials such as sand, silt, and clay, which provide texture, structure, and nutrient retention capacity to soil(Esmaeilzadeh & Ahangar, 2014). Decomposed plant and animal residues, microbial biomass, and humus contribute to soil fertility, water retention, and nutrient cycling. The liquid phase, containing dissolved ions, nutrients, and contaminants, is influenced by soil pH, redox conditions, and organic matter content. Bacteria, fungi, protozoa, and other microorganisms are essential for nutrient transformation, organic matter decomposition, and maintaining soil ecosystem functionality(Biswas & Kole, 2017).

Soil contamination arises from a wide range of anthropogenic and natural sources, introducing various contaminants into the soil environment. Common sources and types of soil contaminants include: Chemicals and heavy metals released from manufacturing processes, mining operations, industrial spills, and waste disposal sites, such as lead (Pb), arsenic (As), mercury (Hg), and polycyclic aromatic hydrocarbons (PAHs)(Priyadarshanee et al., 2022). Pesticides, herbicides, fertilizers, and animal manure applied to agricultural fields, contributing to soil pollution with pesticides residues, nitrate, phosphate, and microbial pathogens(Baweja et al., 2020). Improper disposal of solid waste, landfill leach ate, sewage sludge, and hazardous materials, leading to soil contamination with organic pollutants, heavy metals, and toxic substances. Urban runoff, road salts, atmospheric deposition, and construction activities introducing contaminants such as heavy metals, petroleum hydrocarbons, and road deicing agents into urban soils. Volcanic eruptions, weathering of minerals, erosion, and sedimentation contributing to soil contamination with naturally occurring substances such as radionuclides, asbestos, and trace elements(Baweja et al., 2020).

Soil contaminants undergo various physical, chemical, and biological processes affecting their mobility, bioavailability, and persistence. These processes include:

-Adsorption and Desorption: Contaminants bind to soil particles, reducing mobility and bioavailability, but can be released back into solution under changing conditions.

- Leaching: Contaminants can migrate through the soil to groundwater, surface water, and neighboring ecosystems, posing health and environmental risks.

-Degradation: Microbial activity, chemical reactions, and natural attenuation break down contaminants into less toxic or more stable forms, reducing their concentrations and impact over time.

- Volatilization: Volatile contaminants can evaporate from soil surfaces into the atmosphere, contributing to air pollution and long-range pollutant transport (de Voogt & Jansson, 1993).

To address soil contamination and protect soil quality, various remediation techniques and management strategies are employed, tailored to the specific contaminants and site conditions. These strategies include: Excavation, soil washing, soil vapor extraction, and thermal treatment techniques physically remove or destroy contaminants, reducing their concentrations in soil and groundwater. Soil amendments, phytoremediation, and chemical oxidation techniques enhance contaminant immobilization, degradation, or extraction through chemical reactions and transformations. Bioremediation, bioaugmentation, and microbial-mediated processes utilize indigenous or engineered microorganisms to metabolize contaminants, degrade organic pollutants, and enhance soil remediation Installing impermeable barriers, capping contaminated sites, and implementing land use restrictions prevent exposure to contaminants, reduce migration pathways, and protect human health and the environment. Achieving sustainable soil management requires an integrated approach that combines pollution prevention, remediation, monitoring, and land use planning strategies. Collaboration among stakeholders, including government agencies, industries, landowners, researchers, and communities, is essential for implementing effective soil management practices and ensuring the long-term health and resilience of soil ecosystems. By understanding the principles of soil chemistry and employing innovative remediation techniques, society can address soil contamination challenges, restore soil health, and promote the sustainable use and management of soil resources for current and future generations(Gavrilescu, 2009), (Dermont et al., 2008).

1.12 Chemical Aspects of Hazardous Waste Management

Hazardous waste poses serious risks to human health and the environment. Effective management of this waste requires identifying, handling, treating, disposing, and remediating materials with hazardous substances. Understanding the chemical properties and environmental behavior of hazardous wastes is essential for developing effective management strategies. This chapter examines the chemical characteristics of hazardous wastes, regulatory frameworks, treatment technologies, and best practices for managing hazardous waste(Varshney et al., 2022).

Hazardous wastes are characterized by specific chemical and physical properties that pose potential risks to both human health and the environment. These properties include toxicity, which refers to the ability of hazardous substances to cause adverse health effects or even death when ingested, inhaled, or absorbed by organisms. Common toxic chemicals found in hazardous wastes include heavy metals, pesticides, and various industrial chemicals(Hassan & Saleh, 2022). Flammability is another key characteristic, indicating the potential for these wastes to ignite and sustain combustion under certain conditions. This not only presents fire hazards but also releases toxic by-products like dioxins, furans, and volatile organic compounds (VOCs)(Zhang et al., 2015). Reactivity is also a concern, as hazardous wastes may undergo violent chemical reactions, explosions, or the release of hazardous gases when exposed to heat, water, air, or other substances. This can occur with reactive metals, oxidizers, and explosives. Finally, corrosivity is a property indicating the ability of hazardous wastes to corrode metal containers, storage tanks, and pipelines. This corrosion can lead to leaks, spills, and the contamination of soil and groundwater with corrosive acids, bases, or salts(Groysman & Groysman, 2014).

1.12.1 Sources and Types of Hazardous Wastes:

Hazardous wastes stem from diverse sources encompassing industrial processes, commercial activities, household products, and remediation endeavors. Industries like chemical manufacturing, metal plating, mining, petroleum refining, and electronics production yield hazardous wastes such as solvents, heavy metals, acids, bases, and toxic by-products. Consumer products, including pesticides, paints, batteries, fluorescent lamps, and electronic devices, harbor hazardous constituents like lead, mercury, cadmium, and persistent organic pollutants (POPs)(Slonecker et al., 2010). Healthcare facilities generate biomedical wastes, sharps, pharmaceuticals, and radioactive materials necessitating special handling and disposal due to their potential health risks. Additionally, contaminated sites like brownfields, Superfund sites, and abandoned industrial facilities may host soils, sediments, and groundwater tainted with hazardous substances, mandating remediation and cleanup efforts(Pasupathi et al., 2011).

1.12.2 Regulatory Frameworks for Hazardous Waste Management

Governments and regulatory bodies have devised comprehensive frameworks to ensure the safe and environmentally sound management of hazardous wastes. These frameworks involve the identification of hazardous wastes based on criteria such as toxicity, ignitability, corrosivity, reactivity, and listing in hazardous waste streams. Strategies like pollution prevention, source reduction, recycling, and substitution of hazardous materials aim to minimize waste generation. Proper handling, labeling, packaging, storage, and transportation protocols mitigate the risk of spills, leaks, and exposures. Regulations govern treatment, storage, and disposal facilities (TSDFs) utilizing methods like land disposal, incineration, chemical treatment, and alternative technologies. Environmental monitoring and enforcement actions uphold compliance to prevent environmental contamination and public health hazards(Mmereki et al., 2016).

1.12.3 Treatment Technologies for Hazardous Wastes

Treatment technologies for hazardous wastes strive to mitigate toxicity, volume, and mobility to minimize environmental risks and enable safe disposal or recycling. Physical treatments encompass separation, filtration, evaporation, distillation, and solidification to isolate or concentrate hazardous constituents. Chemical treatments involve oxidation, reduction, precipitation, and neutralization reactions to transform contaminants into less toxic or immobilized forms. Biological treatments employ bioremediation, composting, and microbial degradation processes to metabolize organic pollutants and degrade hazardous wastes. Thermal treatments like incineration, pyrolysis, and thermal desorption subject wastes to high temperatures to decompose organic compounds, volatilize contaminants, and recover energy or resources(Yu et al., 2020).

1.12.4 Best Practices for Hazardous Waste Management

Effective hazardous waste management requires a comprehensive approach integrating pollution prevention, waste reduction, treatment, and disposal practices. Best practices entail implementing pollution prevention strategies, conducting risk assessments, raising public awareness, fostering technology innovation, and promoting collaborative partnerships. By comprehending the chemical aspects of hazardous wastes and implementing suitable management strategies, society can minimize environmental contamination, safeguard human health, and advance sustainable resource management. Compliance with regulations, adoption of best practices, and continuous improvement efforts are imperative for achieving the objectives of hazardous waste management and ensuring a safe and healthy environment for present and future generations(Jha et al., 2022).

By understanding the chemical aspects of hazardous wastes and implementing appropriate management strategies, society can minimize environmental contamination, protect human health, and promote the sustainable use and management of resources. Compliance with regulatory requirements, adoption of best practices, and continuous improvement efforts are essential for achieving the goals of hazardous waste management and ensuring a safe and healthy environment for present and future generations(Abrol et al., 2019).

1.13 Industrial Processes and Pollution Prevention

Industrial processes play a significant role in global economic activities, yet they often generate substantial pollution, contributing to environmental degradation and public health risks. Pollution prevention strategies are pivotal in mitigating these adverse impacts. By integrating cleaner production techniques, optimizing resource utilization, and implementing efficient technologies, industries can minimize waste generation, emissions, and environmental footprint. Moreover, adopting closed-loop systems, recycling initiatives, and eco-friendly practices not only reduce pollution but also enhance resource efficiency and promote sustainable development. Collaborative efforts among industries, regulatory bodies, and research institutions are crucial in fostering innovation and disseminating best practices for pollution prevention across various sectors, ultimately leading to a more sustainable industrial landscape and a healthier environment for communities worldwide(Wu et al., 2023).

1.13.1 Regulations and Policy Frameworks for Pollution Control

Regulations and policy frameworks serve as essential tools in controlling pollution and safeguarding environmental quality. Governments worldwide enact laws and establish regulatory agencies to monitor, enforce, and continuously improve environmental standards. These frameworks typically include emission limits, waste disposal guidelines, and pollution control measures tailored to specific industries and pollutants. By imposing penalties for non-compliance and incentivizing sustainable practices, regulations encourage industries to adopt cleaner technologies and invest in pollution prevention measures(Awewomom et al., 2024). Additionally, international agreements and treaties promote cross-border cooperation, setting global standards and fostering collective action to address transboundary pollution and environmental challenges. Effective implementation of regulations, coupled with public participation and stakeholder engagement, is crucial in ensuring compliance and achieving sustainable development goals while protecting ecosystems and human health for present and future generations(Awewomom et al., 2024).

1.14 Future Directions and Challenges in Environmental Protection

Future directions in environmental protection entail addressing emerging challenges and advancing innovative solutions to safeguard ecosystems and mitigate environmental degradation. With climate change accelerating and biodiversity loss worsening, there's a growing emphasis on transitioning towards sustainable practices and renewable energy sources. Harnessing technological advancements like artificial intelligence, remote sensing, and green infrastructure can enhance environmental monitoring, prediction, and management. Furthermore, promoting circular economy principles, such as resource efficiency, waste reduction, and recycling, can minimize environmental impacts while fostering economic growth(Wichaisri & Sopadang, 2018). However, significant challenges persist, including limited resources, competing interests, and geopolitical tensions. Bridging the gap between science, policy, and implementation is crucial for effective environmental governance. Moreover, addressing environmental injustices and ensuring equitable access to resources and environmental benefits remain imperative. Additionally, strengthening international cooperation and promoting multi-stakeholder partnerships are essential for tackling global environmental issues comprehensively. Ultimately, achieving sustainable environmental protection requires collective action, innovative approaches, and a commitment to balance ecological integrity with societal needs for a resilient and equitable future(O'Riordan, 1985).

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ADVANCES IN ORGANIC COMPOUND SYNTHESIS

Momina ZUBAIR

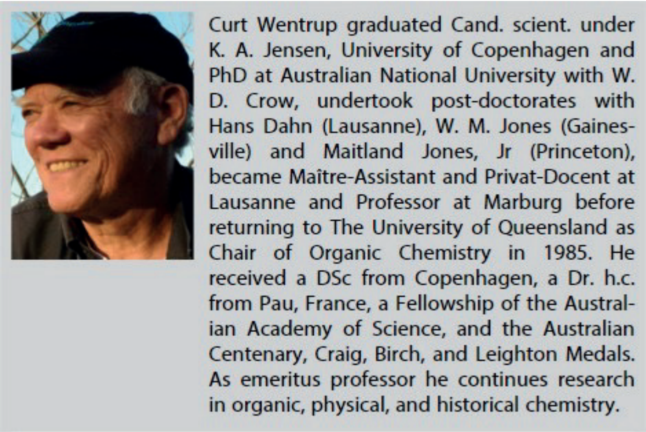
1.1 Introduction

The chemistry of carbon compounds is the contemporary definition of organic chemistry. Entire branch of chemistry is so committed to its compounds that means what makes carbon so special? Carbon setup a bond with broad range of elements and to other carbon atoms, which is distinct trait of carbon.

Heterogeneity of carbon compounds is what gives cornerstone for life on earth. Majority of living things are constituted mainly of complex organic compounds that have ask of structural, chemical or genetic.

The expression organic exactly means "derived from living organism". At first the phenomenon of organic chemistry was simply research of substances taken from living things and from their derivatives. Sugar, urea, wax, starch and plant oil were all seen as organic substances and people agreed to Vitalism, the idea that natural compounds need an essential strength to exist (Wade, 2008).

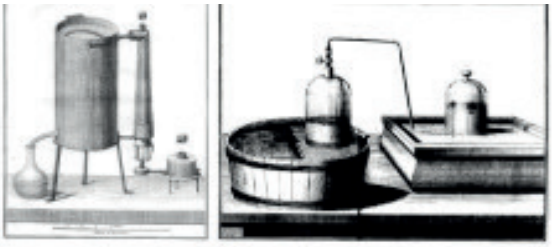
Due to the time constraints and textbooks rarely include much information on it, the instructors of chemistry cannot simply cover the history of organic chemistry in all depths, keeping in mind the vastness of the subject it is not common. For that reason, the students may perhaps not come to have a sound comprehension of why this is called "Organic Chemistry" and of those who teach it as organic chemists (Wentrup, 2022). Organic synthesis is unique branch of chemical synthesis and is linked with the calculated establishment of organic compounds. Organic molecules' synthesis has evolved into one of the most prime branches of organic chemistry and are frequently more complex than inorganic compounds. The principle chemical process is Organic synthesis that also is fundamental to many scientific disciplines. Medical industry, pharmaceutical industry and many others are some specimens of fields that be in need of organic synthesis but are beyond chemistry. Industrial-level production of pharmaceutical products are allowed by organic processes (Tejeda, 2017).



Curt Wentrup graduated Cand. scient. under K. A. Jensen, University of Copenhagen and PhD at Australian National University with W. D. Crow, undertook post-doctorates with Hans Dahn (Lausanne), W. M. Jones (Gainesville) and Maitland Jones, Jr (Princeton), became Maître-Assistant and Privat-Docent at Lausanne and Professor at Marburg before returning to The University of Queensland as Chair of Organic Chemistry in 1985. He received a DSc from Copenhagen, a Dr. h.c. from Pau, France, a Fellowship of the Australian Academy of Science, and the Australian Centenary, Craig, Birch, and Leighton Medals. As emeritus professor he continues research in organic, physical, and historical chemistry.

1.2 Historical overview

The expressions Organic and Synthesis arises from Aristotle; denotes ('instrumental' and 'put together' respectively) but had distinctives meanings from time to time. In 1600s, Iatrochemists put together innumerable pharmaceutical medicines, but had no idea or organic chemistry. Definition of organic bodies as living things was given by Buffon, Bergman and Gren in the 1700s, but discrete organic compounds continue to exist unknown. Scheele and Chevereuil, both isolated organic natural products in the late 1700s and early 1800s, they separated carboxylic acids from saponification of fats. That resulted in Organic chemistry. For organic characterization Lavoisier invented and Berzelius improved combustion analysis. Descartes'



Lavoisier's apparatuses for combustion analysis, 1784.

dictum that Synthesis is needed to show an analysis was validated by Bergman and others. When Wohler and Kolbe prepared organic compounds from element the idea of organic chemistry changed completely. In 1853, modern synthetic organic chemistry came into being as chemistry of carbon compounds when Berthelot's did synthesis of non-natural fats, regardless whether it occurs in nature or not. In the middle ages, the organic chemistry and organic synthesis began way before the concept of molecular compositions were understood. Lavoisier, Chevreuil, Wohler, Liebig, Kolbe and Berthelot caused Paradigm shifts are highlighted.


From left to right: Lavoisier, Chevreuil, and Berthelot.

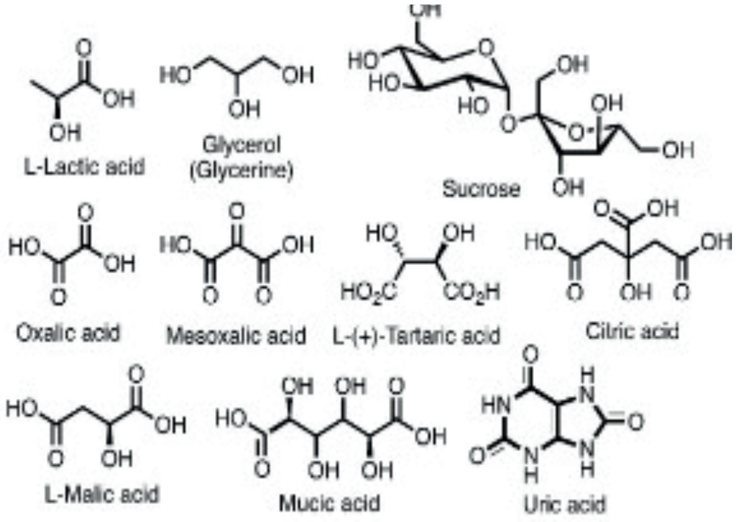
The graphic illustrates early key organic molecules. However, despite the fact that synthesis and analysis had become well established sciences by the 1840s, the chemical structures of these molecules remained largely unknown (Wentrup, 2022). Scarcely any discrete organic substances were known to Bergman in 1777. Since the 12th century, Ethanol by the distillation of wine had been acquired. Some vegetable acids and salts, such as tartaric acid and tartar (potassium hydrogen tartrate and calcium tartrate), sugar (an "essential salt"), "sugar acid" (oxalic acid, prepared by Bergman and Johan Afzelius by oxidation of sugar with nitric acid), acetocella salt (potassium hydrogen oxalate) from sorrel, citric acid, and acetic acid were known. Bergman classified organic and inorganic bodies as follows:

1. The most advanced natural substances found on the Earth's surface can be categorized into organic and inorganic.

2. Organic bodies contain numerous internal systems that extracts, processes, and distribute nourishment, facilitating their growth, maintenance and reproduction.

3. Organic bodies, are also known as living organisms, are classified into two main groups, animals and plants (based on their sensory capabilities) which are commonly regarded as two distinct Kingdoms of Nature.

4. Inorganic bodies are those which lack organic structure and can only grow by external addition of parts" (for the original Swedish and German texts, see Supporting Information, Section S3). The major thanks in large part to Lavoisier and Berzelius for the considerable advancement in organic chemistry that occurred in the late 1700s and early 1800s, so that elemental composition of organic materials could now be established. Other than Bergman and Gren, Berzelius could therefore start talking about organic and inorganic chemistry. Organic nature encompassed living things, but the chemical constituents of the organic bodies were still largely unexplored. Initially, contested by Berzelius, the isolation of discrete organic compounds from organic materials were becoming increasingly common. While the concept of structure was not yet developed, chemical compositions could at least be identified (Wentrup, 2022).



Some organic compounds known by the late 1700s (but structures unknown at the time).

1.3 Modern concept of organic synthesis

By combining few advancements in chemical techniques and methodologies, the contemporary notion of organic chemistry has progressed notably. The branch of chemical synthesis that mainly focuses on constructing organic compounds is Organic Synthesis, compounds that are essentially composed of carbon, hydrogen, oxygen and nitrogen atoms. Many methodologies, applications, and advancements changed the contemporary outlook of organic synthesis and helped in shaping the field.

1.3.1 Green Chemistry

The definition of Green Chemistry is "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances". Green chemistry is generally a new concept of organic chemistry that attempts to function at molecular level in order to obtain sustainability. In order to meet environmental and economic objectives all at once, green chemistry has gained extensive interest in the past decade due to its ability to harness chemical innovations. Framework of Green Chemistry

The three main points about the Green Chemistry framework can be summed up as:

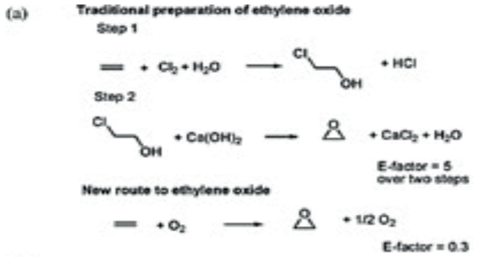
1. Green Chemistry designs across all stages of the chemical life-cycle.

2. Green Chemistry seeks to design the inherent nature of the chemical products and processes to reduce their intrinsic hazard.

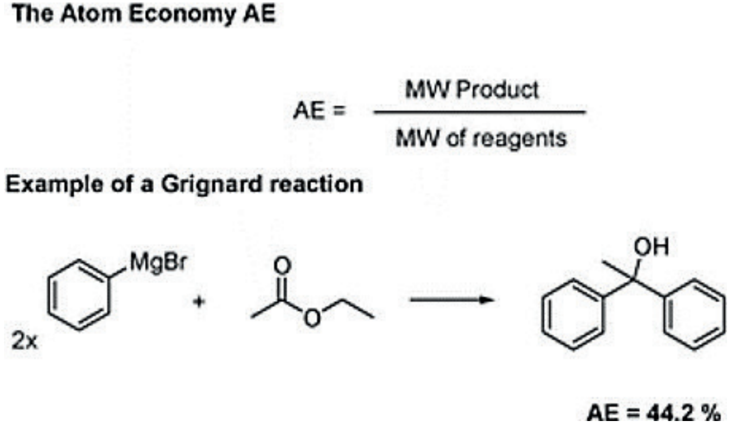
3. Green Chemistry serves as a cohesive system of principles or design criteria.

The Twelve Principles: In 1998 Paul Anastas and John Warner introduced The Twelve Principles of Green Chemistry (Clark, 2006).

1. Prevention: Preventing waste is more effective than dealing with it after it has been produced example Traditional preparation of ethylene oxide and the new route relying on molecular oxygen.



2. Atom Economy: Barry Trost presented the concept of synthetic efficiency in 1990: Atom Economy (AE) also known as Atom Efficiency, refers to the principle that an ideal reaction should utilize all of the atoms of the reactants.



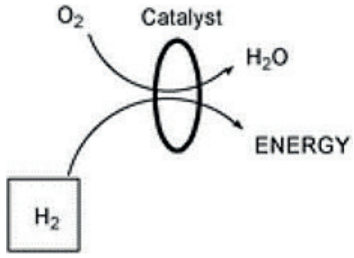
Synthetic methods should aim to maximize the inclusion of all materials used in the process into the final product, thereby minimizing waste. To exemplify this idea, consider the Grignard reaction. Although highly regarded in organic synthesis, The Grignard reaction is relatively inefficient in terms of atom economy. This is because the need for stoichiometric amount of metal reactant and the requirement to put together the Grignard reagent separately. As a result, the atom economy values are 44% and 56% indicating a significant loss of the raw materials. In contrast, the one-step multicomponent coupling reaction, such as the A3 coupling (Alkyne, Aldehyde and Amine), demonstrates greater efficiency and atom conservation, with 92% of original atoms being retained in the final product. Similarly, the Diels–Alder reaction is an excellent example of an atom-economical process, reflecting high atom economy and minimal material waste.

3. Less hazardous chemical synthesis: Wherever feasible, synthetic methods should use and produce substances that have minimal or zero toxicity to human health and the environment.

4. Designing safer chemicals: Chemical products should be engineered to achieve their intended purpose while minimizing toxicity.

5. Safer solvent and Auxiliary: When necessary, the use of auxiliary substances (like solvents) should be reduced or made non-poisonous. Solvents are arguably the most active focus of Green Chemistry research. Wherever possible, the ideal scenario would involve avoiding the use of any solvent, as incorporating an auxiliary necessitates additional effort and energy to remove it from the systems. Consequently, significant efforts have been made towards developing solvent-free systems.

6. Design for energy efficiency: Energy demands should be kept down, ideally by conducting reactions at ambient temperature and pressure. Growing concerns about the depletion of petroleum resources and the rise in energy consumption has accelerated the development of more energy efficient processes and for the pursuit of renewable energies sources; sustainable resources in a time frame relevant to human scale. Chemists can address these challenges by lowering the energy barrier of a chemical reaction or selecting suitable reactants that facilitate the transformation at room temperature, thus acquiring all the direct and indirect benefits associated with it. Furthermore, Proton Exchange Membrane (PEM) fuel cells, which utilize hydrogen and oxygen gases, offer a promising solution to the anticipated surge in energy demand, embodying the core principle of hydrogen fuel cell technology (Ahluwalia et al., 2004).



7. Use of renewable feed stocks: Whenever possible, raw materials should be drawn/sourced from renewable rather than from depleting ones.

8. Catalysis: Catalytic reagents are favored over stoichiometric reagents, as they are effective in smaller quantities and offer great efficiency.

9. Design for degradation: Chemical products should be engineered to decompose into non- harmful substances after their intended use.

10. Real-time analysis for pollution prevention: Processes should integrate real-time monitoring to reduce or prevent the creation of hazardous substances.

11. Minimize the potential for accidents: Chemicals and their physical forms should be engineered to mitigate the risks of accidents, such as explosions or releases into the environment.

12. Reduce derivatives: Minimize unnecessary derivatization that demands extra reagents and contribute to waste generation (Anastas & Warner, 2000).

1.3.2 Automation and Robotics

Organic synthesis is one the influential tool for generating and crafting complex molecules, and its automation has dramatically transformed the field, facilitating faster and more efficient creation of organic compounds. Some advantages of automated organic synthesis include increased productivity, lower costs, and improved safety. However, it’s not that straightforward, where there is automation of organic synthesis there is a requirement of knowledge to operate and specialized tools, where specialized software playing a crucial role in binding the gap between the chemist and the machine.

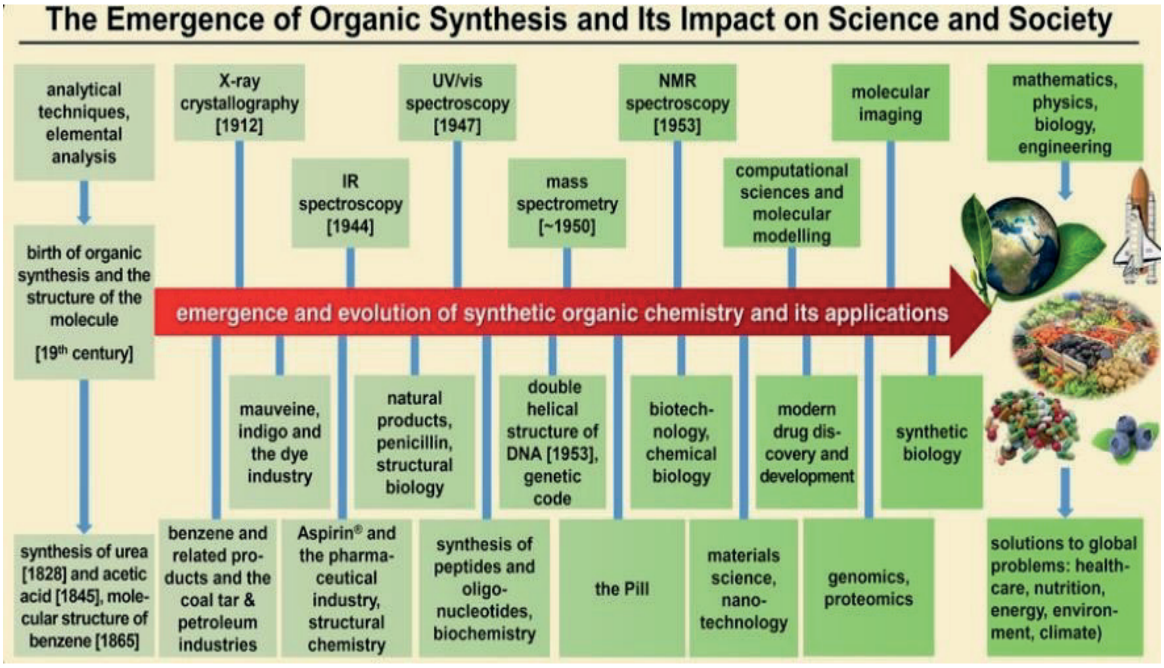
However, many people see software as merely a reaction input system. In reality, the capabilities of software surpass that significantly. Such software can serve to optimize and design synthetic pathways, forecast reaction outcomes and lead to comprehensive reports on the results. It can also serve to simulate reaction conditions, examine reaction data, and maximize process efficiency. Eventually, it can enhance data-driven decision-making by optimizing the organic synthesis process ultimately saving time and reducing cost.

The software should have the following modules to construct an ideal automated organic synthesis management platform (Gangwal & Lavecchia, 2024):

- Computer assisted synthesis planning (CASP)
- Reaction submission system
- Inventory management
- Integration with external databases and ability to interface with ELNs
- Instrument Control Software
- Data Acquisition and Analysis Software
- Database Management Software
- Visualisation Software
- Additional Specialised Software Packages

1.3.3 Computational Chemistry

A career in computational chemistry not only demands a keen interest in computer modeling and statistical analysis but also requires patience, logical thinking, and careful attention to detail. Additionally, strong "People skills" are crucial for this field. Computational chemists must collaborate effectively with other scientists and clearly communicate their findings to clients. Success in this field is greatly supported by excellent communication abilities, an outgoing personality, and a tendency for offering expert advice (Barbiric et al., 2015).



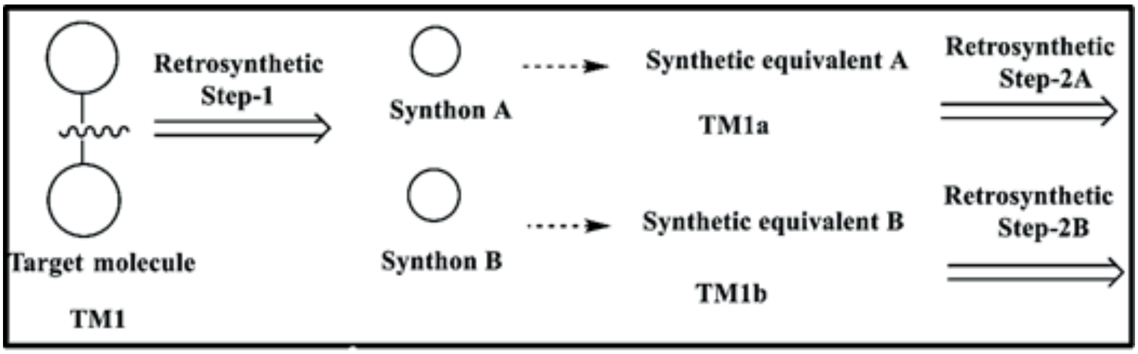
1.4 Applications of Organic Synthesis

► **Pharmaceutical development:** Organic synthesis is essential for developing of pharmaceutical compounds. For example, synthesizing ibuprofen demands multiple steps, such as reduction and carboxylation, to efficiently produce this commonly used pain reliever. Organic synthesis is also pivotal in rational drug design, where chemists use structure-activity relationship (SAR) studies to refine the biological activity of lead compounds. By systematically altering molecular structure, functional groups and stereochemistry, chemists can investigate the structure-activity landscape and pinpoint crucial molecular features responsible for activity.

Organic synthesis enables medicinal chemists to create drug like molecules with optimal pharmacokinetic and pharmacodynamic characteristics. Through rational design and structure-activity relationship (SAR) studies, chemists can adjust the molecular structure, optimize key pharmacophores and improve drug-likeness.

► **The importance of organic synthesis in drug discovery:** Organic synthesis is fundamental to drug discovery, offering a way to create diverse chemical libraries and identify potential lead compounds. It involves designing and constructing target molecules through various chemical transformations, allowing for the efficient and selective synthesis of complex structures. Effective collaboration between synthetic chemists and medicinal chemists is crucial for optimizing synthetic methods, addressing synthetic challenges, and refining the production of drug candidates (Zhang & Cue, 2018).

► **Retrosynthesis:** In Organic chemistry, synthesis involves creating more complex organic molecules from simpler starting compounds. A chemist begins with a basic compound and devises reaction pathways to build upon it. Synthesis and retrosynthesis differ in their approach to designing a sequence of reactions for the creating an organic compound. Synthesis starts with the initial compounds and progress towards the final product, while Retrosynthesis begins with the target compound and work backwards to identify the starting compounds. Both methods that are synthesis and retrosynthesis usually involve three types of transformations (Jabbar & Al-Hamashi, 2024).



General scheme of retrosynthetic analysis.

Retrosynthesis Strategies (Vosburg, 2008)

How to form a carbon-carbon bond

- Reaction of an aldehyde or ketone with a Grignard or organolithium reagent
- Reaction of an alkyl halide with a Gilman reagent
- Reaction of an organometallic reagent with an epoxide How to synthesize particular functional groups

Alcohols:

- Nucleophilic substitution of an alkyl halide with HO- or H2O
- Reduction of an aldehyde with NaBH4
- Reduction of a ketone with LiAlH4
- Reaction of an aldehyde or ketone with a Grignard or organo-lithium reagent
- Reaction of an organometallic reagent with an epoxide

Aldehydes:

- Oxidation of a primary alcohol with PCC

Alkenes:

- β Elimination of an alkyl halide or an alkyl tosylate with base
- Dehydration of an alcohol with acid
- Dehydration of an alcohol using POCl3 and pyridine

Alkyl halides:

- Radical halogenation of an alkane with X2
- Reaction of an alcohol with SOCl2 or PBr3
- Reaction of an alcohol with HX

Carboxylic acids:

- Oxidation of a primary alcohol with Na2Cr2O7

Epoxides:

- Intramolecular SN2 reaction of a haloalcohol using base

Ethers:

- Williamson ether synthesis: SN2 reaction of an alkyl halide with an alkoxide
- Reaction of an alkyl tosylate with an alkoxide

Ketones:

- Oxidation of a secondary alcohol with PCC or Na2Cr2O7

► **Industrial applications:** The European Journal of Organic Chemistry is presenting a special collection on "Industrial Organic Synthesis" which will highlight the impact of organic synthesis within the field of Life Sciences. The collection will cover industrial synthetic organic chemistry projects across various fields of Life Science, including process research, technology application for small molecules, and emerging modalities like PROTACs.

Summary

Organic chemistry, the study of Carbon compounds, explores the unique properties of carbon that enables it to create a diverse range of substances. The key to wide variety of molecules is carbon's ability to bond with variety of other carbon atoms and elements, which are crucial for life on earth. It is documented that, Organic chemistry originated from the isolation of and examination of substances found in living organisms, originally guided by the concept of Vitalism. Important breakthrough in its development includes the synthesis of organic compounds from inorganic materials by Kolbe and Wohler, which challenged the vitalism and paved the way for contemporary Organic chemistry. Organic synthesis, vital part of Organic chemistry, is essential in various fields, including medicine and industry by focusing on the intentional formation of Organic compounds. Applications extends from pharmaceutical development, where organic chemistry facilitate the production of drugs such as ibuprofen, to industrial processes that promote sustainability via Green Chemistry Principles. Automation and computational instrument have transformed organic synthesis by enhancing efficiency and enabling the design of intricate molecules. These advancements are continuously shaping the field, frosting innovation and expanding practical applications across diverse scientific area.

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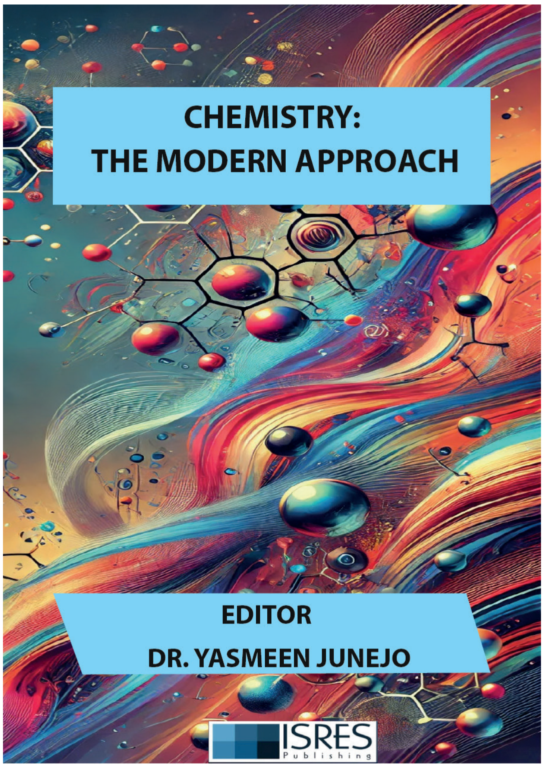

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