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Catalytic Properties of Asymmetric and Symmetric Materials: A Review

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ABSTRACT: This review explores the synthesis and catalytic properties of various symmetric and asymmetric organic molecules, with a particular focus on platinum as a catalyst. The catalytic efficiency of platinum in facilitating chemical reactions is examined, highlighting its role in producing numerous organic compounds, including benzene, ethylene, toluene, and lactic acid. Additionally, this study compares the catalytic capabilities of platinum group metals (PGMs) in contrast to other catalysts, analyzing their environmental impact, economic feasibility, and industrial applications. One of the significant advantages of using PGMs is their ability to enable reactions without the need for stoichiometric concentrations of environmentally harmful reagents, such as transition metals and nitrites, which are commonly used in traditional synthesis methods. This article also discusses various alternative synthesis methods, including thermal cracking and catalyst-free routes, providing a comparative assessment of their efficiency and sustainability. The review critically evaluates the economic and environmental trade-offs associated with PGMs in industrial applications, emphasizing their role in green chemistry. Furthermore, the study highlights recent advancements in catalysis research, shedding light on emerging trends and future directions in the development of novel catalytic systems. Ultimately, this review aims to provide a comprehensive understanding of the catalytic behavior of symmetric and asymmetric materials, their industrial significance, and the potential for innovation in catalyst design to enhance sustainability and efficiency in chemical synthesis.

Keywords: Catalysis, Platinum Group Metals (PGMs), Symmetric and Asymmetric Materials, Green Chemistry.

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1. INTRODUCTION

Catalysis is a crucial process in numerous industries, including the production of chemicals, pharmaceuticals, and

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energy. The effectiveness and specificity of catalytic processes are significantly influenced by the properties of the materials used as catalysts. This article discusses the differences and applications of symmetric and asymmetric catalytic materials [1].

In chemistry, catalysis refers to the process of altering the rate of a chemical reaction—typically accelerating it—by adding a substance that is not consumed during the reaction. The reaction rate is influenced by various factors, including the chemical nature of the reactants and environmental conditions. Catalysts function by lowering the activation energy required for a reaction to proceed, thereby increasing reaction rates. Catalysis is of both theoretical and practical significance, as it provides insight into fundamental chemical reaction mechanisms while also being integral to many industrial processes. Enzymes, for example, serve as biological catalysts essential for sustaining life [2]. A catalyst typically interacts chemically with reactants but is

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regenerated at the end of the reaction, maintaining a constant quantity. Due to this property, a single catalyst molecule can convert multiple reactant molecules. In some cases, a single catalyst molecule can facilitate the transformation of millions of reactant molecules per minute [3].

Catalysts can influence the selectivity of reactions, allowing specific reaction pathways to be favored over others. This selectivity is crucial in industrial applications where the formation of unwanted byproducts must be minimized. By choosing an appropriate catalyst, it is possible to drive one reaction forward while suppressing competing reactions. A catalyst does not alter the equilibrium position of a reaction; it only affects the rate at which equilibrium is reached. However, exceptions exist, such as autocatalytic reactions, where one of the reaction products also serves as a catalyst, further accelerating the reaction [4]. In contrast, some substances, known as inhibitors, reduce the rate of chemical reactions. This process, known as inhibition or retardation, can occur due to the formation of complexes between the inhibitor and catalyst, depletion of reactant concentrations due to interactions with the inhibitor, or termination of chain reactions [5, 6].

The concept of catalysis was first introduced in 1835 by the Swedish chemist Jöns Jacob Berzelius. However, it was not until 1894 that Wilhelm Ostwald provided a more precise definition, stating that catalysts are substances that increase the rate of a chemical reaction without being consumed. Over a century later, catalysis remains a fundamental concept in chemistry. Despite its importance, elementary textbooks often provide limited information beyond describing catalysts as substances that lower activation energy and enable reactions to proceed more efficiently [7].

The field of catalysis has historically been considered an art rather than a precise scientific discipline. However, advances in surface science and experimental techniques have transformed it into a well-defined field of study. Surface science has enabled detailed investigations of molecule adsorption on single-crystal surfaces, significantly advancing our understanding of catalytic mechanisms. However, many early surface science techniques were limited by their inability to replicate real-world catalytic conditions. More recent advancements in nanoscale imaging and reaction monitoring have bridged this gap, allowing researchers to study catalysts in their active state [4, 8].

Heterogeneous catalysis, which occurs at the surface of solid materials, is particularly significant in industrial applications. Porous solids and fine powders often exhibit superior catalytic performance compared to bulk single crystals due to their larger surface areas. However, in porous materials, there is ongoing debate regarding the extent to which catalytic activity is limited to the outermost layers versus occurring within the pores. Additionally, diffusion constraints within pores can influence reaction rates [1, 9]. The use of nanometer-sized catalytic particles instead of micrometer-sized ones is not solely a matter of efficiency. Catalytically active elements such as platinum and other precious metals can be used more effectively at the nanoscale. Moreover, atoms on the surface of nanoparticles exhibit different electronic properties compared to those on larger particles, further influencing catalytic behavior [10-12].

The term "catalysis" was coined by Swedish chemist Jöns Jacob Berzelius in 1835, derived from the Greek words "kata" (down) and "lyein" (loosen). This terminology emerged following discoveries by multiple chemists in the late 18th and early 19th centuries. Among these were Gottlieb Sigismund Constantin Kirchhoff's observation of acid-catalyzed starch conversion to sugar, Sir Humphry Davy's demonstration that platinum accelerates gas combustion, and the oxidation of alcohol to acetic acid facilitated by finely divided platinum. Berzelius proposed that these reactions involved a unique, unidentified catalytic force, and the materials enabling these transformations were termed catalysts [13, 14].

In 1834, English scientist Michael Faraday studied the ability of platinum to facilitate the recombination of gaseous hydrogen and oxygen—byproducts of water electrolysis [15, 16]. He observed that impurities such as carbon monoxide could inhibit this process, highlighting the importance of a clean metal surface for catalytic activity [17-21]. Catalysis has been used unconsciously for centuries in various processes, including the fermentation of alcohol to produce acetic acid and the saponification of fats into soap. Early industrial applications of catalysis included the lead-chamber process for sulfuric acid production, which involved nitrogen oxides as catalysts. In 1812, Sir Humphry Davy proposed improvements to this method [14, 22, 23]. The study of reaction acceleration gained further attention in 1850 when research on sucrose hydrolysis demonstrated that reaction rates were influenced by the amount of sugar present and were accelerated by acids. This discovery contributed to the foundational understanding of reaction kinetics, later explored by Wilhelm Ostwald, Svante Arrhenius, and J.H. van 't Hoff. In the 1890s, Ostwald formally defined catalysts as substances that alter reaction rates without affecting equilibrium, a significant breakthrough in catalysis research [8, 24, 25].

During the 19th century, catalytic processes began to be intentionally applied in industry. English chemist P. Phillips patented a method using platinum to oxidize sulfur dioxide to sulfur trioxide. While initially abandoned due to catalyst deactivation, this process was later revived when researchers identified and mitigated catalyst poisons. In 1871, an industrial method for converting hydrochloric acid to chlorine using cupric ion-impregnated clay bricks was developed, leading to the production of chlorine-based bleaching agents [15, 26, 27]. By the late 19th and early 20th centuries, catalytic processes had transformed industry. advancements Notable included Paul Sabatier's hydrogenation reactions using nickel catalysts and three major German catalytic processes: the contact process for sulfuric acid production, catalytic synthesis of indigo dye, and the Haber-Bosch process for ammonia production developed by Fritz Haber and Carl Bosch. These breakthroughs had a lasting impact on industrial chemistry [15, 27]. Figure 1 shows the timeline of catalyst technologies throughout the history.

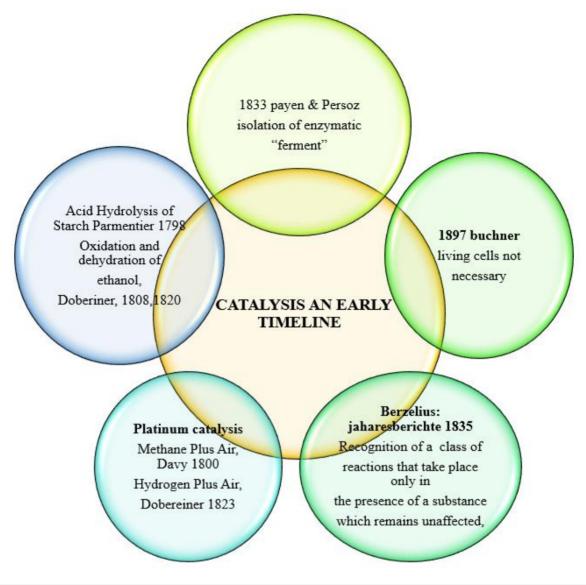


Fig. 1. Timeline of catalyst technologies throughout the history.

2. TYPES OF CATALYSTS

Catalysts play a crucial role in various chemical reactions, enhancing reaction rates without undergoing permanent change themselves. They can be classified based on their physical state, chemical composition, or the specific reactions they facilitate. Catalysts exist in different forms, including solids, liquids, or gases, each exhibiting unique characteristics that influence their efficiency and applications. Broadly, catalysis is divided into homogeneous and heterogeneous catalysis, depending on whether the catalyst shares the same phase as the reactants or exists in a different phase [27-29]. Figure 2 demonstrates various catalysis systems.

In homogeneous catalysis, the catalyst is molecularly dispersed within the same phase as the reactants, typically in liquid or gaseous form. This type of catalysis is widely used in industrial and biochemical applications due to its uniform reaction environment, leading to better control over reaction mechanisms and selectivity. Conversely, heterogeneous catalysis involves catalysts that exist in a different phase from the reactants, often as solid catalysts interacting with gaseous or liquid reactants. This type is widely applied in industrial processes such as petroleum refining, catalytic converters in automobiles, and the Haber-Bosch process for ammonia synthesis.

2.1. Homogeneous Catalysis

Homogeneous catalysis occurs when both the catalyst and the reactants are present in the same phase, typically as gases or liquids [30]. This results in a uniform mixture, allowing for better interaction and reaction kinetics. One of the classic examples of homogeneous catalysis is the lead chamber process used for producing sulfuric acid, where nitrogen oxides serve as catalysts to oxidize sulfur dioxide. Another example is the reaction of carbon monoxide with oxygen, which occurs very slowly under dry conditions but is significantly accelerated in the presence of trace amounts of water vapor. Similarly, the formation of diethyl ether from ethyl alcohol is catalyzed by sulfuric acid.

Homogeneous catalysis plays a pivotal role in various industrial and laboratory reactions [31]. The oxidation of sodium sulfite solutions by dissolved oxygen is an example where the presence of small amounts of copper ions dramatically accelerates the reaction. This particular reaction is of special interest as it follows a chain reaction mechanism. In such cases, the absorption of a few photons of light can initiate a series of reactions, leading to the oxidation of thousands of sodium sulfite molecules. A notable example of this phenomenon is the photochemical reaction between hydrogen and chlorine in sunlight, where a single absorbed photon can trigger the formation of millions of hydrogen chloride molecules.

2.1.1. Reaction Mechanism in Homogeneous Catalysis

A generalized reaction mechanism for homogeneous catalysis, partially based on the Brønsted acid-base theory, involves the catalyst (C) facilitating the transformation of reactant A into product B through an intermediate species (Z). The process can be represented as follows:

Formation of Intermediate: $A + C \rightarrow Z$ (Rate: k_1)

Conversion to Product: $Z \rightarrow B + C$ (Rate: k₃)

Regeneration of Catalyst: $Z \rightarrow A + C$ (Rate: k_2)

If the rate constant k_3 is significantly greater than k_2 , the intermediate decomposes almost as quickly as it forms, leading to rapid product formation. However, if k_2 is greater than k_3 , the reaction rate is limited by the breakdown of the intermediate. These two scenarios highlight different catalytic pathways, each governing reaction speed and efficiency [32]. Homogeneous catalysis also involves promoter effects, where the combined action of multiple catalysts enhances the overall catalytic efficiency beyond what each catalyst could achieve individually. For instance, iron ions in solution can enhance the catalytic ability of copper ions in the reaction between iodine and hydrogen peroxide.

2.1.2. Applications of Homogeneous Catalysis

Homogeneous catalysts find widespread application in the petrochemical industry, one of the most significant modern uses. The oxo process, for example, is employed to produce alcohols and aldehydes by introducing carbon monoxide and hydrogen to olefins under specific temperature and pressure conditions [33].

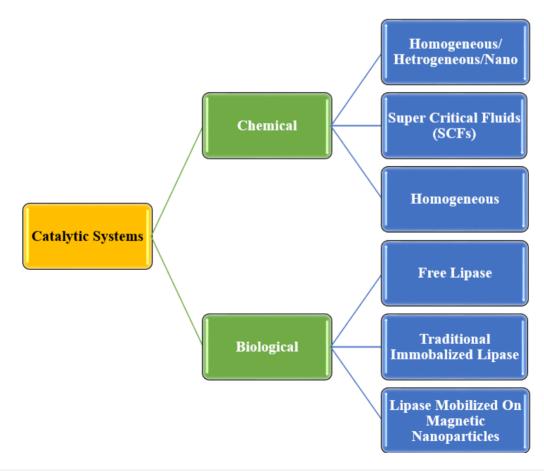


Fig. 2. Various catalytic systems. Adapted from ref. [29].

This reaction utilizes cobalt carbonyl as a catalyst, which is soluble in hydrocarbons and aids in activating hydrogen by forming intermediate species like HCo(CO)₄. The development of such catalytic processes has led to extensive research into organometallic chemistry, as it provides insights into transition metal-mediated transformations.

Another industrial application is the Wacker process, where palladium chloride catalyzes the oxidation of ethylene to acetaldehyde in the presence of cupric chloride. In this system, palladium continuously cycles between its metallic and ionic states, with cupric chloride playing a role in regenerating the palladium catalyst [34]. Furthermore, strong acids such as sulfuric acid, phosphoric acid, and sulfonic acids serve as homogeneous catalysts in polymerization, esterification, hydration, and isomerization reactions. Additionally, homogeneous catalytic systems involve free radical reactions, which are initiated by the breakdown of peroxides or metal alkyl compounds. Free radicals are highly reactive species with unpaired electrons, making them crucial in initiating and propagating chain reactions, particularly in polymer chemistry and organic synthesis [35].

2.1.3. Acid-Base Catalysis

J.N. Brønsted's acid-base theory provides a fundamental understanding of homogeneous catalytic reactions. According to his definition, acids donate protons while bases accept them. This concept explains various catalytic reactions, including acid-catalyzed ester hydrolysis and nitramide decomposition [36]. Brønsted discovered a direct correlation between the concentration of the catalytic agent and the reaction rate. His research laid the foundation for acid-base catalysis, where acids and bases act as catalysts to speed up the conversion of substrates. Some common acids involved in homogeneous catalysis include hydronium ions, ammonium ions, acetic acid, and bisulfate ions, while their corresponding bases include sulfate, acetate, hydroxide, and ammonia [37]. These acid-base pairs participate in numerous reactions, from esterification to carbohydrate hydrolysis. An example of acid-base catalysis is the mutarotation of glucose, where glucose shifts between its alpha and beta anomeric forms. This transformation is catalyzed by acids and bases in aqueous solutions, providing a practical demonstration of the Brønsted acid-base principle in biological and chemical systems.

Homogeneous catalysis plays an essential role in various chemical transformations, providing high reaction efficiency and specificity. It is widely used in industrial processes such as the production of sulfuric acid, oxidation reactions, and the manufacture of petrochemical products. The mechanistic insights provided by Brønsted and subsequent researchers have enhanced our understanding of catalysis, leading to the development of more efficient catalytic systems. Whether through acid-base catalysis, transition metal complexes, or free radical initiation, homogeneous catalysts continue to drive innovation in chemistry and industrial applications [38]. The field of homogeneous catalysis is rich with diverse reaction mechanisms and applications, making it an indispensable tool in both academic and industrial chemistry. Continued research into catalytic efficiency, selectivity, and sustainability will further advance the field, leading to new discoveries and technological advancements in catalysisdriven processes.

2.2. Heterogeneous Catalysis

Heterogeneous catalysis is a crucial process in various industrial and environmental applications, including the production of fuels, chemicals, and pollution control. It involves a catalyst that is in a different phase or state of matter than the reactants. These catalytic processes occur at the surface of solid catalysts when they interact with gases, liquids, or a combination of both [37, 39]. The reactants, typically in the gaseous or liquid phase, must interact with the catalyst's surface for the reaction to occur. The catalyst remains unchanged during the reaction, allowing for continuous cycles of chemical transformation. The efficiency of heterogeneous catalysis depends largely on the surface area and the ability of the catalyst to adsorb reactants. Figure 3 exhibits the interdisciplinary significance in heterogeneous catalysis.

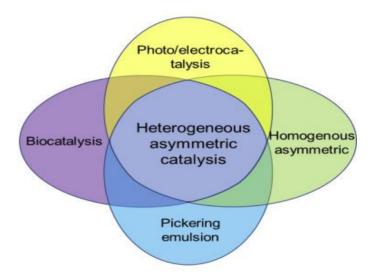


Fig. 3. Interdisciplinary significance in heterogeneous catalysis. Reprinted with permission from ref. [37], Dai, H. and Yang, Q., 2022. The importance of interdiscipline in heterogeneous asymmetric catalysis. *Chem Catalysis*, 2(11), pp.2840-2851. Copyright © Cell Press.

2.2.1. Mechanisms and Catalytic Sites

Heterogeneous catalysts are designed with large surface areas to maximize their effectiveness. As a result, modern catalysts often include finely divided metals, metal oxides, sulfides, or other materials integrated into support structures. These catalysts may be prepared as thin films, metal gauzes, or porous materials to ensure a significant contact area with the reactants. The solid catalyst interacts with gases or liquids at its outermost layer, where reactions typically take place. This interaction is governed by the adsorption of reactant molecules onto the catalyst's surface, a critical step in catalysis [40]. The metal catalysts may undergo transformations, such as the formation of halides, oxides, or sulfides, which can influence their catalytic properties. Catalysts can also be used in their original metallic state for certain reactions, such as hydrogenation or dehydrogenation processes.

When using solid catalysts, at least one of the reactants must be chemisorbed, a process in which the molecules of the reactant form chemical bonds with the catalyst's surface. Chemisorption is typically stronger than physical adsorption, and it often requires specific conditions, such as a particular temperature range. For example, hydrogen can be chemisorbed onto metals at temperatures as low as -180°C (under liquid air temperature), but dehydrogenation and hydrogenation reactions generally occur at higher temperatures. The temperature at which chemisorption occurs plays a significant role in determining the activity and efficiency of the catalyst in a given reaction. Additionally, once the reaction occurs, the products must easily desorb from the catalyst's surface to avoid poisoning the catalyst or blocking further adsorption sites [41].

The catalytic process typically involves the formation and breaking of chemical bonds, a process that differs from the physical adsorption of molecules. Chemisorption, in contrast to physical adsorption, often requires the input of activation energy to initiate the reaction. This energy barrier is lowered in catalyzed reactions, making them more efficient than uncatalyzed reactions, which require higher activation energies. The presence of a catalyst allows the reactants to overcome the activation energy barrier more easily, leading to a faster reaction rate. A typical energy diagram of a catalytic process compares the energy profiles of uncatalyzed and catalyzed reactions, demonstrating the lowering of the activation energy when a catalyst is involved (Figure 4).

2.2.2. Langmuir's Theory and Surface Chemistry

Irving Langmuir, a pioneering physical chemist, was instrumental in the development of the theory of surface catalysis. He proposed that catalytic reactions occur through the chemisorption of reactant molecules onto the catalyst's surface. Once adsorbed, the molecules interact with each other, leading to product formation and desorption. Langmuir's model is still foundational to understanding the surface interactions that occur in heterogeneous catalysis. However, alternate theories have also been proposed to explain the behavior of adsorbed species. These theories suggest that, rather than a simple adsorption-desorption mechanism, the reactant molecules may undergo more complex interactions before reacting on the surface [42].

The study of surface chemistry and the development of methods to quantify the surface area of catalysts marked a

significant milestone in heterogeneous catalysis. The invention of techniques to measure surface area, such as the adsorption of gases (e.g., nitrogen adsorption at liquid nitrogen temperatures), allowed researchers to evaluate the amount of available surface area on catalysts. This was crucial because the catalytic activity of a material is directly related to the available surface area. The surface area can be quantified using the concept of the monolayer volume (Vm), which represents the volume of gas required to form a single layer of adsorbed molecules on the surface. By analyzing the adsorption of gases, scientists could measure the surface area of catalysts and better understand the relationship between surface area and catalytic activity.

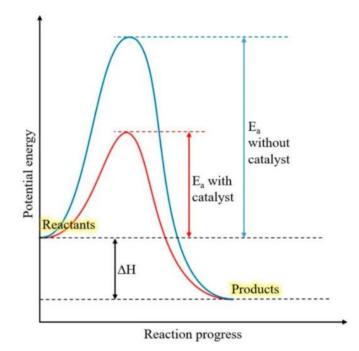


Fig. 4. Impact of Catalyst on energy diagram profile. Reprinted with permission from ref. [35], Sinar Mashuri, S.I., Ibrahim, M.L., Kasim, M.F., Mastuli, M.S., Rashid, U., Abdullah, A.H., Islam, A., Asikin Mijan, N., Tan, Y.H., Mansir, N. and Mohd Kaus, N.H., 2020. Photocatalysis for organic wastewater treatment: From the basis to current challenges for society. *Catalysts*, 10(11), pp. 1260. Copyright © MDPI.

2.2.3. The Role of Promoters and Poisoning

Promoters are substances that are present in trace amounts in the catalytic material but significantly enhance its catalytic activity. These substances work by increasing the effective surface area of the catalyst or by improving the catalyst's surface quality for specific reactions. While promoters are beneficial, certain impurities or undesired components can act as poisons, which hinder the catalyst's effectiveness. Poisons typically work by adsorbing more strongly to the catalyst's surface than the reactants, blocking active sites, and reducing the number of available sites for the catalytic reaction. This phenomenon can significantly reduce the catalyst's performance and lifetime.

Catalyst poisoning is a common challenge in industrial processes where the catalyst may be exposed to impurities in the reactants. For instance, sulfur compounds in natural gas can poison metal catalysts, reducing their efficiency in processes such as the steam reforming of methane. In some cases, the poisons may alter the catalyst's electronic properties, leading to a decline in its overall activity. The ability to minimize catalyst poisoning and regenerate poisoned catalysts is an important area of research in heterogeneous catalysis. Figure 5 shows the industrial role of catalytic processes and relative contribution of heterogeneous catalysis.

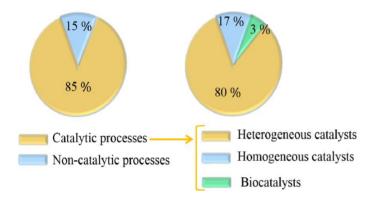


Fig. 5. The industrial role of catalytic processes and relative contribution of heterogeneous catalysis. Reprinted with permission from ref. [38], Saini, S., 2020. Designing clusters for efficient catalytic activity at a realistic condition from first-principles simulation. Copyright © Research gate.

2.2.4. Isotopic Labeling Studies

The study of catalytic mechanisms can be enhanced using isotopic labeling. Isotopes of elements such as hydrogen, nitrogen, and carbon can be incorporated into reactants, allowing researchers to track the movement of atoms during the reaction. This technique has been particularly useful in understanding complex reactions, such as the Haber-Bosch process for ammonia synthesis. The ability to track isotopic species helps clarify the role of various bonds in the reaction mechanism.

In the case of ammonia production, isotopes of hydrogen (such as deuterium) and nitrogen (such as nitrogen-14 and nitrogen-15) have been used to study the activation of nitrogen-hydrogen bonds. For example, the reaction between hydrogen (H₂) and deuterium (D₂) to form HD (H–D) on a reduced iron catalyst can be observed at low temperatures, even near liquid air temperatures. Similarly, the reaction involving nitrogen isotopes, such as $14N_2$ and $15N_2$, demonstrates how the activation of nitrogen molecules

becomes the rate-limiting step in the reaction. These studies reveal that the activation of nitrogen requires higher temperatures (around 400° C or 750° F), which is consistent with the temperature conditions used in industrial ammonia synthesis.

By examining isotopic reactions such as $NH_3 + ND_3 \rightarrow NH_2D + NHD_2$, researchers have gained insight into the formation and breaking of bonds on the catalyst surface. These isotopic studies have also been applied to the study of hydrocarbons and other reactions, providing valuable information about the catalytic mechanisms that govern industrial processes.

2.2.5. The Industrial Role of Heterogeneous Catalysis

Heterogeneous catalysis plays a pivotal role in the chemical industry, where it is used in a wide range of applications, from the production of fuels and chemicals to pollution control. Industrial catalytic processes such as the catalytic cracking of petroleum, the synthesis of fertilizers, and the reduction of pollutants rely on heterogeneous catalysts. The catalytic activity, efficiency, and stability of the catalysts are critical to ensuring that these processes are economically viable and environmentally friendly.

Heterogeneous catalysis also finds applications in renewable energy production, such as the conversion of biomass into biofuels and the generation of hydrogen from water using photocatalytic processes. Researchers are continually exploring new catalysts and improving existing ones to meet the demands of these applications. The development of more efficient catalysts is crucial for reducing energy consumption, minimizing waste, and enhancing the overall sustainability of industrial processes.

The relative contribution of heterogeneous catalysis to industrial processes is significant, as it enables the efficient transformation of raw materials into valuable products. In fact, the majority of chemical transformations in industry are catalyzed by heterogeneous catalysts. This highlights the importance of ongoing research into catalyst design, surface chemistry, and reaction mechanisms to optimize industrial processes and address emerging challenges.

Heterogeneous catalysis is an essential process in modern chemistry, providing an efficient and sustainable means of carrying out chemical reactions. The development of catalysts with large surface areas, the discovery of promoters and poisons, and the use of isotopic labeling techniques have deepened our understanding of catalytic mechanisms. While challenges remain, particularly in terms of catalyst poisoning and the need for more efficient catalysts, the continued advancement of this field promises to improve the efficiency and sustainability of a wide range of industrial processes.

2.3. Characteristics and Structure of Catalysts

The catalytic activity of a material is significantly influenced

by its structural properties, with several factors determining the efficiency and selectivity of reactions. Notably, the behavior of catalysts can be altered by external conditions such as radiation. For instance, when silica gel at liquidnitrogen temperatures is exposed to cobalt-60 gamma radiation, the material becomes purple in color and can catalyze the reaction $H_2 + D_2 \rightarrow 2HD$. This reaction occurs even at normal temperatures, though the color centers (positive "holes" or deficiencies in the material) are destroyed when hydrogen interacts with them. The catalytic activity is thus tied to the presence of these color centers, and the destruction of these sites occurs when the material is sterilized in a vacuum or heated above 200°C (400°F) in the presence of aluminum contaminants [39, 40].

This phenomenon demonstrates the critical role that specific structural characteristics play in catalytic activity. The catalytic properties of materials can be manipulated by altering their structure, particularly at the atomic and molecular levels. One example of this is the study of platinum metals dispersed on carbon carriers or in oxide matrices such as silica and alumina. These materials are vital in industrial applications like gasoline reforming. For example, platinum and palladium, when dispersed in amounts as small as 0.5% by weight, exhibit significant catalytic properties. The dispersion of metal atoms, which refers to the ratio of visible metal atoms to the total metal atoms, plays a critical role in determining catalytic efficiency. In these catalysts, the dispersion of platinum is around 1, while on platinum foil, it is much lower at approximately $4 \times$ 10^{-3} . The metal dispersion is typically measured using techniques such as hydrogen and oxygen titration and adsorption processes [41].

The dispersion of platinum and palladium in catalysts leads to distinct catalytic effects. For certain catalytic reactions, including the hydrogenation of benzene or hydrogenolysis of cyclopentane, the size of the metal particles (typically less than 5 nm) does not significantly affect the outcome. These reactions are termed "structureinsensitive" because they proceed in a manner that does not depend on the dispersion or the specific atomic arrangement of the catalyst particles. On the other hand, some reactions, particularly those involving platinum-alumina catalysts, demonstrate significant variation in their selectivity based on the structure of the catalyst. For example, the isomerization of neopentane to isopentane and the subsequent cracking of isobutane and methane varies drastically with different catalysts. In these cases, the catalytic activity is highly sensitive to the arrangement of metal atoms at the surface. When platinum catalysts are exposed to high temperatures in vacuo (900°C or 1600°F), the catalyst becomes more selective, with an optimal ratio of isomerization to hydrogenolysis. This is attributed to the creation of specific facets on the platinum surface, particularly the (111) planes, which offer unique adsorption sites for the reactants [42-44].

This dependence of catalytic activity on the surface structure has led to the classification of reactions as either "structure-sensitive" or "structure-insensitive." The former category involves reactions where the structure of the catalyst significantly impacts the reaction's outcome, while the latter involves reactions where the catalyst's structure has little to no effect on the catalytic process. The concept of structuresensitive reactions is critical for designing and optimizing catalysts for specific applications, such as selective hydrogenation or isomerization reactions.

2.4. Electronic Characteristics of Catalysts

In addition to the physical structure of the catalyst, its electronic properties also play a vital role in catalytic activity. Many materials used in catalysis are semiconductors, which have unique electronic characteristics that influence their ability to form bonds with reactants. These materials have a lattice structure that creates spaces where unbound lattice electrons can interact with adsorbed species. The reactivity of these species, whether they are atoms, radicals, or ions, depends on how they interact with the catalyst's surface and the availability of electrons or "holes" in the catalyst's electronic structure.

In semiconductor catalysts, the ability to establish bonds with reactants is influenced by factors such as the electronic configuration of the material, the presence of unbound electrons, and the electrochemical properties of the catalyst's surface. When radicals or ions come into contact with the catalyst, their reactivity is determined by how the catalyst's surface can facilitate or hinder the formation of chemical bonds. Research has shown that the d-band character of the catalyst, or the number of electrons present in the d orbitals of the catalyst's atoms, is a critical factor in determining its catalytic activity [45-47]. The d-band character refers to the density of electronic states in the d orbitals, which can be tuned to optimize the catalyst's interaction with reactants.

The relationship between the electronic characteristics of the catalyst and its catalytic activity is complex and requires a detailed understanding of the material's electronic structure. For example, some catalysts may exhibit greater reactivity due to a higher density of states in the d-band, while others may be less reactive due to a lower density of available electrons. This electronic tuning is important in the development of catalysts for specific reactions, such as selective oxidation or reduction processes.

2.5. Characterization of Catalysts

To understand the properties and behavior of catalysts, a variety of experimental techniques have been developed since the 1940s. These methods allow researchers to investigate the structure, composition, and electronic characteristics of catalysts during actual catalytic reactions. Among the most widely used techniques are nuclear magnetic resonance (NMR) and electron spin resonance (ESR), which can provide insights into the behavior of adsorbed species and the dynamics of chemical bonds during reactions. Other techniques, such as flash desorption, infrared spectroscopy, Mössbauer spectroscopy, and

magnetic measurements, allow for the analysis of catalyst surface interactions and the identification of active sites involved in catalysis.

Electron microscopy and field-emission microscopy are invaluable tools for examining the morphology and structure of catalysts at the atomic scale. These techniques allow for the observation of catalyst particles, their dispersion, and the formation of specific crystal facets that are critical for catalytic performance. Low-energy electron diffraction (LEED) studies provide additional information about the arrangement of atoms on the catalyst surface, while electron microprobe methods enable the analysis of the elemental composition of catalysts at high resolution. Additionally, measurements of heats of immersion can provide information about the interaction of reactants with the catalyst surface, helping to elucidate the energetics of the catalytic process [48-52].

These advanced characterization techniques have significantly improved our understanding of catalytic processes, allowing researchers to design more efficient and selective catalysts. By studying the behavior of adsorbed species, the composition of catalyst surfaces, and the electronic characteristics of catalysts, scientists can gain valuable insights into the mechanisms that govern catalytic reactions. This knowledge is crucial for the development of new catalysts for a wide range of applications, from environmental protection to energy production.

The catalytic activity of materials is influenced by both their structural and electronic characteristics. The dispersion of metal atoms on supports, the arrangement of atoms on the catalyst surface, and the electronic properties of the catalyst all play a significant role in determining its effectiveness in catalyzing specific reactions. The development of new techniques for characterizing catalysts has enabled researchers to gain a deeper understanding of the factors that govern catalytic activity. By manipulating these factors, it is possible to design catalysts that are more efficient, selective, and durable, paving the way for more sustainable and economically viable industrial processes.

2.6. Other Catalytic Compounds

In the field of heterogeneous catalysis, certain catalytic compounds are particularly notable for their ability to engage multiple surface components simultaneously. These compounds are known as polyfunctional heterogeneous catalysts. They typically involve catalytic systems where different sites or active components on the catalyst surface interact with various reactants and intermediates, facilitating complex transformations. One well-known example of such a catalyst is the dual-functional catalyst, which combines both metallic and acidic properties. These catalysts, such as nickel or platinum deposited on a silica-alumina base, play a significant role in the interconversion of different types of hydrocarbons, including saturated (paraffins), regular (straight-chain), iso (branched-chain), and unsaturated hydrocarbons (olefins). Additionally, they are crucial in the cracking of hydrocarbon molecules, where larger molecules are broken down into smaller ones, an important process in refining and petrochemical industries.

Dual-functional catalysts have significant importance in industrial processes, particularly in the transformation of hydrocarbons. For example, in the petroleum industry, the conversion of straight-chain alkanes (paraffins) into branched-chain isomers (iso-hydrocarbons) is a key reaction in gasoline production, as the branched isomers exhibit superior performance as fuel components. These catalysts are also instrumental in the cracking of larger hydrocarbons to produce lighter, more volatile products. The acidic sites on the catalyst promote the generation of carbocations, while the metal sites enable hydrogenation reactions, thus making dual-functional catalysts versatile and efficient for such transformations.

2.7. Clarifying Response Mechanisms: Illuminating a Mystery

One of the challenges in catalysis is understanding the exact mechanisms by which a catalyst facilitates a reaction. This is particularly difficult in heterogeneous catalysis, where the reactants and products are not in the same phase, and the reaction typically occurs on the catalyst's surface. To elucidate the mechanism of a reaction, researchers often rely on kinetics, which involves studying the rate of reaction as a function of reactant concentrations. In homogeneous (singlephase) systems, the relationship between the rate and concentration can be used to infer which species are involved in the rate-determining step of the reaction. For example, if the reactant (A), it suggests that A is directly involved in the rate-determining step.

In contrast, heterogeneous catalytic reactions are often more complex. The products of these reactions may differ slightly from the reactants, making it difficult to directly correlate reactant concentrations with the reaction rate. Furthermore, in porous systems, such as those involving zeolite catalysts, the transport and adsorption limitations can affect the concentrations of reactants at the catalyst's surface, adding another layer of complexity. Despite these challenges, researchers have developed techniques to gain insight into the mechanisms of heterogeneous catalytic reactions, such as using isotopically labeled reactants to trace intermediates and products.

For example, in the methanol-to-gasoline (MTG) process, the use of acidic zeolite catalysts such as H-ZSM-5 plays a crucial role in converting methanol into gasoline-like hydrocarbons. This process is known for its complexity, as it involves the formation of multiple intermediates and products in a seemingly random fashion. The catalyst works as a "black box" that facilitates the formation of carbon-carbon bonds in one step, converting methanol (CH3OH) into a mixture of hydrocarbons. To understand this process, one approach is to use isotopic labeling, such as 13C-labeled methanol, to track the formation of intermediates and

products.

In an experiment using 13C-labeled methanol with the SAPO-34 zeolite catalyst, which typically generates C2 to C4 alkenes, researchers were able to observe the intermediate formation process more clearly. For a simple sequential reaction mechanism (e.g., $CH_3OH \rightarrow C_2H_4 \rightarrow C_3H_6 \rightarrow C_4H_8 \rightarrow C_5H_{10}$), one would expect to find 13C labels only in the products in a specific pattern. However, the experiment also revealed products with two labels, indicating that the 13C isotopic label was shuffled between different positions in the molecules. This suggested that the MTG process involves a more complex mechanism, where a pool of hydrocarbons, including fragments such as (CH₂)n, undergoes repeated reactions to generate a variety of intermediates and final products.

This discovery was a crucial step in elucidating the mechanism of the MTG process. The catalytic activity in the MTG process does not follow a simple linear pathway; instead, it involves the creation and recombination of intermediate species. The observation of the isotopic label distribution provided compelling evidence for the existence of a hydrocarbon pool mechanism, in which fragments and intermediates are recycled to form a range of products. The results of this experiment demonstrated that the catalytic system operates through a more intricate network of reactions than originally anticipated, highlighting the importance of isotopic labeling in understanding complex catalytic processes.

Figure 6 illustrates the carbon pool mechanism in the methanol-to-gasoline (MTG) process, where various hydrocarbons are generated as a result of repeated reactions between fragments. This process, which involves the creation of multiple carbon-carbon bonds, is central to the production of gasoline-like products from methanol. The figure provides a visual representation of how the pool of hydrocarbons is formed and how these intermediates contribute to the final product distribution.

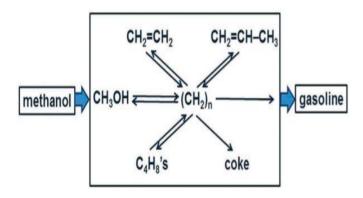


Fig. 6. Mechanism of the carbon pool in methanol's production of gasoline. Reprinted with permission from ref. [11]. Roduner, E., 2014. Understanding catalysis. *Chemical Society Reviews*, 43(24), pp. 8226-8239. Copyright © Royal Society of Chemistry.

Polyfunctional heterogeneous catalysts, such as those

combining metal and acidic sites, are critical in facilitating complex reactions in various industrial processes, particularly in the conversion and cracking of hydrocarbons. These catalysts enable the interconversion of different hydrocarbon types and the breaking of larger molecules into smaller ones, making them indispensable in petroleum refining and chemical manufacturing.

Understanding the mechanisms of heterogeneous catalysis is a challenging task due to the complexity of the reactions and the involvement of multiple phases. However, advancements in experimental techniques, such as isotopic labeling, have provided valuable insights into these mechanisms. The study of the methanol-to-gasoline process using 13C-labeled methanol demonstrated the intricacies of catalytic reactions and highlighted the existence of a hydrocarbon pool mechanism, where intermediates are repeatedly recombined to form a variety of products. These findings not only contribute to our understanding of the MTG process but also pave the way for the development of more efficient catalysts for complex chemical transformations.

2.8. Spectroscopic Monitoring of Catalytic Centers and Reaction Intermediates in Real Time

Spectroscopic techniques have become indispensable tools in both homogeneous and heterogeneous reaction systems for understanding the mechanisms of catalysis. These methods allow for real-time observation of the creation of intermediates and products, as well as the disappearance of reactants during the catalytic process. One of the primary challenges in spectroscopic monitoring is distinguishing the subtle signals from transient intermediates amidst the overwhelming, time-independent signals from the catalyst and solvent, which can dominate the spectra. To address this, spectra that show the change in signal relative to the initial state are often used, enabling researchers to focus on the evolution of the catalyst's behavior and the intermediates' transformations.

Several spectroscopic techniques have gained significant traction in heterogeneous catalysis over the years, each offering unique insights into catalytic processes. As shown in Figure 7, the application of these methods has greatly advanced the understanding of catalytic centers and their interaction with reaction intermediates.

2.8.1. Electronic Spectroscopy (UV/Vis)

One of the most commonly used techniques to investigate catalytic systems is electronic spectroscopy, particularly ultraviolet-visible (UV/Vis) spectroscopy. This technique allows for the identification of the oxidation states of catalytic centers, which are typically transition metals, and can provide valuable information about the changes occurring in the catalyst's electronic structure during the reaction. However, UV/Vis spectroscopy has certain limitations, particularly its relatively low resolution, which

can make it challenging to discern small shifts in absorption bands corresponding to the transient intermediates of interest. Despite this, UV/Vis remains a useful method for monitoring broad catalytic behaviors, such as changes in the oxidation state of metal centers, and is often used in conjunction with other techniques to provide a comprehensive view of the catalytic process.

2.8.2. Vibrational Spectroscopy (IR and Raman)

Vibrational spectroscopy, including both infrared (IR) and Raman spectroscopy, plays a vital role in identifying and characterizing chemical intermediates on the catalyst surface. These techniques are particularly sensitive and are widely applied in the study of heterogeneous catalysis. Infrared (IR) spectroscopy, in particular, is highly favored due to its extraordinary sensitivity to changes in the chemical environment of molecules adsorbed on catalyst surfaces. IR spectroscopy can provide detailed information about the bonding and interactions of intermediates with the catalyst, including the identification of specific vibrational modes, which are affected by the adsorption and reaction processes.

Raman spectroscopy, another powerful vibrational technique, also contributes significantly to the understanding of catalytic processes. Unlike IR spectroscopy, Raman spectroscopy relies on the scattering of light, and it is especially useful for studying molecular vibrations that are not infrared active. When used together, IR and Raman spectroscopy offer complementary information about the intermediates formed during catalysis, providing insights into both the molecular structure and dynamics of these intermediates.

2.8.3. X-ray Absorption Spectroscopy (XAS)

In the past two decades, X-ray absorption spectroscopy (XAS), particularly Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, has developed into a highly effective tool for probing catalytic centers at the atomic level. One of the most significant advantages of XAS is its ability to provide direct, element-selective information about the local environment of catalytic centers, which are often metal atoms. EXAFS can measure distances to neighboring atoms and provide structural information about the catalytic site, including coordination numbers and bond lengths. This technique can probe distances up to approximately 0.5 nm, making it an invaluable tool for understanding the atomic-scale structure of catalysts during reactions.

Moreover, the X-ray absorption near-edge structure (XANES) region of XAS is particularly useful for determining the oxidation state of the metal centers. The details of the absorption edge and the spectral response provide insight into the oxidation states of the catalyst's transition metal centers and their changes during the reaction. This information is crucial for understanding how the metal

centers evolve during the catalytic cycle and how such changes influence the reaction pathway and the catalyst's overall performance.

2.8.4. Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR)

In addition to XAS, nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) spectroscopies are powerful tools for examining catalytic systems. NMR spectroscopy provides precise access to the nuclei of diamagnetic compounds and can be used to detect and identify chemical species present in the reaction medium. This is particularly useful for identifying reaction intermediates and understanding the nature of the bonds between the catalyst and the reacting molecules. EPR, on the other hand, is particularly useful for studying paramagnetic species, such as transition metal centers with unpaired electrons or radicals. EPR spectroscopy provides valuable information about the electronic structure of paramagnetic intermediates, making it a complementary technique to NMR in characterizing catalytic processes.

Both NMR and EPR are element-specific to a limited degree and can provide insights into the coordination environment of the catalytic sites, as well as the nature of the intermediates formed during catalysis. In the case of the methanol-to-olefin (MTO) process, NMR has been employed to study the carbon pools and the intermediate species involved in the reaction mechanism, shedding light on the intricate transformations that occur on the catalyst surface.

2.8.5. Application of Spectroscopic Techniques in Heterogeneous Catalysis

The combination of these various spectroscopic techniques provides a comprehensive toolkit for monitoring catalytic systems in real time. By using a combination of UV/Vis, IR, Raman, XAS, NMR, and EPR, researchers can track the behavior of catalytic centers and the evolution of reaction intermediates throughout the catalytic process. Each technique contributes unique insights into different aspects of the catalytic cycle, from the electronic structure of the catalyst to the molecular identity of intermediates.

For instance, the adsorption characteristics of reactants and intermediates can be investigated using IR spectroscopy. In a study involving benzene adsorption on a copper catalyst, it was found that the n13 in-plane vibrational mode of benzene, which shifts slightly upon adsorption on copper, could be distinguished from other adsorption sites. Furthermore, the shift in the thermal band of the OH group at 3610 cm-1 indicated adsorption on Brønsted acid sites. These spectral shifts provide insights into the nature of the catalyst's active sites and how they interact with reactants, which is critical for understanding the mechanism of catalysis.

However, quantifying the significance of an observed spectral feature requires careful comparison with other

factors, such as the loading of adsorbed precursors and the number of catalytic centers. For example, in the case of benzene adsorption, the extinction coefficient of the observed species does not change significantly upon adsorption, allowing for accurate quantification of the IR spectra and the use of literature values for comparison. This makes vibrational spectroscopy particularly useful for monitoring the concentration of intermediates and determining the efficiency of the catalyst in facilitating specific reactions.

Spectroscopic techniques, including UV/Vis, IR, Raman, XAS, NMR, and EPR, are essential tools for studying catalytic systems in real time. These methods provide critical insights into the structure and behavior of catalytic centers, the formation and transformation of reaction intermediates, and the overall reaction mechanism. By employing a combination of these techniques, researchers can unravel the complexities of catalytic processes and improve the design and efficiency of catalysts for various industrial applications. The ability to monitor catalysts at the atomic and molecular levels opens up new possibilities for advancing catalysis research and developing more efficient catalytic systems for energy production, environmental protection, and chemical manufacturing.

Figure 7, which illustrates various methods used to probe catalytic systems, highlights the growing importance of these spectroscopic techniques in advancing our understanding of catalysis and driving innovation in catalytic technology.

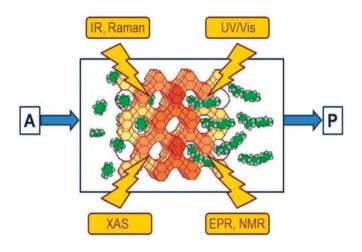


Fig. 7. Methods to shine light to blackbox of catalyst. Reprinted with permission from ref. [11], Roduner, E., 2014. Understanding catalysis. *Chemical Society Reviews*, 43(24), pp. 8226-8239. Copyright © Royal Society of Chemistry.

2.9. Catalysis for Commodity Chemicals

The use of catalysis dates back to early human civilization, though its mechanisms were not understood at the time. Fermentation processes were perhaps the earliest examples of catalytic activity, as humans unknowingly used it to produce items like ether, soap, cheese, sulfuric acid (vitriol oil), wine, and beer. These processes, which were fundamental to ancient cultures, laid the groundwork for more scientific exploration into catalysis and its potential in industrial applications. Over time, scientists sought to understand the chemical stimulation provided by catalysts and began investigating the underlying principles behind these processes.

In 1817, Sir Humphrey Davy made a crucial observation when he noted the rapid ignition of coal gas using oxygen and a platinum wire, marking the first documented example of heterogeneous catalytic oxidation. This marked a significant milestone in the field of catalysis, as it was one of the earliest instances where catalysis was not only observed but also utilized in a controlled setting. While Davy's observation was a key early moment in catalysis research, the fundamental principles and science of catalysis were not yet fully understood.

The field of catalysis expanded as various scientists, such as Berzelius Jons J., a Swedish chemist, began to define and explain catalytic processes. In 1836, Berzelius described catalysis as the acceleration of reactions by substances that do not change in the process. His description laid the foundation for the modern understanding of catalysis, and his work influenced many later researchers in the field, including Wilhelm Ostwald, who furthered the study of catalysis in the 1800s. Notably, Joseph Priestley, Johann Wolfgang Döbereiner, Louis Jacques Thenard, and others made important contributions to the study of catalytic materials, even though they did not necessarily formalize the concept of catalysis at the time.

By the mid-18th century, the industrial applications of catalysis began to take shape. John Roebuck, an English inventor, began manufacturing highly potent sulfuric acid in 1746 using a lead-lined chamber, which, although rudimentary, marked one of the first large-scale catalytic processes. This sulfuric acid production method, known as the Lead Chamber Process, laid the groundwork for later, more efficient methods of acid production. However, it was not until 1831 that a more cost-effective catalytic process was developed with the Contact Process, pioneered by Peregrine Phillips Jr., which used platinum as a catalyst to produce sulfuric acid in a much more controlled and efficient manner.

The Contact Process was a pivotal advancement in industrial catalysis, and the development of catalytic processes continued through the 19th century. In 1838, Frederick Kuhlmann filed a patent for the aerial oxidation of ammonia to nitric acid using platinum as a catalyst. This process was particularly significant for the production of fertilizers and explosives, and its widespread use was delayed until 1906 due to various scientific and geopolitical challenges. The commercialization of catalytic methods for large-scale chemical production became more widespread by the early 20th century.

The Deacon Process for chlorine production, introduced in 1875, used copper chloride (CuCl₂) as a catalyst for the oxidation of hydrochloric acid (HCl) with oxygen. While now obsolete, this process represented an important step in the development of industrial catalysis. Similarly, the introduction of vanadium oxide (V_2O_5) catalysts in 1875 greatly enhanced sulfuric acid production. As catalytic research advanced, more effective catalysts and processes were developed, leading to the commercialization of nitric acid production in 1904 with the introduction of platinum gauzes to oxidize ammonia.

In the early 20th century, catalytic processes underwent another transformative development with the large-scale synthesis of ammonia (NH₃) from nitrogen (N₂) and hydrogen (H₂) at BASF in 1910. This achievement marked a turning point in the production of fertilizers and had a profound impact on agriculture. The use of catalysts for the industrial synthesis of ammonia led to the development of the Haber-Bosch Process, which remains a cornerstone of modern fertilizer production.

In the 1920s, BASF also introduced a high-pressure methanol synthesis process using a zinc oxide-chromia catalyst. This technology signaled the beginning of the largescale production of organic compounds, which were previously limited by the availability of raw materials. The development of Fischer-Tropsch synthesis, commercialized in 1930, allowed for the production of synthetic fuels and was an essential alternative to the extraction of heavy oil. This breakthrough further exemplified the potential of catalytic processes to revolutionize the production of chemicals and fuels.

Throughout the 19th and early 20th centuries, the scientific understanding of catalysis remained limited, with many commercial catalytic processes developed without a solid grasp of concepts like equilibrium or high-pressure reaction conditions. Despite this, the industrial applications of catalysis grew, with major chemical companies such as Dow, General Electric (GE), DuPont, BASF, ICI, and Monsanto establishing research facilities in the 1940s to 1970s to advance catalytic technology.

Simultaneously, universities began to recognize the importance of catalysis research, and many established dedicated research institutes. The Max Planck Institutes in Germany, Boreskov Institute of Catalysis in Russia, and the Netherlands Institute of Catalysis Research (NIOK) became hubs for catalysis research. In the United States, national laboratories such as Oak Ridge, Sandia, and Hanford (now known as PNNL) provided a collaborative environment for government, business, and academia to develop new catalytic technologies. These institutions continue to play a pivotal role in advancing catalysis research.

The history of catalysis for commodity chemicals illustrates the interplay between scientific discovery and industrial application. As catalysts were developed and refined over time, they paved the way for the mass production of essential chemicals, fuels, and pharmaceuticals. The field of catalysis has continued to evolve, fueled by ongoing research in both academic and industrial sectors. With the support of national laboratories and research institutions, catalysis remains a driving force in the development of new technologies and materials that shape the modern world.

2.10. Individuals Lay the Foundation; Teams Drive Progress

At the dawn of the 20th century, individual scientists pioneered fundamental discoveries in catalysis before collaborating in teams to tackle the large-scale challenges of industrial catalyst development. Nicolas Clément, a professor at Paris's Conservatoire des Arts et Métiers, contributed to the development of the Lead Chamber process for sulfuric acid production. Wilhelm Ostwald, a renowned chemist in Latvia and Germany, made groundbreaking contributions to both electrochemistry and catalysis.

French chemist Paul Sabatier was instrumental in early studies on the role of finely divided metals in hydrogenating organic molecules. Meanwhile, Vladimir Ipatieff, a Russian aristocrat and chemistry instructor at the Mikhail Artillery Academy, later became a professor at the University of St. Petersburg. After immigrating to the United States, he held dual positions at Northwestern University and UOP, where he played a crucial role in the discovery of the promoter effect in 1909. His work on solid acid catalysts, particularly phosphoric acid, paved the way for paraffin alkylation by olefins in 1935. Ipatieff's pioneering research in polymerization, alkylation, and isomerization at UOP was instrumental in the development of high-octane aviation fuel.

Carl Bosch, working alongside Alwin Mittasch at BASF, was responsible for scaling up the ammonia synthesis process first developed by Fritz Haber at the Technische Hochschule of Karlsruhe. Their work on catalysts and process optimization represented a major breakthrough in industrial catalysis. Irving Langmuir, initially at Stevens Tech before joining General Electric in 1909, applied his expertise in surface chemistry to improve light bulb technology and advance catalytic principles. In 1915, he introduced the concept of heterogeneous catalysis occurring in a single layer of gas molecules adsorbed onto a solid surface, though this model was later refined.

2.10.1. The Rise of the Chemical Industry

As catalytic principles evolved, a thriving chemical industry emerged, driven by the need for efficient production of key inorganic compounds such as ammonia, nitric acid, and sulfuric acid. These bulk chemicals played a crucial role in agriculture as fertilizers and in wartime applications, particularly during World War I for explosives manufacturing. By 1907, catalysts were also being used in food processing, such as nickel-based catalysts for fat hydrogenation.

In the early 20th century, coal was the primary raw material for organic chemical production, supporting processes such as coal liquefaction, coal gas synthesis (CO/H₂), acetylene production, and coal tar distillation. Although oil drilling began in 1859, and early thermal cracking techniques were developed, the petrochemical industry only gained momentum with the increasing demand for gasoline. The advent of catalytic cracking, pioneered by

Eugène Houdry in the 1930s, marked a shift away from coalbased feedstocks to petroleum refining. This shift became even more pronounced during World War II with the introduction of the Fluid Catalytic Cracking (FCC) process, which was critical in producing high-octane aviation fuel.

The expansion of the petrochemical industry cemented catalysis as a cornerstone of modern chemical manufacturing, enabling the large-scale production of specialized chemicals, polymers, and pharmaceuticals that improved everyday life. While some catalytic advancements were the result of industrial teamwork, many transformative discoveries are credited to individual scientists.

Key catalytic milestones include the oxidation of aromatics and benzene to anhydrides over vanadium pentoxide (V₂O₅) in 1920, and the development of isopropanol—petroleum's first bulk chemical—by Standard Oil of New Jersey using acid catalysts. The 1930s saw the introduction of steam reforming for hydrogen production, while the oxidation of ethylene over silver/alumina in 1937 enabled ethylene oxide synthesis. In 1938, Otto Roelen discovered oxo synthesis while conducting coal research at the Kaiser Wilhelm Institute, marking the beginning of a major homogeneous catalysis process. An overview of the growing demand for heavy metals in industrial catalysis is illustrated in Figure 8 [53-55].

2.3. Symmetry and Asymmetry in Catalysis

2.3.1. Symmetry

Symmetry in molecular structures refers to the balance and self-similarity observed in a molecule's spatial arrangement. In organic chemistry, symmetry plays a crucial role in predicting molecular properties and behavior. Symmetry elements such as rotation axes, planes of symmetry, and inversion centers help define molecular symmetry, which is essential in spectroscopy and molecular characterization. Spectroscopic techniques such as nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy rely on symmetry constraints to interpret experimental data and determine molecular structures [56-59].

Beyond characterization, symmetry also plays a fundamental role in reaction mechanisms. The principles of molecular symmetry govern the selection rules for certain chemical reactions, particularly pericyclic reactions, allowing chemists to predict feasible reaction pathways. The Woodward–Hoffmann rules, for instance, use symmetry considerations to distinguish between allowed and forbidden reaction pathways in pericyclic reactions [60, 61].

2.3.2. Asymmetry

Asymmetry, or chirality, occurs when a molecule lacks symmetry and its mirror image cannot be superimposed onto itself. Chiral molecules exist as two non-superimposable mirror images called enantiomers. Chirality is a critical concept in organic chemistry due to its profound implications in biological systems, pharmaceuticals, and catalysis. Many biologically active compounds, including amino acids, sugars, and drugs, exhibit chirality.

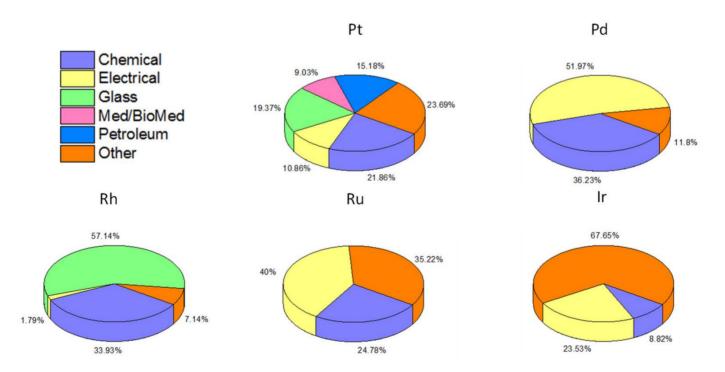


Fig. 8. Demand of heavy metals in industrial applications. Reprinted with permission from ref. [55], Hughes, A.E., Haque, N., Northey, S.A. and Giddey, S., 2021. Platinum group metals: A review of resources, production and usage with a focus on

catalysts. Resources, 10(9), p.93. Copyright © MDPI.

Often, enantiomers of the same molecule display significantly different biological activity. For example, one enantiomer of a drug may be therapeutically beneficial, while the other could be inactive or even harmful. Understanding and controlling chirality is therefore vital in drug design and development [62, 63].

Chirality also plays a crucial role in stereochemistry, where asymmetric carbon atoms (chiral centers) determine molecular configuration and reactivity. The threedimensional arrangement of substituents around a chiral center influences a molecule's interaction with biological targets and other chemical species. This stereochemical aspect is especially relevant in asymmetric synthesis, which aims to selectively produce one enantiomer over the other through chiral catalysis [64-66].

In chemical reactions, chirality affects selectivity and reactivity. Enzymes, as highly selective biological catalysts, often recognize and interact with specific enantiomers of substrates. This enantioselectivity is exploited in asymmetric synthesis, where chiral catalysts enable the selective formation of one enantiomer in preference to its mirror image [64-66].

2.3.3. Symmetric Materials

Materials with symmetrical properties exhibit uniform catalytic activity due to their isotropic nature. Such materials include metals and crystalline solids that provide consistent reaction sites for catalytic processes include:

Metals: Transition metals such as platinum, gold, and palladium are widely used as catalysts due to their high surface area and uniform reactivity. These materials facilitate a range of catalytic transformations, including hydrogenation, oxidation, and carbon-carbon bond formation [67].

Zeolites: Zeolites are microporous, crystalline aluminosilicates with a highly symmetrical structure. Their well-defined pore architecture makes them effective catalysts in processes such as isomerization and cracking, particularly in petrochemical applications [68].

2.3.4. Catalytic Properties of Symmetric Materials

Symmetric materials possess several advantages that contribute to their widespread use in catalysis. The large surface area of symmetric materials enhances molecular interactions, increasing reaction rates [69, 70]. The consistent electronic and structural environment ensures predictable catalytic performance across the material's surface [71]. Symmetric materials are often more stable under reaction conditions, reducing deactivation and extending catalyst lifespan [72].

2.3.5. Asymmetric Materials

Unlike symmetric materials, asymmetric materials exhibit varying properties depending on their orientation, leading to unique catalytic activity. These materials are often engineered to optimize their catalytic performance in selective reactions.

Chiral Catalysts: Enzymes and chiral metal complexes possess inherent asymmetry that enables enantioselective reactions. These catalysts play a crucial role in asymmetric synthesis by selectively producing one enantiomer over the other [73].

Graphene: Graphene, a two-dimensional material, exhibits asymmetric properties due to its layered structure. This characteristic makes it highly suitable for applications in fuel cells, sensors, and electronic devices [74, 75].

2.3.6. Catalytic Properties of Asymmetric Materials

Asymmetric materials offer specialized catalytic properties that make them valuable in selective transformations:

Enantioselectivity: Chiral catalysts enable the production of specific enantiomers, which is essential in pharmaceutical and fine chemical synthesis [76, 77].

Directional Reactivity: Asymmetric materials facilitate controlled reaction pathways, allowing for regioselective and stereoselective transformations [78-80].

Tunable Properties: The catalytic performance of asymmetric materials can be fine-tuned by modifying their structural and electronic properties, optimizing their efficiency for specific reactions [81].

2.3.7. The Role of Symmetry and Asymmetry in Chemistry

The principles of symmetry and asymmetry are fundamental in understanding the behavior and reactivity of chemical compounds. Asymmetry, particularly chirality, is crucial in biological and pharmaceutical sciences due to its impact on molecular interactions and activity. Many biologically relevant molecules, such as sugars, amino acids, and drugs, exhibit chirality, with their enantiomers often displaying distinct biological effects. This makes the study and control of chirality essential in drug development and biomolecular research [81, 82].

Chiral centers, or asymmetric carbon atoms, dictate the stereochemistry of molecules, influencing their physical properties and interactions with other compounds. The configuration of substituents around a chiral center determines molecular stability, reactivity, and binding affinity in biological and catalytic systems [81].

In chemical reactions, chirality significantly influences reaction selectivity. Enzymes, as nature's chiral catalysts, demonstrate high stereoselectivity, recognizing and reacting preferentially with specific enantiomers. This principle is leveraged in asymmetric synthesis, where chiral catalysts guide the selective formation of one enantiomer from achiral precursors [81, 83].

Conversely, molecular symmetry provides valuable

insights into chemical structure and reactivity. Symmetry elements such as rotation axes, inversion centers, and mirror planes help predict molecular behavior and interpret spectroscopic data. Techniques like IR and NMR spectroscopy rely on symmetry principles to clarify molecular structures and characterize compounds [84-86].

Moreover, symmetry considerations extend to reaction mechanisms. The symmetry of molecular orbitals influences reaction feasibility, as seen in pericyclic reactions governed by symmetry-based selection rules. Understanding these principles allows chemists to predict reaction pathways and design efficient synthetic strategies [84-86].

Symmetry and asymmetry are integral to molecular science, influencing everything from structural characterization to reaction dynamics and catalytic performance. Their impact spans diverse fields, including materials science, organic synthesis, and pharmaceutical development, highlighting their profound significance in advancing chemical research and technology.

2.4. Platinum Group Metals

The platinum group metals (PGMs) consist of six transition elements—rhodium, iridium, osmium, ruthenium, palladium, and platinum—found in Groups 8–10 (VIII) of the periodic table. These elements frequently occur together in nature due to their similar geochemical properties and are often extracted from the same mineral deposits [87-89]. They are known for their remarkable physical and chemical properties, such as resistance to oxidation, high melting points, and excellent catalytic activity.

Each subgroup within the PGMs exhibits unique yet overlapping characteristics. For example, platinum and palladium are highly ductile and form highly effective catalysts, making them essential in industrial applications such as automobile catalytic converters and hydrogenation reactions. In contrast, rhodium and iridium are exceptionally resistant to oxidation and chemical degradation, making them suitable for applications requiring high durability and corrosion resistance. Osmium and ruthenium, though less commonly used in mainstream industries, play critical roles in specific niche applications, such as electrical contacts, pen tips, and advanced electronics [90-92].

2.4.1. Historical Background and Early Uses

The historical use of platinum predates the Spanish colonization of South America. Archeological evidence suggests that pre-Columbian indigenous civilizations in Ecuador's Esmeraldas region utilized platinum for jewelry and artifacts. These civilizations developed rudimentary powder metallurgy techniques, combining minute platinum grains with gold dust and subjecting them to heat to create a homogeneous alloy composition. This early metallurgical advancement highlights the ingenuity of ancient craftsmen in manipulating platinum, despite its high melting point and

refractory nature [90-92].

Following the Spanish conquest, platinum was often considered an undesirable contaminant in gold and silver mining and was dismissed as "platina," meaning "small silver." However, interest in platinum's unique properties gradually grew, leading to the first documented shipments of platinum to England for scientific investigation in 1741. By the early 19th century, significant breakthroughs were made platinum refinement. William Hyde Wollaston in successfully developed commercial methods for producing malleable platinum, which enabled broader industrial applications. In the process, Wollaston also discovered three additional PGM elements-palladium, rhodium, and osmium-further expanding the knowledge and utility of this metal group. Additionally, research on platinum ores from the Ural Mountains led to the discovery of ruthenium in 1844, rounding out the modern understanding of the PGMs [90-92].

2.4.2. Technological Advancements and Industrial Applications

The development of electricity and telecommunications in the 19th and early 20th centuries saw increased utilization of platinum. Early electrical pioneers, including Michael Faraday and Humphry Davy, leveraged platinum's superior conductivity and resistance to oxidation in experiments related to electricity and electrochemistry. Platinum was integral in the development of early electrical technologies, including the thermionic switch, electric telegraph, and incandescent light bulbs. Its high resistance to corrosion made it an ideal material for critical components in ignition systems, including magneto contacts and igniter tubes in early internal combustion engines [56, 93-95].

Platinum's most significant modern applications lie in catalysis. It is widely used in petroleum refining, fuel cells, and environmental pollution control systems. In petroleum refining, platinum serves as a key component in catalytic reforming processes that improve fuel quality and efficiency. Platinum-based catalysts are also essential for hydrogen fuel cells, facilitating the electrochemical reactions necessary for sustainable energy production. In pollution control, platinum-containing catalytic converters in automobiles help reduce harmful emissions by converting carbon monoxide, hydrocarbons, and nitrogen oxides into less harmful substances [56, 93-95].

Beyond platinum, the other five PGMs have found diverse industrial applications. Palladium, for example, is extensively used in the electronics industry, particularly in multilayer ceramic capacitors (MLCCs) and connector coatings. It is also a key material in hydrogen storage and purification technologies. Rhodium, due to its exceptional ability to resist oxidation and high-temperature degradation, is used in high-performance thermocouples and corrosionresistant coatings. Iridium's hardness and corrosionresistance make it valuable in spark plugs, crucibles for hightemperature applications, and deep-space exploration instruments. Osmium, though less common, is used in specialized applications such as fountain pen tips and surgical implants due to its extreme hardness. Ruthenium is widely employed in the electronics sector, especially in hard disk drives and advanced microprocessors, due to its ability to improve electrical conductivity and data storage efficiency [56, 93-95].

2.4.3. Challenges and Sustainability Concerns

Despite their technological significance, PGMs pose several challenges regarding their extraction, availability, and environmental impact. These metals are rare in the Earth's crust, and their extraction requires complex and energy-intensive processes. South Africa, Russia, and Canada are the primary sources of PGMs, with South Africa alone accounting for over 70% of global platinum production. However, geopolitical factors, labor disputes, and environmental concerns have led to fluctuations in supply and pricing [90-92].

The environmental impact of PGM mining is another concern. The extraction and refining processes generate significant waste, including toxic byproducts such as sulfur dioxide and heavy metals. To address these concerns, industries are investing in recycling and recovery technologies to minimize reliance on primary mining. Solvent extraction methods, such as those detailed in Figure 9, have been developed to efficiently recover PGMs from spent catalysts, electronic waste, and industrial residues. These advancements help reduce environmental impact and promote the sustainable use of these valuable resources [96].

2.4.4. Future Prospects and Emerging Applications

As industries continue to advance, the demand for PGMs is expected to grow, particularly in the fields of green energy and sustainable technologies. Hydrogen fuel cells, which rely heavily on platinum and palladium catalysts, are being explored as viable alternatives to traditional fossil fuels. The shift toward electric vehicles (EVs) and renewable energy sources will likely drive innovations in PGM recycling and alternative catalytic materials. Additionally, the increasing use of PGMs in medical applications, such as cancer treatments and biomedical implants, highlights their potential for future scientific breakthroughs. Nanotechnology and materials science advancements are also exploring new ways to enhance PGM efficiency and develop cost-effective alternatives that maintain high catalytic performance while reducing dependence on these rare metals [56, 93-95].

The platinum group metals play an indispensable role in modern industry and technology, with applications spanning from catalysis and electronics to medical science. Despite challenges related to scarcity and environmental impact, ongoing research and advancements in recycling and alternative materials are paving the way for a more sustainable and efficient utilization of PGMs. Their continued importance in green energy solutions, medical advancements, and cutting-edge technologies ensures that these metals will remain crucial components of scientific and industrial progress in the coming decades.



Fig. 9. Usage of platinum group metals. Reprinted with permission from ref. [96], Pianowska, K., Kluczka, J., Benke, G., Goc, K., Malarz, J., Ochmański, M. and Leszczyńska-Sejda, K., 2023. Solvent extraction as a method of recovery and separation of platinum group metals. *Materials*, 16(13), p.4681. Copyright © MDPI.

3. PREPARATION OF SYMMETRICAL ORGANIC COMPOUND

3.1. Benzene catalytic preparation

A contemporary method for producing benzene is the dehydrocyclization of alkanes with a catalyst present. This approach is applicable to manufacturing in industries. Dehydrogenation and cyclization are catalytic processes that transform alkanes into benzene [84]. Platinum or rhenium based on alumina (AlO₃) or zeolites serve as typical catalytic for this type of reaction [84]. Additionally the mechanism consist of dehydrogenation: benzene is created by further dehydrogenating cyclohexane [84, 94, 97]. Typically, reaction is given below:

 $C_6H_{14} \rightarrow C_6H_{12} + 2H_2$ (1)

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2 \tag{2}$$

Overall reaction:

 $C_6H_{14} \rightarrow C_6H_6 + 4H_2 \tag{3}$

3.2. Benzene non catalytic preparation

The procedure of thermal cracking is the process of breaking down hydrocarbons, such as alkanes into smaller units, such a benzene by heating them to higher temperatures. Its procedure consist of alkanes are exposed to temperatures that are usually higher than 500 °C (932 °F) [11]. Decomposition: the alkanes and other hydrocarbons breakdown into tiny pieces due to the high temperature, especially benzene [84, 98]. Typically reaction can be expressed in equation form as given below:

$$C_nH_{2n+2} \rightarrow C_xH_v + C_zH_w + \text{others product}$$
 (4)

Thermal cracking of Hexane is given below:

 $C_6H_{14} \to C_6H_6 + C_2H_4 + 2C_2H_6 \tag{5}$

3.3. Ethylene catalytic preparation

The catalytic dehydrogenation of ethane (C_2H_6) can be used to prepare ethylene (C_2H_4) with platinum acting as a catalyst. The following is the representation of a reaction [93, 99]:

$$C_2H_6(Pt) \rightarrow C_2H_4 + H_2 \tag{6}$$

The procedure begins with the selection of feedstock, which in this case is ethane, typically obtained from the refinement of petroleum or natural gas. To accelerate the dehydrogenation process, a platinum-based catalyst is used. This catalyst is often supported by substances such as alumina (Al₂O₃) to enhance its stability and surface area. The reaction takes place under specific conditions. The temperature is maintained at high levels, usually between 500 and 600°C, to overcome the activation energy barrier. Additionally, the process is generally conducted at low pressures to promote ethylene production. One possible reaction mechanism involves the adsorption of ethane onto the platinum catalyst's surface, where dehydrogenation occurs. The platinum surface facilitates the breaking of ethane's C-H bonds and the formation of new bonds, leading to the release of hydrogen gas and the formation of ethylene. After the reaction, the ethylene and hydrogen mixture is cooled, and separation techniques such as membrane filtration or distillation are employed to isolate ethylene from hydrogen and any unreacted ethane [93, 99, 100].

3.4. Ethylene non catalytic preparation

Thermal cracking also referred to as pyrolysis, of hydrocarbons like ethane, naphtha or propane can provide ethylene (Figure 10). Without a catalyst this method involves subjecting the hydrocarbon feedstock to high temperature (usually 750-900°C). Hydrocarbons can disintegrate into lesser molecules such as ethylene due to the elevated temperature [99, 101, 102].

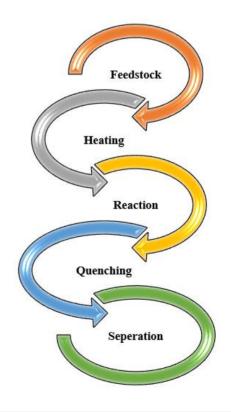


Fig. 10. Flow sheet of thermal Cracking of Ethylene.

Procedure outline consists of, Feedstock: heavy hydrocarbons like naphtha or lighter hydrocarbons like ethane or propane are utilized as raw materials. Heating: to reach the necessary bursting temperatures, the feedstock is quickly heated in a combustion chamber. Reaction: Ethylene, hydrogen, and other byproducts are produced when the heat forces the feedstock molecules to thermally decompose. Quenching: to halt other reactions and stabilize the intended products, the resulting mixing is quickly chilled or quenched. Separation: in order to isolate ethylene, its component undergo separation using techniques such as distillations [99, 101].

4. PREPARATION OF ASYMMETRICAL ORGANIC COMPOUND

4.1. Toluene catalytic preparation

The hydrogenation process of benzene is one of the ways that may be used to produce toluene. Under particular circumstances, benzene (C_6H_6) and hydrogen gas (H_2) are usually involved in the reaction when employing a platinum catalyst [103-105]. Generally, reaction can performed in equation form as:

$$C_6H_6 + H_2(Pt) \rightarrow C_6H_5CH_3 \tag{7}$$

The substance that reacts in the above process is benzene (C_6H_6) . The benzene ring is hydrogenated using hydrogen gas (H_2) . As a catalyst, platinum makes it easier for hydrogen atoms to join the aromatic ring. The product is toluene $(C_6H_5CH_3)$. To increase the platinum catalyst area of contact and activity, it frequently relies on substances like alumina (AIO_3) . For the reaction to continue effectively high temperatures and pressure are usually needed [103].

4.2. Toluene non catalytic preparation

A variety of industrial procedures are often used to manufacture toluene an aromatic hydrocarbon. One technique is the distillation of crude oil which includes toluene or the petroleum product naphtha's catalytic reformation. Although a catalyst is not always needed for the process toluene can be separated from various hydrocarbons using purifying and separation techniques such as fractional distillation [103].

4.3. Lactic Acid (2-Hydroxypropanoic acid) catalytic preparation

When glycerol is converted to lactic acid in a water solution with a base present and at a temperature of 230 °C, palladium and platinum based catalyst seated on activated carbon are effective catalysts. Glycerol first undergoes oxidative dehydrogenation to produce glyceraldehyde as part of the reaction pathway. Under normal circumstances glyceraldehyde and dihydroxyacetone are in balance. It is generally accepted that in alkaline environments, trioses such as glyceraldehyde and dihydroxyacetone reorganize into lactic acid (Figure 11) [104-108].

4.4. Lactic Acid (2-Hydroxypropanoic acid) non catalytic preparation

Nowadays over 90% of commercially available LA is produced using an aerobic fermentation process, which has advantages including low manufacturing temperatures, cheap energy costs, and excellent purity when using the right strain as shown in (Figure 12) [109-112]. Anaerobic fermentation, acidulation, purification and separation of LA and processing of feedstocks are the four basic processes that are typically conducted for the manufacture of LA by conventional fermentation when beginning with biomass that is cellulosic. The primary drawbacks however must be addressed. These include limited productivity, the demand for expensive enzymes (which have precise temperature and PH restrictions), and the difficulty of separation and purification. Since chemocatalysisis a viable alternative approach that might be considered a hotspot in the cutting edge advancement of LA research it is vital to address sustainability problems with upscaling of the current fermentation process [113].

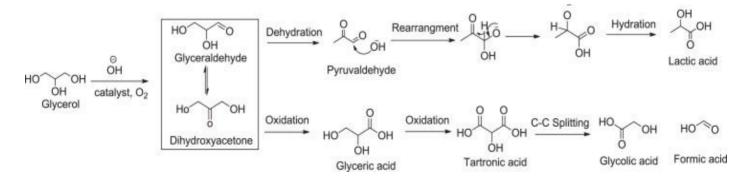


Fig. 11. Conversion of glycerol to lactic acid. Reprinted with permission from ref. [109], Purushothaman, R.K.P., Van Haveren, J., Van Es, D.S., Melián-Cabrera, I., Meeldijk, J.D. and Heeres, H.J., 2014. An efficient one pot conversion of glycerol to lactic acid using bimetallic gold-platinum catalysts on a nanocrystalline CeO₂ support. *Applied Catalysis B: Environmental*, 147, pp.92-100. Copyright © Elsevier.

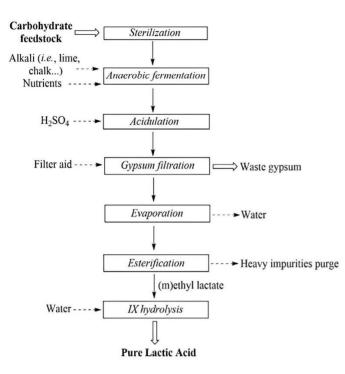


Fig. 12. Lactic acid production through anaerobic fermentation method. Reprinted with permission from ref. [113], Zhang, H., Li, H. and Yang, S., 2020. Lactic acid/lactates production from biomass over chemocatalytic strategies. *Biomass, Biofuels, Biochemicals*, pp.227-257. Copyright © Elsevier.

5. PLATINUM GROUP METALS – CATALYTIC PROPERTIES

The platinum group metals (PGMs) consist of six elements rhodium, iridium, osmium, ruthenium, palladium, and platinum—found in Groups 8-10 (VIII) of the periodic table. These elements are frequently located together in nature and share several chemical and physical characteristics. Each triad of the PGMs exhibits specific similarities; for example, platinum and palladium are both highly ductile metals with exceptional catalytic efficiency. Meanwhile, iridium and rhodium possess outstanding resistance to oxidation and chemical degradation, making them highly durable [114].

The catalytic properties of PGMs, particularly palladium and platinum, make them indispensable in various chemical reactions, including oxidation, hydrogenation, isomerization, and carbon-carbon bond formation. A crucial determinant of catalytic activity is the heat of adsorption, which refers to the strength of interaction between a reactant and a catalyst surface. If the reactant binds too strongly to the catalyst, it will not participate in subsequent reactions. Conversely, if it is bound too weakly, it may desorb before undergoing a reaction. Efficient catalysts operate within an optimal range where reactants interact with the surface without being either permanently immobilized or prematurely released. Platinum is unique in that it can adsorb a diverse range of compounds with moderate strength, including nitrogen compounds, oxygenated compounds (such as imines, oximes, hydrazones, esters, anhydrides, aldehydes, ketones, and acids), sulfur dioxide, ammonia, oxygen, hydrogen, carbon monoxide, and unsaturated hydrocarbons. However, methane exhibits weak adsorption on platinum, necessitating the addition of other metals to enhance its catalytic efficiency in methane combustion.

The catalytic properties of PGMs have been widely exploited in industries such as petrochemical refining, chemical manufacturing, and automotive exhaust treatment. Their ability to facilitate reactions under mild conditions while maintaining stability makes them valuable for industrial applications [114, 115].

5.1. Economic Aspects

In 2009, global platinum consumption in the automotive catalyst industry declined to 69,400 kg. This was largely due to a shift toward smaller gasoline-powered vehicles, which utilize more palladium in their catalytic converters. The market share of light-duty diesel vehicles in Europe decreased to 46%, further reducing the demand for platinum. Additionally, stricter emissions regulations led to reduced vehicle sales in North America. Japan. and other regions. contributing to a decline in platinum use for automotive applications. However, the demand for platinum jewelry surged due to a sharp drop in prices. China remained the largest consumer in this sector, accounting for 64,700 kg or approximately 69% of global consumption. The downturn in global industrial activity also affected platinum use in the chemical sector, where consumption dropped to 9,180 kg as a result of decreased chemical production. Despite fluctuations in demand, the rarity and complexity of PGM extraction and refinement continue to sustain their high economic value [116, 117].

5.2. Environmental Concerns

The impact of PGMs on the environment has been the subject of increasing research. While no uniform regulatory framework exists, much of the focus has been on pollution arising from automotive catalytic converters. Estimates suggest that platinum emissions from these converters range from 0.01 to 6 mg per kilometer. Over the course of a vehicle's lifespan (approximately 160,000 km), around 5% of the catalyst's platinum content—equivalent to about 1 mg/km—may be lost due to wear and tear.

To contextualize this figure, a vehicle running on leaded gasoline emits over 14,000 mg of lead per kilometer. While platinum emissions are detectable, airborne concentrations remain significantly lower than occupational exposure limits. However, platinum also enters the environment through pharmaceutical applications, particularly in chemotherapy drugs. Trace amounts of platinum have been observed in wastewater from cancer treatment facilities. Additionally, industrial processes such as nitric acid production can contribute to platinum contamination. Cosmic dust and meteorites also introduce platinum into the Earth's atmosphere, albeit at negligible levels compared to anthropogenic sources [116, 117].

5.3. Uses of PGMs

The primary application of PGMs is in catalytic converters used in the automotive industry, where platinum, palladium, and rhodium help reduce vehicle emissions. Platinum and palladium are widely used in fine jewelry due to their luster, corrosion resistance, and hypoallergenic properties. PGMs are also found in electrical contacts, capacitors, and hard disk drives due to their excellent conductivity and durability. PGMs are used in crucibles and other equipment for producing high-purity glass. In addition, platinum is employed in anticancer drugs (such as cisplatin) and biomedical implants. Platinum coatings protect turbine blades in jet engines from high-temperature oxidation. Furthermore, platinum is also traded in the form of coins and small bars [118].

5.4. Catalytic Applications

PGMs play a crucial role as catalysts in numerous chemical processes, including oxidation, hydrogenation, dehydrogenation, isomerization, cyclization, and carboncarbon bond formation. The choice between a PGM catalyst and a base metal catalyst is typically guided by economic factors, with PGMs preferred for their superior efficiency and selectivity. A major objective in catalyst development is to enhance activity and selectivity while minimizing energy consumption. Lower reaction temperatures and pressures not only improve efficiency but also reduce capital costs [119-129].

5.4. Advantages and Disadvantages of PGM Catalysts

PGM catalysts offer several advantages. They enable reactions to occur under milder conditions, reducing operational costs. They are highly active and selective, often outperforming base metal catalysts. They are non-toxic and safe to handle. They can be recovered and recycled with efficiency rates of 98-99%, making waste management more sustainable. However, PGM catalysts also have drawbacks such as they are expensive due to their rarity and complex extraction processes. They are sometimes susceptible to poisoning, which can reduce their catalytic efficiency. In certain cases, their high activity makes them more prone to deactivation. To address these challenges, extensive research is conducted to optimize catalyst formulations, including the use of alloyed PGMs and novel support materials [130-136].

5.5. Catalysis in the Chemical Industry

Platinum is the most widely used PGM in the chemical industry. It is essential for large-scale processes such as nitric acid production, silicone manufacturing, and petroleum refining. The chemical sector accounts for approximately 40% of global ruthenium consumption and 30% of iridium usage. Palladium is commonly employed in acetaldehyde and hydrogen peroxide production, as well as in hydrogenation reactions. Its ability to facilitate selective transformations makes it a key catalyst in fine chemical synthesis [137-143]. PGMs play a pivotal role in modern industry, with their catalytic properties driving innovation in automotive, chemical, and environmental applications. While their economic and environmental implications require careful management, their unparalleled efficiency ensures their continued relevance in technological advancements.

6. FUTURE DIRECTIONS

As our understanding of catalytic processes continues to evolve, the development of high-performance catalysts is becoming increasingly precise. Advances in computational chemistry, machine learning, and real-time characterization techniques have allowed researchers to design catalysts with enhanced efficiency, selectivity, and durability. These developments are particularly critical in addressing the growing demand for sustainable and environmentally friendly catalytic processes.

One of the major areas of future research is the transition toward renewable feedstocks and greener catalytic methods. The increasing reliance on fossil fuels for chemical production and energy generation poses significant environmental challenges. By incorporating renewable resources—such as biomass, carbon dioxide, and hydrogen—into catalytic processes, industries can reduce carbon footprints and shift towards more sustainable production methods. Additionally, researchers are exploring ways to minimize or completely eliminate hazardous byproducts from catalytic reactions, improving overall environmental safety [142].

A key challenge in catalysis research is the high cost and limited availability of platinum group metals (PGMs). Future developments will focus on finding cost-effective alternatives or optimizing the efficiency of existing PGMbased catalysts. One promising avenue is the design of bimetallic or alloy catalysts, where PGMs are combined with earth-abundant metals such as iron, cobalt, and nickel to reduce metal dependency while maintaining catalytic efficiency. Another exciting area is single-atom catalysis, where individual metal atoms are dispersed on a support material, maximizing surface area and reactivity while significantly reducing metal consumption.

Nanotechnology and catalyst engineering are also expected to play a crucial role in advancing catalytic processes. The development of core-shell nanostructures, porous materials, and engineered surfaces will enable more efficient and selective catalytic reactions. Additionally, electrocatalysis and photocatalysis are gaining momentum, particularly in applications such as hydrogen production, fuel cells, and carbon dioxide reduction. These technologies could revolutionize the energy sector by providing cleaner and more efficient alternatives to conventional fossil-fuelbased methods.

The industrial demand for novel catalytic processes continues to drive innovation in this field. Competition and market pressures have historically accelerated catalytic advancements, and this trend is expected to continue. The ultimate goal for future catalysis is to develop cost-effective, highly efficient, and environmentally sustainable catalysts that can be applied across various industries, from petrochemicals and pharmaceuticals to renewable energy and environmental remediation [143].

7. CONCLUSION

The use of platinum catalysts in chemical processes has demonstrated remarkable versatility, particularly in the synthesis of both asymmetrical and symmetrical organic compounds such as benzene, toluene, ethylene, and lactic acid. This highlights the significant role of platinum group metals (PGMs) in facilitating various catalytic reactions, including carbon-carbon bond formation, oxidation, isomerization, and hydrogenation. While platinum is widely recognized for its catalytic efficiency, it is also important to acknowledge that these compounds can be synthesized through alternative strategies, such as thermal cracking and non-catalytic processes. However, PGMs remain invaluable enhancing reaction efficiency, selectivity, and in sustainability.

One of the key properties that make platinum unique among PGMs is its ability to adsorb a wide range of compounds with moderate binding strength, allowing it to effectively catalyze numerous chemical reactions. Unlike some catalysts that bind reactants too strongly—hindering reaction progress—or too weakly—failing to facilitate meaningful interactions—platinum achieves an optimal balance, making it an essential material in both industrial and environmental applications.

The study of PGMs extends beyond their catalytic performance, encompassing economic and environmental considerations. The high cost and scarcity of these metals pose significant challenges for widespread industrial applications. As demand for sustainable and cost-effective catalytic solutions increases, researchers are exploring alternative catalyst materials, improved recycling methods, and novel catalyst designs to minimize reliance on PGMs while maintaining high catalytic efficiency.

Moreover, the environmental impact of PGMs, particularly in the form of pollutants from catalytic converters and industrial waste, necessitates the development of greener catalytic processes. With advancements in materials science and nanotechnology, researchers aim to enhance catalyst stability, improve reaction selectivity, and reduce overall waste production. Future innovations in heterogeneous catalysis, electrocatalysis, and photocatalysis will play a crucial role in addressing these challenges and advancing sustainable chemical manufacturing.

PGMs, particularly platinum, continue to be indispensable in modern catalysis due to their unique properties and broad applicability. However, the future of catalysis will likely involve a combination of optimizing PGM usage, developing cost-effective alternatives, and integrating catalysts into environmentally friendly processes. The continued pursuit of innovative catalytic technologies will ensure that chemical industries remain efficient, economically viable, and sustainable in the long run.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

All authors contributed equally in the preparation of this manuscript.

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