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Heterogeneous Catalysis

1.1 What is Heterogeneous Catalysis?

The phenomenon of catalysis applies to a wide range of chemical reactions. By using a catalyst, chemical reactions that are non-selective can be made selective and those that require a high temperature can be conducted at a lower temperature (see Figure 1.1). In this and the next chapter, we will describe the discovery of this phenomenon in the nineteenth century, the understanding of catalysis that followed, and the main chemical industrial processes that developed in the twentieth century.

There are many chemical compounds that show catalytic action. In this book, we will mainly discuss heterogeneous catalysts. These are solid materials that are positioned in a reactor where they are exposed to reacting gasses or liquids. The reagents flow over the catalyst and are converted by it into products. These products and the unconverted reagents are continuously removed from the reactor, while the catalyst remains in the reactor and becomes exposed to fresh reactants. This continuous process operation is possible because the catalyst is in a separate phase.

We will focus primarily on inorganic materials, which were also the main focus of the early exploratory catalytic studies. When the molecular principles of heterogeneous catalyst activity were gradually understood, it became apparent that similarities exist between biochemical enzymatic processes and molecular organometallic catalysts. The knowledge of the molecular chemistry of the catalytic action of enzymes in biochemical systems as well as information about the action of molecular organic and metal–organic complexes has been of great importance to the further development of the molecular scientific basis of heterogeneous catalytic systems discussed later in this book.

Heterogeneous inorganic catalysts are often quite robust, which makes them especially useful for chemical reactions that operate under hostile conditions.

A specific advantage of the heterogeneous catalyst is that it can be used in a continuous process operation, instead of in a batch-type process where it must be separated in an individual step from the reaction product. Continuous process operation made the development of the large-scale chemical process industry possible once heterogeneous catalysis was discovered early in the previous

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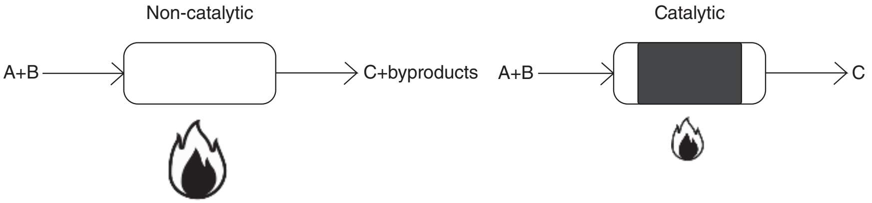

Figure 1.1 Non-catalytic versus catalytic processes. Non-catalytic processes are usually non-selective and require a high temperature of reaction. Catalytic processes are selective and can be conducted at lower temperatures. They save energy, reduce waste, and produce materials that are otherwise not available.

century. Heterogeneous catalysis has become basic to more than 80% of current bulk chemical processes used in the chemical and petrochemical industries [1].

The modern science of heterogeneous catalytic chemistry developed as the understanding of its chemical basis at a molecular level increased. The current understanding of the catalytic reaction mechanism at the physical and chemical levels and its relation to the structure and composition of heterogeneous catalysts is based to a large extent on the computational catalytic results obtained during the past decades. The ultimate aim of catalysis science is to predict the proper catalytic material for a given chemical conversion reaction. This is still far off due to the complexity of experimental catalytic systems, but the large body of empirical chemical information currently available about the reactivity of different catalytic materials is helpful. Computational methods provide tools for estimating the rate and selectivity of a catalytic reaction as a function of catalyst composition. In addition to spectroscopic characterization of a catalyst, this has become indispensable for research.

In this chapter, we will describe the discovery of the basic principles of heterogeneous catalysis. The next chapters will provide an introduction to current catalytic processes, followed by chapters on the principles of physical chemistry and inorganic chemistry of heterogeneous catalysis that are the basis of modern catalysis science.

The discovery of quantum mechanics provided the chemical sciences a predictive foundation, which led to the development of computational catalysis. Combined with the application of advanced spectroscopic techniques and advances in material synthesis, this discovery has provided the molecular foundation of heterogeneous catalysis that is the main topic of part II of this book.

1.2 Early Developments

In its infancy, the science of chemistry was highly exploratory and focused primarily on the categorization of chemical materials and their properties. Heterogeneous catalysis science started in that early period of modern chemistry, before the understanding of the molecular nature of matter. It has its origin in the early part of the nineteenth century, after the founding of modern chemistry by

Lavoisier and colleagues at the end of the eighteenth century. They introduced the law of conservation of mass, and with it an accurate understanding of the nature of oxygen. This knowledge sparked the development of the significant heterogeneous catalytic oxidation processes of the nineteenth century.

The discovery by Davy and Döbereiner of catalytic oxidation contributed to the earlier recognition by Berzelius of catalysis as a separate phenomenon, and to the development of two important heterogeneous catalytic processes: oxidation of HCl to produce chlorine and oxidation of SO_2 to yield oleum, a highly concentrated sulfuric acid.

A second period at the end of the nineteenth century was marked by the development of chemical thermodynamics, which aided in the definition of catalysis by Ostwald and provided its physical chemical foundation. During this period, the rise of coal gasification for domestic lighting and heating made hydrogen readily available. This allowed Sabatier's discovery of catalytic hydrogenation to develop into a practical technology.

Sabatier also discovered an important law of catalysis that defines the condition of maximum activity of a catalyst. The three catalysis laws of Berzelius, Ostwald, and Sabatier are the main topics of this chapter.

This chapter closes with the invention of the Haber–Bosch ammonia synthesis process that is the culminating technological success of this period. As the source for artificial fertilizer, it made a significant impact on the world's growing need for fertilizers. It contributed to chemical technology by creating the continuous heterogeneous catalytic process, which can be operated at high pressure. The development of this process provided the basis for many other modern heterogeneous catalytic processes.

1.2.1 Early Nineteenth Century Discoveries

The early discoveries of heterogeneous catalytic reactions were concurrent with electrocatalytic exploration, which significantly improved the understanding of catalytic reactivity [2]. We will occasionally refer back to this parallel development in the physical chemistry of heterogeneous catalysis and electrocatalysis.

It took some time to recognize the chemical nature of the effect of metals on decomposition reactions as displayed by the decomposition of ammonia or alcohols. These were previously attributed to the effect of heat or electrochemical action, as the latter had been demonstrated in the electrolysis of water [3–5]. A crucial observation by H. Davy was published in 1817. During the course of his studies on the miner's safety lamp, he discovered that a Pt wire remained hot in the presence of coal gas and air. In this experiment, the flame heating the wire was extinguished by exposure to gas enriched with coal gas that is essentially methane. He concluded that the Pt wire assisted in the burning of the gas by air without a flame [3, 6]. In 1823, Döbereiner, another famous chemist from that age, discovered that Pt sponge would react at room temperature with hydrogen to produce a flame. As previously shown by Thénard in the decomposition of ammonia, the effect is material-dependent and could only be observed for particular metals [7].

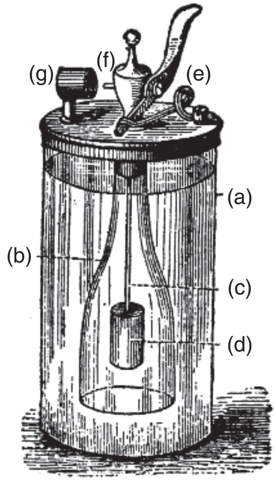

Figure 1.2 An early design of Döbereiner's lamp. This lamp contains hydrogen gas that is ignited using platinum as a catalyst. In a bottle filled with sulfuric acid, zinc metal (e) reacts with sulfuric acid to produce hydrogen gas. $Zn + H_2SO_4 \rightarrow Zn^{2+} + SO_4^{2-} + H_2$. When the stopcock (e) is opened, the hydrogen is directed by a thin tube onto a platinum sponge (g), and then a flame lights instantaneously. The flame goes out when the stopcock is closed. Hydrogen production ceases as gas pressure builds. (a) Glass cylinder, (b) open bottle, (c) wire, (d) zinc, (e) stopcock, (f) nozzle, (g) platinum sponge [7, 8].

Based on his discovery, Döbereiner designed a lamp (Figure 1.2) that generates a flame. The hydrogen is produced by the reaction of sulfuric acid with zinc, which over time is converted into $ZnSO_4$. This lamp became widely used in industry and even in households, until it was replaced by matches and other lighters. Döbereiner's invention can be considered a first practical application of catalysis [7].

Twenty years after Davy's initial experiment, the electro-catalytic analogue of the Döbereiner reaction was discovered by Grove who designed a fuel cell in 1839. Grove ultimately proved that electrical energy, instead of heat, could be produced from an electrochemical reaction between hydrogen and oxygen over a platinum electrode. He called his device a gas voltaic battery. Electricity was stored by the electrochemical decomposition of water and released by the reaction of the products with platinum (Figure 1.3).

The fuel cell is currently attracting renewed interest as a source of electrical energy in the context of a hydrogen-based energy economy, in combination with electricity produced by the electrolysis of water and generated by renewable energy sources such as wind or solar.

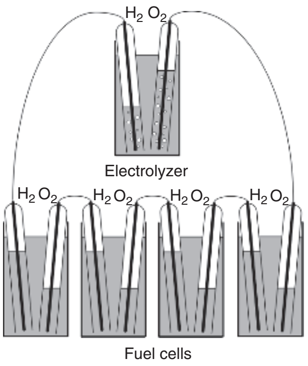

Figure 1.3 Grove cells (gas voltaic battery). This fuel cell consists of five sealed containers (cells) charged with hydrogen (H) and oxygen (O), connected by a voltmeter. Two platinum electrodes each have one end immersed in a container of sulfuric acid and the other end connected to a hydrogen–oxygen cell. The constant flow of energy between the electrodes causes the water level to rise in the cells holding the water and gases [1, 9, 10].

Several other important heterogeneous catalytic reactions were discovered during this same period. The discovery of catalytic oxidation of ammonia to nitrous oxides over Pt by Kuhlmann in 1838 was critical for the development of the ammonia-based fertilizer industry half a century later [3, 6, 11, 12].

Since the Middle Ages, the production of sulfuric acid by burning sulfur was widespread because of its use as an agent to prepare wool for dying. A major innovation in this process was introduced in the eighteenth century. The Lead Chamber Process [13, 14] oxidizes SO_2 to SO_3 by NO_2 yielding NO, which is then re-oxidized by air to NO_2. In this process, NO is the homogeneous gas phase catalyst that drew the attention of Davys and Berzelius.

1.2.2 Later Nineteenth Century Discoveries

At the end of the nineteenth century, the developing synthetic organic dye industry required oleum (fuming sulfuric acid) of substantially higher concentration than the product of the lead chamber process. In 1875, Messel developed the contact process based on the use of Pt as a catalyst, which was later replaced by vanadium oxide [13, 14]. The vanadium-based process is more stable since unlike Pt, vanadium oxide is not deactivated by the arsenic present in the sulfur.

The other large-scale oxidation process that developed during the same period was the catalytic Deacon process (1868) that oxidizes HCl to chlorine. It replaced the commonly used stoichiometric oxidation process by MnO_2. This is an early example of replacing a stoichiometric reaction that consumes expensive chemicals and produces harmful waste with an environmentally friendly catalytic reaction [15–19].

Chloric acid is a co-product of the soda production process. Chlorine is converted with hydroxide into hypochlorite, which is a bleaching chemical. The Deacon process was based on a Cu catalyst of CuO and $CuCl_2$ that reacts to produce a chlorine. The process had several drawbacks, such as the lack of stability of the catalyst under harsh reaction conditions and insufficient activity [20, 21]. This process has been replaced by the electrocatalytic production of chlorine that was discovered in 1800 and developed into a commercial process by Griesheim in 1888. Initially, Fe or graphite electrodes were used, but modern large-scale electrochemical chlorine production facilities use mercury as the cathode and TiO_2 as the anode materials respectively.

Alternative improved catalysts were developed for the Deacon process only recently in the last decade of the twentieth century. RuO_2-based catalysts have been developed by Sumitomo and Bayer showing outstanding stability and activity while producing Cl_2 of high chemical purity [20–22].

1.3 The Three Basic Laws of Catalysis

1.3.1 Berzelius' Catalysis Law

In 1835, Berzelius summarized the chemical reactivity phenomena that he recognized as catalytic for chemical systems: the acid-enhanced conversion of starch into sugar, the oxidation of SO_2 assisted by NO in the lead chamber process, and the many observations of oxidation reactions made possible only by contact with particular materials. He generalized his observation in the following sentences [5, 11, 23, 24]:

> Substances, both simple and compound, in solid form as well as in solution, have the property of exerting an effect on compound bodies, which is quite different from ordinary chemical affinity, in that they promote the conversion of the component parts of the body they influence into other states, without necessarily participating in the process with their own component parts; the body effecting the change does not take part in the reaction and remains unaltered through the reaction.

The definition of a catalyst by Berzelius as a material that enhances a chemical reaction, but itself remains unchanged by reaction, became readily accepted [5, 11, 23, 24]. He proposed the term "catalysis" derived from the Greek words "kata" meaning down and "lyein" meaning loosen. He understood catalysis as the decomposition of a substance by a mysterious force induced by contact with the catalytically active material. Later in 1843, he mentions: "The catalytic force manifests itself by the excitation of the electrical relations that have so far evaded our researches" [3, 4] (Figure 1.4).

This was not an unreasonable suggestion in view of the frequently observed relationship between chemical reactivity and electrochemical activity. Its elucidation had to wait for the next century, once the proper nature of atoms and molecules became understood.

This theory created a great controversy between those who attributed catalysis to a physical force like Ostwald's thermodynamics law, and those who proposed that the interaction was chemical, as was the view of the inorganic chemist Sabatier. In fact, the catalysis laws of Ostwald and of Sabatier essentially complement each other.

Both Ostwald and Sabatier are Nobel laureates that received awards for their contributions to catalysis. Ostwald was awarded for his work on catalysis and fundamental principles governing equilibria in kinetics in 1909, and Sabatier for his work on hydrogenation of organic molecules by finely dispersed metal particles in 1912 [1, 6, 25, 26].

1.3.2 Ostwald's Catalysis Law

Ostwald is the founder of physical chemistry. His main interest was to formulate the chemical laws that regulate chemical transformations. He defined catalysis

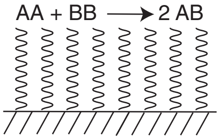

Figure 1.4 Catalytic force as defined by Berzelius. A catalyst influences the course of a reaction, but is not changed by it.

in chemical thermodynamics terms: the catalyst does not alter the equilibrium between the reaction and product molecules, but it enhances or suppresses the rate of their reaction [1, 6, 24, 27, 28].

This so-called Ostwald catalysis law was a breakthrough in catalysis science, because thermodynamics predicts the conditions required by a reaction and provides an essential scientific basis to catalytic investigation. This innovative application of the science of chemical thermodynamics enables selection of the process conditions for reactor experiments to test catalytic materials.

The selection of an appropriate catalyst material could not be determined by prediction and thus required empirical investigation. It is with this strategy that the ammonia synthesis process was discovered (see Insert 1). The process required the discovery of catalytic hydrogenation, the subject of Sabatier's Nobel award.

The two basic physical chemical relationships that were known at that time to govern the rate and equilibrium of a catalytic reaction were the van Hoff equation for the equilibrium constant K_{eq} (Eq. (1.1)) (with ΔG° the Gibbs free energy at standard conditions, R gas constant, and T temperature):

$$K_{\mathrm{eq}} = e^{\left(-\frac{\Delta G^\circ}{RT}\right)} \tag{1.1}$$

and r_A, the Arrhenius reaction rate expression (Eq. (1.2)) (with A the pre-exponential factor, and E the activation energy)

$$r_A = Ae^{\left(-\frac{E}{RT}\right)} \tag{1.2}$$

The constants in the Arrhenius rate expression are dependent on catalyst material and had to be empirically determined, as there was no method available to deduce them using thermodynamics. It was known that the most active catalyst would have a lower Arrhenius activation energy, leading to the general understanding that a catalyst decreases the activation energy of a reaction. The Sabatier principle to be discussed next makes clear that this activation energy is the result of the interplay within the complex reaction network on the catalyst surface.

The character of this relationship within specific catalytic systems is an important topic of this book. As we will describe in the later chapters, a major theoretical advance made at the end of the last century was the development of techniques used to relate the kinetic parameters of the elementary reactions within the catalytic reaction network to the thermodynamic data of the corresponding reaction intermediates.

At the time of the invention of the Haber–Bosch ammonia synthesis process, only the thermodynamics of the overall reaction could be determined. This data, combined with a measurement of the overall reaction rate of the catalytic reaction (which is catalyst-dependent), was used to determine the optimum reaction condition for the process [11, 14, 25].

Insert 1: The Haber–Bosch Ammonia Synthesis Process: The Haber and Nernst Controversy

Haber and Nernst disagreed initially on the proper conditions for ammonia synthesis from nitrogen and hydrogen. Nernst disagreed on Haber's data obtained at atmospheric conditions and concluded that the endothermic reaction can be conducted at higher pressures. However, improved data from Haber indicated that the exothermic reaction ($\Delta H = -92\ \text{kJ mol}^{-1}$) should produce an acceptable yield at a pressure of 200 atmosphere a temperature of around 800 K. He identified Os and Ru as proper catalysts.

The process was purchased by the German company BASF and a commercial plant started in 1913. Carl Bosch solved the substantial engineering problems of the process, such as the required use of high pressures. Nearly 20 000 tests were conducted with reactors designed by Bosch before the optimum, economic catalyst formulation was found. The catalyst was a complex composition of Fe promoted with potassium oxide and alumina. The mechanism and operation of this catalyst only became understood after a 100 years, aided by the studies of Ertl!

This process was integrated in the production of hydrogen from coal and in the selective oxidation of ammonia which became the Ostwald process of high-temperature catalytic oxidation of NH_3.

These revolutionary scientific discoveries were recognized by Nobel awards to all four of these scientists.

Ostwald believed that a catalyst did not induce a reaction, but rather accelerated it without formation of an intermediate. He theorized that catalyzed gas reactions resulted from the absorption of gases in the cavities of the porous metal where compression and local temperature elevation led to chemical combination.

1.3.3 Sabatier's Catalysis Law

Ostwald's view of chemistry of the working catalyst was rejected by Sabatier. He studied reactions such as the hydrogenation of ethylene to ethane and the conversion of CO_2 to methane through the use of transition metal powders, prepared by reducing their corresponding oxides. Based on these studies, Sabatier formulated a chemical theory of catalysis that involves the formation of unstable chemical compounds as intermediates. These determine the product selectivity and the rate of the catalytic reaction. He assumed that a hydrogenation reaction catalyzed by Ni involved various nickel hydrides with concentrations that relate to the reactivity of the nickel [6]. He argued that the formation and decomposition of intermediate compounds formed between reagent and catalyst corresponded to a lowering of the Gibbs energy of the system. This view is completely validated by modern molecular insights into the action of a catalyst [29].

Sabatier's law can be considered the third basic law of catalysis [1, 6, 14, 25, 28, 30]. It is a rule that formulates the condition of optimum catalytic reactivity. In modern terms it can be worded as: *In a catalytic reaction, reacting molecules form intermediate complexes with the catalyst (surface). These complexes should be of intermediate stability. If they are too stable they will not decompose to achieve* *product formation. If they are too unstable reagent molecules will not be activated and surface reaction intermediate complexes will not be formed.*

As we now know, the catalytic reaction is composed of a sequence of elementary reaction steps.

- Molecules adsorb onto the catalyst surface where they become activated and form intermediate reaction complexes.
- These complexes then rearrange and recombine.
- Final product formation occurs by desorption of the product molecules that regenerates the free catalyst surface (Figure 1.5a).

Sabatier's rule is a direct consequence of the cyclic nature of the catalytic reaction sequence. Reacting molecules interact with a catalyst. This chemical reaction

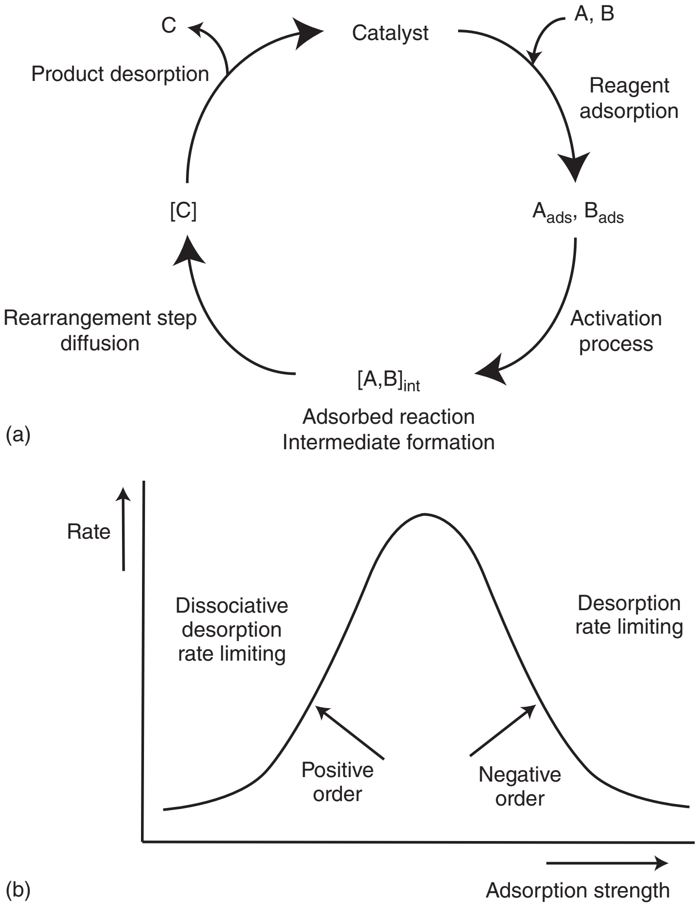

Figure 1.5 (a) Schematic representation of the cyclic nature of the catalytic heterogeneous reaction. (b) Volcano plot illustrating the Sabatier principle. The rate of reaction is shown as a function of the interaction energy of the substrate. The rate is maximized at optimum adsorption strength. To the left of the Sabatier maximum, the rate has a positive order in reactant concentration, and to the right it has a negative order [25].

leads to the formation of the intermediate complexes between reagent molecules and catalyst surface atoms. The strong interaction between catalyst and adsorbed reaction intermediates causes dissociation reactions as chemical bonds in reactants break, and association reactions as new chemical bonds form from the production of different reaction intermediates. The latter leads to the product molecules that in subsequent steps desorb from the surface.

The reaction activation rates of the reagent molecules, the formation of intermediate product molecules, and the desorption of product molecules all compete. Chemical bond activation of the adsorbed molecules requires a stronger interaction with the catalyst surface than the formation of product molecule sand product by association reactions. Because cleavage of the chemical bonds between reaction intermediate and catalyst surface is necessary, the maximum overall rate of the catalytic reaction is determined by the optimum interaction energy of reaction intermediates with the surface. This leads to the volcano-type dependence of the overall catalytic reaction rate on catalyst reactivity as shown in Figure 1.5b.

The kinetics of the full network of interacting elementary reactions must be considered in order to determine the catalyst's maximum performance. As we will discuss in more detail in Chapter 3, at the catalyst's operational maximum other reaction steps compete and there is no longer a single reaction step controlling the reaction rate.

The Sabatier principle is basic to our understanding of the physical chemistry of catalyst activity. The understanding of catalyst selectivity would come later, with the molecular theory of catalysis that is discussed at length in Chapter 5.

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