CATALYST FUNDAMENTALS OF INDUSTRIAL CATALYSIS

1.1 INTRODUCTION

Chemical reactions occur by breaking the bonds of reactants and forming new bonds and new compounds. Breaking stable bonds requires the absorption of energy, while making new bonds results in the liberation of energy. The combination of these energies results in either an exothermic reaction in which the conversion of reactants to products liberates energy or an endothermic process in which the conversion process requires energy. In the former case, the energy of the product is lower than that of the reactants with the difference being the heat liberated. In the latter case, the product energy is greater by the amount that must be added to conserve the total energy of the system. Under the same reaction conditions, the heat of reaction (ΔH) being a thermodynamic function does not depend on the path or rate by which reactants are converted to products. Similarly, ΔG of the reaction is not dependent on the reaction path since it too is a thermodynamic state function. This will be emphasized once we discuss catalytic reactions. The rate of reaction is determined by the slowest step in a conversion process independent of the energy content of the reactants or products.

1.2 CATALYZED VERSUS NONCATALYZED REACTIONS

In the most basic sense, the purpose of the catalyst is to provide a reaction pathway or mechanism that has a lower activation barrier compared to the noncatalyzed (E_{nc}) pathway, as illustrated in Figure 1.1. Also shown is the catalyzed barrier (E_{Mn}). In any reaction, catalyzed or noncatalyzed, the reaction sequence occurs through a series of elementary steps. In a noncatalyzed reaction, the species that participate in the reaction sequence are derived solely from the reactants. In a catalyzed reaction, the catalyst is simply an additional species that participates in the reaction sequence by lowering the activation energy and hence enhances the kinetics of the reaction. Finally, during the catalyzed reaction sequence, the catalyst species returns to its original state. It is the regeneration of the catalyst species to its original state that makes a catalyst a "catalyst"
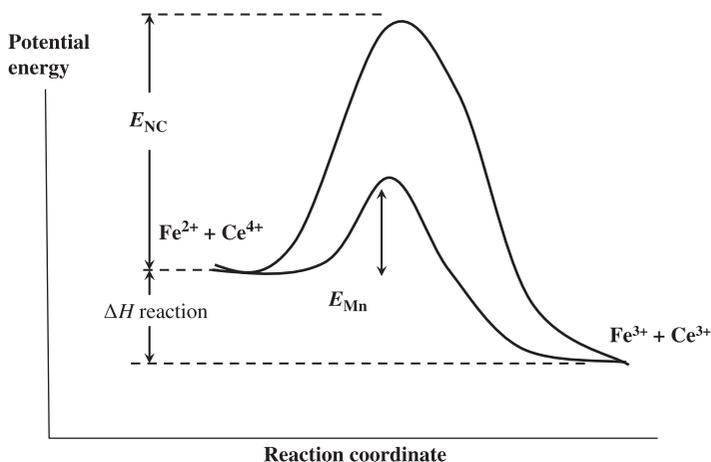
Figure 1.1 Catalyzed and uncatalyzed reaction energy paths illustrating the lower energy barrier (activation energy) associated with the catalytic reaction compared with the noncatalytic reaction. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)
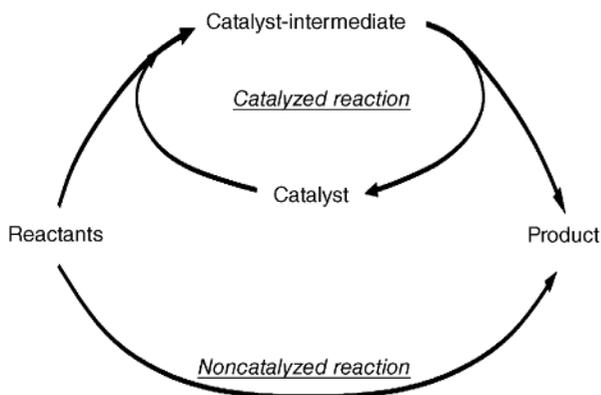
Figure 1.2 Illustration of catalyzed versus noncatalyzed reactions.

and not a "reactant." Thus, a catalyst is a species that participates in the reaction sequence—it interacts with the "reactants" to form an intermediate species that undergoes further reaction to form the "product" with the catalyst returning to its original state. This basic sequence of events is illustrated in Figure 1.2.

1.2.1 Example Reaction: Liquid-Phase Redox Reaction

Let us consider the simple redox reaction between Fe^{2+} and Ce^{4+} in aqueous solution. The reaction below excludes the H_2O present in the coordination sphere for each
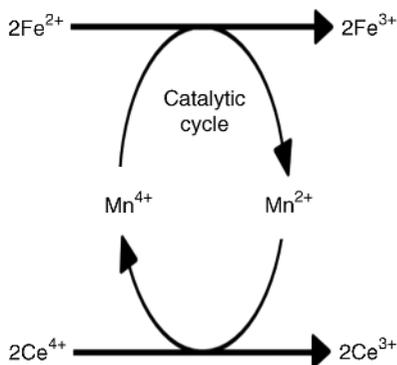
Figure 1.3   Catalytic Fe–Ce redox reaction catalyzed by Mn.

species since it does not directly participate in the reaction.

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+} \tag{1.1a}$$
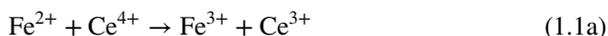
$$K_e = \frac{\left[Fe^{3+}\right]\left[Ce^{3+}\right]}{[Fe^{2+}][Ce^{4+}]} \tag{1.1b}$$

This reaction involves a direct electron transfer from the Fe^{2+} to the Ce^{4+} and by itself occurs very slowly because the electron transfer process occurs slowly. However, in the presence of Mn^{4+} species, the rate dramatically increases because the electron transfer is now facilitated through the Mn^{4+}/Mn^{2+} couple. The Mn^{4+} species is a catalyst, not a reactant. While it does directly participate in the reaction, the reaction pathway results in no overall change in the chemical state of the Mn ion (Figure 1.3).

The reaction profile of both the catalyzed and noncatalyzed reactions can be described kinetically by the Arrhenius profile in which reactants convert to products by surmounting the energy barrier called the activation energy. According to the Arrhenius expression (Equation 1.2), the rate of reaction is proportional to the exponential of absolute temperature (T) and inversely proportional to the exponential of the activation energy (E). The remaining terms in Equation 1.2 include the universal gas constant (R), pre-exponential factor (k_0), and the rate constant (k). Thus, the rate of reaction (i.e., rate constant) will increase as the temperature increases or the activation energy decreases:

$$k = k_0 \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{1.2}$$

Referring back to our redox example, the catalyzed pathway has the lower activation energy and, therefore, will have a higher reaction rate at a given temperature. The energy barrier was lowered by the Mn catalyst providing a chemical shortcut to products. Although it is greater, the reactants and products are the same as the noncatalyzed reaction. Thus, thermodynamic properties remain unchanged and both reaction pathways will have the same reaction enthalpy (ΔH) and reaction free energy (ΔG) and equilibrium constant. The catalyst can only influence the rate at which reactants are converted to products as the equilibrium constant is approached and cannot make thermodynamically unfavorable reactions occur. In industrial practice

reaction conditions, such as temperature, pressure and reactant compositions are varied to maximize product formation consistent with the equilibrium constant.

1.2.2 Example Reaction: Gas-Phase Oxidation Reaction

Consider the conversion of carbon monoxide (CO), a known human poison, to CO_2, a reaction of great importance to the quality of air we breathe. The overall rate of the noncatalytic reaction is controlled by the dissociation of the O_2 molecule to O atoms (rate-limiting step) that rapidly react with CO forming CO_2. The temperature required to initiate the dissociation of O_2 is greater than 700 °C and once provided, the reaction rapidly goes to completion with a net liberation of energy (the heat of reaction is exothermic). The requirement to bring about the O_2 dissociation and ultimately the conversion of CO to CO_2 has activation energy (E_{nc}) in Figure 1.4. Reaction occurs when a sufficient number of molecules (O_2) possess the energy necessary (as determined by the Boltzmann distribution) to surmount the activation energy barrier. The rate of reaction is expressed in accordance with the Arrhenius equation (Equation 1.2).

Let us now discuss the effect of passing the same gaseous reactants, CO and O_2, through a reactor containing a solid catalyst. Since the process is carried out in two
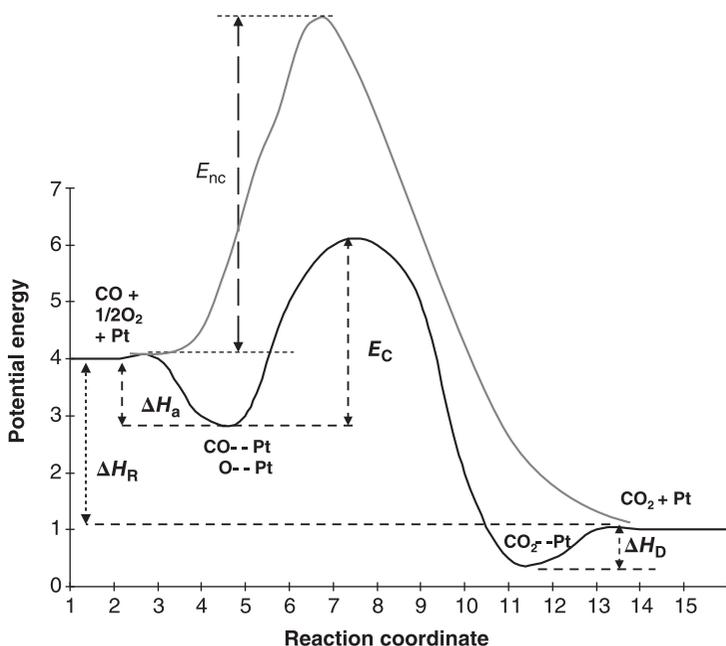
Figure 1.4   Activation energy diagram for the non-catalytic thermal reaction of CO and O_2 (E_{nc}) and the same reaction in the presence of Pt (E_c). Activation energy for the non-catalyzed reaction is E_{nc}. Activation energy for the non-catalyzed reaction is E_{nc}. The Pt catalyzed reaction activation energy is designated Ec. Note that heat of reaction ΔH is the same for both reactions. *Catalytic Air Pollution Control: Commercial Technology*, Chapter 1, Wiley and Sons 2009

separate phases, the term heterogeneous catalytic reaction is used. In the presence of a solid catalyst such as Pt, gaseous O_2 and CO adsorb on separate Pt sites in a process called chemisorption in which a chemical partial bond is formed between reactants and the catalyst surface. Dissociation of chemisorbed O_2 to chemisorbed O atoms rapidly occurs at room temperature. Adsorbed O atoms react with chemisorbed CO on adjacent Pt sites producing CO_2 that desorbs from the Pt completing the reaction and freeing the catalytic site for another cycle. The presence of the Pt catalyst greatly facilitates the dissociation of oxygen, which was the slow energy-intensive step associated with the noncatalytic gas-phase oxidation of CO. Thus, the activation energy for the Pt-catalyzed reaction (E_c), shown in Figure 1.4, is considerably smaller than that for the noncatalyzed reaction, enhancing the conversion kinetics. This difference in activation energy can be easily observed when comparing the light-off temperature of the catalyzed versus the gas-phase reactions, which is illustrated in Figure 1.5. The noncatalyzed reaction has a considerably higher light-off temperature (around 700 °C) due to its higher activation energy. More input energy is necessary to provide the molecules the necessary energy to surmount the activation barrier so that light-off occurs at higher temperatures. It should be noted, however, that the noncatalyzed reaction has a greater sensitivity to temperature (slope of plot). Thus, the reaction with the higher activation energy has greater sensitivity to temperature, making it increase to a greater extent with temperature than that with a lower activation energy. This is a serious problem for highly exothermic reactions, such as hydrocarbon oxidations, where noncatalytic free radical reactions, with large activation energies, can lead to very undesirable products.
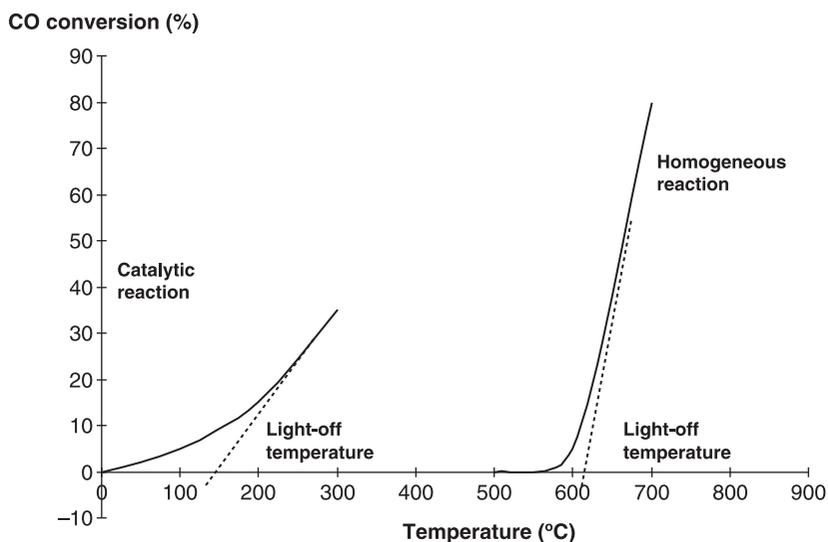
Figure 1.5   Conversion of CO versus temperature for a noncatalyzed (homogeneous) and catalyzed reaction. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)

Equations relating reaction rates to activation energies will be discussed in considerable detail in Chapter 4, but for now it is sufficient to understand that an inverse relationship exists between the activation energy and the reaction rate.

Relative to one that is not catalyzed, kinetic rate studies indicate that the rate-limiting step is the reaction of chemisorbed CO with chemisorbed O atoms on adjacent Pt sites. The reaction occurs around $100\,°C$ far below the $700\,°C$ required for the noncatalytic process described above. Thus, the catalyst provides a new reaction pathway in which the rate-limiting step is altered at a significantly lower temperature. This shows the great importance of catalysis in enhancing rates of reaction allowing them to occur at moderate temperatures. Lower operating temperature translates to energy savings, less expensive reactor materials of construction, and preferred product distributions with greater rates of production with smaller size reactors. For this reason, catalysts are commonly used in many industrial applications: petroleum processing, chemical and energy synthesis, and environmental emission control.

Inspection of Figure 1.4 indicates that an energy decrease associated with the adsorption of CO and O_2 on the Pt surface (ΔH_a) is due to its exothermic nature. This is a consequence of the decreased entropy (ΔS) when molecules are confined in an adsorbed state with the commensurate loss in a degree of freedom. Since ΔG_a must be negative and $-T\Delta S_a$ is positive, ΔH_a must be negative in accordance with $\Delta G_a = \Delta H_a - T\Delta S_a$. Desorption is always endothermic.

1.3 PHYSICAL STRUCTURE OF A HETEROGENEOUS CATALYST

All heterogeneous catalysts are solid substances that can be classified into two general categories: unsupported or supported. Most heterogeneous catalysts fall under the "supported" category, where the active catalytic component is dispersed into an inorganic porous high surface area carrier (often called a support) physically similar to a household porous sponge. The primary function of the carrier is to maintain the dispersion of the active phase; however, it can also participate in the reaction. As an example of supported and unsupported catalysts, consider the process for ammonia synthesis (Equation 1.3) where both supported and unsupported catalysts are used. One catalyst used for this reaction is *unsupported* iron derived from iron oxide. Another catalyst used for this reaction is ruthenium *supported* on a high surface area carbon carrier. In the preparation of this catalyst, a small amount of ruthenium is dissolved into water and impregnated into the carbon carrier. Thus, the bulk of the catalyst is comprised of carbon with small "islands" of well-dispersed ruthenium. Both types of catalyst structures are widely used and the optimal catalyst structure is often a function of several variables, including the nature of the active species, catalyst manufacturing cost, and the desired catalyst form to be used in the industrial process.

$$3H_2 + N_2 \leftrightarrow 2NH_3 \qquad (1.3)$$

Whether supported or unsupported, the catalyst will be comprised of two basic components: *active species* and *promoters* in addition to the carrier. The species that adsorbs the gas-phase reactant and on which the surface reaction occurs is called the

active species. Within the active species, the specific atomic location where adsorption and reaction occur is called the *active site*. It is on the active site where the short-lived reaction intermediates form is called the *active center*. Beyond the active species, there are often other species incorporated into the catalyst structure, called *promoters*, that either improve the activity of the active species by positively participating in the surface reaction sequence (*chemical promoter*) or help maintain the catalyst activity over time by stabilizing the catalyst structure (*textural promoter*).

1.3.1   Active Catalytic Species

Group VIIIB metals and their oxides such as Fe, Co, and Ni are catalytic as are Cu and Ag (Group 1b), V (Group Vb), and Cr and Mo (Group V1b) and in specific combinations are mainly used in the chemical and petroleum industries. These are referred to as base metals (oxides). Precious metals such as Pt, Pd, Ru, and Rh are also in Group VIII that are very commonly used broadly in all industries. Ironically, the precious metals are also referred to as noble metals for their resistance to oxidation, various poisons, and high temperatures, yet they are some of the most catalytically active elements in nature due to their ability to chemisorb and convert adsorbed species with high rates. They are rare and very expensive and thus when no longer performing satisfactorily, they are recycled, purified, and reused. They are primarily mined in South Africa and Russia with small deposits in Canada and the United States. In most cases, both base and precious metals (or their oxides) are deposited on high surface area carriers in order to maximize their accessible catalytic sites.

It should be understood that the active catalytic component is often not present in its native elemental state, but may be present as an oxide. For the oxidation of many hydrocarbons, Pd is catalytically active as PdO; while for the hydrogenation reactions, Ni, Cu, and Pd metals are most active. Vanadium pentoxide (V_2O_5) is an active catalyst for oxidizing SO_2 to SO_3 in the manufacture of sulfuric acid.

Throughout this book you will see the breadth of applications for all of these metals and their oxides as catalysts that enhance activity and selectivity.

1.3.2   Chemical and Textural Promoters

While catalyst activity and selectivity are dominated by the main catalytic component, other metals or metal oxides may also contribute to the overall activity or selectivity. When this is the case, these materials are called *promoters*. Promoters are generally classified as two types: chemical promoters and textural (structural) promoters. In the case of the chemical promoter, the material facilitates the surface reaction. In the case of the textural promoter, the material stabilizes the metal dispersion or the structure of the carrier, which prevents or slows catalyst deactivation over time. There are many examples for a wide variety of petroleum, chemical, environmental, and alternative energy processes that we will discuss in subsequent chapters, but just to give a preview here are some examples. The addition of CeO_2 to a precious metal catalyst such as Pt or Pd in the automotive catalyst promotes the oxidation of hydrocarbons and carbon monoxide decreasing the minimum temperature needed to initiate catalytic oxidation during the cold start portion of the automobile cycle requirement.

Adding Cl^- to a naphtha reforming catalyst $PtRe/\gamma\text{-}Al_2O_3$ used to make high octane gasoline enhances the acidity of the catalyst and catalyzes isomerization reactions generating branched hydrocarbons with high octane. The addition of sulfur to a hydro-desulfurization catalyst $(Co, Mo/Al_2O_3)$ diminishes excessive activity leading to undesired gaseous products in crude oils. The addition of alkali (K_2O) to a Ni/Al_2O_3 steam-reforming catalyst decreases acidity and promotes steam gasification minimizing carbon formation. In the generation of H_2, the gas stream is enriched in H_2 by the oxidation of CO by water in the water gas shift reaction using a Cu-containing catalyst. The addition of 5–10% ZnO to the catalyst suppresses the methanation reaction and avoids the consumption of H_2 and the large exotherm associated with the reaction:

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{1.4}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{1.5}$$

1.3.3   Carrier Materials

In most industrial reactions, the number of reactant molecules converted to products in a given time is directly related to the number of catalytic sites available to the reactants. It is necessary to maximize the number of active sites by dispersing the catalytic components onto a porous material. Maximizing the surface area of the catalytic components, such as Pt, Fe, Ni, Rh, Pd, CuO, PdO, CoO, and so forth increases the number of sites upon which chemisorption and catalytic reaction can occur. The catalytic components are introduced into the carrier by impregnation from aqueous solutions. Maximizing dispersion of the catalytic component requires carriers with a high surface area, such as Al_2O_3, SiO_2, TiO_2, C, $SiO_2\text{-}Al_2O_3$, zeolites, and CeO_2. In most cases, carriers themselves are not catalytically active for the specific reaction in question, but can play a major role in promoting the activity, selectivity, and maintaining the overall stability and durability of the finished catalyst. Such is the case in the hydrogenation of organic functional groups where high surface area carbons are used as carriers for precious metals and Ni. In these cases, the carrier adsorbs the organic compound prior to hydrogenation by the H_2 dissociated on the metallic catalytic component. For now when we speak of the catalyst, it is understood to be composed of catalytic components dispersed on high surface area porous carriers. Exceptions to this broad definition will be discussed in the application section.

1.3.4   Structure of the Catalyst and Catalytic Reactor

In chemical and petroleum applications, many different catalyst structures can be used. The structure depends on a number of factors such as volume of product to be produced, addition or withdrawal of heat, thermodynamic equilibrium, need for frequent regenerations, and life. The rationale for each reactor type will be discussed in the specific application section. For now, it is sufficient to say the catalyst materials are loaded and supported into a tubular reactor through which the reactants pass, interact with the catalyst, and convert to products. Figure 1.6a shows particulate structures, while a cartoon of a fixed bed reactor is shown in Figure 1.6b.
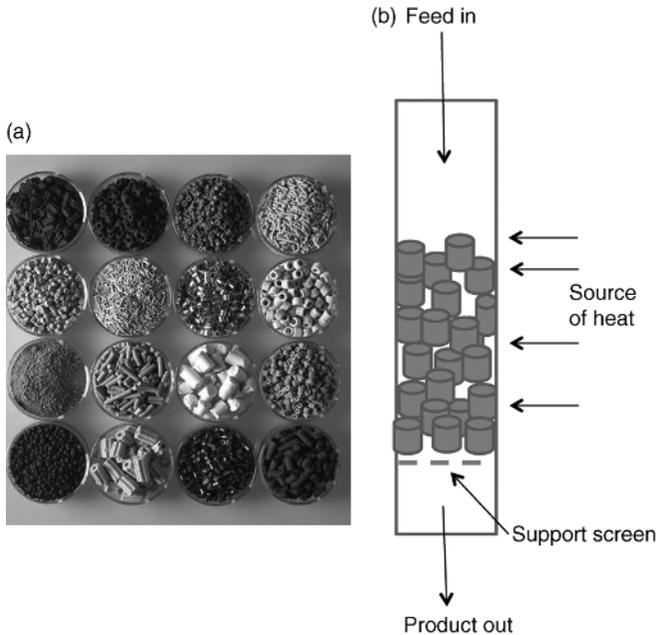
Figure 1.6   Particulate catalysts for fixed bed reactors: spheres, extrudates, and tablets. Powdered catalysts for batch slurry phase processors. A cartoon of a fixed bed reactor loaded with catalyst tablets. (Picture of particulates printed with permission from BASF.)

The catalyst is present in a preshaped particulate containing the catalytic component dispersed on the carrier. The size and shape of the catalyst depend on the nature of flow, permitted pressure drop, requirement for heat management (exothermic or endothermic reactions), mechanical strength, and so on. Spherical and tablet shapes 3–10 mm are commonly used. The desired reaction gas mixture flows through the bed of packed catalyst particulates and reaction occurs. The effluent gas is often monitored with some type of analytical device, such as a gas chromatograph, to monitor conversion. The temperature inside the bed is often measured at several points to monitor the reaction using thermocouples.

The preparation and properties of these materials and catalyzed monolith structures and their influence on catalytic reactions will be discussed in Chapter 2, but, for now, γ-Al_2O_3, most commonly used in catalysis, will be used to develop a model of a heterogeneous catalyst.

The pores of γ-Al_2O_3 are typically 2–10 nm in diameter, but irregularly shaped. The simplistic drawing shown in Figure 1.6 has circular catalytic components dispersed on the walls similar to raisins in a cake. The physical surface area of the carrier is the sum of all internal areas from all the walls of each and every pore. It is upon these internal walls that the catalytic components are bound or dispersed. The catalytic surface area is the sum of all the areas of the active catalytic components in this example. The smaller the individual size of the active catalytic material (higher catalytic surface area), the more the sites available for the reactants

to interact. As a rough approximation, one assumes the higher the catalytic surface area, the higher the rate of reaction for a process controlled by kinetics. This is often the case, but there are exceptions in which a particular reaction is said to be structurally sensitive and the rate is maximum when interacting with a catalytic crystal size of a specific size range.

This procedure maximizes the catalytic surface area but also introduces other physical processes such as mass transfer of the reactants to the catalytic sites. Each of these processes has a rate influenced by the hydrodynamics of the fluid flow, the pore size and structure of the carrier, and the molecular dimensions of the diffusing molecule.

1.4   ADSORPTION AND KINETICALLY CONTROLLED MODELS FOR HETEROGENEOUS CATALYSIS

In heterogeneous catalysis, the initiating and terminating steps for the surface reaction involve the adsorption of the reactant onto and the desorption of the product from the active surface. In chemical terms, adsorption is the formation of chemical bonds between the adsorbing species (adsorbate) and the adsorbing surface (adsorbent). In general, there are two kinds of adsorptions, chemical and physical, typically referred to as chemisorption and physisorption, respectively. Physisorption is weak, nonselective adsorption of gaseous molecules on a solid at relatively low temperatures. In contrast, chemisorption is the relatively strong, selective adsorption of chemically reactive species on available sites of metal or metal oxide surfaces. In chemisorption, the adsorbent–adsorbate interaction involves the formation of chemical bonds and heats of reaction on the order of 40–300 kJ/mol. It is the formation of these strong bonds that alters the chemical nature of the adsorbate, making the newly formed structure more reactive and more easily transformed than the "free" molecule.

The maximum number of reactant molecules adsorbed onto a unit area of active catalyst surface will be the number of available catalytic sites per unit area. In the case where all catalytic sites are covered with an adsorbate molecule, the surface is said to be saturated and the fractional site coverage (θ) is unity. Adsorption and desorption continuously occur even when the net number of adsorbed species reaches a steady state. Thus, a dynamic equilibrium is established, where the fractional coverage at equilibrium is a function of temperature, adsorbate partial pressure, and the chemical nature of the adsorbate.

In heterogeneous catalysis, it is essential to know the amount of reactants that adsorb onto a given area of active catalyst surface. The quantity of adsorbed species is generally characterized by an isotherm, which is a mathematical relationship between fractional site coverage (θ) and temperature. The rate of reaction on the catalyst surface is going to be a function of the surface concentration of reactants, not necessarily the gas-phase reactant concentrations. Thus, the isotherm provides us with the link between the gas-phase concentration (measurable) and the surface concentration (immeasurable directly).

1.4.1 Langmuir Isotherm

There are many different isotherm forms, but the Langmuir isotherm is the simplest and most widely used and is applicable to many reactions. It is based on the key assumption that all sites on the adsorbent surface are of equal energies. Consider the example reaction presented earlier where CO is oxidized on a platinum catalyst. In this reaction, CO and O_2 must adsorb onto the platinum surface for reaction to occur. Further, the O_2-Pt must dissociate to form two Pt-O species. We can use the Langmuir isotherm to predict the surface concentration of each reactant and how the surface concentrations will vary with reaction conditions. We first consider the strong adsorption of CO in equilibrium with the surface of Pt:

$$CO + Pt \leftrightarrow CO\text{-}\text{-}Pt \tag{1.6}$$

The forward rate of Equation 1.6 (CO adsorption) is given by

$$r_{fCO} = k_{fCO}P_{CO}(1 - \theta_{CO}) \tag{1.7}$$

k_{fCO} is the forward rate constant of CO adsorption on Pt, P_{CO} is the partial pressure of CO, and θ_{CO} is the fraction of the surface of Pt covered by CO. The term $(1 - \theta_{CO})$ is the fractional number of sites available for additional CO adsorption. The isotherm also assumes each site is occupied by only one adsorbate molecule and full coverage is a monolayer.

The rate or reverse of Equation 1.6 (CO desorption) is given by

$$r_{dCO} = k_{dCO}\theta_{CO} \tag{1.8}$$

At equilibrium, the forward and desorption rates are equal and the ratio of the forward rate to reverse rate is defined as the adsorption equilibrium constant (Equation 1.9):

$$\frac{k_{fCO}}{k_{dCO}} = K_{CO} \tag{1.9}$$

$$k_{fCO}P_{CO}(1 - \theta_{CO}) = k_{dCO}\theta_{CO} \tag{1.10}$$

$$\theta_{CO} = \frac{K_{CO}P_{CO}}{(1 + K_{CO}P_{CO})} \tag{1.11}$$

Thus, Equation 1.11 provides the surface concentration of adsorbed CO as a function of CO partial pressure and the adsorption equilibrium constant. The adsorption equilibrium constant captures the influence of temperature and chemical nature of the adsorbate since the forward and reverse rate constants are a function of these parameters. Plotting Equation 1.11 generates Figure 1.7.

We can now consider two limiting cases: one where the partial pressure of CO is very low (P_{CO} is small) and one where the partial pressure of CO is very large (P_{CO} is large).

When P_{CO} is large, the denominator in Equation 1.11 $(1 + K_{CO}P_{CO})$ is approximately equal to $(K_{CO}P_{CO})$ since $K_{CO}P_{CO} \gg 1$. Thus, Equation 1.11 reduces to $\theta_{CO} = 1$ that signifies all the catalytic sites are covered with CO molecules and we say the surface is saturated with CO.

$$(\theta_{co}) = K_{co}P_{co}/(1+K_{co}P_{co})$$

Fractional coverage of CO on Pt surface (θ_{co})

$(\theta_{co}) = 1$

Slope = K_{co}

P_{CO}
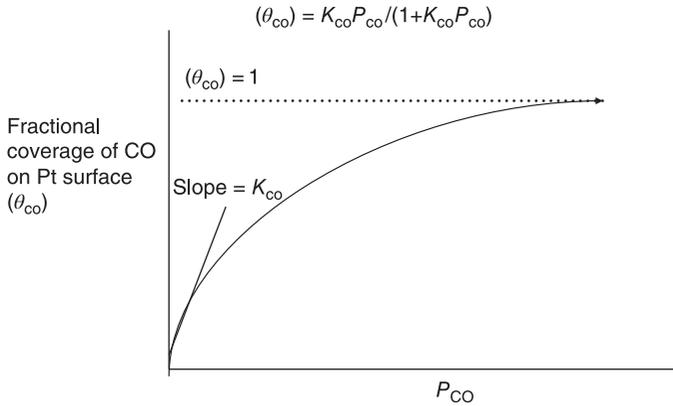
Figure 1.7 Adsorption isotherm (θ_{CO}) for CO on Pt for large, moderate, and low partial pressures of CO. The slope at low partial pressures of CO equals the adsorption equilibrium constant K_{CO}. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)

When P_{CO} is small, the denominator in Equation 1.11 $(1 + K_{CO}P_{CO})$ is approximately equal to 1 since $K_{CO}P_{CO} \ll 1$ and Equation 1.11 reduces to $\theta_{CO} = K_{CO}P_{CO}$. Under these conditions, the surface concentration responds linearly with increasing gas-phase concentration. Recall the equilibrium constant is defined as the ratio of the forward to reverse adsorption rates (Equation 1.9). An adsorbate that strongly adsorbs onto the surface will have a relatively large equilibrium constant and surface coverage will increase rapidly with increasing gas partial pressure. This is the case for CO on Pt, which is illustrated in Figure 1.4 as the steeply sloped trace at low P_{CO}.

At moderate values of P_{CO}, Equation 1.11 applies as written with the curve becoming more shallow as P_{CO} increases. $\theta_{CO} = 1$ at large CO.

The isotherm for dissociative chemisorption of O_2 on Pt is similarly generated where θ_O refers to the fractional coverage by O atoms consistent with the stoichiometry for CO oxidation of one O atom for each CO:

$$O_2 + Pt \leftrightarrow 2O\text{--}Pt \tag{1.12}$$

The rate of the forward (adsorption of O_2 on Pt)

$$r_{fO_2} = k_{fO_2}P_{O_2}(1 - \theta_O)^2 \tag{1.13}$$

The rate of the reverse reaction (O desorption from Pt) is

$$r_{dO_2} = k_{dO_2}\theta_{O_2}^2 \tag{1.14}$$

The square term for both the forward and reverse rates is due to the lower probability that two adjacent Pt sites will be available to accommodate two oxygen atoms from the dissociative chemisorption of O_2. Similarly, two adsorbed O atoms on Pt must be adjacent for desorption and recombination to diatomic O_2 to occur. Also,

the adsorption equilibrium constant (K_{O_2}) for O_2 on Pt is k_{fO_2}/k_{dO_2}. Equating forward and reverse rates,

$$k_{fO_2} P_{O_2} (1 - \theta_O)^2 = k_{dO_2} \theta_O^2 \tag{1.15}$$

$$\theta_O = \frac{K_{O_2}^{1/2} P_{O_2}^{1/2}}{\left(1 + K_{O_2}^{1/2} P_{O_2}^{1/2}\right)} \tag{1.16}$$

Plotting the fractional coverage of oxygen atoms versus $PO_2^{1/2}$ generates a similar plot as Figure 1.7. The slope at low O_2 pressures is equal to $KO_2^{1/2}$, while at high pressures $\theta = 1$.

1.4.2   Reaction Kinetic Models

The isotherm provides us with the relationship for reactant surface concentration as a function of reaction conditions (i.e., temperature and reactant partial pressure). The next step is to use this information to estimate the rate of the chemical reaction occurring on the catalyst surface. To develop an expression for reaction rate, we need to know or assume a mechanism for the surface reaction. Specifically, the mechanism considers which reactants adsorb onto the surface and on which active species do they adsorb? While anything is possible, three general mechanisms are used to describe adsorption and reaction in heterogeneous catalysis:

> *Langmuir–Hinshelwood Mechanism:* Reactants adsorb onto the same active species and thus compete for available active sites (Figure 1.8).

> *Mars–van Krevelen Mechanism:* Reactants adsorb onto different sites, and the two surface intermediates interact and reaction occurs. Since each reactant adsorbs onto different surface species, there is no site competition between reactants (Figure 1.9).

> *Eley–Rideal Mechanism:* One reactant adsorbs onto the catalyst surface forming an intermediate surface species, which then reacts with a gas-phase reactant. Thus, there is no competition for catalytic sites (Figure 1.10).

Each of these three mechanisms is described in more detail in the following sections. The critical question is determining which mechanism a particular reaction follows. For each mechanism, a rate equation can be derived in terms of the appropriate surface and gas-phase reactant concentrations. Once derived, experiments can be conducted to see which rate equation best describes the experimental data. One possibility will be that neither of these three mechanisms describes the
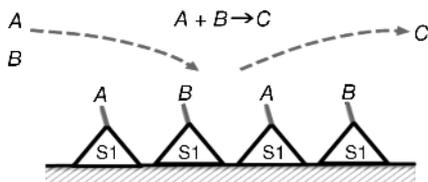
Figure 1.8   Illustration of Langmuir–Hinshelwood reaction mechanism.
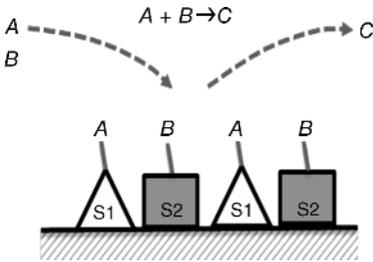
Figure 1.9   Illustration of Mars–van Krevelen reaction mechanism.
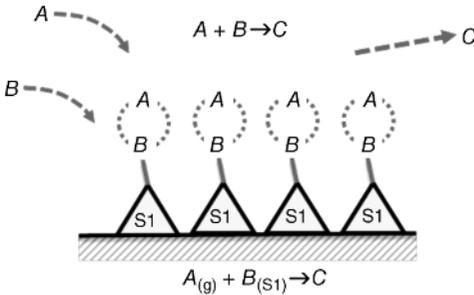
Figure 1.10   Illustration of Eley–Rideal reaction mechanism.

experimental data, which suggests the existence of a complex combination of mechanisms occurring simultaneously on the surface or the existence of an entirely different mechanism.

1.4.2.1 Langmuir–Hinshelwood Kinetics for CO Oxidation on Pt   The widely accepted kinetic model for the CO oxidation reaction on Pt is based on the Langmuir isotherm from which is derived Langmuir–Hinshelwood (LH) kinetics. The adsorption isotherms for CO and O_2 were considered separately in Section 1.4.1, but for the oxidation of CO by O_2 it is necessary to consider both gases each competing for the same sites on Pt. We will use k as the rate constant for the oxidation of CO where the net rate of reaction for CO oxidation will be

$$r_{CO} = k\theta_{CO}\theta_O \tag{1.17}$$

The surface coverage of CO and O, θ_{CO} and θ_O, respectively, must be modified to account for the competitive adsorption that occurs on the active Pt sites. Specifically, the fraction of open sites used to determine the rate of adsorption must include terms for both O and CO, as written in Equation 1.18:

$$r_{fCO} = k_{fCO}P_{CO}(1 - \theta_{CO} - \theta_O) \tag{1.18}$$

However, the desorption rate for CO is still dependent only on the sites occupied by CO and is the same as that given in Equation 1.8:

$$r_{dCO} = k_{dCO}\theta_{CO} \tag{1.19}$$

Equating adsorption (1.18) and desorption (1.19) rates at equilibrium and recognizing that $k_{fCO}/k_{dCO} = K_{CO}$ yields an expression for the surface concentration of CO,

$$K_{CO}P_{CO} = \frac{\theta_{CO}}{(1 - \theta_{CO} - \theta_O)} \tag{1.20}$$

However, Equation 1.20 contains two unknowns, θ_{CO} and θ_O. Before we can solve it, we need an expression for θ_O. Following a similar approach to that used previously, for the rate of adsorption and desorption of O_2, we obtain

$$K_{O_2}^{1/2}P_{O_2}^{1/2} = \frac{\theta_O}{(1 - \theta_{CO} - \theta_O)} \tag{1.21}$$

Simplification is achieved by dividing (1.20) by (1.21):

$$\theta_O = \theta_{CO}\frac{K_{O_2}^{1/2}P_{O_2}^{1/2}}{K_{CO}P_{CO}} \tag{1.22}$$

We now substitute (1.22) into (1.20) to yield an expression for θ_{CO} in terms of known quantities.

$$\theta_{CO} = \frac{K_{CO}P_{CO}}{\left(1 + K_{CO}P_{CO} + K_{O_2}^{1/2}P_{O_2}^{1/2}\right)} \tag{1.23}$$

Similarly, we substitute (1.22) into (1.20) to yield an expression for θ_O in terms of known quantities:

$$\theta_O = \frac{K_{O_2}^{1/2}P_{O_2}^{1/2}}{\left(1 + K_{CO}P_{CO} + K_{O_2}^{1/2}P_{O_2}^{1/2}\right)} \tag{1.24}$$

Now we have an expression for θ_{CO} and θ_O that can be substituted into Equation 1.17 to develop a rate expression for CO oxidation in terms of the surface concentration of CO and O:

$$r_{CO} = k\theta_{CO}\theta_O \tag{1.17}$$

$$r_{CO} = k\frac{K_{O_2}^{1/2}P_{O_2}^{1/2}K_{CO}P_{CO}}{\left(1 + K_{CO}P_{CO} + K_{O_2}^{1/2}P_{O_2}^{1/2}\right)^2} \tag{1.25}$$

Let us now consider the concentration extremes when the concentration of CO is very low and very high. For low P_{CO}, Equation 1.25 reduces to Equation 1.26:

$$r_{CO} = k\frac{K_{O_2}^{1/2}P_{O_2}^{1/2}K_{CO}P_{CO}}{\left(1 + K_{O_2}^{1/2}P_{O_2}^{1/2}\right)^2} \tag{1.26}$$

This shows a direct relationship between the rate and P_{CO} when P_{O_2} is constant. For large P_{CO}, Equation 1.25 reduces to Equation 1.27:

$$r_{CO} = k\frac{K_{O_2}^{1/2}P_{O_2}^{1/2}}{K_{CO}P_{CO}} \tag{1.27}$$

$$\text{Rate} = k\,[K_{CO}P_{CO}\,K_{O2}^{1/2}\,P_{O2}^{1/2}]/[1+K_{CO}\,P_{CO}+K_{O2}^{1/2}\,P_{O2}^{1/2}]^2$$

$$CO + 1/2O_2 \xrightarrow{\text{Pt}} CO_2$$

$\theta_{co} = \Theta_o$

equal sites occupied by CO and O

at high P_{CO}

$$\text{Rate} = \kappa\,[K_{O2}^{1/2}P_{O2}^{1/2}]/[(P_{CO}K_{CO}]$$

at low P_{CO}

$$\text{Rate} = \kappa\,[K_{CO}P_{CO}K_{O2}^{1/2}P_{O2}^{1/2}]/[1 + K_{O2}^{1/2}P_{O2}^{1/2}]^2$$

Rate (vertical axis)

P_{CO} (horizontal axis)

$P_{O2} =$ **Constant**, $T =$ **constant**
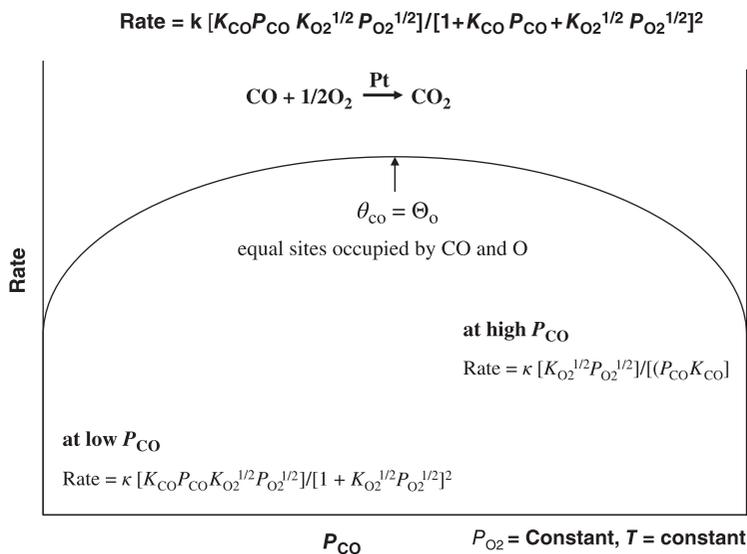
Figure 1.11 L–H kinetics applied to increasing P_{CO} at constant P_{O2}. Maximum rate was achieved when an equal number of CO molecules and O atoms are adsorbed ($\theta_O = \theta_{CO}$) on adjacent Pt sites. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)

Equation 1.28 indicates that the rate of reaction will decrease as the gas-phase concentration of CO becomes high. This means high CO concentrations inhibit the rate of reaction, which is due to CO saturating the catalyst surface and displacing adsorbed oxygen. Thus, the reaction rate approaches zero at high and low CO concentrations, which indicates a maximum of rate exists when $\theta_O = \theta_{CO}$, which is shown graphically in Figure 1.11.

Applying this model was very useful in designing an optimum system for the first gasoline oxidation catalyst for the automobile converter. When the CO was high during the cold start portion of the driving cycle, the addition of extra O_2 (from air) decreased the P_{CO} more than P_{O_2} and the rate of the reaction for CO oxidation increased. Thus, understanding kinetics and the rate expressions helped design a workable system to meet regulations.

From a fundamental point of view, it should be noted that the assumption of uniform energy sites on the catalyst in the Langmuir isotherm is not correct. A heterogeneous catalytic surface consists of a distribution of strong, moderate, and weak sites upon which the reactant molecules adsorb. Increasing temperature allows only the stronger sites to be retained. This results in a change in the overall energy of the adsorbed states on the activation energy profile of Figure 1.2. Fundamentally, with increasing temperature, this causes a small change in the activation energy, but for all intensive purposes it can be ignored when making activation energy measurements. Measurements of activation energies will be discussed later.
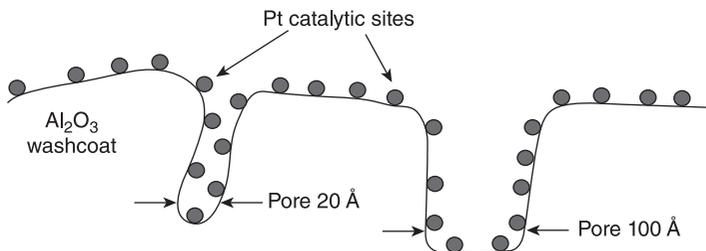
Figure 1.12 Ideal dispersion of Pt atoms on a high surface area Al_2O_3 carrier. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)

1.4.2.2 Mars–van Krevelen Kinetic Mechanism   There are a number of reactions that proceed by a surface redox mechanism where oxygen is provided by one catalytic component to an adsorbed reactant on another catalyst site leading to oxidation. Examples for this mechanism apply when V_2O_5 is the catalyst for the oxidation of sulfur dioxide to sulfur trioxide. It also applies to oxidation of benzene to benzoquinone. We will use an example of the oxidation of CO over copper oxide and iron oxide to demonstrate the mechanism and rate equation. These mechanisms are known as Mars–van Krevelen (MvK). In this case, gas-phase CO reduces Cu^{2+} to Cu^{1+} (Equation 1.29). The FeO contributes its O to reoxidize Cu to Cu^{2+}, with reduced Fe forming gas-phase O_2 that then adsorbs and oxidizes Fe to FeO (Equation 1.30).

$$CO + 2CuO \rightarrow Cu_2O + CO_2 \tag{1.28}$$

$$Cu_2O + FeO \rightarrow 2CuO + Fe \tag{1.29}$$

$$\frac{1}{2}O_2 + Fe \rightarrow FeO \tag{1.30}$$

$$\text{Net reaction}: \quad CO + \frac{1}{2}O_2 \rightarrow CO_2$$

The overall rate of reaction can be written recognizing that Θ equals the fractional coverage of O atoms on the Fe species.

Overall oxidation of CO:

$$r_{CO} = k_1 P_{CO}\theta \tag{1.31}$$

Rate of reoxidation of the Fe:

$$r_o = k_2 P_{O_2}^{1/2}(1 - \theta) \tag{1.32}$$

The overall oxidation rate of the CO can be no faster that the rate at which Fe is reoxidized at steady state, so we can equate the two equations:

$$k_1 P_{CO}\theta = k_2 P_{O_2}^{1/2}(1 - \theta) \tag{1.33}$$

$$\theta = \frac{k_2 P_{O_2}^{1/2}}{k_1 P_{CO} + k_2 P_{O_2}^{1/2}} \tag{1.34}$$

The MvK rate equation for CO oxidation can be written as

$$r_{CO} = \frac{k_1 k_2 P_{CO} P_{O_2}^{1/2}}{k_1 P_{CO} + k_2 P_{O_2}^{1/2}} \tag{1.35}$$

This expression recognizes that the rate is dependent on the gas-phase partial pressure of both CO and O_2:

At low CO/O_2, the rate reduces to $k_1 P_{CO}$.

At high CO/O_2, the rate reduces to $k_2 PO_2^{1/2}$.

1.4.2.3 Eley–Rideal (E–R) Kinetic Mechanism

This model represents a case where a gas-phase reactant adsorbs onto another reactant adsorbed onto the catalyst site:

$$A_{(s)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)} \tag{1.36}$$

Assuming C and D do not adsorb and A adsorbs with an equilibrium constant K_A and gas species B does not compete with A for catalytic sites and only adsorbs on adsorbed A, the expression reduces to

$$r = k\theta_A P_B \tag{1.37}$$

$$r = kP_B \left(\frac{K_A P_A}{(1 + K_A P_A)} \right) \tag{1.38}$$

where $\Theta_A = [K_A P_A/(1 + K_A P_A)]$ is derived by equating the forward and reverse rates of adsorption and desorption at equilibrium. The slope of rate versus P_B is the rate constant k when K_A is very large. Rate versus P_A at low concentrations of P_A relative to P_B is linear with the slope equal to $K_A P_B k$.

The hydrogenation of CO_2 to methane at $300\,°C$ over a supported Ru catalyst obeys the Eley–Rideal mechanism. The empirical rate equation is essentially first order in H_2 and almost zero order in CO_2. The CO_2 is strongly adsorbed onto the Ru sites, while H_2 reacts with adsorbed CO_2 producing methane. In this case, $P_B = P_{H_2}$, $P_A = P_{CO_2}$ and $K_A = K_{CO_2}$.

1.4.2.4 Kinetic versus Empirical Rate Models

Kinetic models are useful in giving us insight into the precise mechanism by which a reaction occurs. It is a goal of catalytic chemistry to fit the experimental data to a model such as the three described above in Sections 1.4.2.1–1.4.2.3. However, often catalytic reactions are much more complicated and no single model can be applied due to many competing rate-limiting steps. For these cases, it is necessary to use what is referred to as an empirical model that permits the calculation of kinetic parameters such as reaction orders and activation energies that allow the process to be designed for the optimum reactant and product concentrations and temperatures for maximizing selectivity. Empirical rate models will be described in Chapter 4.

1.5   SUPPORTED CATALYSTS: DISPERSED MODEL

Most heterogeneous catalyst materials are supported on a high surface area (and highly porous) carrier such as Al_2O_3, carbon, SiO_2, TiO_2, and zeolites composed of SiO_2–Al_2O_3. This disperses the catalytic components into nanosized clusters that generate a high catalytic surface area, which maximizes their accessibility to reactants. Figure 1.12 shows Pt atoms ideally dispersed on high surface area Al_2O_3.

The catalytic sites (Pt in Figure 1.12) are bound moderately to surface functional groups (i.e., OH— not shown) of the carrier. One can envision chocolate chips well dispersed within the cookie. Commonly, the surface of the carriers has functional groups that provide some "anchoring" of the catalytic components maintaining them as nanosized clusters as they function in the reaction. Carriers and catalyst preparation methods will be discussed in Chapter 2. Chapter 3 will cover various characterization methods to provide understanding of their physical and chemical properties and changes that may occur during their operation. Chapter 5 will show how catalysts can undergo changes due to the environmental factors that occur during reaction.

Although supporting a catalytic component offers the benefit of maximizing the catalytic surface area, it does introduce transport issues whereby reactants must diffuse to the dispersed catalytic sites within the porous network of the carrier. These issues are discussed in the next section.

1.5.1   Chemical and Physical Steps Occurring during Heterogeneous Catalysis

To maximize reaction rates, it is essential to ensure accessibility of all reactants to the active catalytic sites dispersed within the internal pore network of the carrier. Once again, let us consider the physical and chemical steps occurring during heterogeneous CO oxidation in a packed bed catalytic reactor.

CO and O_2 molecules are flowing through a bed of a solid particulate catalyst. To be converted to CO_2, the following physical and chemical steps must occur:

1. CO and O_2 must make contact with the outer surface of the carrier. To do so, they must diffuse through a stagnant thin layer of gas or boundary layer forming around the outer surface of the supported catalyst particles. Bulk molecular diffusion rates vary approximately with $T^{3/2}$ and typically have an "apparent" activation energies, $E_1 = 8$–16 kJ/mol (2–4 kcal/mol).

   The term "apparent" activation energy is used here to distinguish the physical phenomena of diffusion from the truly activated chemical processes that occur at the catalytic site. Diffusion reactions are a physical phenomenon and thus are not activated processes. Thus, the term "apparent" activation energy is as convenient as a figure of merit for reaction sensitivity to temperature.

2. Since the bulk of the catalytic components are internally dispersed within the carrier, the CO and O_2 molecules must diffuse through the porous network toward the active catalytic sites. The "apparent" activation energy for pore diffusion, E_2, is approximately 1/2 that of a chemical reaction or about 25–35 kJ/mol (6–9 kcal/mol).

3. Once CO and O_2 arrive at the catalytic site, chemisorption of both O_2 and CO occurs on adjacent catalytic sites. The kinetics generally follow exponential dependence on temperature, that is, $\exp(-E_3/RT)$, where E_3 is the activation energy, which for chemisorption is typically greater than 40 kJ/mol (>10 kcal/mol).

4. An activated complex forms between adsorbed CO and adsorbed O with an energy equal to that at the peak of the activation energy profile since this is the rate-limiting step. At this point, the activated complex has sufficient energy to convert to CO_2 that remains adsorbed on the catalytic site. Kinetics also follow exponential dependence on temperature, that is, $(-E_4/RT)$ with activation energies typically greater than 40 kJ/mol (10 kcal/mol).

5. CO_2 desorbs from the site following exponential kinetics, that is, $\exp(-E_5/RT)$ with activation energies typically greater than 40 kJ/mol (10 kcal/mol).

6. The desorbed CO_2 diffuses through the porous network toward the outer surface with an "apparent" activation energy and kinetics similar to step 2.

7. CO_2 must diffuse through the stagnant layer and, finally, into the bulk gas. Reaction rates follow $T^{3/2}$ dependence. "Apparent" activation energies are also similar to step 1: less than 8–16 kJ/mol (2–4 kcal/mol).

Steps 1 and 7 represent bulk mass transfer, which is a function of the specific molecules, the dynamics of the flow conditions, and the geometric surface area (outside or external area of the catalyst/carrier). Pore diffusion, illustrated in steps 2 and 6, depends primarily on the size and shape of both the pore and the diffusing reactants and products. Steps 3–5 are related to the chemical interactions of reactants and products (i.e., CO, O_2, and CO_2) at the catalytic site(s). The sequence of these three processes are illustrated in Figure 1.13.
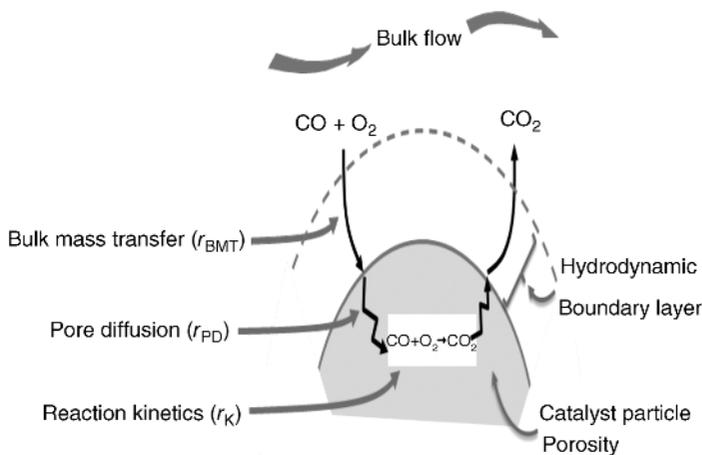
Figure 1.13   Illustration of the sequence of chemical and physical steps occurring in heterogeneous catalysis.

Chemical kinetics, E_a > 10 kcal/mol
Pore diffusion, Apparent E_a = 6–10 kcal/mol
Bulk mass transfer, Apparent E_a = 2–4 kcal/mol
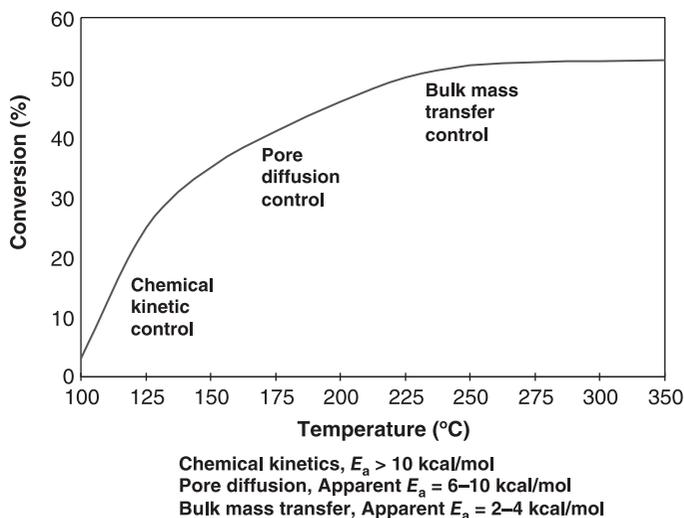
Figure 1.14   Conversion versus temperature profile illustrating regions for chemical kinetics, pore diffusion, and bulk mass transfer control. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)

Any of the seven steps listed above can be rate limiting and control the overall rate of reaction. The rate-controlling process then dictates the overall rate of reaction observed experimentally. In catalytic processes, it is essential to understand what process limits the overall rate of reaction. The rate of each of these processes is a function of reaction conditions, the design of the catalyst bed, and properties of the catalyst. As reaction conditions change, so will the rate of each of these processes and the rate-limiting step may change. For example, consider the effect of temperature on the rate of a hypothetical reaction described in the temperature–conversion plot in Figure 1.14.

At a low temperature, the rate of reaction is chemically controlled. However, the chemical reaction rate is very sensitive to temperature (high activation energy), so its rate increases more with temperature than the diffusion processes. Pore diffusion then becomes rate limiting as the temperature increases, but eventually the least temperature-sensitive bulk mass transfer process becomes rate limiting. This is also demonstrated in Figure 1.15 that depicts the three relative rates of reaction. It shows that of the three rate-limiting phenomena, bulk mass transfer (BMT) is the fastest process at low temperatures but has a shallow dependence on temperature due to its low "apparent" activation energy. Pore diffusion has a lower rate than BMT due to its higher "apparent" activation energy but greater temperature dependence. The highest temperature dependence occurs for a reaction controlled by chemical kinetics, but because of its higher activation energy, the rate is small at low temperatures relative to those controlled by diffusion and thus is the rate-limiting step.
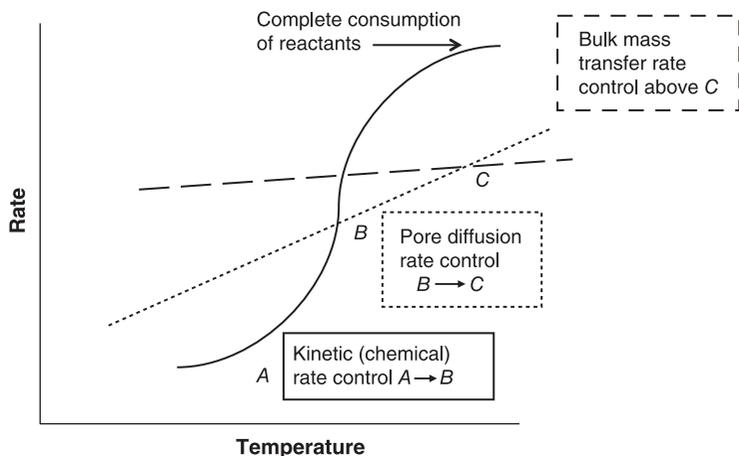
Figure 1.15 Relative rates of bulk mass transfer, pore diffusion, and chemical kinetics as a function of temperature. Chemical kinetics controls the rate between temperatures *A* and *B*. Pore diffusion controls from *B* to *C* temperatures, while bulk mass transfer controls at temperatures greater than *C*. (Reproduced from Chapter 1 of Heck, R.M., Farrauto, R.J., and Gulati, S.T. (2009) *Catalytic Air Pollution Control: Commercial Technology*, 3rd edn, John Wiley & Sons, Inc., New York.)

1.5.2   Reactant Concentration Gradients within the Catalyzed Material

In the chemical kinetic control region, the reaction of chemisorbed CO with chemisorbed O is slow relative to diffusion and thus is rate limiting. As the temperature is further increased, control of the overall rate will shift to pore diffusion. Here, the surface reaction between CO and O is faster than the rate at which gaseous CO and O_2 can be supplied to the sites and a concentration gradient exists within the carrier. This is referred to as intraparticle diffusion in which the catalytic components deep within the carrier are not being completely utilized or have an effectiveness factor less than 1. The effectiveness factor is the ratio of the actual rate versus the theoretical maximum rate if all catalytic sites are functioning. It can be thought of as a measure of the utilization of the catalytic component(s). At higher temperatures, the rate of diffusion of the CO and O_2 from the bulk gas to the external surface of the catalyst is slow relative to the other processes and the rate becomes controlled by bulk mass transfer. In this regime, the CO and O_2 are converted to CO_2 as soon as they arrive at the external surface of the carrier. The concentration of reactant and product is essentially zero at the external interface of the catalyst and the bulk fluid. The effectiveness factor is close to zero. Figure 1.16 graphically shows the relative gradients in concentration for reactants for the three rate-controlling processes in the catalyzed carrier.

1.5.3   The Rate-Limiting Step

The efficiency with which a catalyst functions in a process depends on what controls the overall reaction rate. If the kinetics of a process are measured and found

Chemically limited reaction reactant concentration is constant radially within the particle

Pore diffusion control reactant concentration decreases toward the particle center

Bulk mass transfer reactant concentration is zero at the outer carrier surface

Reactant concentration

Reactant concentration is zero with the particle

Radial distance within carrier particle

Radial distance with carrier particle

Reactant concentration

Radial distance with carrier particle

Figure 1.16   Reactant concentration gradients within a spherical structured catalyst for three regimes controlling the rate of reaction.

to be in a regime where chemical kinetics are rate controlling, the catalyst should be made with as high a catalytic surface area as possible. This is accomplished by increasing the catalytic component loading and/or dispersion so that every catalytic site is available to the reactants with an effectiveness factor approaching 1. Process parameters, such as an increase in temperature, promote a reaction controlled by chemical kinetics.

When it is known that a process will have significant pore diffusion limitations, the carrier should be selected with large pores and locate the catalytic components as close to the surface as possible to improve the effectiveness factor. Alternatively, a special geometry such as a carrier with holes (donut shape) can be used that also decreases the diffusion path. To enhance the transport rate, one can decrease the diameter of the carrier to decrease the diffusion path of reactants and products. A temperature increase will have some effect of enhancing the rate, but to a lesser extent than for those reactions controlled by chemical kinetics.

The rate of mass transfer is enhanced by increasing turbulence in the bulk gas and by increasing the geometric surface area (i.e., external area) by decreasing the particle size of the catalyst. This can be accomplished by selecting a catalyst with a high geometric surface area (small particle size or density of channels per unit area as is possible for monolith catalysts). Clearly, increasing the catalytic components surface area, the loading of the catalytic components or the size of the pores will have no effect on enhancing the rate of mass transfer since these catalyst properties do not participate in the rate-limiting step. Also, temperature will have virtually no impact on the BMT rate. This kinetics of all these rate-limiting steps will be more thoroughly discussed Chapter 4.

1.6   SELECTIVITY

The selectivity (S) of a reaction is defined as the ratio of the amount of desired product formed compared to the amount of reactant converted.

$\%S$ = moles of a specific product/moles of reactant converted

$\times$ (reactant/product stoichiometry) $\times$ 100

A general equation for selectivity of reactant A converting to product C is

$$xA + zB \rightarrow yC \tag{1.39}$$

$$S_C = \frac{(\text{moles } C \text{ produced})(x/y)}{(\text{moles } A \text{ consumed})} \tag{1.40}$$

The catalyst has the potential to greatly influence selectivity by preferentially lowering the activation energy for a particular step in the reaction sequence and increasing the rate at which this step proceeds. For the same reactants at the same conditions, different catalysts will influence the product distribution (selectivity) differently. By choosing the proper catalyst, the selectivity toward the desired product can be enhanced even if other products are more thermodynamically favored. For example, consider the oxidation of ammonia for the production of nitric acid (Chapter 8). Two ammonia oxidation reactions are possible, which are given in Equations 1.41 and 1.42. For the production of nitric acid, it is the formation of NO that is the desired reaction. From a thermodynamic perspective, the equilibrium constant for the N_2-forming reaction is four orders of magnitude more favorable than the desired NO reaction. However, when this reaction occurs in the presence of a Pt–Rh catalyst, the formation of NO greatly exceeds that of N_2. Thus, the Pt–Rh catalyst greatly favors the reaction sequence to form NO and selectively enhances the rate of this reaction over the formation of N_2.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{1.41}$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{1.42}$$

Another example of a catalyst influencing product selectivity is the oxidation of ethylene. Consider the comparison between the products produced when Pt is used as a catalyst as opposed to oxides of vanadium. In the case of Pt, the carbon in the ethylene is completely oxidized to CO_2 with a selectivity of 100%:

$$C_2H_4 + 3O_2 \xrightarrow{\text{Pt}} 2CO_2 + 2H_2O \tag{1.43}$$
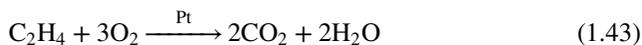
However, the V_2O_5 catalyst favors the selective partial oxidation of only one carbon in the ethylene yielding an aldehyde because this reaction pathway has the lowest activation energy compared to complete combustion to CO_2 and H_2O:

$$C_2H_4 + 3O_2 \xrightarrow{V_2O_5} CH_3CH = O \tag{1.44}$$
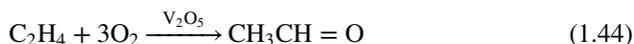
For Pt, the reaction products are exclusively CO_2 and H_2O; thus, selectivity is essentially 100%, making it a good catalyst for pollution abatement. For V_2O_5, the selectivity is about 80–90% toward the aldehyde with the balance 20–10% being

CO_2 and H_2O. Clearly, V_2O_5 would not be desirable for conversion of hydrocarbons such as ethylene to harmless CO_2 and H_2O, but is used commercially for selective partial oxidation reactions to desirable chemicals. So it is the function of the catalyst and reaction conditions to provide the right path that will yield the most desirable product. The ability to (i) enhance reaction rates and (ii) direct reactants to specific products makes catalysis extremely important in the environmental, petroleum, chemical, and alternative energy industry.

An important reaction in the automotive catalytic converter is the reduction of NO by H_2 during a specific driving mode. Two parallel reaction pathways are possible: one desirable leading to N_2 formation and the other undesirable producing toxic NH_3:

$$2H_2 + 2NO \xrightarrow{\text{Rh}} N_2 + 2H_2O \tag{1.45}$$

$$5H_2 + 2NO \xrightarrow{\text{Pt}} 2NH_3 + 2H_2O \tag{1.46}$$
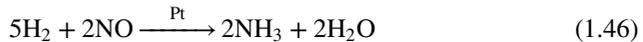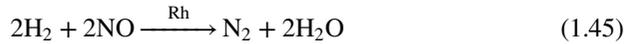
Clearly, Rh is more selective and dominates the NO to N_2 pathway with a rate considerably higher than that with undesired pathway leading to NH_3 formation when Pt is used.

The reaction conditions also have a pronounced effect on product distribution depending on activation energies for all possible reactions. For example, NO (component of acid rain and a contributor to ozone formation) emitted from automobile engines and power plant exhausts can be reduced using a V_2O_5-containing catalyst with high selectivity provided the temperature is maintained between 250–300 °C:

$$2NH_3 + NO + O_2 \xrightarrow{250-300\ °C} 3/2N_2 + 3H_2O \tag{1.47}$$

$$2NH_3 + NO + 5/2O_2 \xrightarrow{>300\ °C} 3NO + 3H_2O \tag{1.48}$$

Ammonia also decomposes to N_2 above 300 °C and thus is not available to reduce the NO:

$$2NH_3 + 3/2O_2 \xrightarrow{>300\ °C} N_2 + 3H_2O \tag{1.49}$$
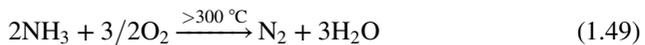
The desired reaction is favored below 300 °C since it has the lowest activation energy of the other two reactions. Once the temperature exceeds 300 °C, the reactions with the higher activation energy (greater temperature sensitivity) become favored and mixed products form.

1.6.1 Examples of Selectivity Calculations for Reactions with Multiple Products

General equation for selectivity:

$$xA + x/2B \rightarrow yC \tag{1.50}$$

$$S_C = \frac{(\text{moles } C \text{ produced})(x/y)}{(\text{moles } A \text{ consumed})} \tag{1.40}$$

To convert to a percent, multiply by 100.

In the example below, we assume 1 mol of NO is converted producing 0.45 mole of N_2:

$$2NO + 2H_2 \rightarrow N_2 + 3H_2O + N_2O + NH_3 \qquad (1.51)$$
$$\text{(1 mol)} \qquad\qquad \text{(0.45 mol)}$$

$$S_{N_2} = \frac{\text{(mole } N_2 \text{ formed)}(2)}{\text{(mole NO converted)}}$$

$$S_{N_2} = \frac{(0.45 \text{ mol})(2)}{(1 \text{ mol})} = 0.90$$

The balance of the NO is converted to a mixture of N_2O and NH_3.

1.6.2 Carbon Balance

In many organic processes, there are several thermodynamically favorable pathways to which reactants can be converted. It is the function of the catalyst and process conditions to direct the reactants to the most desired products. Seldom is selectivity 100% and, therefore, it is necessary to know what other products are being formed and to account for all of the carbon. This is especially important when the feedstock is expensive. The desired product must have a certain purity for commercial use and thus separation from the other products must be conducted, which can be costly. For these cases, it is necessary to know the other compounds containing carbon.

Take for example the catalytic partial oxidation of ethylene to ethylene oxide where the latter is used for the production of terephthalate polyesters and ethylene glycol (antifreeze). An undesired side product is CO_2.

$$H_2C=CH_2 + 1/2 O_2 \longrightarrow \overset{\overset{O}{\diagup\diagdown}}{H_2C-CH_2} \text{ (desired)} \qquad (1.52)$$
$$\longrightarrow CO \text{ (undesired)}$$

The general carbon balance equation can be written as shown below (1.53) and should approach 100%. Although not shown, there may be carbon-containing compounds present on the catalyst in the form of "coke" and should be included in the products. However, often its value is small and is not directly considered in the balance, but is certainly important for the life of the catalyst:

$$\text{Carbon balance} = \frac{(C \text{ atoms in ethylene oxide} + C \text{ atoms in } CO_2)}{(C \text{ atoms in ehtylene})} \qquad (1.53)$$

To convert to a percent, multiply by 100.

In the example above, the carbon in the product is distributed between the desired ethylene oxide and undesired CO_2. Detailed product analysis permits determination of carbon in each, which can then be used to account for all the carbon introduced in the process from ethylene.

1.6.3 Experimental Methods for Measuring Carbon Balance

Many gas-phase reactions lead to either an increase or a decrease in product volume. A conventional way to perform a material balance is to use an internal standard that undergoes no reaction. Commonly N_2 is used. The ratio of grams/time of N_2 to grams/time of total C distributed among many different products will not change. Thus, if the N_2 concentration signal in the product decreases (as measured in a gas chromatograph (GC) by its calibrated peak area), it means there has been a volume expansion that will dilute all the gas components. The ratio of the N_2 concentration in the feed $N_{2\ (in)}$ to the $N_{2\ (prod)}$ concentration in the product gives a measure of the extent of volume increase. The total product flow rate is determined as shown below:

$$(\text{Total flow rate in})\frac{N_{2,in}}{N_{2,prod}} = \text{Total flow rate produced} \qquad (1.54)$$

Equation 1.55 is used for the carbon material balance in which grams/time of carbon in is equal to grams/time of carbon in the product where [] is concentrations:

Flow rate [liter/time] $\times$ Concentration [grams/liter] $=$ grams/time
$(\text{Flow rate})_{in} \times [\text{carbon in reactant}]_{in} = (\text{Flow rate})_{prod} \times [\text{carbon in products}]_{prod}$

$$(1.55)$$

The material balance is achieved by comparing all of the carbon distributed in the products with the carbon introduced from the reactants. Ideally, it should be 100%. If less, there is some carbon that has not been measured, which may be a small amount of coke (i.e., carbon) deposited on the catalyst.

QUESTIONS

1. Distinguish a homogeneous catalyst and process from a heterogeneous catalyst and process.

2. Why is it important to maximize the number of active sites in a heterogeneous catalyst?

3. In your own words, what is activation energy and how is it measured experimentally?

4. What is the practical value in preparing a catalyst or adjusting the process conditions by knowing the activation energy of a reaction?

5. How would you change the process conditions by knowing that in a hydrocarbon oxidation reaction, the hydrocarbon has a very large inhibition effect as in the following equation:
$$\text{Rate} \sim k[(\text{Kads}_{HC}\ PP_{HC})(\text{Kads}_{O_2}\ PP_{O_2})]/(\text{Kads}\ PP_{HC})$$

6. **a.** How does the presence of a catalyst change the thermodynamic equilibrium constant of a reaction?

   b. Two reactions are thermodynamically feasible (both have negative free energies), but one is much more negative than the other. Can a catalyst direct the reactants to the least favorable?

7. What are the benefits of using a catalyst for abating emissions?

8. Derive the L–H rate expression for the decomposition of PH_3 on a W metallic catalyst where no products adsorb:

$$PH_3 \rightarrow P + 3/2H_2$$

9. Write the L–H for N_2O decomposition on Pt where both the N_2O and the product O_2 strongly adsorb onto the Pt. Make a plot of rate versus conversion of N_2O.

10. What catalyst properties (assume the catalyst is Pt dispersed on porous Al_2O_3 present as a thin coating (washcoat) on a ceramic monolith) and process conditions will enhance the rate of a gas-phase reaction if the reaction is controlled by

   a. chemical kinetics?

   b. pore diffusion?

   c. bulk mass transfer?

11. What temperature is required for a catalyst with an activation energy of 15,000 cal/mol to operate with the same volume as one with an activation energy of $E = 12,000$ cal/mol (operation temperature is 227 °C) with the same conversion? Assume k_0 is the same for both catalysts. $R = 2$ cal/°K.

12. How will the rate constant (and hence the reaction rate) change when the temperature is increased from 100 to 110 °C? Assume an activation energy of 20 kcal/mol with the universal gas constant $= 2$ cal/(deg mol). Feel free to use joules also for activation energy with ($R = 8.3$ J/(mol °K)).

13. a. Consider a reaction with two possible product distributions: one desired and the other not. Why is it important to know their respective activation energies?

   b. What conditions temperature and concentrations would you use in the process to favor the desired reaction? Plot their respective relative rates versus temperature.

14. What properties of the particulate catalyst and process conditions can be changed to enhance the rate-limiting step for each of the four separate cases of rate control?

   1. Bulk mass transfer

   2. Pore diffusion

   3. Chemical

   4. Heat transfer

15. Consider a scenario where one reactant could undergo two different reactions leading to two products. Why is it important to know the respective activation energy of each possible reaction?
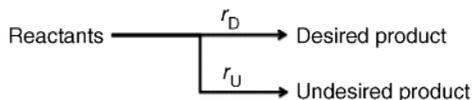
16. You are hired to troubleshoot a fixed bed catalyst, oxidizing a pollutant (CO) with air (O_2) to CO_2. The operator tells you that conversion does not increase significantly as the temperature is increased by 30 °C.

   a. What could cause such an observation?

   b. How would you verify this by doing one experiment?

17. Sketch out the conversion–temperature profile and Arrhenius plot for the above catalyst if the reaction operates up to 200 °C in kinetic control, from 200–250 °C in pore diffusion control, and above 250 °C in bulk mass transfer control. A maximum conversion of 99% is achieved at 300 °C.

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