PART I

Fundamentals

1 Catalyst Fundamentals

1.1 INTRODUCTION

Chemical reactions occur by breaking chemical bonds of reactants and by forming new bonds and new compounds. Breaking stable bonds requires the absorption of energy, whereas 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 the rate by which reactants are converted to products. Similarly, the free energy of reaction (ΔG) of the reaction is not dependent on the reaction path because 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

A few decades ago, chlorofluorocarbons (i.e., CF_2Cl_2), emitted primarily from refrigerants, were found to catalyze the destruction of the ozone (O_3) layer in the stratosphere necessary to protect us from harmful ultraviolet (UV) radiation and its skin cancer consequences. Fortunately alternative chemicals are now used, and this problem is no longer of great concern. It does, however, serve as an excellent example of a homogeneous gas phase catalytic reaction. First let us consider the very slow noncatalytic reaction between gaseous O_3 and O atoms produced by dissociation of O_2 by solar radiation in the upper atmosphere:

$$O_3 + O \rightarrow 2O_2 \tag{1.1}$$

Catalytic Air Pollution Control: Commercial Technology, by Ronald M. Heck and Robert J. Farrauto, with Suresh T. Gulati.

Chlorine atoms, produced by solar radiation of chlorofluorohydrocarbons, catalyze the decomposition of ozone by reacting with it to form ClO and O_2 (1.2). The ClO then reacts with the O atoms regenerating Cl and producing more O_2 (1.3).

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \tag{1.2}$$

$$\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2} \tag{1.3}$$

Adding both reactions results in Eq. (1.1) and completes the catalytic cycle since the Cl and ClO are both consumed and regenerated in the two reactions. Thus, Cl is a homogeneous catalyst for the destruction of O_3. The uncatalyzed reaction is very slow, and its reaction profile can be described kinetically by the Arrhenius profile in which reactants convert to products by surmounting the noncatalytic activation energy barrier (E_{NC}) as shown in Figure 1.1. The rate constant k of the reaction is inversely related to the exponential of the activation energy, where T is the absolute temperature, R is the universal gas constant, and k_o is the preexponential constant. The Arrhenius equation (1.4) indicates that the rate constant k decreases the higher the activation energy (E).

$$k = k_o \mathrm{Exp}\,(-E/RT) \tag{1.4}$$

Since the catalyzed reaction has a lower activation energy (E_C), its reaction rate is greater. The barrier was lowered by the Cl catalyst providing a chemical shortcut to products. Although the rate is greater for the catalyzed reaction, the enthalpy (ΔH) and free energy (ΔG) are not changed. Similarly the equilibrium constant for both catalyzed and noncatalyzed reactions is not changed

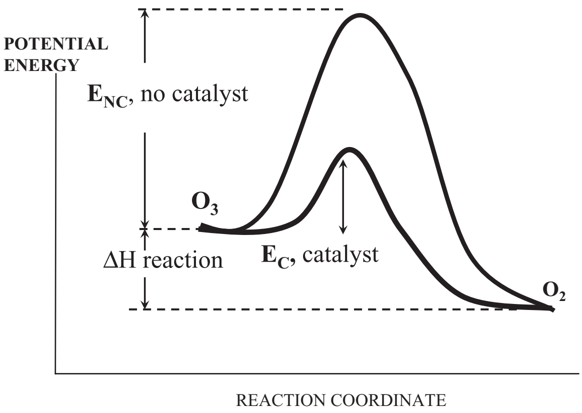
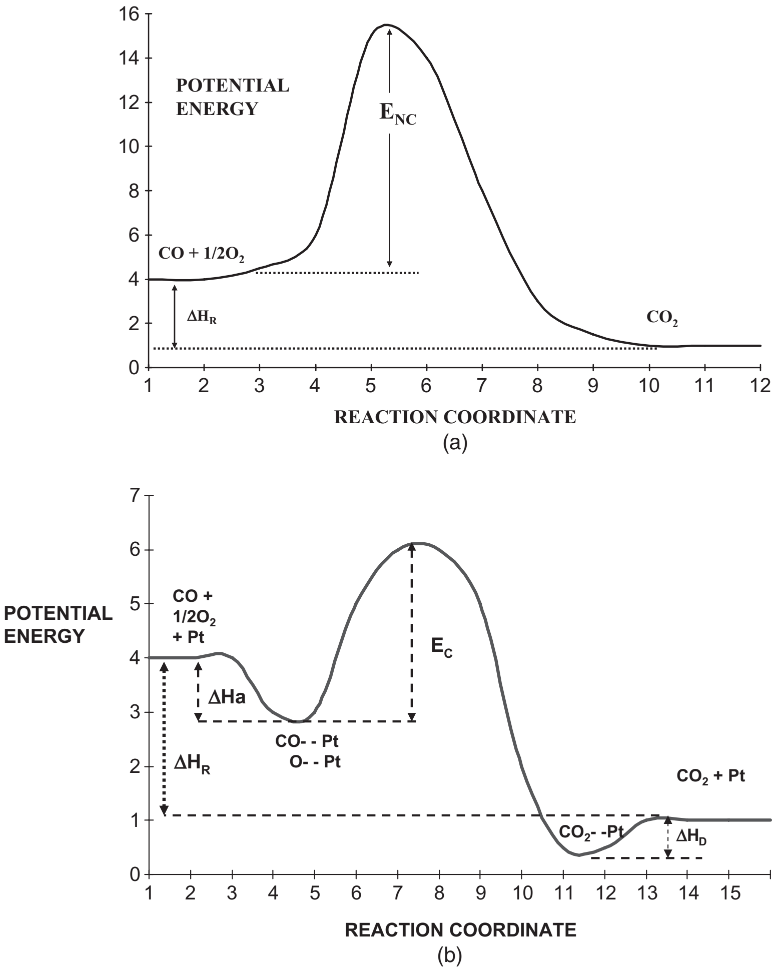


FIGURE 1.1. Catalyzed and uncatalyzed reaction energy paths for O_3 decomposition to O_2. Activation energy for catalyzed reaction E_C is lower, and the reaction is faster than the noncatalyzed E_{NC}.

since both operate under the same reaction conditions in the stratosphere. The catalyst can only influence the rate of which reactants are converted to products in accordance to the equilibrium constant and cannot make thermodynamically unfavorable reactions occur. In industrial practice, reactions conditions, such as temperature and pressure, are varied to bring the free energy to a desirable value to permit the reaction to occur.

Now we will 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 daily. The overall rate of the noncatalytic reaction is controlled by the dissociation of the O_2 molecule to O atoms (rate-limiting step), which 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 an activation energy (E_{NC}). 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 (E_{NC}) shown in Figure 1.2a). The rate of reaction is expressed in accordance with the Arrhenius equation (1.4). Typically the activation energy for the noncatalytic or thermal conversion of CO to CO_2 is about 40 Kcal/mole.

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 now carried out in two separate phases, the term *heterogeneous catalytic reaction* is used. In the presence of a catalyst such as Pt, the O_2 and CO molecules adsorb on separate 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 molecules to chemisorbed O atoms is rapid, occurring essentially at room temperature. Highly reactive adsorbed O atoms react with chemisorbed CO on adjacent Pt sites producing CO_2, which desorbs from the Pt site, completing the reaction and freeing the catalytic site for another cycle. Thus, the activation energy for the Pt catalyzed reaction (E_c), shown in Figure 1.2b), is considerably smaller than that for the noncatalyzed reaction, enhancing the conversion kinetics. Typically the activation energy for Pt catalyzed CO to CO_2 is less than about 20 Kcal/mole. Figure 1.3 shows the initial lightoff of a conversion versus temperature plot for the catalyzed reaction occurring around 100 °C. The noncatalyzed reaction has a considerably higher lightoff temperature (around 700 °C) because of its higher activation energy. More input energy is necessary to provide the molecules the necessary energy to surmount the activation barrier so lightoff 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 the activation energy has the 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 CO and hydrocarbon oxidation, where noncatalytic free radical reactions, with large



(a)

(b)

FIGURE 1.2. Activation energy diagram for a) thermal reaction of CO and O_2 and b) the same reaction in the presence of Pt. Activation energy for the noncatalyzed reaction is E_{NC}. The Pt catalyzed reaction activation energy is designated E_c. Note that the heat of reaction ΔH_R is the same for both reactions. ΔH_a = heat of adsorption; ΔH_D = heat of desorption.

activation energies, can lead to undesirable products. Thus, the temperature must be carefully controlled within the reactor.

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.

The environmental significance of catalyzed reactions is now apparent; a reaction can be carried out at much lower temperatures consistent with startup conditions in an automobile converter. Kinetic rate studies indicate that the

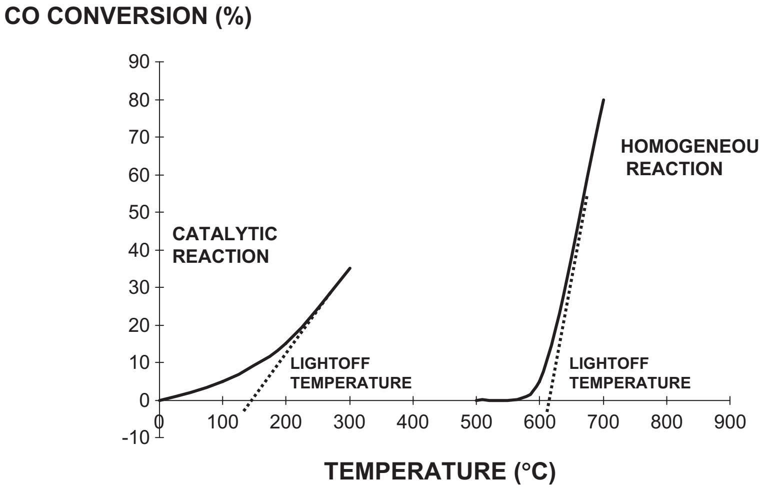


FIGURE 1.3. Conversion of CO versus temperature for a noncatalyzed (homogeneous) and a catalyzed reaction.

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 from one of high-temperature dissociation of O_2 to that of the reaction between two adsorbed moieties on adjacent Pt sites at a significantly lower temperature. This shows the great importance of catalysis in enhancing rates of reaction, allowing them to occur at moderate temperatures as indicated in this example. A lower operating temperature translates into 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 ranging from petroleum processing, chemical and energy synthesis, to environmental emission control (Bartholomew and Farrauto 2006).

Inspection of Figure 1.2b) indicates an energy decrease associated with the adsorption of CO and O_2 on the Pt surface (ΔH_a) because of its exothermic nature. This is a consequence of the decreased entropy (ΔS) when the molecules are confined in an adsorbed state with the commensurate loss in a degree of freedom. Because 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.

The catalytic reaction is usually carried out in a fixed-bed reactor similar to that shown in Figure 1.4. Here we introduce the monolithic support upon the walls of which is deposited the catalysts called a catalyzed washcoat. This is the common support used in environmental applications for reasons to be given in later chapters. The proper flow of inlet reactant gas is established by

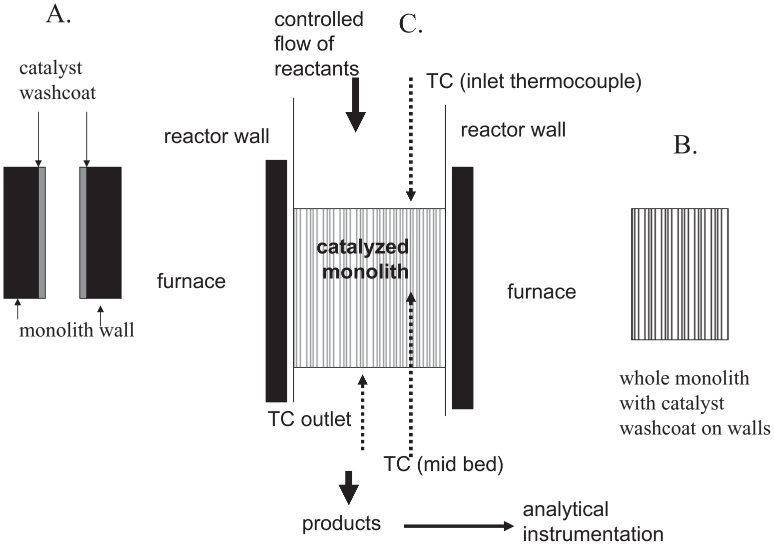


FIGURE 1.4. Fixed bed reactor containing a catalyzed monolith for measurement of conversion versus temperature. A) Single channel of catalyzed monolith. B) Monolith structure with walls coated with catalyzed washcoat. C) Catalyzed washcoat on a monolith in the reactor surrounded by a furnace.

individually controlled mass flow meters. The mixed reactants are continuously preheated, and the conversion of reactants and the appearance of products are observed using analytical instrumentation such as a gas chromatograph or other suitable equipment specific for reactants and products such as a CO and CO_2 analyzer, hydrocarbon analyzer, and so on. The inlet, mid-bed, and outlet temperatures are commonly measured using thermocouples.

1.2.1 Adsorption and Kinetic Models for CO Oxidation on Pt: Langmuir–Hinshelwood Kinetics

1.2.1.1 Langmuir Isotherm. The most 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 (Hinshelwood 1940; Hougen and Watson 1943). The Langmuir isotherm is based on the key assumption that all sites on the adsorbent surface are of equal energies. It also assumes the rate-limiting step is the surface reaction between adsorbed species with all others fast and in equilibrium. Despite this ideal view, its application yields reasonable predictions.

Consider the strong adsorption of CO in equilibrium with the surface of Pt.

$$CO + Pt \leftrightarrow CO\text{ - - - }Pt \tag{1.5}$$

The rate of forward (CO adsorption) is given by

$$(\mathrm{Rate})_{\mathrm{fCO}} = \mathrm{k_{fCO}P_{CO}}(1-\theta_{\mathrm{CO}}) \tag{1.6}$$

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

The rate of reverse (CO desorption) is as follows:

$$(\mathrm{Rate})_{\mathrm{dCO}} = \mathrm{k_{dCO}}\theta_{\mathrm{CO}} \tag{1.7}$$

At equilibrium, the forward and desorption rates are equal and the ratio of the forward rate to reverse rate is

$$\mathrm{k_{fCO}/k_{dCO} = K_{CO}} \tag{1.8}$$

$$\mathrm{k_{fCO}P_{CO}}(1-\theta_{\mathrm{CO}}) = \mathrm{k_{dCO}}\theta_{\mathrm{CO}} \tag{1.9}$$

$$\theta_{\mathrm{CO}} = \mathrm{K_{CO}P_{CO}/(1+K_{CO}P_{CO})} \tag{1.10}$$

Plotting Eq. (1.10) generates Figure 1.5.

When $\mathrm{P_{CO}}$ is large,

$$\mathrm{(1+K_{CO}P_{CO}) \sim K_{CO}P_{CO}} \tag{1.11}$$

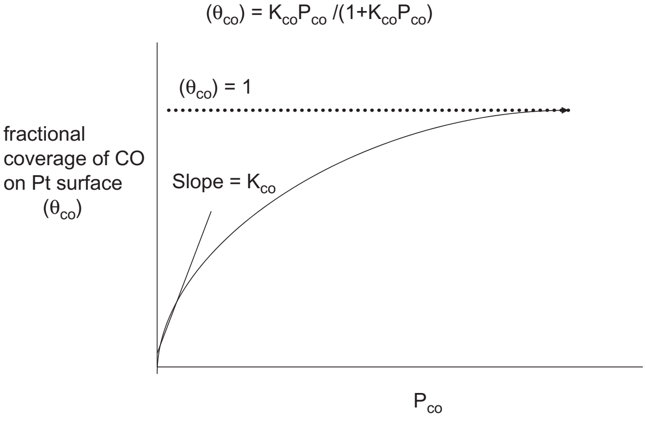


FIGURE 1.5. Adsorption isotherm (θ_{CO}) for CO on Pt for large, moderate, and low partial pressures of CO. The slope at low partial pressures of CO equals the adsorption equilibrium constant $\mathrm{K_{CO}}$.

Eq. (1.10) reduces to $\theta_{CO} = 1$ representing monolayer coverage of the surface by CO.

When CO is small,

$$(1 + K_{CO}P_{CO}) \sim 1 \tag{1.12}$$

and Eq. (1.10) reduces to $\theta_{CO} = K_{CO}\ P_{CO}$ with the slope equal to K_{CO}.

At moderate values of P_{CO}, Eq. (1.10) applies as written with the curve becoming more shallow as P_{CO} increases.

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 stiochiomety for CO oxidation of one O atom for each CO.

$$O_2 + Pt \leftrightarrow 2O \text{ - - - } Pt \tag{1.13}$$

The rate of the forward (adsorption of O_2 on Pt) is as follows:

$$(\text{Rate})_{fO2} = k_{fO2}P_{O2}(1 - \theta_O)^2 \tag{1.14}$$

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

$$(\text{Rate})_{dO2} = k_{dO2}\theta_O^2 \tag{1.15}$$

The square term for both the forward and reverse rates is from the lower probability that two adjacent Pt sites will be available to accommodate two oxygen atoms resulting from the dissociative chemisorption of O_2 on Pt. Similarly two adsorbed O atoms on Pt must be adjacent for desorption and recombination of diatomic O_2 to occur. Also the adsorption equilibrium constant (K_{O2}) for O_2 on Pt is $k_{fO2/}k_{dO2}$.

Equating forward and reverse rates,

$$k_{fO2}P_{O2}(1 - \theta_O)^2 = k_{dO2}\theta_O^2 \tag{1.16}$$

$$\theta_O = K_{O2}^{1/2}P_{O2}^{1/2} / (1 + K_{O2}P_{O2})^{1/2} \tag{1.17}$$

Plotting the fractional coverage of oxygen atoms versus $P_{O2}^{1/2}$ generates a similar plot as in Figure 1.5, but the slope at low $P_{O2} = K_{O2}^{1/2}$. At high P_{O2} $\theta_O = 1$.

1.2.1.2 Langmuir–Hinshelwood Kinetics for CO Oxidation on Pt.

The adsorption isotherms for CO and O_2 were considered separately in Section 1.2.1.1, but for the oxidation of CO by O_2, it is necessary to consider both gases present with each competing for the same sites on Pt. We will use k as the rate constant for the oxidation of CO.

The net rate of reaction for CO oxidation will be

$$[\text{Rate}]_{CO} = k\theta_{CO}\theta_{O} \tag{1.18}$$

Coverage for both θ_{CO} and θ_{O} must be modified to include competitive adsorption on Pt sites.

To account for the sites occupied by O atoms, the rate for forward adsorption of CO is written as follows:

$$(\text{Rate})_{fCO} = k_{fCO}P_{CO}(1-\theta_{CO}-\theta_{O}) \tag{1.19}$$

The desorption rate for CO only depends on the sites occupied by CO [as shown in Eq. (1.7) and reprinted below]:

$$(\text{Rate})_{dCO} = k_{dCO}\theta_{CO}$$

Equating adsorption (1.19) and desorption (1.7) rates at equilibrium and recognizing that $k_{fCO} / k_{dCO} = K_{CO}$

$$K_{CO}P_{CO} = \theta_{CO}/(1-\theta_{CO}-\theta_{O}) \tag{1.20}$$

For the rate of adsorption and desorption of O_2, we obtain

$$K_{O2}^{1/2}P_{O2}^{1/2} = \theta_{O}/(1-\theta_{CO}-\theta_{O}) \tag{1.21}$$

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

$$\theta_{O} = \theta_{CO}K_{O2}^{1/2}P_{O2}^{1/2}/K_{CO}P_{CO} \tag{1.22}$$

Substitute Eq. (1.22) into Eq. (1.20):

$$\theta_{CO} = K_{CO}P_{CO}/(1+K_{CO}P_{CO}+K_{O2}^{1/2}P_{O2}^{1/2}) \tag{1.23}$$

Substitute Eq. (1.23) into Eq. (1.22):

$$\theta_{O} = K_{O2}^{1/2}P_{O2}^{1/2}/(1+K_{CO}P_{CO}+K_{O2}^{1/2}P_{O2}^{1/2}) \tag{1.24}$$

Now we have an expression for θ_{CO} and one for θ_{O}, so substituting these terms into [as shown in Eq. (1.18) and reprinted below]:

$$[\text{Rate}]_{CO} = k\,\theta_{CO}\theta_{O}$$

$$[\text{Rate}]_{CO} = k\,K_{CO}P_{CO}K_{O2}^{1/2}P_{O2}^{1/2}/(1+K_{CO}P_{CO}+K_{O2}^{1/2}P_{O2}^{1/2})^{2} \tag{1.25}$$

For low P_{CO}, Eq. (1.25) reduces to Eq. (1.26):

$$[\text{Rate}]_{CO} = k\, K_{CO} P_{CO} K_{O2}^{1/2} P_{O2}^{1/2} \big/ \left(1 + K_{O2}^{1/2} P_{O2}^{1/2}\right)^2 \tag{1.26}$$

This shows a direct relationship between the rate and the P_{CO} when P_{O2} is constant

For large P_{CO}, Eq. (1.25) reduces to Eq. (1.27):

$$[\text{Rate}]_{CO} = k\, K_{O2}^{1/2} P_{O2}^{1/2} / (P_{CO} K_{CO}) \tag{1.27}$$

This shows that at high P_{CO}, the reaction rate is inhibited by CO and its rate of oxidation decreases. Thus, a maximum in rate exists when

$$\theta_O = \theta_{CO}$$

This is shown graphically in Figure 1.6.

Applying this model was 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_{O2} 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.

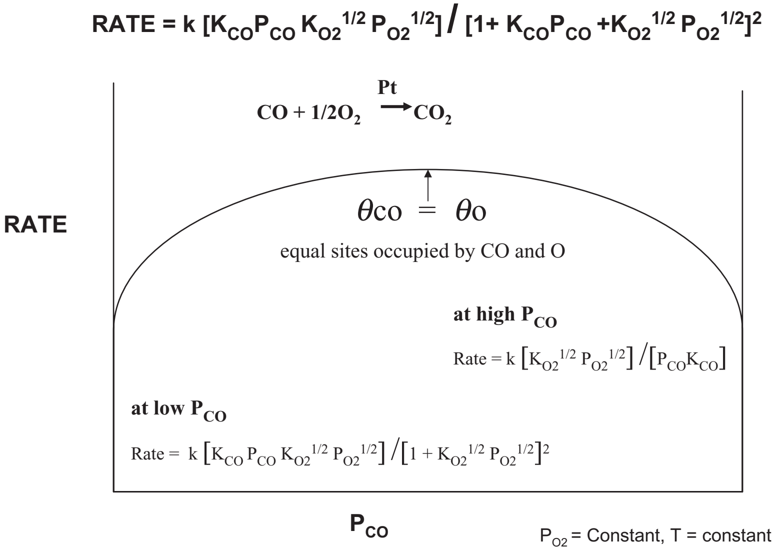


FIGURE 1.6. LH kinetics applied to increasing P_{CO} at constant P_{O2}. Maximum rate was achieved when an equal number of CO molecules and O atoms is adsorbed ($\theta_O = \theta_{CO}$) on adjacent Pt sites.

A heterogeneous catalytic surface consists of a distribution of strong, moderate, and weak sites upon which the reactant molecules adsorb. Naturally with increasing temperature, only the stronger sites retain adsorbed molecules and the fractional coverage decreases. This action results in a change in the overall energy of the adsorbed states on the activation energy profile of Figure 1.2b). Fundamentally, with increasing temperature, this causes a small change in the activation energy but for all intents and purposes can be ignored when making activation energy measurements. Measurements of activation energies will be discussed later.

1.3 CATALYTIC COMPONENTS

Precious metals (often referred to as the Pt group metals or PGMs) are located in group VIIIB of the periodic table and consist of Ru, Rh, Pd, Ir, Pt, and Os. For environmental emission control applications, Pt, Pd, and Rh dominate as the main catalytic components individually or in combinations; however, they also are commonly used in processing petroleum to transportation fuels and for the synthesis of many important chemicals (Bartholomew and Farrauto 2006). Ironically the PGMs are also referred to as the noble metals for their resistance to oxidation, various poisons, and high temperatures; yet they are some of the most catalytically active elements in nature because of their ability to chemisorb and convert adsorbed species with high rates. They are rare and 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.

Other group VIIIB metals and their oxides such as Fe, Co, and Ni are also catalysts as are Cu and Ag (group IB) , V (group VB), and Cr and Mo (group VIB) for industrial applications (Bartholomew and Farrauto 2006). Some of these base metals have modest catalytic activities relative to Pt, Pd, and Rh but are much less expensive and, in certain cases, more selective. It is common practice in commercial applications, especially in automotive catalysts, to pursue base metal materials as replacements for precious metals; however, because of their lower activity, vulnerability to poisons, and lack of hydrothermal stability in the severe environment of an automobile exhaust, this quest has not been successful.

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

1.4 SELECTIVITY

The catalyst also affects the selectivity or rate of desired product formation by preferentially lowering the activation energy for a particular step in the reaction sequence and increasing the rate at which this step proceeds. Selectivity is an issue for many reactions in which multiple products can occur in parallel. Different catalysts and/or reaction conditions can preferentially enhance the rate at which reactants are converted to desired products even though many other paths are thermodynamically more or less favorable. Selectivity is the rate of one reaction compared with the rate of parallel paths the reactants may take to other products. Industry describes a process based on the % selectivity to a particular product. The most desirable catalyst and process conditions will have the highest selectivity.

Consider the comparison between the products produced when Pt is used as a catalyst as opposed to oxides of vanadium for the oxidation of ethylene, a hydrocarbon component in automobile exhaust:

$$C_2H_4 + 3O_2 \xrightarrow{Pt} 2CO_2 + 2H_2O \tag{1.28}$$

V_2O_5 catalyzes the formation of the aldehyde because this pathway with this catalyst has the lowest activation energy compared with the complete combustion to CO_2 and H_2O:

$$C_2H_4 + 1/2\,O_2 \xrightarrow{V_2O_5} CH_3CH{=}O \tag{1.29}$$

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. However, for V_2O_5, the selectivity is about 80–90% toward the aldehyde, with the balance of 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 it is used commercially for selective partial oxidation reactions to desirable chemicals. So it is the function of the catalyst with optimum reaction conditions to reduce the activation energy of the path that will yield the most desirable product. The ability to (1) enhance reaction rates and (2) direct reactants to specific products makes catalysis extremely important in the environmental, petroleum, and chemical industries.

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

$$2H_2 + 2NO \xrightarrow{Rh} N_2 + 2H_2O \tag{1.30}$$

$$5H_2 + 2NO \xrightarrow{Pt} 2NH_3 + 2H_2O \tag{1.31}$$

Clearly Rh is more selective and dominates the NO-to-N_2 pathway with a rate considerably higher than that undesired pathway leading to NH_3 formation when Pt is used.

The reaction conditions also have a pronounced effect on product distribution depending on the activation energies for all possible reactions. For example, NO (a 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 °C and 400 °C:

$$2NH_3 + NO + O_2 \xrightarrow{250-400°C} 3/2\,N_2 + 3H_2O \tag{1.32}$$

$$2NH_3 + NO + 5/2\,O_2 \xrightarrow{>400°C} 3NO + 3H_2O \tag{1.33}$$

Ammonia also decomposes to N_2 above 400 °C and, thus, is not available to reduce the NO:

$$2NH_3 + 3/2\,O_2 \xrightarrow{>400°C} N_2 + 3H_2O \tag{1.34}$$

The desired reaction is favored below 400 °C since it has the lowest activation energy of the other two reactions. Once the temperature exceeds 400 °C, the reactions with the higher activation energy (greater temperature sensitivity) become favored and mixed products form.

1.5 PROMOTERS AND THEIR EFFECT ON ACTIVITY AND SELECTIVITY

The main catalytic component dominates the activity and the selectivity, but oxides or metal promoters, which may or may not be catalytic for the reaction of interest, can promote the activity or enhance one reaction over another. There are many examples in the industrial literature for a wide variety of petroleum and chemical processes (Bartholomew and Farrauto 2006), but we will focus on environmental applications. 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. It has other functions as well, which will be described in the catalytic converter chapter. Using TiO_2 as a carrier for Pt enhances the rate of oxidation reactions for some and finds use in low-temperature applications (Bollinger and Vannice 1996; Grisel and Nieuwenhuys 2001; Bond et al. 2006). One can speculate that the presence of TiO_2 as a carrier for metals promotes the oxidation rate by providing sites for O_2 to dissociate and adsorb, minimizing competition with CO for metal. The addition of a small amount of iron oxide as a promoter to a Pt-containing catalyst enhances the kinetics of the oxidation of CO in the presence of large excesses of H_2. This purification technique, called preferential oxidation or PROX, is used to produce fuel cell quality H_2 with less than 10 vppm of CO. In the presence of a Pt catalyst promoted with oxides of Fe, the O_2 added reacts selectively with the CO without oxidizing appreciable amounts of the H_2. The O_2 dissociatively chemisorbs on the iron oxide and reacts with the CO adsorbed on Pt. In the absence of the promoter oxide, the reaction rate is considerably slower and seems to obey LH-type kinetics where the CO and O_2 compete for Pt sites. Thus, a competitive reaction is altered to one that is noncompetitive and the kinetics are significantly enhanced (Liu et al. 2002; Korotkikh and Farrauto 2000).

One may also consider a mechanism in which the lattice oxygen associated with the TiO_2 or CeO_2 contributes the O atom directly to the species to be oxidized and is replenished by gas phase O_2. This mechanism is called Mars–van Krevlen and has been applied to reactions involving reducible oxide carriers as well as to base metal oxides that are active for both CO and hydrocarbon oxidation reactions (Mars and van Krevelen 1954). It has also been suggested for the oxidation of methane on Pd/Al_2O_3 (Hurtado et al. 2004; Avgouropoulos et al. 2002).

One more example will be instructive in demonstrating the important role of small amounts of promoters in altering catalyst selectivity. In the generation of fuel cell quality H_2, the gas stream is enriched in H_2 by promoting the oxidation of CO by water in the water gas shift reaction using a Pt-containing catalyst (1.35). For a Pt-only catalyst, appreciable amounts of undesired methane are formed during the reaction at 300 °C. The addition of 5–10% ZnO to the catalyst suppresses the methanation reaction (1.36) and avoids the consumption of H_2 and the large exotherm associated with the reaction (Korotkikh et al. 2003):

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{1.35}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{1.36}$$

1.6 DISPERSED MODEL FOR CATALYTIC COMPONENT ON CARRIER: PT ON AL_2O_3

In many 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, therefore, common practice to maximize the number of active sites by dispersing the catalytic components onto a surface. 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. It is common practice to disperse the catalytic components on a high-surface-area carrier, such as Al_2O_3,

SiO_2, TiO_2, SiO_2-Al_2O_3, zeolites, CeO_2, and so on. In some cases, but not for environmental applications, nonoxides such as high-surface-area carbons are also used as carriers. The carriers themselves usually are not catalytically active for the specific reaction in question, but they do play a major role in promoting the activity and selectivity as well as in maintaining the overall stability and durability of the finished catalyst.

The preparation and properties of these materials and their influence on catalytic reactions will be discussed in Chapter 2, but, for now, Al_2O_3 (the most commonly used carrier in catalysis especially for environmental applications) will be used to develop a model of a heterogeneous catalyst. Figure 1.7 is a drawing of a few select pores of a high-surface-area Al_2O_3.

The drawing shown has 20 and 100 Å (2–10 nanometers) pores into which Pt, or any other catalytic component, has been deposited by solution impregnation. The Pt particles or crystallites are represented as dots. When the Al_2O_3 is bonded to a monolithic honeycomb support, which will be described in Chapter 2, it is called a *washcoat*. The internal surface of the Al_2O_3 is rich in surface OH^- groups (not shown), depending on the type of Al_2O_3 and its thermal history. These OH^- species that cover the entire internal surface and are part of the walls of each pore represent sites upon which one can chemically or physically bond a catalytic substance. The physical surface area of the Al_2O_3 is the sum of all internal areas of the oxide from all the walls of each and every pore. It is upon these internal walls and at the OH^- sites that the catalytic components are bound. The catalytic surface area is the sum of all the areas of the active catalytic components in this example, Pt. The smaller the individual size of the crystallites of the active catalytic material (higher catalytic surface area), the more sites are 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

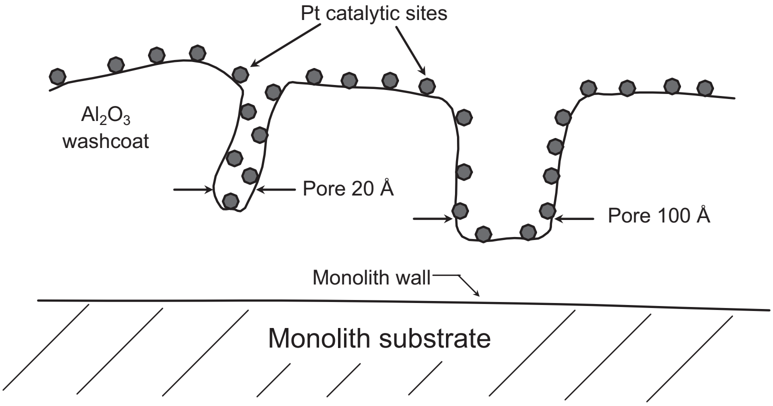


FIGURE 1.7. Conceptual, highly idealized model for catalytic sites dispersed on a high-surface-area Al_2O_3 carrier bonded to a monolith support.

the case, but there are exceptions in which a particular reaction is said to be structurally sensitive and the rate is a maximum when interacting with a catalytic crystal size of a specific size range.

The tiny Pt-containing particles shown in Figure 1.7 are dispersed throughout the porous Al_2O_3 carrier network and generate a high-Pt surface area. As it is shown, every Pt atom is available to the reactants. This model is highly idealized since the Pt sites typically vary in size and usually are not 100% dispersed as shown. This procedure maximizes the catalytic 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 (Bartholomew and Farrauto 2006; Morbidelli et al. 2001). These are discussed below.

1.7 CHEMICAL AND PHYSICAL STEPS IN HETEROGENEOUS CATALYSIS

To maximize reaction rates, it is essential to ensure the accessibility of all reactants to the active catalytic component sites dispersed within the internal pore network of the carrier. Consider a reaction in which CO and O_2 molecules are flowing through a bed of a heterogeneous 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 (or washcoat in the case of a monolithic-supported catalyst) containing the catalytic sites. To do so, they must diffuse through a stagnant thin layer of gas or boundary layer in close contact with the catalyzed carrier. Bulk molecular diffusion rates vary approximately with $T^{3/2}$ and typically have "apparent" activation energies, $E_1 = 2$–4 Kcal/mole.

   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 physical phenomena and thus are not activated processes. The term "apparent" activation energy is a convenient term used to give a figure of merit for reaction sensitivity to temperature.
2. Since the bulk of the catalytic components are internally dispersed, most 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 6–10 Kcal/mole.
3. Once molecule CO and O_2 arrive at the catalytic site, O_2 dissociates quickly and chemisorption of both O and CO occurs on adjacent catalytic sites. The kinetics generally follow exponential dependence on tem-

perature; i.e., exp ($-E_3/RT$), where E_3 is the activation energy, which for chemisorption is typically greater than 10 Kcal/mole.

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, which remains adsorbed on the catalytic site. Kinetics also follow exponential dependence on temperature, i.e., ($-E_4/RT$), with activation energies typically greater than 10 Kcal/mole.
5. CO_2 desorbs from the site obeying exponential kinetics, i.e., exp($-E_5/RT$), with activation energies typically greater than 10 Kcal/mole.
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 are less than 2–4 Kcal/mole.

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, as illustrated in steps 2 and 6, depends primarily on the size and shape of both the pore and the diffusing reactants and product. 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).

Any of the seven steps listed above can be rate limiting and control the overall rate of reaction. Let us take, for example, the conversion of any reactant to product using a heterogeneous catalyst. This is shown graphically in Figure 1.8.

Chemically controlled reactions determine the overall reaction rate initially, but their high sensitivity to temperature (high activation energy) relative to those controlled by diffusion is apparent by its steep rise in conversion with temperature. 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 1.9, which 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 because of its lower "apparent" activation energy. Pore diffusion has a lower reaction rate than BMT because of its higher "apparent" activation energy, but its temperature dependence is greater. The highest temperature dependence occurs for a reaction controlled by chemical kinetics, but because of its higher activation energy, the rate is low at low temperatures relative to those controlled by diffusion (Morbidelli et al. 2001).

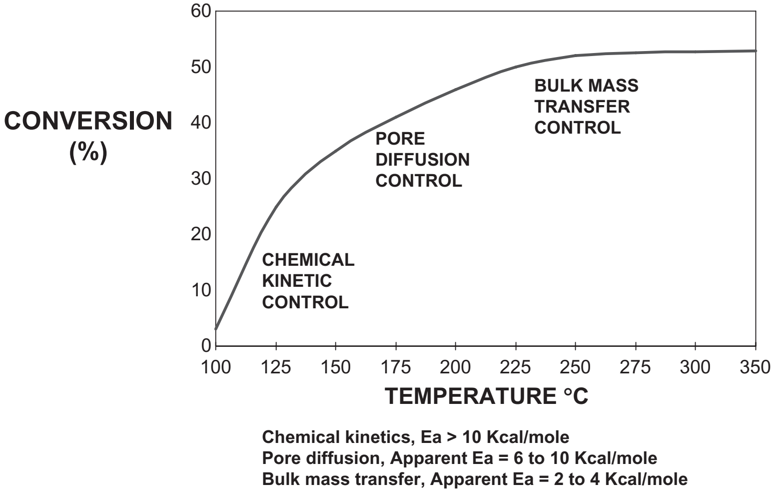


FIGURE 1.8. Conversion versus temperature profile illustrating regions for chemical kinetics, pore diffusion, and bulk mass transfer control.

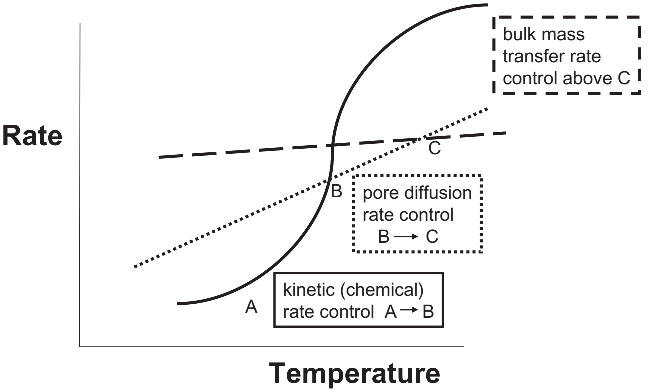


FIGURE 1.9. Relative rates of bulk mass transfer, pore diffusion, and chemical kinetics as a function of temperature. Chemical kinetics controls the rate between temperatures A and B. Pore diffusion controls from B to C, whereas bulk mass transfer controls at temperatures greater than C.

1.7.1 Reactant Concentration Gradients within the Catalyzed Washcoat

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 gaseous CO and O_2 can be supplied to the sites and a concentration gradient exists decreasing within the washcoat. This is referred to as intraparticle diffusion in which the catalytic components deep within the washcoat are not

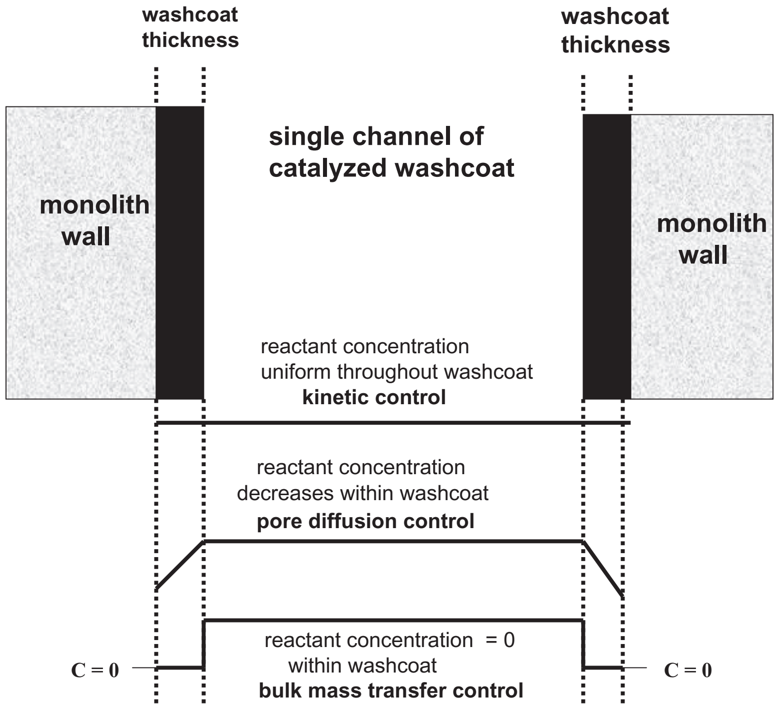


FIGURE 1.10. Reactant concentration gradients within a single channel of washcoat for three regimes controlling the rate of reaction.

being completely used or have an effectiveness factor less than 1. The effectiveness factor is the ratio of the actual rate versus the theoretical maximum rate and 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 washcoat 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 washcoat. The concentration of reactant and product is essentially zero at the external interface of the washcoat and the bulk fluid. The effectiveness factor is close to zero. Figure 1.10 graphically shows the relative gradients in concentration for reactants for the three rate-controlling processes in a catalyzed washcoat.

1.8 PRACTICAL SIGNIFICANCE OF KNOWING 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 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. Furthermore, the catalytic components should be dispersed uniformly throughout the interior of the carrier 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. To enhance the transport rate, one can decrease the thickness of the washcoat to decrease the diffusion path of reactants and products. A temperature increase will have some effect on 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) of the washcoated monolithic catalyst. This can be accomplished by selecting a monolith with a high geometric surface area or density of channels per unit area. 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.

REFERENCES

Avgouropoulos, G., Ioannides, T., Papadopoulos, C., Hocevar, S., and Matralis, H. "A comparative study of Pt/Al_2O_3, Au/Ce-Fe_2O_3 and CuO-CeO_2 catalysts for the selective oxidation of carbon monoxide in excess hydrogen," *Catalysis Today* 75: 157 (2002).

Bartholomew, C., and Farrauto, R. *Fundamentals of Industrial Catalytic Processes*, Second Edition, Wiley and Sons, Hoboken, NJ (2006).

Bollinger, M., and Vannice, M. A. "A kinetics and Drift study of low temperature carbon monoxide oxidation over Au-TiO2 catalysts," *APCAT B: Environmental* 8: 417 (1996).

Bond, G., Lous, C., and Thompson, D. *Catalysis by Gold* Imperial College Press, London, England (2006).

Grisel, R., and Nieuwenhuys, B. "A comparative study of the oxidation of CO and CH_4 over Au/MO_x/Al_2O_3 catalysts," *Catalysis Today* 64: 69 (2001).

Hinshelwood, C. N. *The Kinetics of Chemical Change*, Oxford, Clarendon Press, London, England (1940).

Hougen, O., and Watson, K. "Solid catalysts and reaction rates general principles," *Industrial Engineering Chemistry* 35: 529 (1943).

Hurtado, P., Ordonez, S., Sastre, H., and Diez, F. "Development of a kinetic model for the oxidation of methane over Pd/Al_2O_3 at dry and wet conditions," *Applied Catalysis B: Environmental* 51: 229–238 (2004).

Korotkikh, O., and Farrauto, R. "Selective catalytic oxidation of CO in H_2: Fuel cell applications," *Catalysis Today* 62: 2 (2000).

Korotkikh, O., Ruettinger, W., and Farrauto, R. "Suppression of methanation activity by water gas shift reaction catalyst," U.S. patent 6, 562, 315 (2003).

Liu, X., Korotkikh, O., and Farrauto, R. "Selective catalytic oxidation of CO in H_2: A structural of Fe oxide promoted Pt/alumina catalyst," *Applied Catalysis B: Environmental* 226: 293 (2002).

Mars, P., and Van Krevelen, D. "Oxidations carried out by means of vanadium oxide catalysts," *Chemical Engineering Series* 3: 41 (1954).

Morbidelli, M., Garvriilidis, A., and Varma, A. *Catalyst Design: Optimal Distribution of Catalyst in Pellets, Reactors and Membranes*, Cambridge University Press, Cambridge, England (2001).

CHAPTER 1 QUESTIONS

1. Give everyday examples of how you encounter rate-limiting steps using analogies to intrinsic, pore diffusion, and mass transfer-controlled reactions.
2. Give examples of how in your everyday life you make decisions regarding selectivity.
3. List three examples for each of the petroleum and chemical products produced by catalytic processes.
4. Distinguish a homogeneous catalyst and process from a heterogeneous catalyst and process.
5. Why is it important to maximize the number of active sites in a heterogeneous catalyst?
6. What is the practical value in preparing a catalyst or in adjusting the process conditions by knowing the activation energy of a reaction?
7. 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 equation:

$$\text{Rate} \sim k[(\text{Kads}_{HC}\ P_{HC})(\text{Kads}_{O2}\ P_{O2})]/(\text{Kads}_{HC}\ P_{HC})$$

8.
   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?
9. What are the benefits of using a catalyst for abating emissions?