1 Catalyst Fundamentals

1.1 THE BASICS: ACTIVITY AND SELECTIVITY

A catalyst in its simplest term is a material that increases the rate (molecules converted by unit time) of a chemical reaction while itself not undergoing any permanent change. Ethylene and oxygen adsorb onto specific sites on a Pt catalyst and rapidly convert to carbon dioxide and water:

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O \tag{1.1}$$

The adsorption onto the catalyst provides a chemical shortcut in which reactants are converted to products more rapidly than if no catalyst were present. From a practical point of view, this translates to reactions occurring at lower temperatures, leading to savings in energy and reactor material. Because reaction rates are increased, the throughput of reactants and the amount of products produced is greatly increased, allowing the use of smaller reaction vessels.

In the ethylene example above, the platinum catalyst produces carbon dioxide and water exclusively, in contrast to a vanadium (V_2O_5) catalyst, which selectively produces mostly partially oxidized product such as aldehyde, as shown below:

$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3CH{=}O \tag{1.2}$$

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.

Reactants undergoing conversion must pass through various energy barriers, called *activation energies* (E), before the final product is produced. The diagram shown in Figure 1.1 plots the net enthalpy change against reaction coordinate and shows the energy path of reactants to products. In effect, the catalyst provides a lower energy barrier or activation energy (E) in the transformation of reactants to products that increases the net rate of reaction.

The rate of reaction is inversely proportional to the exponential of the activation energy. This relationship is expressed through the rate constant k, as in equations (1.3) and (1.4), where C_a and C_b represent the concentrations at any given time of the reactants and superscripts x and y denote their respective reaction orders. The rate constant is related to the preexponential function k_0,

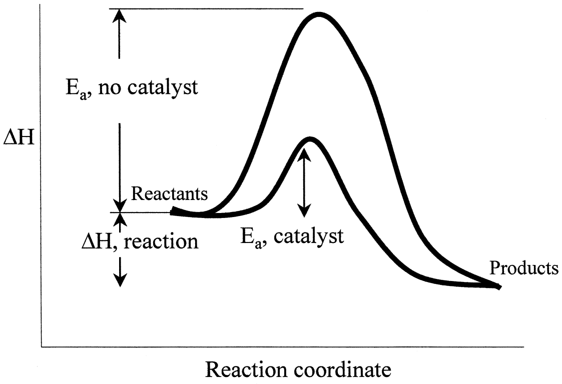


Figure 1.1 Catalyzed and uncatalyzed reaction energy paths for reactants converted to products. Activation energy for catalyzed reaction is lowest.

which is a mechanistic term, but also is proportional to the number of active sites on the catalyst. R and T are the universal gas constant and the absolute temperature, respectively.

$$\text{Rate} = kC_a^x C_b^y \tag{1.3}$$

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{1.4}$$

The activation energy for the entire reaction represents the slowest of all steps involved in converting reactants to products. The overall rate can never be greater than the slowest step. The difference between the energy states of the reactants and products is the exothermic heat of reaction.

An instructive example of how the catalyst functions to decrease the activation energy is illustrated by the important environmental application of the oxidation of the pollutant CO to CO_2:

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2 \tag{1.5}$$

This reaction requires about 700°C, in the absence of a catalyst, because the rate-limiting step is the thermal dissociation of O_2 into O atoms. The activation energy has been determined experimentally to be about 40 kcal/mol. In the presence of Pt or Pd, the dissociation of O_2 occurs catalytically on the metal surface and the rate-limiting step becomes the reaction of adsorbed CO with adsorbed O atoms. The activation energy is reduced to less than 20 mol/mol and the reaction occurs at 100°C. Thus, the catalyst changed the rate-limiting step and provided a less energetic path for the product to be formed. The catalyst provides a chemical shortcut and lowers the energy necessary for the reaction. This is a key reason why CO can be abated from vehicles and power plants at modest temperatures.

It is of great importance to recognize that neither the net enthalpy nor the net free energy is affected by the presence of the catalyst. A catalyst changes neither the energetics of the initial and final states nor the equilibrium, but affects only the rate of approach to the final product state. The catalyst enhances the kinetics of reaching equilibrium. Thus, the reaction enthalpy, ΔH, and reaction free energy, ΔG (and consequently the equilibrium constant, K_e) are not altered by the presence of a catalyst.

The catalyst influences selectivity by preferentially lowering the activation energy for a particular step in the reaction sequence and increases the rate at which this step proceeds. Selectivity is an issue for many reactions in which multiple products can occur in parallel. For the example with the V_2O_5 catalyst, the reaction path leading to the formation of the aldehyde product is favored because it has a lower activation energy than the complete combustion to CO_2 and H_2O. For the reaction using Pt the opposite is true. It is the job of the catalyst to reduce the activation energy of the reaction that will yield the desirable product.

In catalytic air pollution control, all the processes utilize solid heterogeneous catalysts through which gaseous reactants pass. This is distinguished from a homogeneous liquid-phase catalyst, which is soluble in the reaction medium.

1.2 DISPERSED CATALYST MODEL

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, and CoO, increases the number of sites on 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, and SiO_2–Al_2O_3. In some cases, but not for environmental applications, nonoxides such as high surface area carbons are also used as carriers. The carriers themselves seldom are catalytically active, but do play a major role 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 1.2 illustrates a few select pores of a high-surface-area Al_2O_3.

Figure 1.2 shows 20- and 100-Å pores into which Pt 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

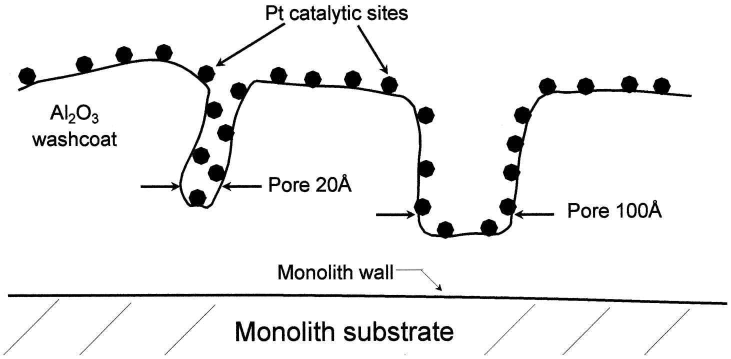


Figure 1.2 Conceptual model for catalytic sites dispersed on a high-surface-area Al_2O_3 carrier bonded to a monolith.

described in Chapter 2, it is called a *washcoat*. The internal surface of the Al_2O_3 is rich in surface OH^- (hydroxyl) groups (not shown), depending on the type of Al_2O_3 and its thermal history. These OH^- species, which cover the entire surface and are part of the walls of each pore, represent sites on 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 on 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 that the higher the catalytic surface area, the higher the rate of reaction for a process controlled by kinetics rather than mass transfer.

The tiny Pt-containing particles shown in Figure 1.2 are dispersed throughout the porous Al_2O_3 carrier network and generate a high-Pt surface area. This procedure maximizes the catalytic area but also introduces other possible rate controlling 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 (Farrauto and Bartholomew 1997; Morbidelli et al. 2001). These are discussed below.

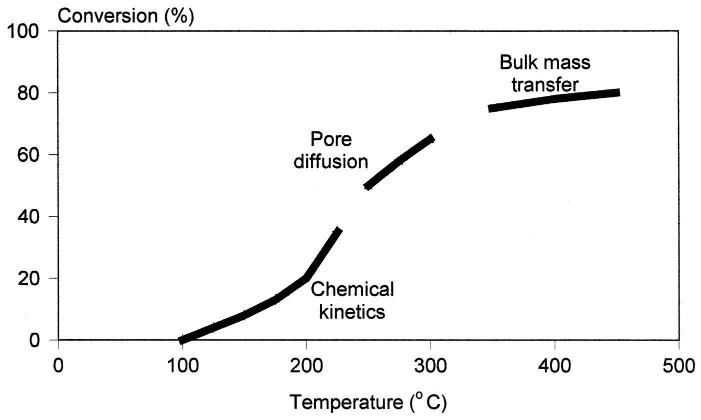
1.3 THE STEPS IN HETEROGENEOUS CATALYSIS

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. Consider reaction (1.5), 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 contact the outer surface of the carrier containing the catalytic sites. To do so, they must diffuse through a stagnant thin layer of gas in close contact with the catalyzed carrier. Bulk molecular diffusion rates vary approximately with $T^{3/2}$ and typically have activation energies, $E_1 = 2\text{–}4$ kcal/mol.
2. Since the bulk of the catalytic components are internally dispersed, the majority of CO and O_2 molecules must diffuse through the porous network toward the active sites. The activation energy for pore diffusion, E_2, is approximately half that of a chemical reaction, or about 6–10 kcal/mol.
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 temperature, for example, $\exp(-E_3/RT)$, where E_3 is the activation energy, which for chemisorption is typically greater than 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 adsorbed CO_2. Kinetics also follow exponential dependence on temperature, for instance, $(-E_4/RT)$ with activation energies typically greater than 10 kcal/mol.
5. CO_2 desorbs from the site following exponential kinetics, for example, $\exp(-E_5/RT)$ with activation energies typically greater than 10 kcal/mol.
6. The desorbed CO_2 diffuses through the porous network toward the outer surface with an activation energy and kinetics similar to those in step 2.
7. CO_2 must diffuse through the stagnant layer and, finally, into the bulk gas. Reaction rates follow $T^{3/2}$ dependence. Activation energies are also similar to step 1, less than 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 or 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 product. Steps 3, 4, and 5 are related to the chemical interactions of reactants and products (CO, O_2, and CO_2, respectively) 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 CO and O_2 to CO_2 as the temperature of the catalyst is increased. This is shown graphically in Figure 1.3.

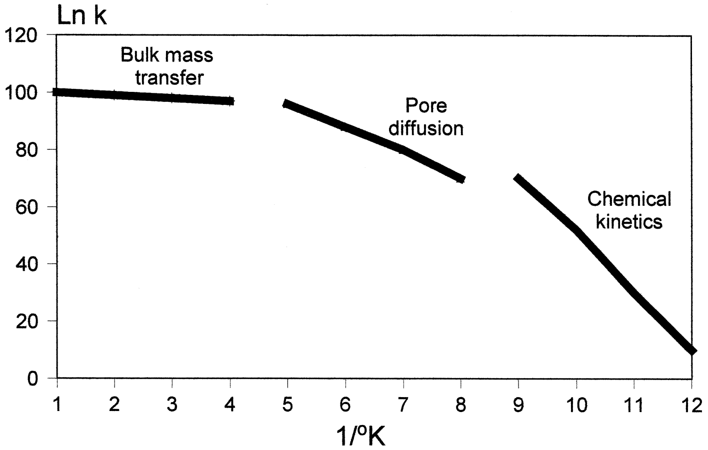


Chemical kinetics, $E_a > 10$ Kcal/mole
Pore diffusion, $E_a = 6$ to 10 Kcal/mole
Bulk mass transfer, $E_a = 2$ to 4 Kcal/mole

Figure 1.3 Conversion–temperature profile illustrating regions for chemical kinetics, pore diffusion, and bulk mass transfer control.

In the chemical kinetic control region the reaction of adsorbed CO with adsorbed O is slow relative to diffusion and thus is rate limiting. As the temperature is further increased, the higher activation energy chemical steps with exponential dependence increase the fastest, and control of the overall rate will shift to pore diffusion. Here the rate of conversion of CO and O is faster than the rate at which they can be supplied and a concentration gradient exists decreasing within the particle. This is referred to as *intraparticle diffusion*, in which the catalytic metals 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 verses the theoretical maximum rate and can be thought of as a measure of the utilization of the metal. At higher temperatures the rate of diffusion of the CO and O_2 from the bulk gas to the catalyst/carrier 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 outer or external surface of the catalyst/carrier. The concentration of reactant and product is essentially zero within the particle. The effectiveness factor is close to zero. This is a result of its smaller temperature dependence compared to the other processes.

The slope of the conversion versus temperature curve can give a qualitative picture of the rate-controlling steps. The steeply rising lower part of the curve is indicative of chemical control (either step 3, 4, or 5). The relatively flat temperature-insensitive portion reflects bulk mass transfer control (either step 1 or 7), while the intermediate portion is characteristic of pore diffusion control (either step 2 or 7).



k = rate constant
Ln ko = intercept
Slope = Ea/R where R = gas constant

Figure 1.4 Arrhenius plot for determining activation energies.

1.4 THE ARRHENIUS EQUATION

We can derive a very simply expression to aid us in determining which step is rate determining by use of the Arrhenius equation. By taking the natural logarithm of equation (1.4) a linear expression results [see equation (1.6)] in which one can generate a series of straight lines whose slopes are directly related to the activation energy of the rate-controlling step, as shown in Figure 1.4:

$$\ln k = \ln k_0 - \frac{E}{R}\left(\frac{1}{T}\right) \tag{1.6}$$

The plot of $\ln k$ versus $1/T$ shows three distinctly different slopes, each related to a possible rate-limiting step. The largest slope is for chemical, intermediate slope for pore diffusion and the smallest slope is for bulk mass transfer.

When the reaction of CO plus O_2 to CO_2 is controlled by one of the chemical steps, bulk and pore diffusion of reactants to the active sites is fast. The concentration of reactants within the catalyst/carrier is essentially uniform. With pore diffusion control, the concentration of reactants decreases from the outer periphery of the catalytic surface toward the center of the particle or bottom of the washcoat. Finally, with mass transfer control, the concentration of reactants approaches zero at the boundary layer near the outside surface of the catalyst.

1.5 SIGNIFICANCE OF 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.

When it is known that a process will have significant pore diffusion limitations, the carrier should be selected with large pores and the catalytic components located as close to the surface as possible to improve the effectiveness factor. To enhance the transport rate, one can decrease the thickness of the carrier or washcoat to decrease the diffusion path of reactants and products.

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 support. Clearly, increasing the catalytic 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.

These concepts will be further applied in Chapter 4, on catalyst deactivation, in determining the causes of catalyst deactivation.

REFERENCES

Farrauto, R. and Bartholomew, C., *Fundamentals of Industrial Catalytic Processes*, Kluwer Scientific Publishers, Amsterdam (1997).

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