CHAPTER 8

CATALYSIS

As kinetic information began to accumulate during the last century, it appeared that the rates of a number of reactions were influenced by the presence of a material which itself was unchanged during the process. In 1836 J. J. Berzelius[1] thoroughly reviewed these reactions and came to the conclusion that a "catalytic" force was in operation in such cases. Among the cases which he studied were the conversion of starch into sugar in the presence of acids, the decomposition of hydrogen peroxide in alkaline solutions, and the combination of hydrogen and oxygen on the surface of spongy platinum. In these three examples the acids, the alkaline ions, and the spongy platinum were the materials which increased the rate and yet were unchanged as the result of the reaction. Although the concept of a catalytic force proposed by Berzelius has now been discarded, the term *catalysis* is retained to describe all processes in which the rate of a reaction is influenced by a substance that remains chemically unaffected.

GENERAL CHARACTERISTICS

8-1. The Nature of Catalytic Reactions. Although the catalyst remains unchanged at the end of the process, there is no requirement that the material not take part in the reaction. Indeed, present-day theories attempting to explain the activity of catalysts postulate that the material does actively take part in the reaction. From the concept of the energy of activation developed in Chap. 3 the mechanism of catalysis would have to be such that the free energy of activation is lowered by the presence of the catalytic material. In other words, a catalyst is effective in increasing the rate of a reaction because it makes possible an alternative mechanism, each step of which has a lower free energy of activation than that for the uncatalyzed process. For example, in the case of the reaction between hydrogen and oxygen in the presence of spongy platinum this concept would suggest that hydrogen combines with the spongy platinum to form an intermediate substance, which reacts with oxygen to provide the final product and reproduce the catalyst.

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[1] J. J. Berzelius, *Jahresber. Chem.*, **15**:237 (1836).

It is also required that this mechanism involving the platinum surface occur at a faster rate than the reaction between the hydrogen and oxygen alone. That is, the energies of activation for forming the intermediate compounds and for their decomposition into the products are lower than that for the homogeneous combination of hydrogen and oxygen.

In addition to the concept that the catalytic material is unchanged during reaction there are other important characteristics of catalytic reactions. The first is that a relatively small amount of catalyst can cause conversion of a large amount of the reactants. For example, Glasstone[1] points out that cupric ions in the concentration of 10^{-9}-normal appreciably increase the rate of the oxidation of sodium sulfide by oxygen. However, the idea that a small amount of the catalyst can cause a large amount of reaction does not mean that the catalyst concentration is unimportant. In fact, when the reaction does not involve a chain mechanism, it is generally true that the rate of the reaction is proportional to the concentration of the catalyst. This is perhaps most readily understood by considering the case of surface catalytic reactions. To continue with the example of hydrogen and oxygen and a spongy platinum catalyst, the extent of the surface of the platinum influences the rate of the reaction. Indeed, the rate is found to be directly proportional to the platinum surface. Similarly the hydrolysis of esters in an acid solution will depend upon the concentration of hydrogen ion acting as a catalyst.

A second property of a catalytic reaction is that the position of equilibrium in a reversible reaction is not changed by the presence of the catalyst. This conclusion has been verified experimentally in several instances. For example, the oxidation of sulfur dioxide by oxygen has been studied using three catalysts, platinum, ferric oxide, and vanadium pentoxide. In all three cases the equilibrium compositions were the same.

It was shown in Chap. 2 that the equilibrium constant of a chemical reaction is equal to the ratio of the reaction-velocity constants for the forward and reversed reactions. That is,

$$K = \frac{k}{k'} \tag{8-1}$$

If the equilibrium constant is unchanged by the presence of the catalyst, it is apparent that the ratio of the reaction-velocity constants for the forward and reverse reactions must be the same. Therefore the catalyst for promoting the forward direction must also be a catalyst for the reverse process. This has also been verified in the study of the oxidation of sulfur dioxide. Thus platinum, which is an effective catalyst for the

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[1] S. Glasstone, "Textbook of Physical Chemistry," p. 1104, D. Van Nostrand Company, Inc., New York, 1940.

forward reaction, also has been found to speed up the decomposition of sulfur trioxide.

Examples have been observed of so-called negative catalysis where the rate is decreased by the catalyst. Indeed, the definition of catalysis in its general form suggests only that the material has an influence on the rate of reaction. Perhaps the most reasonable theory of negative catalysis has been developed for chain reactions. In these cases it is postulated that the catalyst breaks the reaction chains, or sequence of steps in the mechanism of the process. For example, nitric oxide reduces the rate of decomposition of acetaldehyde and ethyl ether. Apparently nitric oxide has the characteristic of combining with the free radicals involved in the reaction mechanism. The halogens, particularly iodine, also act as negative catalysts in certain homogeneous gaseous reactions. In the combination of hydrogen and oxygen, where a chain mechanism is probably involved, iodine presumably acts by destroying the radicals necessary for the propagation of the chains.

8-2. Classification of Catalytic Reactions. Catalytic reactions are conveniently divided into two main groups, depending upon whether the catalyst and the reaction mixture form a homogeneous phase. We have mentioned examples of both homogeneous and heterogeneous cases. The hydrolysis of an ester in an aqueous solution containing hydrogen ions is an example of homogeneous catalysis. On the other hand, the combination of hydrogen and oxygen to form water vapor in the presence of spongy platinum is heterogeneous since the platinum catalyst forms a separate phase from the reaction mixture. Heterogeneous catalysis need not involve only gas and solid phases. For example, in emulsion polymerization the reactants may be in the liquid phase and the catalyst in a solid phase or separate liquid phase.

One of the most common and important industrial examples of homogeneous catalysis is the gas-phase oxidation of sulfur dioxide involved in the chamber process for the manufacture of sulfuric acid. The direct combination of sulfur dioxide and oxygen in accordance with the following reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

is a very slow process. However, termolecular reactions (combinations of three molecules of reactants) involving nitric oxide are well known and occur at reasonable velocities. On this basis, the most likely mechanism which has been proposed for the chamber process consists of the following two reactions:

1: $$2NO + O_2 \rightarrow 2NO_2$$
2: $$NO_2 + SO_2 \rightarrow NO + SO_3$$

Doubling the second and adding it to the first result in an over-all reaction equivalent to the noncatalytic combination of SO_2 with oxygen to form SO_3. The actual mechanisms involved in the chamber process are not definitely known, and the entire process may be quite complicated. However, the mechanism just proposed is probably involved and indicates how the presence of a catalyst, in this case NO, can result in two fairly fast reactions replacing a noncatalytic, slow step.

Homogeneous catalytic reactions can be subdivided into two classifications, gaseous and liquid. The chamber process for the manufacture of sulfuric acid is an example of the first. Homogeneous liquid catalytic reactions are numerous and used widely in industry. Most applications of this type are carried out in batch or continuous-tank-type reactors, such as the hydrolysis of organic esters in acid solutions and the nitration of aromatic liquids with nitric acid in the presence of sulfuric acid.

Reactions in the heterogeneous classification are of considerable significance to engineers. A few industrial applications of current importance are the oxidation of sulfur dioxide on vanadium pentoxide catalysts, the catalytic cracking of petroleum stocks using fixed or fluidized beds of solid catalysts, the oxidation of naphthalene to phthalic anhydride using vanadium pentoxide catalyst, and the manufacture of vinyl chloride by the reaction of acetylene and hydrogen chloride gas on a catalyst of mercuric chloride. In all these examples the reaction mixture is in the gas phase. There are other cases where the reaction mixture is either in both the gas and the liquid phase or in the latter alone. For example, a recently developed desulfurization process for the removal of mercaptans and sulfides from petroleum stocks involves the flow of a liquid-phase reaction mixture over a solid catalyst.

The study of catalysis in such heterogeneous cases is intimately connected with the subject of surface chemistry since surface processes play a dominant part in determining the kinetics of the reactions. The kinetics of this important class of reactions are discussed in Chap. 9, and the basic concepts of surface chemistry are considered in Sec. 8-4. However, before proceeding to these subjects it is worthwhile to consider a simple kinetic treatment of catalytic reactions which frequently may be applied to both homogeneous and heterogeneous cases.

8-3. Elementary Mechanism of Catalytic Reactions.[1] The concept that a catalyst provides an alternate mechanism for accomplishing a reaction, and that this alternate path is a more rapid one, has been developed in many individual cases. The common feature of this idea, in all instances, is that the catalyst and one or more of the reactants

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[1] This presentation of a simple mechanism of catalysis follows closely the treatment of K. J. Laidler, "Kinetics and Catalysis," McGraw-Hill Book Company, Inc., New York, 1950.

form an intermediate complex, a loosely bound compound which is unstable. This complex then takes part in subsequent reactions which result in the final products and the regenerated catalyst.

Homogeneous catalysis can frequently be explained by using this concept. Applications of these ideas in homogeneous systems can be illustrated by reference to catalysis by acids and bases. In aqueous solutions acids and bases can increase the rate of hydrolysis of sugars, starch, and esters. The kinetics of the hydrolysis of ethyl acetate catalyzed by hydrochloric acid can be explained by the following mechanism:

1: $CH_3COOC_2H_5 + H^+ \rightarrow CH_3COOC_2H_5[H^+]$
2: $CH_3COOC_2H_5[H^+] + H_2O \rightarrow C_2H_5OH + H^+ + CH_3COOH$

For this catalytic reaction to be rapid with respect to the noncatalytic hydrolysis, the free energy of activation of steps 1 and 2 must each be less than the free energy of activation for the noncatalytic reaction,

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

In a similar way the heterogeneous catalytic hydrogenation of ethylene on a solid catalyst might be represented by the following steps:

1: $C_2H_4 + H_2[C] \rightarrow C_2H_4[C]H_2 \qquad \Delta F_1^*$
2: $C_2H_4[C]H_2 \rightarrow C_2H_6 + [C] \qquad \Delta F_2^*$

where [C] is the solid catalyst and $C_2H_4[C]H_2$ represents the complex formed between the reactants and the catalyst. In the second step the complex decomposes directly into the product and the catalyst.[1] The homogeneous reaction, according to the absolute theory of reaction rates discussed in Chap. 3, would be written

$$C_2H_4 + H_2 \xrightarrow{\Delta F^*} \underset{\text{Activated complex}}{C_2H_4 \cdot H_2} \rightarrow C_2H_6$$

where the free-energy change for the formation of the activated complex ΔF^* is the free energy of activation for the homogeneous reaction. The effectiveness of the catalyst is explained on the basis that the free energy of activation of each of the two steps in the catalytic mechanism, ΔF_1^* or ΔF_2^*, is less than ΔF^*.

ADSORPTION ON SOLID SURFACES

8-4. Surface Chemistry and Adsorption. We have seen that the effectiveness of solid surfaces in catalyzing heterogeneous reactions must be due to the interaction between reactants and the surface. Therefore

it is necessary to investigate how molecules of a fluid can attach themselves to solid surfaces. Even the most carefully polished surfaces are not smooth in a microscopic sense, but irregular with valleys and peaks alternating over the area. The areas of irregularity are particularly susceptible to the presence of residual-force fields. At these locations the surface atoms of the solid may attract other atoms or molecules in the surrounding gas or liquid phase.

Physical Adsorption. As the result of developments in the last few decades it is generally accepted that two main types of adsorption may occur. The first, called physical adsorption, is somewhat similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak, and the heat evolved during the adsorption process is of the same order of magnitude as the heat of condensation, that is, 1 to 20,000 cal/g mole. Since the forces of attraction between the fluid molecules and the surface atoms correspond to those assumed in the van der Waals equation of state of gases, this kind of process is frequently called van der Waals' adsorption. Equilibrium between the solid surface and the gas molecules is rapidly attained and easily reversible, because the energy requirements are small. Considered as a reaction, the energy of activation for physical adsorption must be small and in the neighborhood of 1000 cal/g mole. This result follows directly from the fact that the forces involved in physical adsorption are weak. Because of the small forces the energy states of adsorbed molecules are very similar to those of molecules in the gas phase. This in turn means the mechanism of reaction involving such adsorbed molecules cannot have activation energies much different from the corresponding homogeneous reaction. It is concluded that physical adsorption cannot explain the catalytic activity of solids for reactions between stable molecules, because there is no possibility of large reductions in activation energy. Reactions of atoms and free radicals at surfaces sometimes involve small activation energies. In these cases physical adsorption may play a role.

The effect of temperature on the extent of physical adsorption is such that the amount adsorbed decreases rapidly as the temperature is raised and is generally very small above the critical temperatures of the adsorbed component. This is further evidence that physical adsorption cannot play an important part in the actions catalyzed by solids. Thus such adsorption cannot account for the formation of intermediate products between reactants and solid catalysts where the reactant is a gas above the critical temperature. For example, the rate of oxidation of sulfur dioxide on a platinum catalyst is not appreciable below 300°C; yet this is considerably above the critical temperature of sulfur dioxide, 157°C, or oxygen, −119°C. Physical adsorption is not highly dependent upon

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[1] In other more complicated cases the formation of the catalyst and products may require more than one reaction.

the irregularities in the nature of the surface but is usually directly proportional to the amount of surface. The extent of adsorption is not limited to a monomolecular layer on the solid surface, especially near the condensation temperature. As the layers of molecules build up on the solid surface, the process becomes progressively more like one of condensation.

While not of direct importance in surface catalysis of reactions of stable molecules, physical-adsorption studies are valuable in determining the physical properties of solid catalysts. Thus the questions of surface area and pore-size distribution in porous catalysts can be answered from physical-adsorption measurements. This aspect of physical adsorption is considered in Secs. 8-6 and 8-7.

Chemisorption. The second type of adsorption involves forces much stronger than in physical adsorption. According to Langmuir's pioneer work[1] the adsorbed molecules are held to the surface by valence forces of the same type as those occurring between atoms in molecules. Evidence for these valence forces was presented by Langmuir in his work with the adsorption of oxygen or tungsten. He observed that a stable oxide film was formed on the surface of tungsten wires in the presence of oxygen. This material was not the normal oxide WO_3, because it exhibited different chemical properties. However, analysis of the walls of the vessel holding the wire indicated WO_3 was given off from the wire surface on decomposition. This suggested the following type of process:

$$3O_2 + 2W \rightarrow 2[W \cdot O_3]$$
$$2[W \cdot O_3] \rightarrow 2WO_3$$

where $[W \cdot O_3]$ represents the adsorption compound on the surface of the wire.

Further evidence for the theory that such adsorption involves valence bonds is found in the large heats of adsorption. Observed values are of the same magnitude as the heat of ordinary chemical reactions, that is, 10,000 to 100,000 cal/g mole, and much larger than the corresponding heats of physical adsorption.

Taylor[2] suggested the name chemisorption for describing and distinguishing this second type of combination of gas molecules with solid surfaces. Because of the high heat of adsorption the energy possessed by chemisorbed molecules can be considerably different from that of the molecules by themselves. Hence the energy of activation for reactions involving chemisorbed molecules can be considerably less than that for reactions involving the molecules alone. It is on this basis that chemisorption offers an explanation for the catalytic effect of solid surfaces.

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[1] I. Langmuir, *J. Am. Chem. Soc.*, **38**:221 (1916).

[2] H. S. Taylor, *J. Am. Chem. Soc.*, **53**:578 (1931).

Using the concept of such adsorption, an alternative mechanism can be postulated which may have a lower energy of activation in each step than that for the noncatalytic homogeneous process.

The term activated adsorption has also been commonly used to describe chemisorption, since the adsorbed molecules have received a considerable amount of energy and are now in a more activated, more energetic state. The free energy of activation is much greater than for physical adsorption, which means that the rate of the activated-adsorption process is slower than for the physical process. Thus activated adsorption is a slow process at low temperatures. On the other hand physical adsorption, owing to its similarity to simple condensation, is rapid at low temperatures. Hence at these temperature levels the quantity of material adsorbed is determined entirely by the physical process. The relationship between temperature and quantity adsorbed is as shown in the low-temperature range of Fig. 8-1. As the critical temperature of the component is exceeded, physical adsorption approaches a very low equilibrium value and equilibrium would be reached in a short time, because of the low energy of activation associated with the physical process. However, as the temperature is raised, the amount of activated adsorption becomes important, because the rate is high enough for significant quantities to be adsorbed in a reasonable amount of time. In an ordinary adsorption experiment involving the usual time periods the adsorption curve actually rises with increasing temperatures from the minimum value, as shown in Fig. 8-1 by the solid line. When the temperature is increased still further, the decreasing equilibrium value for activated adsorption begins to be significant and the quantity adsorbed passes through a maximum. At these high temperatures even the rate of the relatively slow activated process will be sufficient to give results closely approaching equilibrium. Hence the solid curve representing the amount adsorbed would approach the dotted equilibrium value for the activated adsorption process, as shown in the figure.

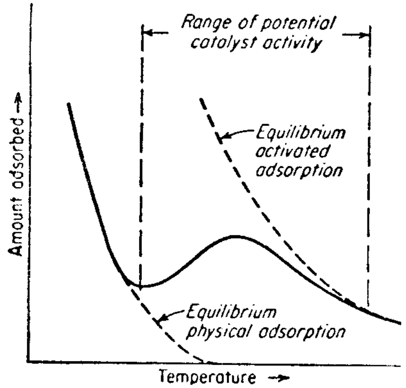

Fig. 8-1. Effect of temperature upon physical and activated adsorption.

It has been explained that the effectiveness of solid catalysts for reactions of stable molecules is dependent upon chemisorption, while the physical process is not significant. Granting this, the temperature range over which a given catalyst is effective must coincide with the range where chemisorption of one or more of the reactants is appreciable. This is indicated on Fig. 8-1 by the dotted vertical lines. Therefore there is a definite relationship between the extent of chemisorption of a gas on a solid and that solid's effectiveness as a catalyst for reactions. For example, many metallic and metallic-oxide surfaces adsorb oxygen easily, and these materials are also found to be good catalysts for oxidation reactions.

An important feature of chemisorption is that its magnitude will not greatly exceed that corresponding to a monomolecular layer. This limitation is due to the fact that the valence forces holding the molecules on the surface diminish rapidly with distance. These forces become too small to form the adsorption compound when the distance from the surface becomes much greater than the usual bond distances.

It was Taylor's[1] concept that the irregularities on the surfaces of a solid lead to particular locations where unbalanced forces of the magnitude of valence forces are in existence. Taylor called these points activated centers. That catalytic surfaces can be highly irregular has been verified by examination in the case of ceramic-type catalysts. However, surface films produced by the condensation of evaporated metal have been shown to have significant catalytic activity, and in this case the irregularities in the surface are less extreme. Beeck and his coworkers[2] formulated catalytic activity, not in terms of active centers on the surface, but in terms of the normal properties of particular faces of the crystalline metals. These properties were assumed to stem from the geometric arrangement of the atoms in the several crystal faces. Regardless of the difficulties in explaining the activity of the solid catalyst surfaces, the concept of activated or chemisorption processes, involving large energies of activation, seems well established. The treatment of the kinetics of solid reactions in Chap. 9 will be developed on the basis of the validity of this concept.

8-5. Quantitative Treatment; Adsorption Isotherms. In order to develop the kinetics of solid catalytic reactions, it is necessary to have available an expression relating the rate and amount of adsorption to the partial pressure of the gas in contact with the adsorbed layer of the surface. At equilibrium and constant temperature this relationship between the pressure and the amount is known as the adsorption isotherm.

A thorough review of the theories of adsorption has recently been presented by Ries.[3] The modern developments are based upon the early work of Langmuir, Freundlich, and Polanyi. The results of both

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[1] H. S. Taylor, *Am. Scientist*, **34**:553 (1946).

[2] O. Beeck, A. E. Smith, and A. Wheeler, *Proc. Roy. Soc.* (*London*), **A177**:62 (1940).

[3] P. H. Emmett (ed.), "Catalysis," vol. I., chap. 1, Physical Adsorption, Reinhold Publishing Corporation, New York, 1954.

Freundlich and Polanyi, in their present state of development, are not suitable for chemisorption, and hence not useful as a steppingstone toward establishing the kinetics of solid catalytic reactions. Freundlich[1] proposed an empirical relationship for the isotherm,

$$v = \beta(p)^{1/n} \tag{8-2}$$

where v = volume of gas adsorbed
p = pressure of gas
β, n = specific constants for system of gas and surface

This equation has been found best suited for correlating experimental data in the region where there are several layers of adsorbed molecules. The Polanyi potential theory[2] originally supposed an adsorption layer several molecules in depth. It was an attempt to treat quantitatively the decrease in attractive forces between molecules and surface atoms as the number of layers increased.

Langmuir's treatment[3] was specifically for chemisorption and limited in its original form to a monomolecular layer. Hence it is the most suitable method upon which to base the kinetics of solid catalytic reactions. His derivations may be carried out by using as a measure of the amount adsorbed either the fraction of the surface covered or the concentration of the gas adsorbed on the surface. Both methods of procedure will be illustrated, although the second is the more useful for kinetic developments and will be used exclusively in Chap. 9.

Several assumptions are pertinent to the Langmuir treatment of the adsorption isotherm:

1. All the surface of the catalyst has the same activity for adsorption; i.e., it is a smooth surface. However, the concept of an irregular surface with active centers can be employed, if it is assumed that all the active centers have the same activity for adsorption and that the rest of the surface has none, or that an average activity can be used.
2. There is no interaction between adsorbed molecules. This means that the amount adsorbed has no effect on the rate of adsorption.
3. All the adsorption occurs by the same mechanism.

Langmuir considered that, in the system of a solid surface and a gas, the molecules of gas will be continually striking the surface and a fraction of these will adhere. However, because of their kinetic, rotational, and vibrational energy the more energetic molecules will be continually leaving the surface. An equilibrium will be established under steady-

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[1] H. Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m.b.H., Leipzig, 1923.

[2] M. Polanyi, *Verhandl. deut. physik. Ges.*, **18**:55 (1916); *Z. Elektrochem.*, **26**:370 (1920).

[3] *Loc. cit.*; *J. Am. Chem. Soc.*, **40**:1361 (1918).

state conditions such that the rate at which molecules strike the surface and remain for an appreciable length of time will be exactly balanced by the rate at which molecules detach themselves from the surface.

The rate of adsorption will be equal to the number of collisions, n_c, of gas molecules with the surface per second, multiplied by a factor F representing the fraction of the colliding molecules that adhere. At a fixed temperature the number of collisions will be proportional to the pressure p of the gas, and the fraction F will be constant. Hence the rate of adsorption per unit of bare surface will be n_cF. This is equal to kp, where k is a constant involving the fraction F and the proportionality between n_c and p.

Since the adsorption is limited to a monomolecular layer, the surface may be divided into two parts, the fraction θ covered by the monomolecular layer of adsorbed molecules and the fraction $1 - \theta$ which is bare. Since only those molecules striking the uncovered part of the surface can be adsorbed, the rate of adsorption per unit of *total* surface will be proportional to $1 - \theta$; that is,

$$r'_a = kp(1 - \theta) \tag{8-3}$$

The rate of desorption will be proportional to the fraction θ of covered surface and is given by the expression

$$r'_d = k'\theta \tag{8-4}$$

Equating the two rates at equilibrium and solving for the fraction of the surface that is covered,

$$\theta = \frac{kp}{k' + kp} = \frac{K_A p}{1 + K_A p} \tag{8-5}$$

where $K_A = k/k'$ = adsorption equilibrium constant.

The fraction covered is proportional to volume of gas adsorbed, since monomolecular adsorption is assumed. Hence Eq. (8-5), like the Freundlich expression [Eq. (8-2)], may be regarded as a relationship between the pressure of the gas and the volume adsorbed. The Brunauer-Emmett-Teller equation for determining surface areas from the amount adsorbed may be considered an extension of the Langmuir derivation to multilayer physical adsorption. The usefulness of the Brunauer-Emmett-Teller approach in studying catalytic surfaces is considered in Sec. 8-6.

The development of Eq. (8-5) has supposed a smooth surface such that all parts are equally effective for adsorption (assumption 1). If the adsorption occurs only on certain active centers, θ in the equations must be defined as the fraction of the active centers covered, not of the total surface. Similarly the bare surface would be only the fraction of the active centers that was unoccupied.

Langmuir himself proposed a more general equation than (8-5) for the case of a nonuniform surface where there were n_i adsorption sites of different activity. If each site had an adsorption equilibrium constant K_i, the fraction of the surface covered by all the sites was proposed to be

$$\theta = \sum_{i=1}^{i=n} \frac{K_i p}{1 + K_i p} \tag{8-6}$$

Because of the assumptions involved Langmuir's isotherm seldom fits experimental data in a satisfactory way. However, the basic concepts upon which it is based, the ideas of a dynamic equilibrium between rate of adsorption and desorption and a finite adsorption time, appear sound and are of great value in developing the kinetics of solid catalytic reactions. Laidler[1] has termed the Langmuir isotherm an ideal treatment, somewhat analogous to the ideal-gas law. Few systems follow the ideal law, but it serves as a foundation for building modifications to fit experimental results. A number of other isotherms have been proposed for quantitatively explaining chemisorption. These have been reviewed by Laidler.[2] He has summarized also the experimental information available for this type of adsorption.

For developing catalytic rate equations, it is convenient to adapt Eq. (8-5) to a form involving surface concentrations rather than a fraction of the surface. Suppose that the total number of active centers, or adsorption sites, per unit area of catalyst is S. Also, suppose S_v is the number of vacant sites per unit area. The rate of adsorption, analogous to Eq. (8-3), will be proportional to the partial pressure of the gas and to S_v. If a molecule of gas A is adsorbed on one site s, according to the equation

$$A + s \rightarrow A{\cdot}s$$

the rate will be in units of molecules adsorbed per unit area of surface per unit time. It is given by the expression

$$r'_a = kpS_v \tag{8-7}$$

For practical purposes it is desirable to express the rate in terms of moles per unit mass of catalyst. If S_g represents the catalyst area per unit mass and N_0 the molecules per mole (Avogadro's number), such a rate is given by

$$r_a = r'_a \frac{S_g}{N_0} = kp \frac{S_v S_g}{N_0} \tag{8-8}$$

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[1] Emmett, *op. cit.*, chap. 3, Chemisorption.

[2] *Ibid.*

The group S_vS_g/N_0 represents the number of vacant adsorption sites per unit mass of catalyst divided by Avogadro's number. This may be regarded as a molal surface concentration of adsorption sites per unit mass of catalyst and will be given the symbol C_v. Hence

$$r_a = kpC_v \tag{8-9}$$

where r_a = rate of adsorption in moles per unit time per unit mass of catalyst
p = pressure of gas at surface, atm
C_v = molal concentration of vacant adsorption sites per unit mass of catalyst
k = adsorption velocity constant, $\text{time}^{-1}\ \text{atm}^{-1}$

The rate of desorption from the surface is proportional to the concentration of adsorbed molecules. If this concentration is S_A molecules per unit area of catalyst, the molal surface concentration of sites occupied by A per unit mass may be defined by the expression

$$C_A = \frac{S_AS_g}{N_0} = \text{moles/unit mass of catalyst} \tag{8-10}$$

Hence the rate of desorption, r_d, is

$$r_d = k'C_A \tag{8-11}$$

At equilibrium, the rates will be the same. Equating Eqs. (8-9) and (8-11),

$$kpC_v = k'C_A$$

$$\frac{k}{k'} = K_A = \frac{C_A}{pC_v} \tag{8-12}$$

The ratio of the rate constants K_A is equal to the adsorption equilibrium constant for A on the catalyst surface.

Equation (8-12) and the usual form of the Langmuir adsorption isotherm [Eq. (8-5)] may be shown to be equivalent. Thus the concentration C_A of adsorbed A is proportional to the fraction of the surface covered, θ, while the concentration of vacant sites is proportional to the vacant fraction $1 - \theta$. Hence the ratio $C_A/C_v = \theta/(1 - \theta)$, so that Eq. (8-12) may be written

$$K_A = \frac{\theta}{p(1 - \theta)}$$

or

$$\theta = \frac{K_Ap}{1 + K_Ap}$$

This is identical with Eq. (8-5).

PHYSICAL PROPERTIES OF SOLID CATALYSTS

It has long been known that increasing the surface area of a solid has a pronounced effect on its ability to adsorb gases and hence on its activity as a catalyst. For example, if a small piece of Raney nickel (highly porous, with a large surface area) is held in the hand, the heat of adsorption is immediately felt. With the same weight of nonporous metal no heating effect is evident. This fact has led to the development of materials[1] with surface areas of as high as 1,000 sq m/g for use either directly as catalysts or as carriers to which the catalytic material can be added. However, until recent times no reliable method was available for measuring such areas. This made it impossible to study different materials for their catalytic activity alone, because the surface areas of the materials might not be the same. In general the relationship between area and catalytic activity had to be on a qualitative basis until a satisfactory method of surface measurement was developed.

The method finally developed is based upon the physical adsorption of gases on the solid at temperatures near the boiling point. Under these conditions adsorption of several layers of molecules on top of each other is possible. Identification of the amount adsorbed when one molecular layer is attained is sufficient to determine a quantity proportional, and perhaps very nearly equal, to the surface area. The historical steps in the development of the Brunauer-Emmett-Teller method[2] are clearly explained by Emmett.[3] There may be some uncertainty as to whether the numbers given by the method are exactly equal to the surface area. However, this is relatively unimportant since the procedure is standardized and results can be reproduced in different laboratories by different investigators. If, as Taylor[4] has proposed, the Brunauer-Emmett-Teller area measurement is included in all publications on solid catalysts, progress in the field would be significantly advanced.

Other properties of solid catalysts may also have an important effect on activity. For example, the surface of a porous catalyst may be very large but the pore size too small to permit the reactants to diffuse into the interior rapidly enough to use all the surface effectively. In addition the pore-size distribution in some instances may be significant. The remainder of this division of the chapter is devoted to a discussion of the measurement of these properties of solid catalysts.

[1] The size of the over-all particles varies from a few microns in the case of fluidized-bed catalysts up to fractions of an inch for fixed-bed applications. Further details of size and shape are given in a later section on catalyst preparation.

[2] S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**:309 (1938).

[3] Emmett, *op. cit.*, vol. I, chap. 2.

[4] H. S. Taylor, *Am. Scientist*, **34**:553 (1946).

8-6. Surface-area Determination. By surface area is meant the sum of the external, or outer, surface, plus the internal surface formed by walls of pores, cracks, and crevices in the porous material. Usually the inner part is of an order of magnitude greater than the outer surface. However, when carriers are used, the catalytic material may not, in some instances, impregnate all the interior surface of a porous catalyst carrier. In this case the catalyst surface will consist of the external area plus the part of the inner surface covered with catalytic material. The Brunauer-Emmett-Teller method described in this section does not differentiate between the total surface and that covered by catalyst.

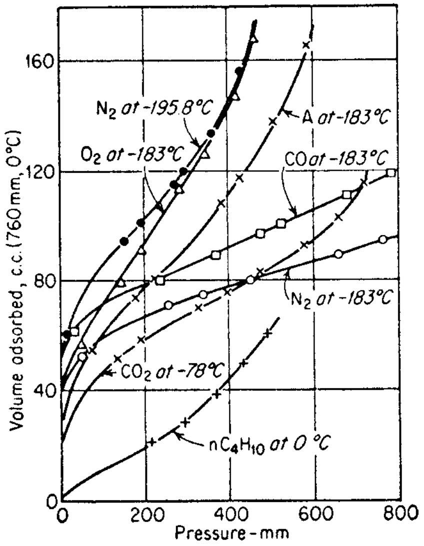

FIG. 8-2. Adsorption isotherms for various gases on a 0.606-g sample of silica gel. [*Reproduced by permission from "Catalysis," vol. I, by P. H. Emmett (ed.), Reinhold Publishing Corporation, New York,* 1954.]

The experimental part of the surface determination requires an all-glass apparatus[1] for measuring the volume of gas adsorbed on a sample of the solid material. The apparatus operates at a low, but variable, pressure from nearly zero up to about 1 atm. Since physical adsorption is desired, the operating temperature is in the range of the normal boiling point. The data obtained are gas volumes at a series of pressures in the adsorption chamber. The observed volumes are corrected to cubic centimeters at 0°C and 1 atm, standard temperature and pressure (STP), and plotted vs. the pressure in millimeters, or the ratio of the pressure to the vapor pressure at the operating temperature. Typical results from Brunauer and Emmett's work[2] are shown in Fig. 8-2 for the adsorption of several gases on a 0.606-g sample of silica gel.

The curves in Fig. 8-2 are similar to the extent that at low pressures they rise more or less steeply, then flatten out for a linear section at intermediate pressures, and finally increase in slope at higher pressure levels. After careful analysis of many data it was concluded that the lower part

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[1] For a complete description of apparatus and techniques see L. G. Toyner, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Co., Pittsburgh, 1949. Also see S. Brunauer, "The Adsorption of Gases and Vapors," vol. 1, Princeton University Press, Princeton, N.J., 1943.

[2] S. Brunauer and P. H. Emmett, *J. Am. Chem. Soc.*, **59**:2682 (1937).

of the linear region corresponded to complete monomolecular adsorption. That is, at this point all the surface was covered with a layer of adsorbed gas one molecule thick, and the second layer had not yet accumulated. If this point could be located with precision, the volume of one layer of gas, v_m, could be read from the curve and the surface area evaluated. The Brunauer-Emmett-Teller method locates this point from an equation obtained by extending the Langmuir isotherm to apply to multilayer adsorption. The development is briefly summarized in the following way: Equation (8-5) can be written in terms of the volume adsorbed, v,

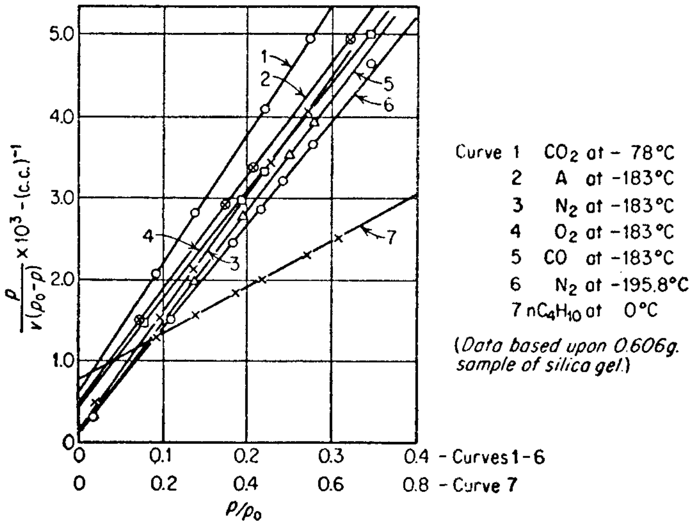

FIG. 8-3. Plot of Brunauer-Emmett-Teller equation for data of Fig. 8-2. [*Reproduced by permission from "Catalysis," vol. I, by P. H. Emmett (ed.), Reinhold Publishing Corporation, New York,* 1954.]

by noting that the fraction covered, θ, is equal to the ratio of the actual volume adsorbed to the volume v_m required to cover completely the surface with a monomolecular layer. In other words,

$$\frac{v}{v_m} = \frac{Kp}{1 + Kp} \tag{8-13}$$

This expression may be rearranged to read

$$\frac{p}{v} = \frac{1}{Kv_m} + \frac{p}{v_m} \tag{8-14}$$

Brunauer, Emmett, and Teller,[1] by adapting this equation to apply to

---

[1] *Loc. cit.*

multilayer adsorption, arrived at the following result,

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c-1)p}{c v_m p_0} \tag{8-15}$$

where p_0 = saturation or vapor pressure

c = a constant for the particular temperature and gas-solid system

If physical adsorption data are in agreement with Eq. (8-15), a plot of $p/v(p_0 - p)$ vs. p/p_0 should give a straight line. The data of Fig. (8-2) are replotted in this fashion in Fig. (8-3), where they do follow a straight-line pattern. Of additional significance is the fact that such straight lines can be safely extrapolated to p/p_0 equal to zero. The intercept obtained from this extrapolation, along with the slope of the straight line, gives two equations from which v_m, and ultimately the surface area, can be obtained. These equations are

$$\text{Intercept (at } p/p_0 = 0\text{)},\ I = \frac{1}{v_m c} \tag{8-16a}$$

$$\text{Slope, } m = \frac{c-1}{v_m c} \tag{8-16b}$$

Solving them for the volume of gas corresponding to the monomolecular layer gives

$$v_m = \frac{1}{I + m} \tag{8-17}$$

The volume v_m can be readily converted to the number of molecules adsorbed. However, to determine the absolute surface area, it is necessary to select a value for the area covered by one adsorbed molecule. If this area per molecule is α, the total surface area is given by the relation

$$S_g = \left[\frac{v_m N_0}{V_m}\right] \alpha \tag{8-18}$$

where N_0 = Avogadro's number (6.02×10^{23} molecules/mole)

V_m = volume of 1 mole of gas at conditions of v_m

Since v_m is recorded at STP, V_m = 22,400 cc/g mole. The term in brackets represents the number of molecules adsorbed. If v_m is based upon a 1-g sample, the area is S_g, the total surface per gram of solid adsorbent.

The value of α has been the subject of considerable investigation. Emmett and Brunauer[1] proposed that α is the projected area of a molecule on the surface when the molecules are arranged in close two-dimensional packing. The result they obtained is slightly larger than that obtained by assuming that the adsorbed molecules are spherical and their projected area on the surface is circular. The proposed equation is

$$\alpha = 1.09 \left[\frac{M}{N_0 \rho}\right]^{\frac{2}{3}} \tag{8-19}$$

where M = molecular weight

ρ = density of adsorbed molecules

The term in brackets represents the volume of one adsorbed molecule. The density is normally taken as that of the pure liquid at the temperature of the adsorption experiment. For example, for N_2 at −195.8°C, ρ = 0.808 g/cc.

In theory the adsorption measurements can be made with a number of different gases. However, it is found that even though the values of α calculated from Eq. (8-19) for each gas are used, the results are somewhat different (see Example 8-2). Therefore it has become customary to employ N_2 at its normal boiling point (−195.8°C) as a standard procedure. The reason for the variation in areas obtained by using different gases is not well understood. Nevertheless, by carrying out the measurements with one gas at one temperature the results for different catalysts may be compared with confidence.

Using the value of ρ for N_2 at −195.8°C, the area per molecule from Eq. (8-19) is 16.2×10^{-16} sq cm, or 16.2 sq A. If this result is used in Eq. (8-18), along with the known values of N_0 and V_m, the area is

$$S_g = 4.35 \times 10^4 v_m \qquad \text{sq cm/g of solid adsorbent}$$

In the usual unit of area of square meters per gram the expression becomes

$$S_g = 4.35 v_m \tag{8-20}$$

In using Eq. (8-20) it should be remembered that it is based upon adsorption measurements with N_2 at −195.8°C.

Values of the surface area range from less than 1 sq m/g for relatively nonporous substances up to several hundred for solids such as activated carbon and silica gel. Table 8-1 shows surface areas determined by the Brunauer-Emmett-Teller method for a number of common catalysts and carriers.

The calculations of surface areas from adsorption data are illustrated in Examples 8-1 and 8-2.

Example 8-1. From the Brunauer-Emmett-Teller plot in Fig. 8-3 estimate the surface area per gram of the silica gel. Use the data for adsorption of nitrogen at −195.8°C.

Solution. From Fig. 8-3, curve 6, the intercept on the ordinate is

$$I = 0.1 \times 10^{-3}\ \text{cc}^{-1}$$

---

[1] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**:1553 (1937).

The slope of the curve is

$$
\begin{aligned}
m &= \frac{(5.3 - 0.1) \times 10^{-3}}{0.4 - 0} \\
&= 13 \times 10^{-3}\ \text{cc}^{-1}
\end{aligned}
$$

These values of m and I may be substituted in Eq. (8-17) to obtain v_m.

$$
\begin{aligned}
v_m &= \frac{10^3}{0.1 + 13}\,\frac{1}{0.606} \\
&= 126\ \text{cc/g of catalyst}
\end{aligned}
$$

The factor 0.606 is introduced since the data in Fig. 8-3 are for a silica gel sample of 0.606 g, while v_m is the monomolecular volume per gram.

TABLE 8-1. SURFACE AREA, PORE VOLUME, AND MEAN PORE RADII FOR TYPICAL SOLID CATALYSTS†

Catalyst	Surface area, S_g, sq m/g	Pore volume, V_g, cc/g	Mean pore radius, A
1. Activated carbons......	500–1,500	0.6–0.8	10–20
2. Silica gels.............	200–600	0.4	15–100
3. SiO_2-Al_2O_3 cracking catalysts..............	200–500	0.2–0.7	33–150
4. Activated clays........	150–225	0.4–0.52	100
5. Activated alumina......	175	0.39	45
6. Celite (Kieselguhr).....	4.2	1.1	11,000
7. Synthetic ammonia catalysts, Fe...........	....	0.12	200–1,000
8. Pumice...............	0.38		
9. Fused copper..........	0.23		

† Taken in part from A. Wheeler, "Advances in Catalysis," vol. III, pp. 250–326, Academic Press, Inc., New York, 1950.

For nitrogen at −195.8°C Eq. (8-20) is applicable.

$$
\begin{aligned}
S_g &= 4.35 \times 126 \\
&= 550\ \text{sq/g}
\end{aligned}
$$

Example 8-2. For comparison purposes estimate the surface area of the silica gel by using the adsorption data for oxygen at −183°C. The density of the liquefied oxygen at −183°C from the International Critical Tables is 1.14 g/cc.

Solution. First the area of an adsorbed molecule of O_2 must be calculated from Eq. (8-19).

$$
\begin{aligned}
\alpha &= 1.09\left(\frac{32}{6.02 \times 10^{23} \times 1.14}\right)^{\frac{2}{3}} \\
&= 14.2 \times 10^{-16}\ \text{sq cm}
\end{aligned}
$$

With this value of α the area equation [Eq. (8-18)] becomes

$$
\begin{aligned}
S_g &= \frac{v_m \times 6.02 \times 10^{23}}{22{,}400} \times 14.2 \times 10^{-16} \\
&= 3.8 \times 10^4 v_m\ \ \text{sq cm/g}
\end{aligned}
$$

From Fig. (8-3), curve 4,

$$
\begin{aligned}
I &= 0.40 \times 10^{-3}\ \text{cc}^{-1} \\
m &= \frac{(5.4 - 0.4) \times 10^{-3}}{0.38 - 0} \\
&= 13.2 \times 10^{-3}\ \text{cc}^{-1}
\end{aligned}
$$

Then the monomolecular volume per gram of silica gel is, from Eq. (8-17),

$$
\begin{aligned}
v_m &= \frac{10^3}{0.4 + 13.2}\,\frac{1}{0.606} \\
&= 122\ \text{cc/g of catalyst}
\end{aligned}
$$

Finally, substituting this value of v_m in the area expression gives S_g.

$$
\begin{aligned}
S_g &= 3.8 \times 10^4 \times 122 \\
&= 465 \times 10^4\ \text{sq cm/g, or 465 sq m/g}
\end{aligned}
$$

The difference in areas determined from the N_2 and O_2 data is somewhat larger than normally expected for these gases. The adsorption curve for N_2 at −183°C gives a value in closer agreement with 465 sq m/g (see Prob. 1 at end of chapter).

8-7. Pore Size. While a large surface area indicates a high activity, it is not safe to compare catalysts entirely on the basis of surface areas per unit mass. This is because the interior surface of a porous catalyst may not be readily available for reaction. There are many possible reasons for this,[1] but one of the most important is that the size of the openings, or pores, into the interior of a catalyst particle may be too small to allow easy access of the reactants to the inner surface. Hence it is not enough to know the surface area of the catalyst. In order to be able to understand fully how reactions occur in pores, it is necessary to know, in addition, the average pore radius, perhaps the pore-size distribution, and a knowledge of how the pores are interconnected.

The surface area per gram, S_g, determined by the Brunauer-Emmett-Teller method can be used to determine the average pore diameter, provided the total pore volume is also known. If the pores are assumed to be cylindrical and V_g is the pore volume per gram of catalyst, equations can be written for both S_g and V_g in terms of the average radius $\bar{r}$,

$$
m_p S_g = 2\pi\bar{r}(n\bar{L}) \tag{8-21}
$$

$$
m_p V_g = \pi\bar{r}^2(n\bar{L}) \tag{8-22}
$$

---

[1] The effectiveness of internal surfaces is considered in connection with the kinetics of catalytic reactions in Chap. 9.

The quantities in parentheses represent the number of pores in a catalyst particle times the average pore length $\bar{L}$. The mass of one particle is m_p. Dividing these equations gives

$$\bar{r} = \frac{2V_g}{S_g} \tag{8-23}$$

In an excellent review of solid catalyst structure, Wheeler[1] has pointed out that this equation gives results which agree well with other measurements even though there are two major errors. The effect of surface roughness in the pores is not accounted for, since a smooth cylindrical shape is assumed. Also, intersections of pores would affect both the volume and the surface, and this has not been taken into consideration. Wheeler suggests that these opposing errors just about cancel each other.

The pore volume V_g can be estimated in a simple manner by boiling a weighed sample of catalyst in a liquid such as water. After the air in the pores has been displaced, the sample is superficially dried and weighed. The increase in weight divided by the density of the liquid gives the pore volume.

A more accurate procedure is the helium-mercury penetration method. The volume of helium displaced by a sample of catalyst is measured first. Then the helium is removed, and the volume of mercury displaced is measured. Since mercury will not fill the pores of most catalysts, the difference in volumes gives the pore volume of the catalyst sample.

The volume of helium displaced is a measure of the volume occupied by the solid material. From this and the weight of the sample the so-called chemical density, ρ_t, can be obtained. This is the density of the actual solid material in the catalyst. Then the void fraction, or porosity, δ_p, of the particle is available from the equation

$$\delta_p = \frac{\text{void, or pore volume, of particle}}{\text{total volume of particle}} = \frac{m_p V_g}{m_p V_g + m_p(1/\rho_t)}$$

$$\delta_p = \frac{V_g \rho_t}{V_g \rho_t + 1} \tag{8-24}$$

Hence from the helium-mercury method both the pore volume and the porosity of the catalyst particle can be determined. Values of δ_p are about 0.5, indicating that the particle is about half void space and half solid material. Since over-all void fractions δ in packed beds are about 0.4, a rule of thumb for a fixed-bed catalytic reactor is that about 30 per cent of the volume is pore space, 30 per cent solid catalyst and carrier, and 40 per cent void space between catalyst particles. Individual catalysts may show results considerably different from these average values.

Table 8-1 in the third and fourth columns gives typical pore volumes and mean radii in angstroms (10^{-8} cm). The range 10 to 200 A includes most catalytic materials.

---

[1] Emmett, *op. cit.*, vol. II, chap. 2.

Measuring the pore-size distribution is a difficult problem. The larger-size pores can be measured by forcing mercury under pressure into the catalyst particle. This is called the mercury-porosimeter method.[1] Very high pressures are required to study pores less than 10 A in diameter. For small pores the capillary condensation of a condensable vapor in the pores can be used. Wheeler[2] has made a careful analysis of this method and its recent improvements.

Example 8-3. In an experiment to determine the pore volume, catalyst-particle porosity, and average pore radius the following data were obtained on a sample of activated silica (granular, 4-12 mesh size):

1. Mass of catalyst sample placed in chamber = 101.5 g.
2. Volume of helium displaced by sample = 228.4 cc.
3. Volume of mercury displaced by sample = 266.0.

From adsorption measurements and the Brunauer-Emmett-Teller equation the surface area of the gel is 560 sq m/g.

Calculate the required properties.

Solution. The volume of mercury displaced, minus the helium displacement volume, is the pore volume. Hence

$$V_g = \frac{266.0 - 228.4}{101.5}$$
$$= 0.371 \text{ cc/g}$$

The helium volume also is a measure of the density of the solid material in the catalyst. That is,

$$\rho_t = \frac{228.4}{101.5}$$
$$= 2.25 \text{ g/cc}$$

Substituting the value of V_g and ρ_t in Eq. (8-24) gives the porosity of the silica-gel particles,

$$\delta_p = \frac{0.371 \times 2.25}{0.371 \times 2.25 + 1} = 0.455$$

The average pore size is obtained from Eq. (8-23),

$$\bar{r} = \frac{2 \times 0.371}{560 \times 10^4}$$
$$= 13 \times 10^{-8} \text{ cm, or } 13 \text{ A}$$

---

[1] H. L. Ritter and L. C. Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**:787 (1945).

[2] Emmett, *op. cit.*, vol. II, chap. 2.

CATALYST PREPARATION AND GENERAL BEHAVIOR

Now that a brief treatment of the physical properties of solid catalysts has been presented, some attention should be given to methods of preparation. Also, the effect of physical characteristics on the activity of catalyst materials will be considered and catalyst life, poisons, promoters, and inhibitors discussed.

8-8. Preparation Methods. Experimental methods and techniques for catalyst manufacture are particularly important because chemical composition is not enough by itself to determine activity. The physical properties of surface area, pore size, particle size, and particle structure frequently exert a pronounced effect on the activity. These properties are determined to a large extent by the preparation procedure.

To begin with, a distinction should be drawn between preparations in which the entire material constitutes the catalyst and those in which the active ingredient is supported by an inert material, commonly called the carrier. The first kind of catalyst is usually made by precipitation, gel formation, or simple mixing of the components.

Precipitation. Precipitation provides a method of obtaining the solid material in a porous form. It consists, in a general way, of adding a precipitating agent to aqueous solutions of the desired components. Washing, drying, and sometimes calcination and activation are subsequent steps in the process. For example, a magnesium oxide catalyst can be prepared by precipitating the magnesium from nitrate solution by adding sodium carbonate. The precipitate of $MgCO_3$ is washed, dried, and calcined to obtain the oxide. Such variables as concentration of the aqueous solutions, temperature, and time of the drying and calcining steps may influence the surface area and pore structure of the final product. This explains the difficulty in reproducing catalysts and indicates the necessity of carefully following tested recipes. Of particular importance is the washing step to remove all traces of impurities, which may act as poisons.

Gel Formation. A special case of the precipitation method is the formation of a colloidal precipitate which gels. The steps in the process are essentially the same as for the usual precipitation procedure. Catalysts containing silica and alumina are especially suitable for preparation by gel formation since their precipitates are of a colloidal nature. Detailed techniques for producing catalysts through gel formation or ordinary precipitation are given by Ciapetta and Plank.[1]

Mixing of Catalyst Components. In some instances a porous material can be obtained by mixing the components with water, milling to the desired grain size, drying, and calcining. Finally such materials must be ground and sieved to obtain the proper particle size. A mixed magnesium and calcium oxide catalyst can be prepared in this fashion. The carbonates are milled wet in a ball machine, extruded, dried, and the carbonates reduced by heating in an oven.

Preparation of Catalysts on Carriers. Materials such as silica gel and alumina have a very large surface area. Hence they serve as effective carriers for those catalytic materials which by themselves are difficult to produce in a highly porous form. Carriers are also of value as a means of obtaining a large surface area with a small amount of active material. This is important when expensive agents such as platinum, nickel, and silver are used. Berkman, Morrell and Egloff[1] have treated the subject of carriers in some detail.

The steps in the preparation of a catalyst impregnated on a carrier may include the following: (1) evacuating the carrier; (2) contacting the carrier with the impregnating solution; (3) removing the excess solution; (4) drying; (5) calcination and activation. For example, a nickel hydrogenation catalyst can be prepared on alumina by soaking the evacuated alumina particles with nickel nitrate solution, draining to remove the excess solution, and heating in an oven to decompose the nitrate to nickel oxide. The final step, reduction of the oxide to metallic nickel, is best carried out with the particles in place in the reactor by passing hydrogen through the equipment. Activation in place is necessary to prevent contamination with air and other gases which might react with, and poison, the reactive nickel.

In the example just described no precipitation was required. This is a desirable method of preparation, since thorough impregnation of all the interior surface of the carrier particles is relatively simple. On the other hand, if the solution used to soak the carrier contains potential poisons such as chlorides or sulfates, it may be necessary to precipitate the required constituent and wash out the possible poison.

Little work has been done on determining the optimum amount of catalyst that should be impregnated on a carrier. The amount of gas necessary to cover the surface with a monomolecular layer is available from adsorption measurements. The values of v_m determined from the Brunauer-Emmett-Teller equation [Eq. (8-15)] are generally within the range of 0.1 to 100 cc (STP)/g of catalyst. For N_2 these values correspond to a mass of 1.07×10^{-4} to 0.107 gram, or 0.01 to 10.7 per cent by weight of the carrier. It seems doubtful that more than a monomolecular layer would improve the catalyst performance. Since all parts of the surface are probably not active, less than a complete monomolecular layer is more reasonable. These calculations suggest that the amount of catalyst should be only a fraction of 1 per cent, or at most a few per cent of

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[1] Emmett, *op. cit.*, vol. I, chap. 7.

[1] S. Berkman, J. C. Morrell, and G. Egloff, "Catalysis," Reinhold Publishing Corporation, New York, 1940.

the mass of the carrier. Platinum catalysts on an alumina carrier with as little as 0.1 to 0.5 per cent by weight platinum have shown good activity for oxidation of sulfur dioxide.

Miscellaneous Procedures. There are numerous special procedures for preparing specific catalysts. An illustration is Raney nickel, a porous material obtained by dissolving the aluminum out of an alloy of nickel and aluminum with an alkaline solution. Ciapetta and Plank[1] have described several of these special techniques.

8-9. Activity and Surface Area. The desirability of a catalytic material having a high surface area is readily understandable. If the activity of a catalyst for a specific reaction is defined as the amount of product produced per unit time per unit mass of catalyst, the activity will increase as S_g increases. However, the activity is frequently not directly proportional to the surface area. One reason, inaccessibility of interior surface due to small pore size, has already been mentioned. It has been found that a direct proportionality is more likely to exist in comparing different batches of the same catalyst with the same reaction. Under these limited conditions surface area is likely to be the only variable. When different catalysts are compared for the same reaction, S_g is not so good a measure of activity. One of the main reasons is based upon the concept that reaction occurs only on certain parts, active centers, of the surface. If the fractions of the total surface that contain active centers are different for different catalysts, then activity will not be proportional to the surface.

8-10. Catalyst Life, Catalyst Poisons. In some reaction systems the catalyst activity decreases so slowly that exchange for new material or regeneration is required only at yearly or longer intervals. Examples are synthetic ammonia catalysts and those containing metals such as platinum and silver. On the other hand, cracking catalysts require frequent regeneration. The decrease in activity is due to poisons, which will be defined here as substances, either in the reactants stream or produced by the reaction, which lower the activity of the catalyst. The frequent regeneration of cracking catalysts is necessary because of the deposition of one of the products, carbon, on the surface.

Poisons can be differentiated by means of the way in which they operate. Many summaries listing specific poisons and classifying groups of poisons are available.[2-4] The following arrangement has been taken in part from Innes.[5]

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[1] Emmett, *op. cit.*, vol. I, chap. 7.

[2] Berkman, Morrell, and Egloff, *op. cit.*

[3] R. H. Griffith, "The Mechanism of Contact Catalysis," p. 93, Oxford University Press, New York, 1936.

[4] E. B. Maxted, *J. Soc. Chem. Ind. (London)*, **67**:93 (1948).

[5] Emmett, *op. cit.*, vol. I, chap. 6.

Deposited Poisons. Carbon deposition on catalysts used in the petroleum industry comes under this category. The carbon covers the active sites of the catalyst and may also partially plug the pore entrances. Both result in less active surface and decrease the activity. This type of poisoning is at least partially reversible, and regeneration can be accomplished by burning off the carbon with air. If the carbon is actually deposited as a high-boiling hydrocarbon, it may be possible to regenerate with steam.

Chemisorbed Poisons. Compounds of sulfur and other materials are frequently chemisorbed on nickel, copper, and platinum catalysts. The decline in activity of this type of poisoning stops when equilibrium is reached between the poison in the reactant stream and that on the catalyst surface. If the strength of the adsorption compound is low, the activity will be regained when the poison is removed from the reactants. If the adsorbed material is tightly held, the poisoning is more permanent. The mechanism appears to be one of covering the active sites, which could otherwise adsorb reactant molecules.

Selectivity Poisons. The selectivity of a solid surface for catalyzing one reaction with respect to another is not well understood. However, it is known that some materials in the reactant stream will adsorb on the surface and then catalyze other undesirable reactions, thus lowering the selectivity. The very small quantities of nickel, copper, iron, etc., in petroleum stocks may act as poisons in this way. When such stocks are cracked, the metals deposit on the catalyst and act as dehydrogenation catalysts. This results in increased yields of hydrogen and coke and lower yields of gasoline.

Stability Poisons. When water vapor is present in the sulfur dioxide–air mixture supplied to a platinum-alumina catalyst, a decrease in oxidation activity occurs. This type of poisoning is due to the effect of water on the structure of the alumina carrier. Temperature has a pronounced effect on stability poisoning. Sintering and localized melting may occur as the temperature is increased, and this, of course, changes the catalyst structure.

Diffusion Poisons. This kind of poisoning has already been mentioned in connection with carbon deposition on cracking catalysts. Blocking the pore mouths prevents the reactants from diffusing into the inner surface. Entrained solids in the reactants or fluids which can react with the catalyst, forming a solid residue, can cause this type of poisoning.

Table 8-2[1] lists poisons for various catalysts and reactions.

8-11. Promoters, Inhibitors. Innes[1] has defined a promoter as a substance, added to the catalyst during its preparation, which gives improved activity, selectivity, or stability, for the desired reaction. The promoter

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[1] In part from W. B. Innes in Emmett, *op. cit.*, vol. 1, chap. 7, p. 306.

is present in small amount and by itself has little activity. There are various types of promoters, depending on how they act to improve the catalyst. Adding alumina to the iron synthetic ammonia catalyst increases the surface area and in this way increases the activity. Some promoters are also believed to increase the number of active centers and thus make the existing catalyst surface more active.

The published information on promoters is largely in the patent literature. Innes has summarized the data appearing from 1942 to 1952 in tabular form.

TABLE 8-2. POISONS FOR VARIOUS CATALYSTS†

Catalyst	Reaction	Type of poisoning	Poisons
Silica-alumina......	Cracking	Chemisorption Deposition Stability Selectivity	Organic bases Carbon, hydrocarbons Water Heavy metals
Nickel, platinum copper	Hydrogenation Dehydrogenation	Chemisorption	Compounds of S, Se, Te, P, As, Zn, halides, Hg, Pb, NH_3, C_2H_2, H_2S, Fe_2O_3, etc.
Cobalt.............	Hydrocracking	Chemisorption	NH_3, S, Se, Te, P
Silver.............	$C_2H_4 + O \rightarrow C_2H_4O$	Selectivity	CH_4, C_2H_6
Vanadium oxide....	Oxidation	Chemisorption	As
Iron...............	Ammonia synthesis Hydrogenation Oxidation	Chemisorption, Chemisorption Chemisorption	O_2, H_2O, CO, S, C_2H_2 Bi, Se, Te, P, H_2O VSO_4, Bi

† In part from W. B. Innes in P. H. Emmett (ed.), "Catalysis," vol. 1, chap. 7, p. 306, Reinhold Publishing Corporation, New York, 1954.

An inhibitor is the opposite of a promoter. When added in small amounts during catalyst manufacture, it causes poorer activity, stability, or selectivity. Theoretically inhibitors can be useful for reducing the activity of a catalyst for an undesirable side reaction. Actually voluntary uses seem to be few.

The materials that are added to reactant streams to improve the performance of a catalyst are called accelerators. They are the counterparts of poisons. For example, steam added to the butene feed of a dehydrogenation reactor appeared to reduce the amount of coke formed and increase the yield of butadiene. The catalyst in this case was iron.[1]

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[1] K. K. Kearly, *Ind. Eng. Chem.*, **42**:295 (1950).

NOMENCLATURE

C_v	Molal concentration of vacant adsorption sites = S_vS_g/N_0
C_A	Molal concentration of adsorbed A = S_AS_g/N_0
c	Constant in Brunauer-Emmett-Teller equation [Eq. (8-15)]
I	Intercept on Brunauer-Emmett-Teller plot (Fig. 8-3)
K_A	Adsorption equilibrium constant for component A
$\bar{L}$	Mean pore length in a catalyst particle
M	Molecular weight
m_p	Mass of a single catalyst particle
n	Number of pores of mean length $\bar{L}$ and $\bar{r}$ in a catalyst particle
N_0	Avogadro's number, 6.02×10^{23} molecules/mole
p	Pressure of gas which is adsorbed on catalyst
p_0	Vapor pressure of gas at temperature of adsorption experiment
$\bar{r}$	Mean radius of pores in a catalyst particle
r_a	Rate of adsorption, moles per unit mass of catalyst per unit time
r_d	Rate of desorption
r_a'	Rate of adsorption, molecules per unit surface of catalyst per unit time
r_d'	Rate of desorption
S	Total number of adsorption sites per unit area of catalyst
S_v	Number of vacant sites per unit area
S_g	Total surface area, external plus internal, per gram of catalyst
V_g	Volume of interior pores/g of catalyst
V_m	Volume at STP of 1 mole of gas (22,400 cc for a perfect gas)
v	Volume at STP of gas adsorbed at a pressure p, per gram of catalyst
v_m	Volume at STP of a monomolecular layer of gas, per gram of catalyst
α	Projected area on the catalyst surface of one molecule of adsorbed gas, sq cm
β	Constant in Freundlich adsorption isotherm
δ	Void fraction for catalyst bed = volume of void space between particles/total volume
δ_p	Void fraction of a single catalyst particle, pore volume/volume of particle
θ	Fraction of surface covered by adsorbed gas (in a monomolecular layer)
ρ	Density of liquefied or solidified gas at temperatures of adsorption, g/cc
ρ_t	Density of solid material in a catalyst particle = mass of catalyst particle divided by volume of solid material in the particle

PROBLEMS

1. Figure 8-3, curve 3, is a Brunauer-Emmett-Teller plot for the adsorption data of N_2 at −183°C on the sample of silica gel. The density of liquid N_2 at this temperature is 0.751 g/cc. Estimate the area of the silica gel in square meters per gram from these data, and compare with the results of Example 8-1.

2. The "point B" method of estimating surface areas was frequently used prior to the development of the Brunauer-Emmett-Teller approach. It involved choosing from an absorption diagram, such as Fig. 8-2, the point where the central linear section began. This procedure worked well for some systems, but it was extremely difficult, if not impossible, to select a reliable point B on an isotherm such as that shown for n-butane in Fig. 8-2.

On the other hand the Brunauer-Emmett-Teller method was found to be reasonably satisfactory for this type of isotherm. Demonstrate this by estimating the surface area of the silica-gel sample from the *n*-butane curve in Fig. 8-3. The density of liquid butane at 0°C is 0.601 g/cc.

3. An 8.01-g sample of Glaucosil is studied with N_2 adsorption at − 195.8°C. The following data are obtained:

Pressure, *p*, mm	Volume adsorbed, cc at STP
6	61
25	127
140	170
230	197
285	215
320	230
430	277
505	335

The vapor pressure of N_2 at −195.8°C is 1 atm. Estimate the surface area (square meters per gram) of the Glaucosil sample.

4. Low-temperature (−195.8°C) N_2 adsorption data were obtained for an $Fe\text{-}Al_2O_3$ ammonia catalyst. For a 50.4-g sample the results were:

Pressure, *p*, mm	Volume adsorbed, cc at STP
8	103
30	116
50	130
102	148
130	159
148	163
233	188
258	198
330	221
442	270
480	294
507	316
550	365

Estimate the surface area for this catalyst.

5. Drake and Ritter[1] give the chemical density of the solid material in an activated alumina particle as 3.675 g/cc. The density of the particle determined by mercury displacement is 1.547. The surface area by adsorption measurement is 175 sq m/g.

From this information compute the pore volume per gram, the porosity of the particles, and the mean pore radius.

The bulk density of a bed of the alumina particles in a 250-cc graduate is given as 0.81 g/cc. What fraction of the total volume of the bed is void space between the particles, and void space within the particles?

6. Two samples of silica-alumina cracking catalysts have particle densities of 1.126 and 0.962 g/cc determined by mercury displacement. The chemical density of the solid materials in each case is 2.37 g/cc. The first sample has a surface area of 467 sq m/g and the second 372 sq m/g. Which sample has the larger mean pore radius?

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[1] *Loc. cit.*