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Diffusion Effects in the Preparation of Impregnated Catalysts

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The distribution of metal within silver-alumina catalysts was studied using autoradiography. When the solute in the impregnating solution was strongly adsorbed on a high-surface-area support, the distributions agreed with predictions from the transient diffusion equations. For low-surface-area supports, mass transfer during drying gave irregular distributions. Theory and results are also given for distribution of metal resulting from fast reaction of a dissolved salt and a reducing agent within the support particle.

Catalysts prepared by impregnating a porous support with a salt solution may have a nonuniform distribution of active material within the pellet. In some metal catalysts, most of the metal is in a thin band in the outer few percent of the pellet radius. The local metal concentration is then much higher than the average value, and the metal surface area is generally lower than if the metal were uniformly dispersed. Such catalysts are also more affected by attrition; in one case (*1*), a rotary-dried catalyst had only one-fourth as much platinum as a sample carefully dried in a dish. A possible advantage of having all the metal near the outside is that the effectiveness factor for a very fast reaction will be increased, since the average diffusion distance is decreased. However, even for this case, there would be an optimum radial distribution of metal, and some control over the distribution would be desirable.

Nonuniformity can arise because of strong adsorption of solute on the support, as shown by Maatman and Prater (*2*, *3*) for platinum-on-alumina catalysts. In this study, autoradiography was used to obtain quantitative data for the distributions of silver within alumina supports. The results for strong adsorption are correlated using the theory of diffusion plus irreversible adsorption, which was extended to allow for depletion of the external solutions. Theory and results are also given for distribution of metal resulting from fast reaction of a dissolved salt and a reducing agent within the support particles.

NOMENCLATURE

A	(Moles solute adsorbed/g support)/(moles solute in pore fluid/g support)
C	Concentration (moles/cm^3)
D	Diffusivity in the liquid-filled pores (cm^2/sec)
f	Fraction approach to equilibrium
r	Radial distance (cm)
R	Particle radius (cm)
S	BET surface area (m^2/g)
t	Time
V_g	Pore volume (cc/g)
W	Metal concentration (g/100g support)
τ	Tortuosity

DIFFUSION–ADSORPTION THEORY

Impregnation of a catalyst support is generally carried out by adding the particles to a stirred solution of active material. When the solute is irreversibly adsorbed, a shell of a saturated solid forms as solute diffuses inside the particle, and the rate of adsorption is limited by the rate of diffusion through this shell. If the amount of solute

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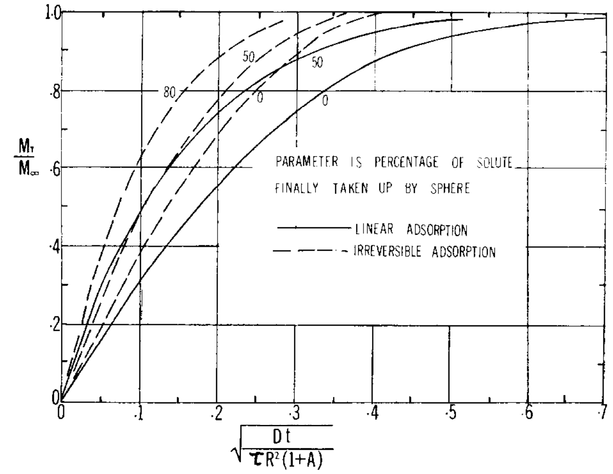

FIG. 1. Fractional approach to equilibrium for irreversible and for linear adsorption in a sphere.

held in the pore liquid is small compared to the amount adsorbed, and if a large excess of solution is used, the fractional approach to equilibrium for various shapes can be obtained from the equations of Weisz and Goodwin (*4*) and Weisz (*5*). Weisz showed that the solutions for irreversible adsorption are similar to those for linear adsorption, and solutions for intermediate cases (Langmuir isotherms) were presented by Weisz and Hicks (*6*). However, these solutions for nonlinear adsorption are for constant external concentrations, and in many catalyst impregnations there is appreciable depletion of the external solution.

The effect of external solution depletion for diffusion plus adsorption in a sphere is shown in Fig. 1. The dashed lines for irreversible adsorption with 50% and 80% uptake were obtained by a stepwise computation. The curves for linear adsorption are from Crank (*7*). The parameter τ is the tortuosity and A is the equilibrium ratio of adsorbed solute to solute in the pore fluid. For linear adsorption, A is the adsorption constant divided by the void fraction. For irreversible adsorption, A varies inversely with the final solution concentration, since the amount adsorbed at equilibrium is constant.

With linear adsorption, equilibrium is approached more rapidly when there is a large change in the external concentration. With nonlinear adsorption, depletion of the external solution actually decreases the rate of approach to equilibrium, since the total amount transferred is almost independent of solute concentration, and depletion lowers the driving force for diffusion. However, if the comparison is made at the same final concentration or same value of A, the higher average driving force obtained with 50% depletion displaces the curve above that for zero depletion. The effect of depletion is not as pronounced for irreversible as for linear adsorption, and for a high percentage uptake, the curves for linear adsorption start out above those for irreversible adsorption. This makes the curves for the limiting cases even closer than at zero depletion.

IMPREGNATION TESTS

Catalysts were prepared by soaking 6–8 mm spheres of activated alumina (S = 324 m^2/g, V_g = 0.44 cc/g) in silver nitrate solutions, drying, and reducing in hydrogen. Analyses of the external solution and of the solid indicated moderately strong adsorption of the silver nitrate, as shown in Fig. 2. The dashed line indicates the concentration expected if the silver came only from salt dissolved in the pore fluid. One test in which W was reduced from 7 to 4.2 by soaking in distilled water showed that the adsorption was reversible.

The rate of adsorption was followed by analysis of the external solution, and the

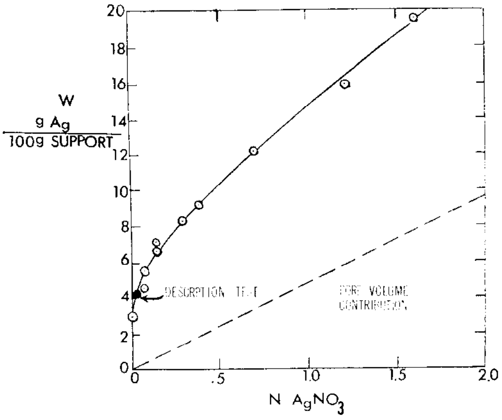

Fig. 2. Adsorption of silver nitrate on activated alumina.

results are shown in Fig. 3. The rate of approach to equilibrium is greatest for the highest external concentration, as expected for nonlinear adsorption. The theoretical curve for irreversible adsorption, adjusted to allow for 25% uptake, fits the lowest set of data quite well, though the reversible adsorption curve would fit almost as well. Based on $D = 1.76 \times 10^{-5}$ cm²/sec, the tortuosity, τ, is 6.0. This is 2 to 3 times the expected value, probably because the diffusivity in the small pores is less than the free solution value.

Some impregnations were carried out with $^{110}AgNO_3$ to show quantitatively the distribution of silver inside the particles. After drying at 170°C and reduction by hydrogen at 200°C, the particles were sanded to hemispheres, glued to metal plates, and sanded to form discs about 0.2 mm thick. Hemispheres were not satisfactory, since enough radiation from the back side penetrated the support to blur the outline of the metal zones. Autoradiographs were made by placing the discs on X-ray film, and the negatives were analyzed with a densitometer. The intensity was approximately proportional to the concentration of silver.

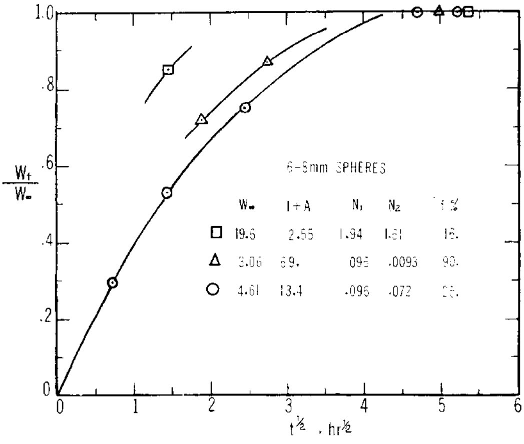

Fig. 3. Rate data for impregnation of alumina with $AgNO_3$.

Exposure of a 6-mm sphere to 0.17 *N* $AgNO_3$ for 1 hr gave a band of silver about 1.5 mm thick, as shown in Fig. 4(a). The concentration was uniform in this band, and the fractional approach to equilibrium was about 0.55–0.6, in agreement with the results in Fig. 3. Impregnation for 1 hr with 1 *N* $AgNO_3$ produced silver throughout the particle, and the concentration at the center was about half that near the outside [Fig. 4(b)]. At the higher solute concentrations, a less sharp adsorption band is expected, since an appreciable fraction of the silver comes from solute dissolved in the pore solution. After 30 hr exposure [Fig. 4(c)] there was no significant gradient in silver concentration.

Further tests were made using alumina spheres that had been heated at 1000°C to reduce the surface area (S = 55 m²/g) and the amount of adsorbed $AgNO_3$. Although the distribution was presumably uniform after 24 hr in the impregnating solution, the final catalysts had local regions of high silver concentration, as shown by a typical autoradiograph, Fig. 4(d). This is attributed mainly to the uneven rate of heat transfer for particles resting on a hot surface in an oven. Certain portions of the pore fluid become supersaturated, crystals form, and diffusion of solute to these crystals leads to a nonuniform distribution. There is some redistribution during hydrogen reduction at 200°C, as shown by comparing a typical distribution of $AgNO_3$ [Fig. 4(e)] with that for Ag [Fig. 4(d)]. The faint rings in Fig. 4(d) and Fig. 4(f) may have been caused by a difference in support porosity. The alumina support itself often showed a banded structure.

The rapid drying step did not appreciably

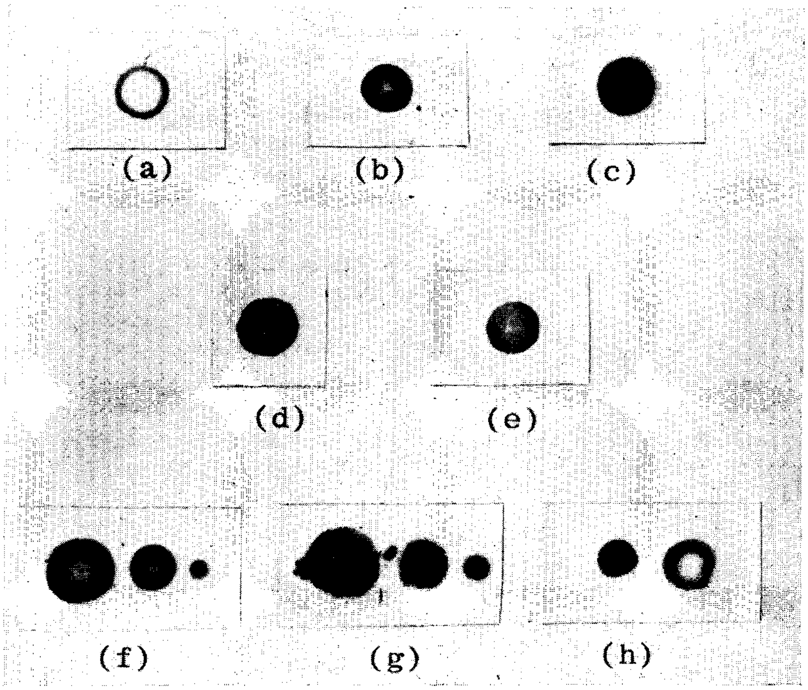

FIG. 4. Autoradiographs of silver-alumina catalysts: (a) 0.17 N $AgNO_3$, 1 hr; (b) 1 N $AgNO_3$, 1 hr; (c) 1 N $AgNO_3$, 30 hr; (d) Ag on low-surface-area support; (e) (d) before reduction; (f) reduction with formaldehyde; (g) precipitation with caustic; (h) silver lactate, slow drying.

alter the distribution of silver in the high-surface-area alumina, because most of the silver came from strongly adsorbed silver nitrate and not from a supersaturated pore solution. Later tests (not illustrated) showed that a nearly uniform distribution of silver nitrate could be obtained with the lower area alumina by drying slowly at 40°C. However, slow drying did not give a uniform distribution for spheres soaked in silver lactate solution. Figure 4(h) shows a 4-mm sphere with a high concentration in the center and a 7-mm sphere with no silver in the center. Both were exposed to the same conditions, and the reason for the different patterns is not known.

DIFFUSION AND REACTION INSIDE A PARTICLE

Tests with low-surface-area supports showed that it is often difficult to get a uniform or even reproducible distribution of active material because of mass transfer during drying. A reproducible distribution should be obtainable by reducing the salt or forming a precipitate within the particle before the drying operation. If a pellet uniformly impregnated with solution is placed in a solution of a strong reducing agent, solute and reducing agent will diffuse towards a reaction zone which slowly advances into the pellet. The equations for unsteady state diffusion with infinitely rapid second order reaction have been solved (*8*) to give the rate of absorption at a plane interface with infinite depth of solution.

Here the interest is in the total amount reacted as a function of sphere radius, and previous solutions can be used only for the initial stage of reaction. The following equations were solved numerically using an explicit difference method for the reaction A + B → Metal:

$$\frac{\partial C_A}{\partial t} = D_A \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right)$$

$$\frac{\partial C_B}{\partial t} = D_B \left(\frac{\partial^2 C_B}{\partial r^2} + \frac{2}{r} \frac{\partial C_B}{\partial r} \right)$$

$$D_A \left(\frac{\partial C_A}{\partial r} \right) = -D_B \left(\frac{\partial C_B}{\partial r} \right)$$

$$\text{at radius where } C_A = 0,\ C_B = 0$$

$$C_B = C_{B_0} \text{ at } t = 0$$

$$C_A = C_{A_0} \text{ at } r = R$$

For the calculation, the sphere was divided into 40 radial zones, and the movement of the reaction interface across each zone was calculated using the condition of equal fluxes at this plane. The amount of metal deposited in each zone was found by integrating to get the B remaining after the reaction plane reached a zone boundary. The theoretical distributions are shown as solid lines in Fig. 5 for several ratios of initial concentrations. For equal initial concentrations and diffusivities, the concentration at the outer surface is 1.9 times the average concentration. As the external concentration is increased, the distribution becomes more uniform, and the maximum concentration is only 1.32 times the average when $A_0/B_0 = 6$. A higher diffusivity for A also favors a more uniform distribution, as shown by the dotted line for $D_A = 4D_B$. The variations in concentration shown in Fig. 5 may seem large, but such catalysts would be better than those with a uniform distribution for fast reactions and have almost as much surface area as if the metal were uniformly dispersed.

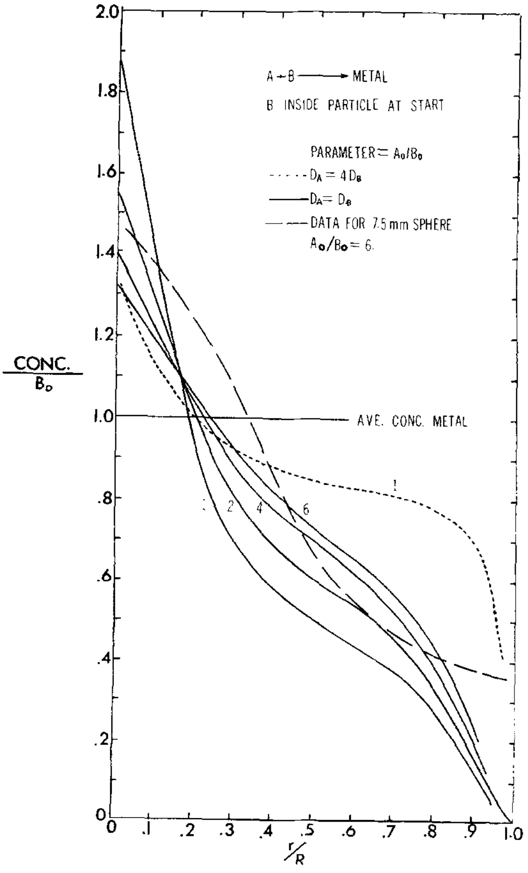

FIG. 5. Distribution of precipitated metal inside a porous catalyst particle.

The technique of internal precipitation was tested by allowing concentrated formaldehyde to diffuse into spheres that had been soaked in $Ag(NH_3)_2NO_3$ solution. Autoradiographs of catalyst sections are shown in Fig. 4(f). Quantitative data obtained with a densitometer are plotted as a smoothed curve in Fig. 5. The distribution is in fair agreement with the theory, though the silver concentration does not drop to zero at the center as predicted, and the curve has the wrong shape near the outer surface. These differences are partly explained by errors in the measurement technique. The spread of radiation from a spot on the surface and the finite aperture area of the densitometer introduce error when the density gradient is rapidly changing. The departure from the predicted shape might also be due to finite rates of nucleation and crystal growth. An instantaneous reaction rate was assumed in the derivation. The main conclusions are that the technique of internal precipitation can be used to prepare catalysts with a radial distribution of metal, and that the slope of the distribution curve is in reasonable agreement with diffusion theory.

Attempts to precipitate Ag_2O inside pellets were not successful. Because of supersaturation effects or pore blockage, most of the silver deposited at or near the exterior surface. Figure 4(g) shows dark inner bands stronger than those attributed to the support itself in Fig. 4(d) and 4(f).

The bands of silver oxide resemble Liesegang rings and suggest a supersaturation–precipitation cycle in the pellet.

ACKNOWLEDGMENT

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