JOURNAL OF CATALYSIS 57, 504-508 (1979)

NOTES

Splitting of Supported Metal Catalysts

Noble metals supported on oxide substrates are routinely being used as catalysts in applications ranging from refineries to pollution control equipment in automobiles. Aging, or loss of performance, of these catalysts can occur either by chemical means (poisoning) or due to thermal effects (sintering) during the process. It is important to regenerate the catalyst to maintain the economics of the process.

Sintering of the catalyst occurs when noble metal particles agglomerate, increase in size, and thus decrease the total surface area of noble metal particles available for reaction. Sintering has been modeled by noting that a larger particle is thermodynamically more stable than several smaller ones. However, the reverse process—splitting of larger noble metal particles to form smaller particles having greater total surface area—has been noted on several occasions. Kluksdahl and Houston (*1*) noticed that exposure of a prereduced commercial-type platinum catalyst to gaseous oxygen led to a dramatic increase in the fraction of platinum available in so-called "soluble" form (removable by aqueous hydrofluoric acid or acetylacetone). The effect was independent of the nature of the support. Kluksdahl and Houston postulated the formation of a Pt–chemisorbed oxygen complex. Johnson and Keith (*2*) interpreted the results of similar experiments to mean that formation of the complex splits the particles on the surface. Subsequent reduction by H_2 then removes oxygen from the complex, leaving Pt metal particles in an active, dispersed state. They found that increasing the temperature first increases and then decreases the formation of the complex. They postulated that, after a given temperature, the partial pressure of oxygen in the gas phase was less than a "decomposition pressure" for the complex, leading to the eventual breakup of the complex. Ruckenstein and Malhotra (*3*) found appreciable sintering of Pt (supported on an Al_2O_3 film) at 400 and 600°C, but at 500°C the average particle size was very much lower. They concluded that the complex was formed and particles ruptured within a temperature range lying inside the larger range 400 to 600°C. The rupture was qualitatively related to strain energy considerations. They postulated that the complex would not be formed at too low a temperature and would not be stable at too high a temperature. The goal of the present note is to obtain a simple quantitative description for the splitting phenomenon in a form that is useful for further kinetic studies.

Oxygen is known to chemisorb readily on bulk Pt metal, although the amount chemisorbed is somewhat less than an entire monolayer at room temperature (*4*). It seems possible then that platinum oxides, say PtO, can be formed with little difficulty on isolated particles at 400°C and higher temperatures. However the lattice parameter of the metal oxide is expected to be much larger than the lattice parameter of the pure metal. This

0021-9517/79/060504-05$02.00/0

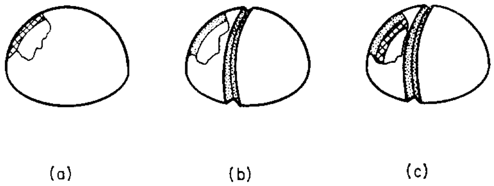

FIG. 1. Model of splitting—I. The hatched portion denotes stressed PtO. The dotted area denotes stress-relieved PtO. Clear centers represent (unstressed) Pt metal. (a) Oxide thickness is less than the critical thickness for splitting. (b) At the critical thickness, a crack splits the oxide layer and the stress is relieved. The metal is not split. (c) Oxidation now continues and a stressed layer of oxide builds inside the stress-relieved layer until the thickness of the stressed layer again approaches the critical thickness. The particle then again resembles (b), and the process continues.

creates a strain and the corresponding force tends to fracture the particle. At temperatures much below that required for significant plasticity of the oxide, the force due to the lattice mismatch is countered by the force required to create a new surface. If the oxide is thick enough that the difference between the surface force and the mismatch force is less than a certain critical value (which may well be zero), the stress in the oxide layer will be relieved by splitting the particle. For higher temperatures, the stress due to the mismatch may be relieved by plastic flow of the oxide layer of the particle. Plastic flow (creep, for example) has been shown to occur in oxide layers on bulk metals at high temperatures (*5*).

Splitting of the particle may occur in one of at least two ways. In both, the stress is to be relieved when the oxide thickness reaches a critical value, l_{crit}. In the first model, the particle cracks only up to a depth not much greater than l_{crit}. Oxidation then continues until the new stressed oxide film is again to be relieved by cracking. The process continues until two quarter-spheres are formed. This model is illustrated in Fig. 1. In the second model the oxide, as before, cracks to relieve the stress due to lattice mismatch. In this case, however, the crack quickly spreads through the particle, dividing it into two quarter-spheres. Each quarter-sphere contains an outside shell of PtO and an inside kernel of Pt. It rearranges itself into the most favorable conformation—a hemisphere, smaller than the initial particle with PtO in a uniform layer on the outside. The thickness of the layer is smaller than the critical thickness, so oxidation continues. After some time, cracking occurs again and the process is repeated. This model is illustrated in Fig. 2.

Of course both models are extreme cases, involving infinitely slow crack propagation in the first case and infinitely fast crack propagation in the second. The first model implies that the initial particle separates only after all the Pt has been converted to PtO. Hence the two quarter-spheres formed after the split cannot be further decreased in size. Only one split is allowed per particle—after that, its constituents cannot be split again unless the PtO is first reduced back to Pt (say by passing hydrogen gas over the catalyst) and the process is started over again. Particles of different sizes exist on the substrate sur-

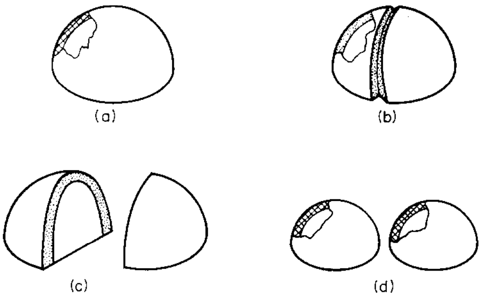

FIG. 2. Model of splitting—II. Hatched, dotted, and clear portions have the same significance as in Fig. 1. (a) Oxide thickness is less than the critical thickness. (b) The crack is initiated when the oxide approaches critical thickness. (c) The crack propagates through the particle, forming two quarter-spheres. (d) The particles form two hemispheres. The oxide thickness is less than the critical thickness.

face, and these may split at different times. Hence the overall increase in surface area with time would be smooth and not a step function. Some cases have been observed (*6*) which would imply a mechanism close to this model. However, the second model, with its infinitely fast propagation of the crack, is used in this work. This model implicitly accounts for the presence of imperfections, thus far neglected, in the structure of the metal particle. Crack propagation will generally be helped rather than hindered by these imperfections. Consequently the second model can be considered closer to the physical picture in the general case.

In the following analysis, the critical oxide thickness for a hemispherical particle is first calculated. This is used to determine the dimensions of the two new hemispherical particles formed. Finally a simple kinetic equation is obtained for the splitting process.

Consider a hemispherical particle containing an inner hemisphere of metal, diameter d, and an outer shell of oxide of uniform thickness l. The assumption of no plastic flow requires that the overall particle diameter d_o $(= d + 2l)$ remain constant as oxidation proceeds, although of course l increases. Then the force due to lattice disregistry in the shaded area of Fig. 3 is

$$F_d = E(\Delta a/a_{\mathrm{Pt}}) \cdot \frac{\pi}{8} \{d_o^2 - (d_o - 2l)^2\} \quad (1)$$

where E is Young's modulus for PtO. The term $(\Delta a/a_{\mathrm{Pt}})$ represents the strain, $\Delta a \equiv a_{\mathrm{PtO}} - a_{\mathrm{Pt}}$, and a_i is the lattice parameter of species i. The surface force can be written

$$F_s = \sigma\pi(d_o/2), \quad (2)$$

where σ is the surface tension of the oxide. The critical force, the difference between F_s and F_d required for actual cracking, can be written in terms of a critical surface tension, σ_c, as

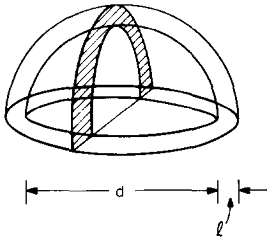

FIG. 3. Geometry of hemispherical particle containing an inner metal hemisphere of diameter d and an outer oxide shell of thickness l. The overall diameter of the particle $d_o = d + 2l$.

$$F_c \equiv \sigma_c\pi(d_o/2). \quad (3)$$

Recall that it may well be that F_c, and therefore σ_c, are equal to zero. When the oxide thickness reaches the critical value, the difference between F_s and F_d is sufficient to cause the initial crack. Then

$$F_s - F_d \lesseqgtr F_c \qquad \text{at } l \gtreqless l_{\mathrm{crit}}. \quad (4)$$

From equations (1) through (4) the critical thickness of the oxide is

$$l_{\mathrm{crit}} = \frac{d_o}{2}\left\{1 - \left[1 - \frac{4(\sigma - \sigma_c)}{E(\Delta a/a_{\mathrm{Pt}})} \cdot \frac{1}{d_o}\right]^{\frac{1}{2}}\right\}. \quad (5a)$$

Consider simpler forms of equation (5a). In the limiting case $4(\sigma - \sigma_c)/E(\Delta a/a_{\mathrm{Pt}}) \ll d_o$,

$$l_{\mathrm{crit}} \approx \frac{(\sigma - \sigma_c)}{E(\Delta a/a_{\mathrm{Pt}})}. \quad (5b)$$

Hence for sufficiently large particles, the critical thickness is independent of the particle diameter. On the other hand, when $4(\sigma - \sigma_c)/E(\Delta a/a_{\mathrm{Pt}}) = d_o$,

$$l_{\mathrm{crit}} = d_o/2. \quad (5c)$$

This implies that the entire particle must be stressed before a crack can form. Particles smaller than this value of d_o will require an oxide thickness greater than the particle dimension before sufficient stress is obtained to generate a crack. Clearly such particles will never crack, and consequently will not split. Therefore

$$d_{\min} = \frac{4(\sigma - \sigma_c)}{E(\Delta a/a_{\mathrm{Pt}})} \tag{6}$$

denotes the minimum diameter required of a particle to split. Note that this value can be decreased by decreasing the surface tension (or more correctly, decreasing $\sigma - \sigma_c$), or by increasing E and /or$\Delta a/a_{\mathrm{Pt}}$.

The parameters of the particles formed after the split can now be found. Assuming that the new particles are also perfect hemispheres, each with half the material of the initial particle, the diameter of the new particle is

$$d'_o = (0.5)^{\frac{1}{3}} d_o. \tag{7a}$$

Similarly, the thickness l' of the oxide in the new particle is

$$l' = (0.5)^{\frac{1}{3}} l_{\mathrm{crit}}. \tag{7b}$$

It follows that the increase in surface area is

$$\begin{aligned} s' - s &= 2\,\{2\pi(d'/2 + l')^2\} \\ &\quad - 2\pi(d/2 + l_{\mathrm{crit}})^2 \\ &\simeq \{2^{\frac{1}{3}} - 1\}\, 2\pi(d/2 + l_{\mathrm{crit}})^2 \end{aligned}$$

or

$$\Delta s \simeq 0.26 s, \tag{8}$$

where s is the surface area of the initial particle, s' is the combined surface area of the two particles after the split, and $\Delta s \equiv s' - s$.

Now the time between two cracking processes, t_p, is the sum

$$t_p = t_a + t_s.$$

Here t_a is the time for a new crack to appear, and t_s is the time required for a crack to spread until relieved, including if necessary the time for split particles to form hemispheres. According to the model of Fig. 2, the time required for propagation of the crack is infinitely small so that

$$t_s \approx 0.$$

Hence t_p equals the time for a new crack to appear. In other words, t_p is the time taken for the oxide thickness to increase from l' to the critical thickness corresponding to the overall diameter of the particle. If the overall diameter is sufficiently large, then Eq. (5b) applies and l_{crit} is independent of d_o. Consequently

$$t_p = \int_{l'}^{l_{\mathrm{crit}}} \frac{dx}{(dx/dt)}$$

where l_{crit} is given by Eq. (5b). Here (dx/dt) is the rate of growth of oxide of thickness x. For metal oxides where cracking is expected, growth is often linear (7). Hence let

$$\frac{dx}{dt} = k_1.$$

This yields

$$t_p = \frac{(l_{\mathrm{crit}} - l')}{k_1}. \tag{9}$$

Note that Eq. (9) also follows if a nonlinear growth rate between $x = l'$ and $x = l_{\mathrm{crit}}$ can be averaged to a constant value k_1.

Consider now a distribution of particle sizes of the catalyst on the substrate. If the time dependence of the size distribution, and hence of the useful surface area of the system, can be described in terms of an average particle diameter D, then the active surface area S per area of substrate is

$$S = (\pi D^2/2)N. \tag{10}$$

From Eqs. (8) and (10), the change in surface area of the catalyst per cracking phenomenon is

$$\Delta S = 0.26 S.$$

Recall that particle size, and hence surface area, is assumed not to change during oxidation. Hence the rate of change of surface area can be written

$$\frac{dS}{dt} \simeq \frac{\Delta S}{t_p} = \frac{0.26k_1}{(L_{\mathrm{crit}} - L')} S,$$

where L_{crit} and L' correspond to l_{crit} and l' for a particle of diameter D. From Eqs. (5b) and (7),

$$\frac{dS}{dt} = \frac{1.3k_1E(\Delta a/a_{\mathrm{Pt}})}{(\sigma - \sigma_c)} \cdot S. \qquad (11)$$

Equation (11) is a simple linear relationship between the splitting rate and the surface area, and was obtained using the simplest expressions for t_p, L_{crit}, and L'. If experimental work, in progress, indicates that the linear relationship is not valid, it may be necessary to consider a more elaborate formulation. The general splitting kinetics may be of the type

$$\frac{dS}{dt} = kS^p,$$

similar to the expression used for the sintering process. In the present case we have

$$p = 1$$

and

$$k = 1.3\, k_1E(\Delta a/a_{\mathrm{Pt}})/(\sigma - \sigma_c).$$

REFERENCES

1. Kluksdahl, H. E., and Houston, R. J., *J. Phys. Chem.* **65**, 1469 (1961).
2. Johnson, M. F. L., and Keith, C. D., *J. Phys. Chem.* **67**, 200 (1963).
3. Ruckenstein, E., and Malhotra, M. L., *J. Catal.* **41**, 303 (1976).
4. Hayward, D. O. *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, Ed.), p. 226 et seq. Academic Press, New York, 1971.
5. Stringer, J., *Corros. Sci.* **10**, 513 (1970).
6. Weller, S. W., and Montagna, A. A., *J. Catal.* **20**, 394 (1971).
7. Lawless, K. R., *Rep. Prog. Phys.* **37**, 231 (1974).

Dady B. Dadyburjor

Department of Chemical
and Environmental Engineering,
Rensselaer Polytechnic Institute,
Troy, New York 12181

Received June 12, 1978; revised December 8, 1978