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Kinetics of Crystallite Sintering During Heat Treatment of Supported Metal Catalysts

Models are developed to describe sintering of metal crystallites during heat treatment. The growth rate of such crystallites is assumed to depend upon particle migration over the surface of the support as well as on the rate the colliding particles merge (sinter) into a single unit. The theory predicts that the rate of decay of exposed metal surface area S is given as in Equation (1a). The exponent n is related to the assumed size dependence of the diffusion coefficients or of the rate constant of the merging process. It varies from 4 to 8 for diffusion controlled decay and it is less than 3 for sintering controlled decay, that is, when the rate controlling step is the merging of two colliding particles. Diffusion control is associated with strong interactions between the metal and the support, but in sintering control there is a weaker metal-support interaction.

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SCOPE

The degree of dispersion of a metal on a support affects the activity and selectivity of the supported metal catalyst. In freshly prepared catalyst, the metal is generally highly dispersed so that a large number of the metal atoms are accessible to reactants. Deactivation observed after excessive heating is associated with aggregation and sintering of the small crystallites (Adler and Keavney, 1960; Mills et al., 1960; Maat and Moscou, 1965).

The goals of the present paper are:

1. to develop a model as those used in chemical kinetics to describe the sintering process caused by heat treatment,
2. to obtain an equation for the rate of decrease of the exposed metal surface area during heat treatment,
3. to explain the effect of temperature and of the chemical atmosphere upon the decay of the exposed surface area of metal.

In the model one assumes migration of the metal crystallites upon the surface of the support and sintering of the colliding particles.

CONCLUSIONS AND SIGNIFICANCE

The decay of the exposed surface area of metal (S) during heat treatment is obtained both by a numerical solution of a population balance and by an analytical solution based on a similarity transformation. The rate of decrease of (S) is obtained as a power function of S. The exponent is very sensitive to the mechanism of the process. It is larger than 4 when the diffusion of the crystallites on the surface of the support controls the rate of the process. It is smaller than 3 when the rate is controlled by the sintering of the colliding particles. The value of the exponent is related to the assumed size dependence of the diffusion coefficient or of the rate constant of the merging process. Diffusion control is associated with strong interactions between metal and support, while in sintering control there is a weaker metal-support interaction.

The physical model suggested in the paper gives some insight concerning the mechanism of sintering of the metal crystallites and also allows one to stress the main parameters (diffusion coefficient, reaction rate constant for the merging process) which are of significance for the process. The effect of temperature and of the atmosphere are explained taking into account their influence on the mentioned parameters.

In several studies (Adler and Keavney, 1960; Mills, et al., 1960; and Maat and Moscou, 1965) it has been shown that supported metal catalysts may lose activity as a result of aging processes associated with the growth of the crystallites. Possible explanations of aging advanced by Luss (1970) and Ruckenstein and Petty (1972) are based on the assumption that hot spots (points of high temperature) occur on the catalyst surface during exothermic reactions.

There is experimental evidence that heating to high temperature is sufficient to cause sintering of the crystallites. Herrmann et al. (1961) subjected various samples of Pt-on-alumina catalyst to a series of heat treatments and used hydrogen chemisorption and X-ray diffraction to obtain information about the state of platinum. They concluded that platinum was present in the original catalyst in a highly dispersed form and that heat treatment caused the formation of platinum crystallites and their growth. These conclusions have been confirmed by Maat and Moscou (1965) and by Zaidman et al. (1969). The kinetic equation suggested by Herrmann et al. (1961) to describe the evolution of the exposed surface area S of the metal is of the form

$$\frac{dS}{dt} = -KS^2 \tag{1}$$

Analyzing the available experimental results of Maat and Moscou (1965), Gruber (1962) and Hughes et al. (1962) we have observed that in reality

$$\frac{dS}{dt} = -KS^n \tag{1a}$$

where the range of the exponent n is between 2 and 8.

It will be shown that the decay during heat treatment of the exposed surface area of the metal is very sensitive to the mechanism of the process and that the process can be either diffusion or sintering controlled. The rate of decay depends strongly upon the interaction between the metal and support, which is affected by the temperature, by the method of preparation of the metal supported catalyst, and by the chemical atmosphere in which the decay takes place.

The aging of a supported metal catalyst during the catalytic process is a more complex phenomenon than that which occurs during the thermal treatment, but a first step in the understanding of the more complex situation can be made by analyzing the simpler case. The goal of the present paper is to develop a model such as those used in chemical kinetics in order to describe the sintering process caused by thermal treatment. A quantitative description of the time dependence of the exposed metal surface area is to be obtained.

PHYSICAL MODEL

Let us consider an initially highly dispersed state of platinum on the surface of a support which is assumed for the sake of simplicity to be planar. The evolution of the sintering with time, hence the formation of crystallites and their growth with time, will be assumed to depend upon the rate of surface migration of agglomerates of metal atoms and the nature of their interaction when they are very close.

For sufficiently high temperature, exceeding the so-called "Tammann temperature" (0.4 × melting point in °K), the mobility of the agglomerates of platinum atoms on the surface of the support is expected to be increased. Lyon and Somorjai (1967), using low energy electron diffraction to study structures of the clean (100), (111), and (110) faces of platinum crystals as a function of temperature up to 1769°C, observed, for temperature higher than about 750°C, some more or less disordered surface structures (perhaps a kind of liquid-like structure due to a surface premelting phenomenon). These disordered structures remain the only ones evidenced by low energy diffraction near the melting point. Because the platinum crystallites existing on the support are at most of the order of 10^2 Å in size, and the interactions between platinum atoms and support are weaker than those between platinum atoms themselves, it appears reasonable to assume that for temperatures higher than the Tammann temperature the crystallites are in a quasiliquid state and hence that they have an increased mobility and can migrate as a whole on the surface of the support. The migration mechanism is not yet clear, but it is probable that the migration is due to the thermal motions of the atoms at the metal support interface.

Concerning the interaction between particles when they are close together, two limiting situations will be considered. In one case the interaction will be assumed so strong that if two particles are in contact they form a single unit within a time which is short compared to the time in which the migration process takes place. The rate of sintering is then diffusion controlled. In the second case the merging into a single unit is assumed to be slow compared to the diffusion process. For this case the name sintering control will be used.

This model, in particular the diffusion controlled case, is similar to that used by Smoluchovski in his coagulation theory (von Smoluchovski, 1917; Chandrasekhar, 1943). Important differences arise, however, from the bidimensional situation of interest here instead of the tridimensional occurring in the coagulation theory and from the kinetics of merging of two colliding particles which is taken here into account.

KINETIC EQUATIONS

Let us denote by c_k the number of crystallites per unit surface area of support, composed of k platinum atoms. The concentration c_k increases by collision of particles composed of i and $k - i$ atoms and decreases by the collisions of the particles composed of k atoms with any other particles.

In analogy with chemical kinetics, the rate of collision between particles composed of i and j units will be written as

$$b_{ij} = K_{ij}c_ic_j \tag{2}$$

where K_{ij} are rate constants dependent upon the mobility of the particles on the support and on the nature of the interaction between the particles.

The rate of change of c_k is thus given by

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij}c_ic_j - c_k \sum_{i=1}^{\infty} K_{ik}c_i \tag{3}$$

To obtain information concerning the rate constants K_{ij}, the problem of the collision rate between particles of various sizes will be examined in more detail.

Consider the center of the surface of contact between a particle composed of j units and the support as the origin of a cylindrical coordinate system. The migration of the particles composed of k units upon the surface of the support is due to the thermal motion of the atoms in contact with the support and, therefore, has a random character; consequently, it may be represented by a diffusional model. Because of radial symmetry no dependence on the polar angle exists. Consequently

$$\frac{\partial c_k}{\partial \theta} = D_{kj}\left[\frac{\partial^2 c_k}{\partial r^2} + \frac{1}{r}\,\frac{\partial c_k}{\partial r}\right] \tag{4}$$

where D_{kj} is the diffusion coefficient of the particle k with respect to that of the particle j, and θ is the time.

Some comments concerning the kinetic Equations (3) and (4) must be made, with particular reference to the two scales of time involved in their formulation: A large scale of time, introduced in Equation (3), which coincides with the time of the process, and a small scale of time, introduced in Equation (4). Equation (4) is used to obtain the rate of collisions between a particle selected at a given time t, and the other particles, during a time interval θ_0 which must be small compared to the time in which an appreciable modification of the particle distribution takes place. The present approach can be used only if during the largest part of the time interval θ_0 the rate of collision is practically independent of θ. It will be shown below that this condition is satisfied.

The particle containing j units, selected as the origin of the coordinate system, is also subject to thermal motions which are independent of the motions of the k-particles. The diffusion coefficient D_{kj} is thus given by

$$D_{kj} = D_k + D_j \tag{5}$$

The following initial and boundary conditions will be used for the situation in which both the diffusion process and the merging into a single unit are important:

$$\text{at } \theta = 0 \quad c_k = c_{k0} \qquad r > R_{kj} \tag{6a}$$

$$\text{for } \theta > 0 \quad \alpha_{kj}c_k = D_{kj}\frac{\partial c_k}{\partial r} \qquad r = R_{kj} \tag{6b}$$

TABLE 1. SOLUTION OF EQUATIONS (4) AND (8) WHEN BOTH THE DIFFUSION AND MERGING PROCESSES ARE TAKEN INTO ACCOUNT

$$c_k(\theta, r) = -\frac{2c_{k0}}{\pi}\left\{h\int_0^{\infty} e^{-D_{kj}u^2\theta}\frac{J_0(ur)\,[uY_1(uR_{kj}) + hY_0(uR_{kj})] - Y_0(ur)\,[uJ_1(uR_{kj}) + hJ_0(uR_{kj})]}{[uJ_1(uR_{kj}) + hJ_0(uR_{kj})]^2 + [uY_1(uR_{kj}) + hY_0(uR_{kj})]^2}\,\frac{du}{u}\right.$$
$$\left. + \int_0^{\infty} e^{-D_{kj}u^2\theta}\,\frac{J_0(ur)\,Y_0(uR_{kj}) - J_0(uR_{kj})\,Y_0(ur)}{J_0^2(R_{kj}u) + Y_0^2(R_{kj}u)}\,\frac{du}{u}\right\} \tag{T1-1}$$

$$\Phi_{kj} = 4\alpha_{kj}\,h\,R_{kj}c_{k0}\int_0^{\infty} e^{-D_{kj}u^2\theta}\,\frac{[J_0(uR_{kj})\,Y_1(uR_{kj}) - Y_0(uR_{kj})\,J_1(uR_{kj})]\,du}{[uJ_1(uR_{kj}) + hJ_0(uR_{kj})]^2 + [uY_1(uR_{kj}) + hY_0(uR_{kj})]^2} \tag{T1-2}$$

For short times ($T \to 0$)

$$\Phi_{kj} = c_{k0}\,2\pi\,R_{kj}\alpha_{kj}\left\{1 - \alpha_{kj}\,2\sqrt{\theta/\pi\,D_{kj}} + \alpha_{kj}\,\theta\left[\frac{1}{2R_{kj}} + \frac{\alpha_{kj}}{D_{kj}}\right]\cdots\right\} \tag{T1-3}$$

For long times ($T \to \infty$) (Ritchie and Sakakura, 1956)

$$\Phi_{kj} = c_{k0}\,4\pi\,R_{kj}\alpha_{kj}\left\{I_0^{-1}(T/\beta) + \left[-\frac{1}{2}(3/2\text{-}2/hR_{kj})\right]I_1^{-1}(T/\beta)\right.$$
$$\left. + \frac{1}{4}\left(1 - \frac{2h^{-1}}{R_{kj}} + \frac{2h^{-2}}{R^2_{kj}}\right)I_1^{-2}(T/\beta)\cdots\right\} \tag{T1-4}$$

where $T = \dfrac{D_{kj}\,\theta}{(R_{kj})^2}$, $h = \dfrac{\alpha_{kj}}{D_{kj}}$, $\beta = (4/e^{2\gamma})e^{2/hR_{ij}}$, $\gamma = 0.5772$

and the function $I_j^k(T/\beta) = \dfrac{1}{2\pi i}\displaystyle\int_{-\infty}^{(0+)} e^{zT/\beta}z^{(j-1)}\,[\ln z]^k\,dz$

Table 2. Solution of Equations (4) and (8) when Either the Migration Process or the Sintering Process is Rate Controlling

Diffusion Control (Carslaw and Jaeger, 1959):

$$c_k(r,\theta) = -\frac{2c_{k0}}{\pi}\int_0^\infty e^{-D_{kj}u^2\theta}\,\frac{J_0(ur)\,Y_0(uR_{kj}) - J_0(uR_{kj})\,Y_0(ur)}{J_0^2(R_{kj}u) + Y_0^2(R_{kj}u)}\,\frac{du}{u} \qquad \text{(T2-1)}$$

$$\Phi_{kj} = \frac{8D_{kj}c_{k0}}{\pi}\int_0^\infty e^{-D_{kj}u^2\theta}\,\frac{1}{[J_0^2(R_{kj}u) + Y_0^2(R_{kj}u)]}\,\frac{du}{u} \qquad \text{(T2-2)}$$

For short times (T2-2) leads to

$$\Phi_{kj} \simeq 2D_{kj}\pi c_{k0}\left[(\pi T)^{-1/2} + \frac{1}{2} - \frac{1}{4}(T/\pi)^{1/2} + \frac{1}{8}T \ldots\right] \qquad \text{(T2-3)}$$

For large times (T2-2) leads to

$$\Phi_{kj} \simeq 4\pi D_{kj}c_{k0}\left[\frac{1}{\ln(4T) - 2\gamma} - \frac{\gamma}{[\ln(4T) - 2\gamma]^2}\ldots\right] \qquad \text{(T2-4)}$$

Sintering control:

$$\Phi_{kj} = 2\pi R_{kj}\alpha_{kj}c_{k0}$$

where $T = \dfrac{D_{kj}\,\theta}{(R_{kj})^2}$, $\gamma = 0.5772$ (T2-5)

where α_{kj} is the reaction rate constant for the merging process and R_{jk} is the radius of interaction of the two colliding particles. This radius will be assumed to be

$$R_{kj} = r_k + r_j \qquad (7)$$

where r_j and r_k are the radii of particles containing j and k units, respectively.

For very high reaction rates ($\alpha_{kj} \to \infty$) the process is diffusion controlled and the concentration c_k for $R_{jk} = r_j + r_k$ is zero.

For reaction rates constants sufficiently low compared to the diffusion coefficient, the rate of the process is sintering controlled.

The solution of Equation (4) for the boundary conditions (6) is given in Table 1, Equation (T1-1).

The rate of collision Φ_{kj} is equal to the diffusion flux times the perimeter $2\pi R_{kj}$. Therefore,

$$\Phi_{kj} = \left|\, 2\pi\, R_{kj}\, D_{kj}\left(\frac{\partial c_k}{\partial r}\right)_{R_{kj}}\right| \qquad (8)$$

Equations (T1-2), (T1-3), and (T1-4) of Table 1 give various expressions for the rate of collisions. The first of them has a general character, while the other two represent asymptotic behaviors for short and long times.

In Table 2 the equations valid for the diffusion controlled case are first given (Equations (T2-1 ÷ T2-4)). Equation (T2-5) gives the rate of collision for the sintering controlled case. The diffusion controlled case occurs when $D_{kj}/\alpha_{kj}R_{kj}$ is sufficiently small while the sintering controlled case occurs when $2\alpha_{kj}\sqrt{\theta/\pi\, D_{kj}} << 1$ (see Equation (T1-3) of Table 1).

Consequently, the rate constants K_{ij} are given by the equations

$$K_{ij} = 4\alpha_{ij}\, h\, R_{ij}\int_0^\infty e^{-D_{ij}u^2\theta} \times \frac{[J_0(uR_{ij})Y_1(uR_{ij}) - Y_0(uR_{ij})J_1(uR_{ij})]}{\left[\begin{array}{l}[uJ_1(uR_{ij}) + hJ_0(uR_{ij})]^2 \\ \qquad + [uY_1(uR_{ij}) + hY_0(uR_{ij})]^2\end{array}\right]}\,du \qquad (9)$$

For the diffusion controlled process one obtains

$$K_{ij} = \frac{8D_{ij}}{\pi}\int_0^\infty e^{-D_{ij}u^2\theta}\,\frac{1}{J_0^2(uR_{ij}) + Y_0^2(uR_{ij})} \times \frac{du}{u} \qquad \text{(9a)}$$

For small values of $T = D_{ij}\theta/R_{ij}^2$, Equation (9a) leads to

$$K_{ij} = 2D_{ij}\pi\left[(\pi T)^{-1/2} + \frac{1}{2} - \frac{1}{4}(T/\pi)^{1/2} + \frac{1}{8}T \ldots\right] \qquad \text{(9'a)}$$

and for large values of T, it leads to

$$K_{ij} = 4D_{ij}\pi\left[\frac{1}{\ln(4T) - 2\gamma} - \frac{\gamma}{[\ln(4T) - 2\gamma]^2}\ldots\right] \qquad \text{(9''a)}$$

where $\gamma = 0.5772\ldots$ is Euler's constant. If $\ln 4T >> 2\gamma \simeq 1$, then Equation (9″a) may be further simplified to give

$$K_{ij} = \frac{4\pi\, D_{ij}}{\ln 4T} \qquad \text{(9'''a)}$$

For the sintering controlled case one obtains

$$K_{ij} = 2\pi R_{ij}\alpha_{ij} \qquad \text{(9b)}$$

It is of interest to observe that in the sintering controlled case the rate constants are independent of the small scale time and that in the diffusion controlled case, although they depend on the small scale time, this dependence is after a very short time very weak (Figure 1). Consequently, a quasisteady state is achieved for diffusion in a time which is much smaller than the infinitesimal variation of the time t of the process.

There are some important questions which can be raised, particularly with respect to Equation (4), and these do not concern only the present problem but also that of coagulation. For instance, when is it appropriate to ignore in the diffusion Equation (4) the collision between various particles? It appears that they can be neglected if the small time interval needed to achieve the quasisteady state is within the infinitesimal variation of the

Table 3. Rate Constants K_{ij} for the Two Limiting Models

Diffusion controlled case				
Case 1	$D_{ij} = c_1\left(\frac{1}{r_i^2} + \frac{1}{r_j^2}\right)$	(T3-1)	$K_{ij} = c_1'\left(\frac{1}{r_i^2} + \frac{1}{r_j^2}\right)$	(T3-1′)
Case 2	$D_{ij} = c_2\left(\frac{1}{r_i} + \frac{1}{r_j}\right)$	(T3-2)	$K_{ij} = c_2'\left(\frac{1}{r_i} + \frac{1}{r_j}\right)$	(T3-2′)
Case 3	$D_{ij} = c_3$	(T3-3)	$K_{ij} = c_3'$	(T3-3′)
Sintering controlled case				
Case 4	$\alpha_{ij} = c_4$	(T3-4)	$K_{ij} = c_4'(r_i + r_j)$	(T3-4′)
Case 5	$\alpha_{ij} = c_5\left(\frac{r_i^2 + r_j^2}{r_i + r_j}\right)$	(T3-5)	$K_{ij} = c_5'(r_i^2 + r_j^2)$	(T3-5′)

time t of the process.

The kinetic equations describing the sintering process are now formulated. They are used in what follows to obtain the time evolution of the exposed surface area of metal.

NUMERICAL SOLUTION OF KINETIC EQUATIONS

The kinetic Equations (3) will be solved for the limiting cases in which the rate of the process is either diffusion controlled or sintering controlled. Equations (9‴a) will be used for the rate constants in the case of diffusion control. This limiting equation is selected because an order of magnitude evaluation of the dimensionless time T shows that T is very large after a very short time θ. Considering D_{ij} a kind of surface diffusion coefficient, it must be of the order of 10^{-4} to 10^{-10} sq.cm./sec. (Satterfield, 1970). The collision radius is of the order of the particle sizes present in the system, hence of the order of 10^{-6} to 10^{-7} cm. Consequently, T is of the order of $(10^2 \text{ to } 10^{10}) \times \theta$ and is large even for small values of θ. Since for such a large value of T the strong inequality $\ln 4T >> 1$ is satisfied, Equation (9‴a) becomes a good approximation for Equation (9a). Equation (9b) will be used for the rate constants in the case of sintering control.

The rate of change of c_k is given by equation

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} M_{ij}4\pi D_{ij}c_ic_j - c_k\sum_{i=1}^{\infty} M_{ki}4\pi D_{ik}c_i \tag{11}$$

where

$$M_{ij} = \frac{1}{\ln\left(\frac{4D_{ij}\theta}{R_{ij}^2}\right)} \tag{11a}$$

for the diffusion controlled case, and by equation

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} 2\pi R_{ij}\alpha_{ij}c_ic_j - c_k\sum_{i=1}^{\infty} 2\pi R_{ik}\alpha_{ik}c_i \tag{12}$$

for the case of sintering control.

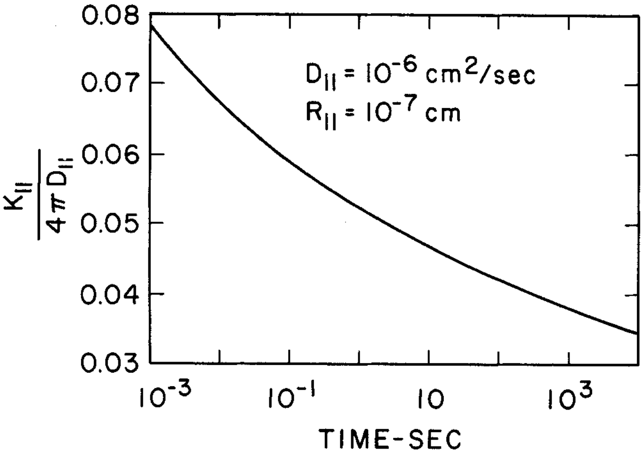

Fig. 1. Dimensionless rate constant in the diffusion controlled case vs. time.

In Equation (11a) the time dependence of M_{ij} is weak. For a variation of θ from 10^{-3} to 10^4 sec, hence within 7 orders of magnitude, M_{ij} varies only by a factor of two (see also Figure 1) and therefore can be considered independent of time. In this manner the difficulty occurring because of the two time scales is avoided. The size dependence of M_{ij}, furthermore, is also weak and can be neglected. To compute the "constant" M_{ij} one may take $\theta^* = 1$ sec, $D_{ij} = D_{11}$ and $R_{ij} = R_{11}$.

The diffusion coefficient and the reaction rate constants may depend also upon the size of the particles. It is expected that the diffusion coefficient will become smaller as the size of the particles increases. In Table 3 various size dependencies of the diffusion coefficient together with the corresponding rate constants are given. All the situations listed in Table 3 are contained in the expression

$$K_{ij} = C[r_i^{3m} + r_j^{3m}] \tag{13}$$

where C is independent of the particle size.

The exposed surface area S of the catalyst is given by

$$S = \sum_{k=1}^{\infty} S_kc_k \tag{14}$$

where S_k is the exposed surface area of the particles containing k units. It is now assumed that the general shape of the particles is preserved during the growth process. Consequently, the ratio of volume to exposed surface area is proportional at each instant of the sintering process to the first power of some characteristic length of the particle, and S_k is given by

$$S_k = S_1k^{2/3} \tag{15}$$

where S_1 is the exposed surface area of a particle containing one unit. The time evolution of the rate of change of exposed surface area is thus given by

$$\frac{dS}{dt} = S_1\sum_{k=1}^{\infty} k^{2/3}\frac{dc_k}{dt} \tag{16}$$

For an initially unisized distribution which closely resembles the physical situation of the platinum crystallites present in the catalyst, the equations for the discrete spectrum of particle sizes [Equations (11) and (12)] have been solved numerically using a fourth-order Runge-Kutta method.

The numerical results obtained for the exposed surface area on the basis of the various rate constants are plotted in Figure 2. The rate of decrease of the exposed surface area can be represented very well in all cases by equations of the form

$$\frac{dS}{dt} = -c_i''S^p \qquad (17)$$

where p is an integer (Figures 3 and 4). In Table 4 these results are summarized. One may observe that the rate of decay of the exposed metal surface area depends strongly upon the mechanism of the process. In the sintering controlled cases exponents of 3 or 2 are obtained, while in the diffusion controlled cases, the exponent is 4 or larger.

In the sintering controlled case an exponent of 2 is obtained if the rate constants K_{ij} are of the form

$$K_{ij} = c_5' \, (r_i^2 + r_j^2) \qquad (18)$$

For the time being we shall bring an experimental argument to support Equation (18): Matsuura and Schuit (1972) have studied the sintering of particles of Bi_2MoO_6 catalyst in contact. In this case the decay of surface area depends only upon the sintering process taking place between the crystals in contact. They have observed that the decay of the exposed surface area is second order in S.

COMPARISON WITH EXPERIMENT

Maat and Moscou (1965) measured the rate of sintering during heat treatment of a platinum reforming catalyst at a temperature of 780°C. They found that the exposed platinum area followed a second-order reaction, which, according to the present considerations shows a sintering controlled decay. Herrmann et al. (1961) reported results regarding the sintering of platinum reforming catalysts in the temperature range of 564° to 625°C. Hydrogen chemisorption was used to measure the exposed surface area of metal. They found, in particular at 625°C, that the rate of decrease of the chemisorptive capacity is second order, indicating also a sintering controlled decay.

Gruber (1962) reported data on the sintering behavior during heat treatment of Pt-on-Alumina catalyst prepared from tetraamino-platinum hydroxide solutions. The sintering experiment was carried out at 500°C in a reducing atmosphere. Their data can be represented by a sixth-order reaction, which, according to the present considerations, indicates a diffusion controlled decay. Similar results have been obtained by Hughes et al. (1962) for Pt-on-alumina reforming catalyst also in a reducing atmosphere. Their data, obtained at 483° and 538°C led to an exponent of 7.7 to 8 indicating a diffusion controlled mechanism, with a strongly size dependent diffusion coefficient.

While the rate of decay of S in the sintering controlled cases is very rapid, being, for instance, a 15-fold one after 17 hours at 780°C (Maat and Moscou, 1965), the rate of decay of S in the diffusion controlled cases is slow, for instance a 2.5-fold one after 1200 hours at 500°C (Gruber, 1962).

From the above results one is tempted to attribute the increased mobility of the crystallites primarily to the temperature. The rate of sintering depends, however, also on the method of preparation of the metal-supported catalyst and upon the chemical atmosphere in which the decay takes place because they affect the strength of the interaction between the crystallites and support and, consequently, the diffusion coefficients of the crystallites upon the support and the rate constant of the merging process.

These problems will be discussed extensively in a future paper. Let us observe here in passing that the chemical atmosphere affects the process strongly because via chemisorption the surface diffusion and the surface free energies

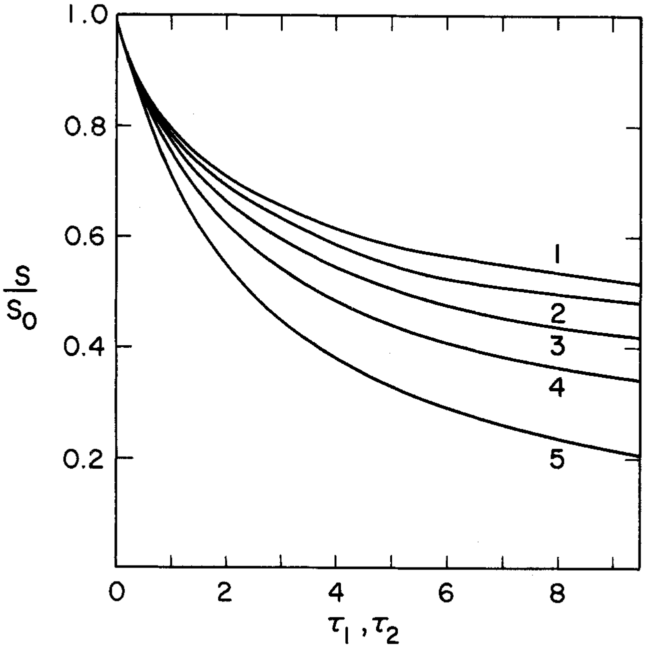

Fig. 2. Exposed surface area of metal vs. dimensionless time for various models on the basis of numerical calculations. Numbers on curves refer to different cases in Table 3.

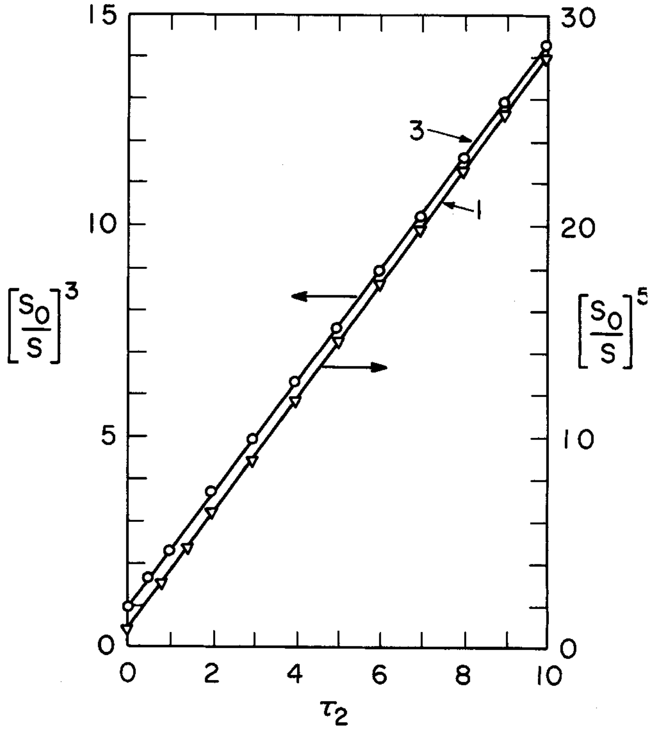

Fig. 3. Plot of $\left(\frac{S_0}{S}\right)^{p-1}$ vs. dimensionless time for the diffusion controlled process. Numbers on curves refer to different cases in Table 3.

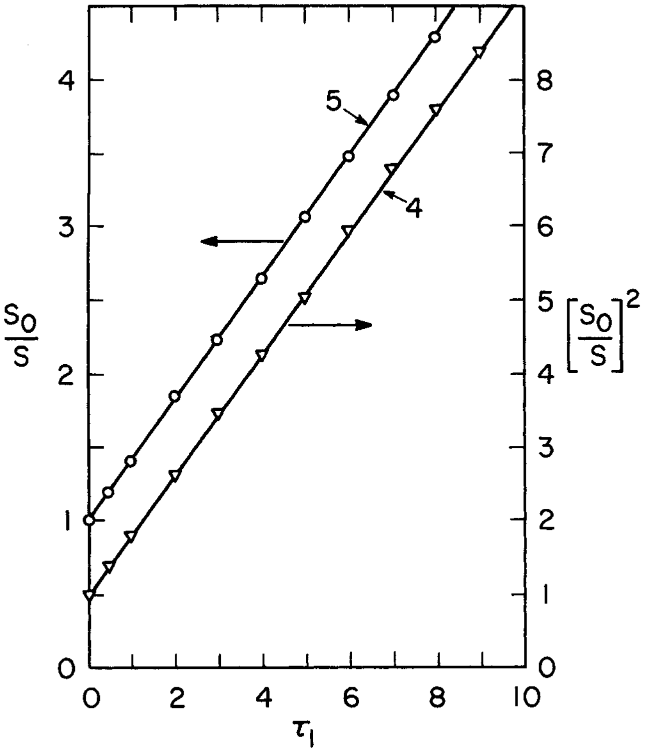

Fig. 4. Plot of $\left(\frac{S_0}{S}\right)^{p-1}$ vs. dimensionless time for the sintering controlled process. Numbers on curves refer to different cases in Table 3.

are modified. The wetting angle of the metal crystallite on the support depends upon the surface free energies. If due to chemisorption the wetting angle is decreased, the surface area of contact between crystallite and support is increased and the mobility of the crystallites (their diffusion coefficient) upon the support decreased. Also the merging of two colliding particles into one depends upon the surface diffusion of the metal and the surface free energies and consequently upon the chemical atmosphere.

We would like to add here that there are possibilities to decrease the mobility and consequently to increase the stability to sintering of the metal supported catalysts by introducing in the metal an impurity able to modify in a convenient manner the surface free energies so that the angle of wetting and mobility be decreased. The increased stability observed with some alloys may probably be explained in this manner.

SIMILARITY SOLUTION OF KINETIC EQUATIONS

The expressions obtained by numerical analysis of the kinetic equations for the decay of the exposed surface area can also be established in closed form by means of a similarity solution.

First a continuous distribution function $n(v, t)$ is introduced such that $n(v, t)dv$ is the number of particles per unit surface area having a volume in the range v to $v + dv$. For the class of rate constants given by Equation (13), a continuous formulation of the discrete representation from Equation (3) may be written in the form

$$\frac{\partial n(v,t)}{\partial t} = \frac{K^*}{2}\int_0^v n(\tilde{v},t)n(v-\tilde{v},t)[\tilde{v}^m + (v-\tilde{v})^m]d\tilde{v} - K^* n(v,t)\int_0^\infty n(\tilde{v},t)(v^m+\tilde{v}^m)d\tilde{v} \quad (19)$$

In Equation (19) the distribution function n depends on two variables v and t. The aim of a similarity solution is to find a change of variables able to reduce the integro-differential equation with partial derivative, Equation (19), to an integro-differential equation. It is important to observe (this point will be shown later) that it is not necessary to solve the resulting integro-differential equation in order to obtain an expression for the decay of the exposed surface area.

In the similarity transformation the total number of particles per unit surface area of support N will have an important part, so first an equation for the rate of change of the total number of particles per unit area of support is written. This equation is obtained by integrating Equation

TABLE 4. TIME EVOLUTION OF THE SURFACE AREA AS GIVEN BY THE TWO LIMITING MODELS

Diffusion controlled case Assumed size dependence of D_{ij}	Rate equation for exposed area	Time dependence of exposed area
$D_{ij} = c_1\left(\frac{1}{r_i^2}+\frac{1}{r_j^2}\right)$	$\frac{dS}{dt} = -c_1''S^6$ (T4-1)	$\frac{1}{S^5} = \frac{1}{S_0^5} + 5c_1''t$ (T4-1′)
$D_{ij} = c_2\left(\frac{1}{r_i}+\frac{1}{r_j}\right)$	$\frac{dS}{dt} = -c_2''S^5$ (T4-2)	$\frac{1}{S^4} = \frac{1}{S_0^4} + 4c_2''t$ (T4-2′)
$D_{ij} = c_3$	$\frac{dS}{dt} = -c_3''S^4$ (T4-3)	$\frac{1}{S^3} = \frac{1}{S_0^3} + 3c_3''t$ (T4-3′)
Sintering controlled case Assumed size dependence of α_{ij}	Rate equation for exposed area	Time dependence of exposed area
$\alpha_{ij} = c_4$	$\frac{dS}{dt} = -c_4''S^3$ (T4-4)	$\frac{1}{S^2} = \frac{1}{S_0^2} + 2c_4''t$ (T4-4′)
$\alpha_{ij} = c_5\frac{r_i^2+r_j^2}{r_i+r_j}$	$\frac{dS}{dt} = -c_5''S^2$ (T4-5)	$\frac{1}{S} = \frac{1}{S_0} + c_5''t$ (T4-5′)

(19) over all particle sizes:

$$\frac{dN}{dt} = -\frac{K^*}{2}\int_0^\infty \int_0^\infty n(v,t)n(\tilde{v},t)[\tilde{v}^m + v^m]dv d\tilde{v} \tag{20}$$

New variables η and $\Psi(\eta)$ are now introduced

$$\eta = \frac{v}{v^*(t)} \tag{21a}$$

$$n(v,t) = h(t)\psi(\eta) \tag{21b}$$

where $h(t)$ and $v^*(t)$ are functions of time, the form of which can be determined from the expressions which give the total number of particles and the total volume of the particles per unit surface area. The total number of particles per unit surface area is given by

$$N = \int_0^\infty n(v,t)dv \tag{22}$$

and the total volume of the particles per unit surface area by

$$\phi = \int_0^\infty vn(v,t)dv \tag{23}$$

If Equations (21a) and (21b) are introduced into Equations (22) and (23), one obtains

$$h(t) = \frac{B}{A^2}\frac{N^2}{\phi} \tag{24}$$

$$v^*(t) = \frac{A}{B}\frac{\phi}{N} \tag{25}$$

where

$$A \equiv \int_0^\infty \psi(\eta)d\eta \tag{26a}$$

and

$$B \equiv \int_0^\infty \eta\psi(\eta)d\eta \tag{26b}$$

are universal constants.

The similarity variables given by (21a) and (21b), can be written as

$$\eta = \frac{BvN}{A\phi} \tag{21'a}$$

$$n^* = \frac{\phi n(v,t)}{N^2} = \psi(\eta)\frac{B}{A^2} \tag{21'b}$$

Such a similarity transformation was first used in a different problem by Friedlander (1961) and Swift and Friedlander (1964). Inserting (21'a) and (21'b) into Equation (20), *one obtains*

$$\frac{dN}{dt} = -b_1 N^{2-m} \tag{27}$$

where

$$b_1 = \frac{K^*}{2}\phi^m\frac{A^{m-2}}{B^m}\int_0^\infty\int_0^\infty \psi(\eta)\psi(\tilde{\eta})$$

$$(\eta^m + \tilde{\eta}^m)d\eta d\tilde{\eta} \tag{28}$$

Equations (21'a), (21'b), (27), and (19) lead to the following integro-differential equation:

$$\left[2\psi(\eta) + \eta\frac{d\psi(\eta)}{d\eta}\right]\int_0^\infty\int_0^\infty \psi(\eta)\psi(\tilde{\eta})$$

$$(\eta^m + \tilde{\eta}^m)d\eta d\tilde{\eta} + \left(\int_0^\infty \psi(\eta)d\eta\right)$$

$$\int_0^\eta \psi(\tilde{\eta})\psi(\eta - \tilde{\eta})[\tilde{\eta}^m + (\eta - \tilde{\eta})^m]\,d\tilde{\eta}$$

$$-2\psi(\eta)\left(\int_0^\infty \psi(\eta)d\eta\right)\int_0^\infty \psi(\tilde{\eta})(\eta^m + \tilde{\eta}^m)d\tilde{\eta} = 0 \tag{29}$$

Equation (29) is an ordinary integro-differential equation for ψ with η as the independent variable. One may thus conclude that the *similarity transformation* leads to a particular solution of Equation (19). Of course, this particular solution is not compatible with any initial distribution. However, our numerical calculations have shown that after a short time the decay of the exposed surface area S is insensitive to the initial size distribution. For this reason one may suspect that the above similarity solution might lead to reasonable results for the decay of S. In order to prove this assertion, it is necessary to compare the solution of the integral equation with the numerical results. It is our intention to do this in the near future. For the time being, let us observe that if we accept the similarity solution then we do not need the form of the function ψ to obtain the law of decay of the exposed surface area.

The total exposed surface area of the metal per unit surface area of support is given by

$$S = b_2\int_0^\infty v^{2/3}n(v,t)dv \tag{30}$$

where b_2 is a geometric factor dependent on the shape of the particles. From Equations (21'a), (21'b), and (30) one obtains

$$S = b_3 N^{1/3} \tag{31}$$

Consequently

$$\frac{dS}{dt} = \frac{1}{3}b_3 N^{-2/3}\frac{dN}{dt} \tag{32}$$

or, taking into account Equations (27) and (31), it follows that

$$\frac{dS}{dt} = -b_4 S^{4-3m} \tag{32a}$$

Equation (32a) is equivalent to those established on the basis of numerical computation (Table 4).

CONCLUSION

The main conclusion of the paper is that the rate of decay of the exposed surface area of metal during heat treatment is given by an equation of the form

$$\frac{dS}{dt} = -KS^n$$

The value of the exponent n depends on the mobility of the crystallites upon the support and upon the rate of merging of two colliding particles into a single particle. For sufficiently low mobilities the process is diffusion controlled and n is 4 or larger, depending on the size dependence of the diffusion coefficients D_{ij}; for sufficiently large mobilities the rate of decay of the exposed surface area of metal is controlled by the rate of merging of two colliding particles into a single particle and n is 2 or 3, depending on the size dependence of the rate constant for the merging process.

NOTATION

A, B = universal constants defined by Equations (26a) and (26b)

b_1, b_2, b_3, b_4 = constants in Equations (27), (28), (30) to (32), and (32a)

b_{ij} = rate of collision between particles composed of i and j atoms

C = constant independent of particle size used in Equation (13)

c_1, c_2, c_3, c_4, c_5 = constants independent of particle size used in Equations (T3-1) to (T3-5)

$c_1', c_2', c_3', c_4', c_5'$ = constants independent of particle size used in Equations (T3-1′) to (T3-5′)

$c_1'', c_2'', c_3'', c_4'', c_5''$ = rate constants used in Equations (T4-1) to (T4-5) and in Equations (T4-1′) to (T4-5′)

c_k = number of crystallites per unit surface area of support, composed of k platinum atoms

c_{k0} = number of crystallites per unit surface area of support, composed of k platinum atoms at $\theta = 0$

D_k, D_j = surface diffusion coefficients of particles containing k and j atoms, respectively

D_{kj} = apparent surface diffusion coefficient of the particle k with respect to that of the particle j

$h(t)$ = function of time defined by Equation (21b)

$h = \alpha_{ij}/D_{ij}$ = ratio of reaction rate constant α_{ij} and the diffusion coefficient D_{ij}

$i = \sqrt{-1}$ = imaginary unit

J_0, J_1 = Bessel functions of the first kind and zero and first order, respectively

K = rate constant in Equation (1)

K^* = constant independent of particle volume used in Equation (19)

K_{ij} = rate constants defined by Equation (2)

N_0, N = total number of particles per unit surface area of support for $t = 0$ and $t = t$

N_v = number of particles per unit surface area of support having a volume v

n^* = dimensionless density distribution function

$n(v, t)$ = continuous density distribution function

M_{ij} = constant defined by Equation (11)

m = exponent used in Equations (13), (19), (20), (27), and (32a)

p = exponent in Equation (17)

R_{kj} = radius of interaction between the two colliding particles j and k

r = coordinate in cylindrical system

r_j, r_k = radius of particles containing j and k atoms, respectively

S = total exposed surface area of the metal per unit surface area of support

S_0 = initial total exposed surface area of the metal per unit surface area of support

S_k = exposed surface area of particle containing k units

S_1 = exposed surface area of a particle containing one unit

$T = D_{ij}\theta/R_{ij}^2$ = dimensionless time in diffusion model

t = process time

u = dummy variable

$v, \tilde{v}$ = volume of a particle

v_1 = volume of a particle containing one unit

$v^*(t)$ = function of time defined by Equation (21a)

Y_0, Y_1 = Bessel functions of the second kind and zero and first order, respectively

z = complex variable

Greek Letters

α_{kj} = reaction rate constant for the merging process of the particles containing k and j units

β = constant in Equation (T1-4)

γ = Euler's constant = 0.5772

$\tilde{\eta}, \eta$ = dimensionless similarity variable

θ = small scale time

θ^* = 1 sec

θ_0 = time interval

$\tau_1 = t\alpha_{11}2\pi R_1 N_0$ = dimensionless time in sintering controlled case

$$\tau_2 = \frac{t4\pi D_1 N_0}{\ln\left[\dfrac{4D_{11}\,\theta^*}{(R_{11})^2}\right]}$$ = dimensionless time in diffusion controlled case

Φ_{kj} = rate of collisions of the k-particles with a j-particle, as defined by Equation (8)

ϕ = total volume of the particles per unit surface area of support

ψ = dimensionless distribution function

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