Effect of the Size Dependence of Particle Diffusion and Surface Tension on the Sintering of Supported Metal Catalysts

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When sintering occurs in supported metal catalysts, there is an increase in the average size of the metal crystallites, thus decreasing the total metal surface area and hence the number of active sites. This leads to a loss of catalytic activity. The phenomena of sintering of metal crystallites on a substrate are mainly migration of crystallites, and single-atom diffusion or Ostwald ripening. Both these mechanisms are known to take place simultaneously. Ruckenstein and Pulvermacher (1973) proposed the particle migration and coalescence model, while Flynn and Wanke (1974) developed a model based on interparticle transport of single atoms to and from a single particle. These and other related processes have been reviewed by Flynn and Wanke (1975), and Ruckenstein and Dadyburjor (1983).

A mathematical analysis of Ostwald ripening between a collection of hemispherical particles on a substrate, as in the case of supported metal catalysts, has been developed by Dadyburjor et al. (1986). They modeled a collection of particles on a flat substrate by considering the ensemble of particles as an ensemble of point sources/sinks of solute atoms (adatoms). The magnitude of the source/sink strength of a particle would then indicate its rate of growth or shrinkage. This analysis is briefly described below, since it is essential to the present treatment.

The quasi-static diffusion field problem of interest is treated as a potential field problem, where the potential C is the concentration of adatoms. The governing equation for a collection of N point sources/sinks is the Poisson equation, and the solution in two dimensions and time is:

$$C(\vec{r}, t) = C_o\left[B_o(t) + \sum_{j=1}^{N} B_j(t)\log|\vec{r} - \vec{r}_j|\right] + C_o \tag{1}$$

where C_o is the equilibrium concentration of adatoms on a flat surface, B_o is the reference potential, B_j is the source strength of the jth particle, $\vec{r}$ is the vector locating the field point, and $\vec{r}_j$ is the vector locating the center of the jth particle on the plane. Each B_j (which is dependent on the size and location of all particles) contributes to the potential or adatom concentration, C.

To solve for B_o and the parameters B_j for N point sources/sinks, $(N + 1)$ conditions are needed. These include a conservation of mass criterion and N boundary conditions, each derived from the Gibbs-Thomson equation relating the concentration of the adatoms at the particle interface, $\vec{r}_p$, to the radius of each particle, R_j:

$$C(\vec{r}_p, t) = C_o \exp\left[\frac{l_c}{R_j(t)}\right] \tag{2a}$$

where l_c is a characteristic length given by

$$l_c = 2V_m\sigma/kT \tag{2b}$$

To solve for the source strengths (B_o, B_j) a decomposition summation procedure is used, similar to that introduced by Ewald (1921). Such a treatment sidesteps the problem of dealing with the divergent logarithmic term in Eq. 1 for widely separated particles. The procedure introduces additional terms added and subtracted to the potential term on the righthand side of the Poisson equation before the integration is performed. Further, it is assumed that the large but finite number N of irregularly-located and -sized particles (source/sink terms) in the system can be replaced by a basis set of N' irregularly-located and -sized particles, where $N' \ll N$, and the images of the basis set repeated a doubly infinite number of times in both dimensions. Note that the number of particles in the system has not been decreased from N to N'; in fact, there is now a fourfold infinite number of particles, due to the repetition of the basis set in all

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four directions. (Of course, particles sufficiently far apart do not influence each other, so increasing the number of particles simplifies the mathematics without changing the physical picture appreciably.) The number of particles in the basis set, N', represents the minimum number required to represent the essentially irregular character of the system. For details, see Dadyburjor et al. (1986).

Using this procedure, the source/sink strengths B_j for each particle in the basis set can be calculated. Equating the volumetric growth rate of a particle to the rate of diffusion of adatoms to the particle yields the relation

$$\frac{dR_j(t)}{dt} = \frac{B_j(t) l_c D_o}{[R_j(t)]^2} \tag{3}$$

where D_o is the diffusion coefficient of a single adatom. From Eq. 3, the new radius of each particle can be calculated.

In the work described above, the effect of particle migration and coalescence was neglected for the sake of simplicity. In the present work, the combined effect of Ostwald ripening and particle migration and coalescence is considered, to study the sintering mechanism in supported metal catalysts. Previous comparisons of the two sintering mechanisms, e.g., by Ruckenstein and Dadyburjor (1977), did not appropriately take into account the ensemble effect of a collection of metal crystallite particles on the substrate.

Analysis

The mathematical analysis described above is used in this work, with added modifications. These modifications allow the particles to diffuse, in random directions, on the substrate surface.

The distance Δd_j moved by each particle on the surface is calculated using the relation

$$\Delta d_j = 2(D_j)^{1/2} (\Delta t)^{1/2} \tag{4}$$

where D_j is the diffusion coefficient of the jth particle and Δt is the time step. Each time step is small enough to maintain a quasi-static diffusion field, but large enough to permit evolution of the sintering system at a reasonable rate.

The direction in which the jth particle moves is obtained from the angle α_j. Values of α_j are obtained using random number generation. The IMSL subroutine GGUBFS is used for basic uniform (0,1) random number generation. In this subroutine, an input seed value sets off the random number generation. The input seed is replaced by a new seed on output, so that a series of independent sequences is obtained in making a series of calls to the subroutine GGUBFS. The value of α_j is obtained by multiplying the numbers generated by a factor of 2π.

From Δd_j and α_j, the new location of each particle is calculated at each time step. As a result, Ostwald ripening takes place with simultaneous migration of each particle.

It is expected that the diffusion coefficient of a multiatom particle is size-dependent. Although the exact form of the dependence is not clear, the diffusion coefficients can be generally expected to be monotone, decreasing with increasing size. Ruckenstein and Dadyburjor (1977) earlier assumed the diffusion coefficient to be inversely proportional to the area of the crystallite-substrate interface. For hemispherical particles, this implies that D_j is proportional to R_j^{-2}. In the present work, we assume that D_j is proportional to R_j^{-n}, with the index n allowed to vary. Then

$$D_j = \left[\frac{R_o}{R_j(t)}\right]^n D_o \tag{5}$$

where R_o is the radius of an adatom and D_o is the diffusion coefficient of the adatom. As an extreme case, setting n equal to zero would physically mean that all particles diffuse at the same rate, i.e., the diffusion coefficient of each particle is equal to the diffusion coefficient of a single solute atom. By varying the value of n between 0 and 2, the effects of particle migration and coalescence on average particle sizes can be compared.

In the present work, the nondimensionalizing parameter l_c is assigned two values and the average particle sizes arising from both cases are compared. From the Gibbs-Thomson relation, Eq. 2, it can be seen that the characteristic length l_c is directly proportional to the surface tension σ between the particles and the substrate at a given temperature T. Thus, by using two values of l_c, the effect of surface tension on the average particle sizes during sintering can be obtained.

Procedure

The problem is analyzed using numerical techniques. Using transmission electron micrographs of the surface of experimentally prepared Pt/Al_2O_3 catalyst samples, we obtain the initial particle size distribution, particle locations, cell length a_o, and the number of particles N' in the basis cell, as described by Dadyburjor et al. (1986). With these parameters, we obtain the initial values of the source strengths B_j using the relations derived in Dadyburjor et al. (1986). Then the difference form of Eq. 3 is used to evaluate the new values of the particle radii. Simultaneously, the new coordinates of the particles are calculated from Eq. 4 and the value of the angle α_j through which the jth particle moves. The new values of B_j for all particles are then calculated as before, and the whole process is repeated. The particle sizes are thus calculated as a function of time. Finally the surface-area-averaged radius is found as a function of time.

Results

The initial particle size distribution used in this analysis was obtained from experimental data for Pt/Al_2O_3 catalyst. The basis cell used from the micrographs had the dimension a_o = 1,102.4 nm. The number of particles in the basis cell N' was 74 and the initial surface-area-averaged radius was 5.4 nm. The values of the characteristic length l_c used were 1.2 nm (which is typical for Pt/Al_2O_3 catalyst) and a value an order of magnitude lower, i.e., 0.12 nm. The diffusion coefficient of a single solute atom of Pt was taken as $D_o = 5 \times 10^{-19}$ m²/s, and the radius of each Pt atom was taken as $R_o = 0.2$ nm.

Figure 1 shows the results of several calculations of average particle size as a function of time. On examination of the plots, several jumps can be seen. There is of course a finite number of particles used in the basis set, and the smallest of these eventually tend to dissolve away completely. As a (small) particle dissolves, the average particle radius shows a sudden increase. Since the calculated values of average particle radius are not smoothed in Figure 1, the plots show several jumps.

For both values of l_c, it can be seen that when the index n equals zero, in other words when the diffusion coefficient of particles is size-independent, the average particle sizes predicted

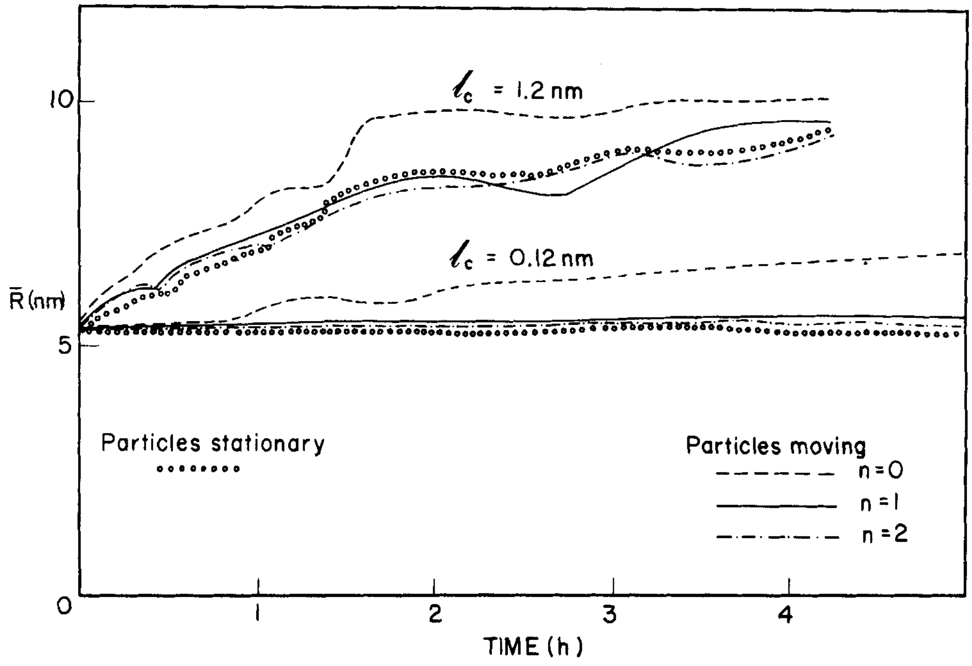

Figure 1. Surface-area-averaged radii $\bar{R}$ as a function of sintering time t for different characteristic lengths l_c and different power indices of surface diffusion coefficient size dependence n.
Parameter l_c is a measure of crystallite-substrate interfacial tension.

are higher. Physically, this seems reasonable as the diffusion coefficient is high, even for the larger particles, and this would contribute to particle migration and coalescence to a large extent. However, when n takes the value of 1 and 2, the average particle sizes predicted by the model at any time are almost the same as for the case previously considered, when the particles were assumed to be stationary. This seems to suggest that only if the diffusion coefficient of the large particles is high, will particle migration and coalescence affect sintering rates appreciably. In other words, the diffusion coefficient of each particle would have to approach the diffusion coefficient of each solute atom for particle migration and coalescence to be the predominant mechanism of sintering of crystallites in the metal form.

Physically, the surface tension would decrease when the crystallite and the substrate are more similar; for example, if the crystallites were the metal oxide and the substrate were also an oxide. The effect of surface tension on average particle sizes can be seen by comparing the curves for the two values of l_c in Figure 1. It can be observed that when l_c = 0.12 nm, the average particles sizes predicted for the same sintering time are much lower than when l_c = 1.2 nm. This means that when the supported species is converted to oxide, migration of particles and adatoms takes place to a lesser extent. In other words, as the surface tension increases, the adatoms have greater mobility and particle migration increases; this leads to coalescence of particles and an increase in the average particle size. The rate of sintering is thus greater for higher surface tension between substrate and particle.

In summary, when particle migration is almost independent of particle size, the average particle sizes are higher than when particle migration is neglected. For lower surface tension between the solute and substrate, migration takes place to a lesser extent and the average particle size is smaller.

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Notation

a_o = length parameter of unit cell containing basis set
B_j = source/sink strength of jth particle
B_o = reference potential or average adatom concentration
C = adatom concentration at a point on two-dimensional surface
C_o = adatom concentration in equilibrium with infinitely large particle (flat interface)
d_j = distance of jth particle
Δd_j = distance moved by jth particle during time interval Δt
D_j = diffusion coefficient of jth particle on two-dimensional surface
D_o = diffusion coefficient of adatoms on two-dimensional surface
k = Boltzman constant
l_c = characteristic length parameter
n = power index of surface diffusion coefficient size dependence
N = number of particles in system
N' = number of particles in basis set
$\vec{r}$ = location of point in system
$\vec{r}_j$ = location of center of jth particle
r_p = location of interface of jth particle
R_j = radius of jth particle
R_o = radius of adatom
t = time
T = absolute temperature
V_m = molar volume of particle

Greek letters

α_j = angle along which particle j moves
Δ = difference operator
π = 3.14
σ = particle-substrate interfacial tension

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