JOURNAL OF CATALYSIS 48, 73–86 (1977)

Mechanisms of Aging of Supported Metal Catalysts

ELI RUCKENSTEIN AND DADY B. DADYBURJOR

Faculty of Engineering and Applied Sciences, State University of New York at Buffalo,
Buffalo, New York 14214

Received August 31, 1976; revised February 28, 1977

The behavior of a population of small metal crystallites on a substrate is accounted for by the splitting of single metal atoms and multiatom particles from larger particles, their diffusion along the substrate and the coalescence of particles (or of a particle and an atom) that collide. The equations are stochastic, allowing for the treatment of a large number of particles. The rate at which one particle is captured by another is determined by the rate of diffusion of particles from the bulk to the interface of the other particles and the kinetics of the capture process at the interface. The rate of emission is proportional to the equilibrium concentration, on the original particle interface, of particles having the size of the particle to be emitted. If emission is an activated process, the probability of multiatom emission is negligibly small compared to single atom emission. Hence, even if particles can lose single atoms to the substrate by activated breaking of bonds the loss of aggregates of two or more atoms must occur via another mechanism. This alternate process is not entirely clear but is probably related to the existence of cracks on the crystallite and their propagation due to internal stresses caused either thermally or by the formation of a chemical compound. The present model can account for an increase or a decrease in the total surface area with time, as well as an initial increase followed by a decrease or an initial decrease followed by an increase. In any particular case the path followed depends upon the metal loading, the saturation concentration of metal atoms, the diffusion rate and the emission rate.

NOMENCLATURE

A_0	Preexponential factor in capture, emission coefficients, Eqs. (12a), (15), (17)
A_j	Radius of the area "governed" by a j-atom particle, Eqs. (18a) and (22)
a	Lattice parameter
C_j, C_j'	Creation rate of j-atom particles from particles of larger, smaller, size, Eqs. (5) and (8)
$C_{j,1}$	Rate of creation of j-atom particles by capture or emission of single atoms, Eq. (3)
$\bar{C}_p$	Concentration of metal atoms on facet of nucleating crystal
$D_{j,i}$	Diffusion coefficient of i-atom particle near a j-atom particle, Eq. (18a)
$E_{a,j,i}$, $E_{b,j,i}$	Activation energies for emission, capture of an i-atom particle from a j-atom particle, Eqs. (12), (15), (17)
E_{mm}	Energy required to remove a metal atom surrounded by other metal atoms, Eq. (12b)
E_{ms}	Energy required to remove metal atom surrounded by atoms of substrate species, Eq. (12b)
G	Growth rate of a crystal
ΔG_c	Free energy of formation of a crystal nucleus
ΔH_c	Migration energy of an atom over a crystal

ISSN 0021-9517

i, j	Number of atoms in a particle
$J_{j,i}$	Diffusion flux of i-atom particles from j-atom particles, Eqs. (18)
K	Rate constant of sintering equation, Eq. (1)
k	Boltzman constant
$k_{a,j,i}$	Coefficient of emission of an i-atom particle from a j-atom particle, Eq. (15)
$k_{b,j,i}$	Coefficient of capture of an i-atom particle by a j-atom particle, Eq. (17)
L_j, L_j'	Loss rate of j-atom particles to form particles of larger, smaller size, Eqs. (6) and (7)
$L_{j,1}$	Rate of loss of j-atom particles by capture or emission of single atoms, Eq. (2)
m	Exponent of the size dependence of the diffusion coefficient on size, Eq. (23)
$n_j(t)$, $n(j, t)$	Concentration of j-atom particle at time t
$n_{1\infty}{}^s$	Equilibrium concentration of single atoms at the interface of an infinitely large crystallite
$n_{i,j}{}^s$	Equilibrium concentration of i-atom particles at the interface of a j-atom particle
$n_{i,j}{}^0$	Concentration of i-atom particles at the interface of a j-atom particle
N_0	Total number of metal atoms present per unit area of substrate, Eq. (10)
P^+	Probability of atoms arriving at the surface of a crystal
$P_q{}^-$	Probability of an atom leaving a crystal surface with q occupied sites
p	Index of sintering equation, Eq. (1)
p_q	Ratio of $P_q{}^-$ to P^+
Q	Maximum number of sites on crystal surface
q	Number of sites occupied on crystal surface
R	Gas constant
r_j	Radius of a j-atom particle
r_{crit}	Critical radius of metal species, Eq. (14c)
S	Total exposed surface area of metal at time t
S_0	Total exposed surface area of metal at $t = 0$
t	Time
T	Temperature
V_m	Molar volume of metal
$\alpha_{j,i}$	Emission rate; number of i-atom particles emitted from a j-atom particle per unit time
$\beta_{j,i}$	Capture rate; number of i-atom particles captured by a j-atom particle per unit time
δ	Constant in Eq. (14), $2\sigma V_m/RT$
δ_{ij}	Kronecker delta; $=1$ if $i = j$, $=0$ otherwise
ν_p	Vibration of an atom on a crystal
π	3.14159
ρ_c	Radius of crystal nucleus
σ	Interfacial free energy between metal and substrate per unit area

INTRODUCTION

Supported metal catalysts consist of metal crystallites 10 to 100 Å in size dispersed upon the internal surface of a porous substrate. The catalyst loses its activity after excessive heating and during the catalytic process. In the absence of chemical "poisoning," this aging phenomenon is generally recognized as being due to sintering or loss of active surface area by coalescence of the metal crystallites to form larger particles. Experimental evidence for sintering has been reviewed in a number of recent papers (*1–3*). Under certain conditions, however, sintered crystallites have been shown to split and redisperse, thus regaining the activity lost by coalescence. The results of the splitting process have been observed directly by using transmission electron microscopy (*4*).

Some indirect experimental evidence exists (*5–9*) that small metal crystallites in a model system migrate over the surface of substrate. The model system contained a high density of metal islands.

Assuming that sintering occurs because of the migration of the islands, an effective diffusion coefficient D of 10^{-15} cm^2/sec was obtained (*2*) for 10 Å gold particles on a silicon substrate. For a commercial catalyst containing a total of N_0 metal atoms per surface area of the substrate, uniformly distributed as j-atom particles, the distance between particles can be written as $(j/N_0\pi)^{\frac{1}{2}}$. Assuming that metal particles in a commercial catalyst diffuse in a manner similar to that of particles in the model system, the time t taken for two particles to diffuse towards one another can be obtained by equating this distance to $2(Dt)^{\frac{1}{2}}$. For a metal loading N_0 equal to 1×10^{13} atoms/cm^2 of substrate and uniform particles containing 16 atoms (corresponding to 0.5% Pt/Al_2O_3 containing particles of 10 Å) the distance is approximately 70 Å. If the diffusion coefficient equals that above for the model system, the time involved is only a few minutes. Hence, diffusion of metal crystallites may play a part in the overall sintering of the supported metal catalysts.

A crystallite has many bonds between metal and substrate atoms that would have to be broken before the crystallite can diffuse along the surface, while a free metal atom requires fewer bonds to be broken. Hence, it might be supposed that crystallite migration would be slow compared to the motion of free atoms. However, the spacings of metal and substrate atoms are such that only a fraction of metal atoms on the crystallite base are in an energy well between atoms of the substrate. On the other hand, free metal atoms can almost always be placed without hindrance between substrate atoms. Hence, although the number of metal–substrate bonds may be much greater in the case of a large crystallite, the intensity of each bond is generally less than that for a single atom. This makes possible some motion of metal crystallites on the substrate. Further, by virtue of their size, crystallites may be able to overcome obstacles such as valleys on the irregular substrates that might trap and immobilize the smaller single atoms.

Of course migration is size dependent and will be very small for particles larger than about 50 Å. Assuming that the diffusion coefficient is proportional to the base area of the crystallite, then for a 0.5% Pt/Al_2O_3 system containing 10^2 Å particles uniformly distributed, the distance between particles is of the order of 10^3 Å. In this case, the time for particles to diffuse towards each other is of the order of 10^2 hr (as opposed to a few minutes calculated above for 10 Å particles). However, for systems containing both large and small metal crystallites, the larger crystallites, despite their own lack of mobility, would nevertheless increase in size when smaller particles collided against them and coalesced. Recent controlled atmosphere electron microscopy (CAEM) experiments cannot observe particles smaller than approximately 25 Å (*10, 11*); the fact that no migration could be observed here is perhaps due to this size limitation.

A phenomenological model was developed (*1*) based upon migration of particles and coalescence of particles that collide. Solution of the kinetic equations led to a family of rate equations for the total exposed surface area S of metal of the form,

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

The index p was found to have values dependent upon the relative magnitudes of the diffusion coefficient and the coalescence constant as well as the particular size dependencies used for these parameters. Analysis of experimental work from other laboratories yielded values of p from 2 to 8 (*12–15*). These values correspond to different, but feasible, size dependencies for the model parameters. For example, $p = 2$ corresponds to coalescence controlled process with the coalescence constant proportional to particle radius. On the other hand, $p = 6$ corresponds to a diffusion controlled process with the diffusion coefficient inversely proportional to the square of the particle radius. If the diffusion coefficient is inversely proportional to higher powers of the radius then larger values of p can be obtained.

Wynblatt and Gjostein (*3*) comment that such a model is valid for particles smaller than about 50 Å but invalid for larger particles because the latter cannot move. We disagree with this. As mentioned above, the size dependence of the diffusion coefficient in the diffusional model accounts for the fact that the larger particles have a negligible migration. However, the larger particles grow because the smaller particles, which migrate much faster, would coalesce with them.

Wynblatt and Gjostein (*16*) obtained values of p equal to about 13 in their sintering experiments on supported Pt. They attempted to explain this by starting with an alternate mechanism, whereby large particles grow while smaller particles decay. This occurs via capture and emission of single atoms which are the only mobile species. However, this Ostwald ripening-like phenomenon could yield only values of p that were even smaller ($p = 3$ to 5) than those of the migration and coalescence model (*1*). In later work (*17*) they have attempted to resolve the differences between experiment and theory by considering an additional, slow, nucleation step in the growth of the larger particles during the ripening process.

Flynn and Wanke (*18*) also considered only single atom emission and transfer, but the formulation of their equations was different. They used a model system containing a relatively small number of particles. They calculated the individual rates of single atom emission and capture of each particle. The initial absence of single atoms in their systems restricted their results to predicting either total redispersion, i.e., a continuous increase in the exposed surface area (for metal loadings less than the saturation concentration of the metal atoms), or an initial increase followed by a decrease in the exposed surface area.

Allowing only single atoms to move on the substrate would seem like too strong a restriction. If monomers can move on the surface, it might be argued that dimers could also be expected to move, albeit at a marginally slower rate, and so on. Flynn and Wanke (*18*) assume that all particles of less than 14 atoms are inherently unstable and reduce instantaneously to single atoms, but this comes about by assuming that all particles are in the form of fcc crystal structures. Certainly small clusters of atoms will not have the same structure as the bulk metal, but this does not mean that they cannot exist in some other form. Further, Geus (*19*) observes that many experimental results indicate that dimers are stable on a substrate.

In this work we suggest a model for the behavior of metal crystallites supported on a substrate that entails the emission, migration and coalescence of particles of every size, including single atoms. In this manner we have an alternate mechanism to explain large values of p without having to postulate what in the model of Ref. (*1*) might be unfeasible size dependences of the diffusion coefficient. Instead, these large values of p are explained by allowing the emission of particles as a mechanism that offsets the capture of particles. In contrast to the model of Ref. (*1*), the present model will also predict particles of smaller size than the smallest initial particle. We show later that the present model can predict a continuous decrease in surface area with time and a decrease followed by an increase in surface area, as well as continuous increase in surface area with time and an increase followed by a decrease. The behavior depends upon the relative magnitudes of emission, diffusion, and capture, although the final state depends upon the metal loading and the saturation concentrations of the metal species on the substrate.

METHODS

1. Single Atom Emission and Capture

For simplicity we consider first the equations of emission and capture of single atoms. They will be extended to the more general case of multiatom transfer below.

The total rate at which particles containing j atoms are lost by capture or emission is

$$L_{j,1} = (\beta_{j,1} + \alpha_{j,1})n_j. \tag{2}$$

Here the first term represents the number of j-mers per unit time that capture an atom to become $(j + 1)$-mers, and the second term represents the number of j-mers per unit time that become $(j - 1)$-mers by the loss of an atom. The creation rate of j-mers is given by

$$C_{j,1} = \beta_{j-1,1}n_{j-1} + \alpha_{j+1,1}n_{j+1}. \tag{3}$$

Now since the net rate of change of j-mers can be written as

$$\frac{dn_j}{dt} = C_{j,1} - L_{j,1},$$

we get for the continuity equation for the j-atom particles

$$\frac{dn_j}{dt} = (\alpha_{j+1,1}n_{j+1} - \beta_{j,1}n_j) - (\alpha_{j,1}n_j - \beta_{j-1,1}n_{j-1}). \tag{4}$$

In the Appendix we derive the differential form of Eq. (4) and note that it is different from the continuity equation of Lifshitz and Slyosov (*20*) frequently used in the treatment of Ostwald ripening [see for example Ref. (*21*)].

It is important to realize that Eq. (4), considering as it does solely the emission and capture of single atoms, is a more rigorous formulation of the mechanism of Wynblatt and Gjostein (*16*) or that of Flynn and Wanke (*18*) that leads in supersaturated situations to Ostwald ripening.

2. The Migration–Coalescence–Emission Model

We now extend each term in Eq. (4) to include multiatom processes. The first term in Eq. (4) represents the rate at which the concentration of j-atom particles is increased by emission of atoms from larger particles. The corresponding term for multiatom transfer is

$$C_j = \sum_{i=1}^{\infty} (1 + \delta_{ij})\alpha_{j+i,i}n_{j+i}, \tag{5}$$

where the Kronecker delta, δ_{ij}, accounts for the formation of two j-atom particles if $i = j$. The second term in Eq. (4) is the rate at which j-atom particles are lost when they capture atoms. Noting that two j-atom particles are lost when $i = j$, we write

$$L_j = \sum_{i=1}^{\infty} (1 + \delta_{ij})\beta_{j,i}n_j, \tag{6}$$

as the loss rate of j-atom particles to larger particles. The emission of i atoms by j-atom particles, described for single atom transfer by the third term in Eq. (4), is equivalent to the emission by the same particle of $(j - i)$ atoms. To avoid duplication we write the corresponding term as

$$L_j' = \tfrac{1}{2} \sum_{i=1}^{j-1} \alpha_{j,i}n_j. \tag{7}$$

The final term in Eq. (4) represents the increase in the concentration when smaller particles capture the required number of atoms. Since the capture of an i-atom particle by a $(j - i)$-atom particle is identical to the capture of a $(j - i)$-atom particle by an i-atom particle we write, following Eq. (7),

$$C_j' = \tfrac{1}{2} \sum_{i=1}^{j-1} \beta_{j-i,i} n_{j-i}. \tag{8}$$

From Eqs. (5) through (8), the rate of change of the concentration of j-atom particles is given by

$$\begin{aligned} \frac{dn_j}{dt} &= \sum_{i=1}^{\infty} (1 + \delta_{ij}) \alpha_{j+i,i} n_{j+i} \\ &+ \tfrac{1}{2} \sum_{i=1}^{j-1} \beta_{j-i,i} n_{j-i} \\ &- \sum_{i=1}^{\infty} (1 + \delta_{ij}) \beta_{j,i} n_j \\ &- \tfrac{1}{2} \sum_{i=1}^{j-1} \alpha_{j,i} n_j. \end{aligned} \tag{9}$$

We have implicitly assumed that this form of the continuity equation for the j-atom particle is valid only for aggregates of atoms and not for single atoms; that is, for $j \geq 2$. The concentration of single atoms emerges from the additional equation,

$$\sum j n_j(t) = N_0, \tag{10}$$

where N_0 is the metal loading, i.e., the total number of metal atoms present per unit area of the substrate. Equation (10) ensures the conservation of metal atoms.

In reality the surface of the substrate is nonhomogeneous from a geographic and energetic point of view. These nonhomogeneities trap some of the mobile particles, for example those caught in a grain boundary of the substrate, or those trapped by acid sites or impurities on the substrate. A treatment has been developed (*1*) to take into account the behavior of these fixed particles by modifying the rate equation to consider the probabilities of formation of fixed and mobile particles. However, we do not consider this in the present paper.

3. Evaluation of Capture and Emission Rates

Metal crystallites on a substrate, like crystals in a solution, may be subjected to a number of complicated processes which lead to increases or decreases in the crystallite size. In the previous section we have simply written the rate of emission of i atoms from a j-atom particle as $\alpha_{j,i}$ and the rate of capture of i atoms by a j-atom particle as $\beta_{j,i}$; however, the evaluation of these terms will depend upon the processes by which capture and loss take place.

A. Single Atom Transfer

Let us first consider some mechanisms by which crystallites may grow. Jackson's model (*22*) involved a crystal containing a maximum of Q sites on its surface. A crystal with, say, q sites occupied gains and loses atoms until Q sites are occupied. This is, of course, identical to having no occupied sites on the next surface, and so the process continues in this manner. If the probability, P^+, of atoms arriving on the surface is independent of the number of sites occupied, the steady state volume rate of growth of the crystal is

$$\begin{aligned} G = QP^+(1 - p_0 p_1 \cdots p_{Q-1}) / \\ \Big\{Q + \sum_{q=0}^{Q-1} (p_q) + \sum_{q=0}^{Q-1} (p_q p_{q+1}) \\ + \cdots + \sum_{q=0}^{Q-1} (p_q p_{q+1} \cdots p_{q-2})\Big\}, \end{aligned}$$

where $p_q \equiv P_q^-/P^+$ is the ratio of the rates at which a surface with q occupied sites loses and gains atoms. Hence, the rate at which the crystal grows by capturing single atoms is proportional to the rate at which atoms approach the surface and hence to the concentration of single atoms near the surface.

For a crystal with facets, growth may be slow until a certain number of sites are occupied (a nucleus is formed), after which there is rapid formation of a monolayer surrounding the original crystal. Growth will then be reduced until a nucleus is formed again on the new crystal. If nucleation is the rate determining step, the volume rate of growth may be written as (*17*, *23*)

$$G = 4\pi r_j^2 \left(\frac{\Delta G_c}{\pi RT}\right)^{\frac{1}{2}} \exp\left[-\frac{\Delta G_c}{RT}\right] \frac{V_m}{\rho_c a} \nu_p \times \exp\left[-\frac{\Delta H_p}{RT}\right] \tilde{C}_p,$$

where ΔG_c and ρ_c are the free energy and radius of a nucleus, a is the lattice parameter of the substrate, ν_p and ΔH_p are the vibration frequency and migration energy of an atom over the crystal and $\tilde{C}_p$ is the concentration of single atoms on the facet.

In either of these cases, the volume growth rate of the crystal, i.e., the rate at which it captures single atoms, depends upon the concentration of single atoms. In a formal sense, therefore, no rigor is lost if the usual condensation equation is used to obtain $\beta_{j,1}$. Here $\beta_{j,1}$ depends upon the perimeter of the j-atom particle and the interfacial concentration of single atoms, i.e.,

$$\beta_{j,1} = k_{b,j,1} 2\pi r_j n_{1,j}^0, \tag{11}$$

where $k_{b,j,1}$ is a rate constant and $n_{1,j}^0$ is the monomer concentration at the interface of the particle. In Eq. (11) the perimeter of the single atom is ignored with respect to that of the larger particle. The rate constant can be written

$$k_{b,j,1} = A_0 \exp[-E_{b,j,1}/kT]. \tag{12a}$$

The activation energy $E_{b,j,1}$ can be expressed in terms of metal–metal and metal–substrate energies, E_{mm} and E_{ms}, as

$$E_{\mathrm{act},j,1} = \tfrac{1}{2}(E_{\mathrm{mm}} + E_{\mathrm{ms}}). \tag{12b}$$

The factor $\frac{1}{2}$ is considered because the number of nearest neighbors is one half of those corresponding to the bulk solid.

When the diffusion of metal atoms on the substrate is very fast, the concentration of single atoms is uniform so that $n_{1,j}^0 = n_1$, the bulk concentration of single atoms.

Analogous to the condensation relation, Eq. (11), we can write the evaporation equation for the loss of single atoms from a j-atom particle to the substrate as

$$\alpha_{j,1} = k_{a,j,1} 2\pi r_j n_{1,j}^s, \tag{13}$$

where $n_{1,j}^s$ is the concentration of single atoms in equilibrium with a j-atom particle. This concentration is given by the well known Gibbs–Thomson relation

$$n_{1,j}^s = n_{1\infty}^s \exp\left[\frac{2\sigma V_m}{RTr_j}\right] \tag{14a}$$

$$\simeq n_{1\infty}^s \left(1 + \frac{\delta}{r_j}\right). \tag{14b}$$

Here r_j is the particle radius and $n_{1\infty}^s$ refers to the equilibrium solubility of the monomer species, i.e., monomer concentration in equilibrium with an infinitely large crystallite.

From Eqs. (11) and (13), with $n_{1,j}^0 = n_1$, when the bulk monomer concentration equals the equilibrium concentration at the interface of some particle, then growth of the particle by addition of single atoms is exactly countered by the decay of the particle by loss of single atoms. Such a particle, which suffers no change in size at this point, is said to have a critical size. The critical radius is given by

$$r_{\mathrm{crit}} \equiv \delta n_{1\infty}^s/(n_1 - n_{1\infty}^s). \tag{14c}$$

The critical radius is significant only when $n_1 > n_{1\infty}^s$, i.e., in supersaturated systems. Under these conditions, particles of radius smaller than r_{crit} will undergo a net loss by monomer transfer while particles larger than r_{crit} will undergo a net gain by monomer transfer. This is of course the mechanism of Ostwald ripening.

B. Multiatom Transfer

The rate of emission of multiatoms from larger particles to the substrate can perhaps be written similar to Eq. (13), viz,

$$\alpha_{j,i} = k_{a,j,i} 2\pi r_j n_{i,j}{}^{s}, \qquad (15a)$$

where $k_{a,j,i}$ is the rate constant of the activated step,

$$k_{a,j,i} = A_0 \exp[-E_{a,j,i}/kT], \qquad (15b)$$

and $E_{a,j,i}$ is the activation energy. Chen (*24*) has computed values of $E_{a,j,i}$ for various values of i and j. The activation energy for emission of dimers, for instance, from j-atom particles was found to be about twice that for single atom emission; since $E_{a,j,i}$ is exponentially related to $\alpha_{j,i}$, the rate of emission of dimers is many orders of magnitude smaller than the corresponding rate for single atoms. Hence, even when emission of single atoms occurs by an activated process, emission of $i \geq 2$ atom particles by a similar process is probably not to be expected. A more plausible mechanism of multiatom emission is one associated with fracture of the particles because of the propagation of some preexisting cracks. The detailed mechanism by which this fracture takes place has not been completely understood but we suspect that in some conditions some compounds are formed in the metal crystallites. This generates stresses in the crystallites which consequently fracture. It is not yet possible to model the dynamics of this process. Since there may be conditions in which no fracture occurs, we consider here the emission of only single atoms.

Analogous to the condensation equation for the capture of single atoms, Eq. (11), the rate of capture of an i-atom particle by a j-atom particle can be written

$$\beta_{j,i} = k_{b,j,i} 2\pi (r_j + r_i) n_{i,j}{}^{0}, \qquad (16)$$

where $k_{b,j,i}$ is the rate constant of the kinetics of combination of two adjacent particles, given by

$$k_{b,j,i} = A_0 \exp[-E_{b,j,i}/kT]. \qquad (17)$$

In Eq. (16) $n_{i,j}{}^0$ is the concentration of i-atom particles at the interface of the j-atom particle. Hence, $n_{ij}{}^0$ depends upon the rate at which particles diffuse towards one another as well as the rate at which touching particles combine.

To obtain an expression for $n_{i,j}{}^0$, consider the steady state diffusion flux of i-atom particles from a j-atom particle, given in Ref. (*1*) as

$$J_{j,i} = \frac{2\pi D_{ji}}{\ln\,[A_j/(r_i + r_j)]}\,(n_{i,j}{}^0 - n_i). \qquad (18a)$$

Here A_j is a measure of the area "governed" by a particle of size j. Under quasi steady state conditions, $J_{j,i}$ is equal to the rate at which $(j + i)$-atom particles lose i atoms, less the rate at which j-atom particles capture i-atom particles. Hence

$$J_{j,i} = \alpha_{j+i,i} - \beta_{j,i}. \qquad (18b)$$

At equilibrium $J_{j,i} = 0$ and, by definition, the interface concentration of i-atom particles is the equilibrium concentration. Equations (15), (16) and (18b) now yield

$$k_{a,j+i,i} r_{j+i} = k_{b,j,i}(r_i + r_j). \qquad (18c)$$

This is of course the principle of microscopic reversibility and must be valid even far from equilibrium.

Using Eqs. (15a) and (16) and equating Eqs. (18a) and (18b), the concentration of i-atom particles at the interface of a j-atom particle is

$$n_{ij}{}^0 = \frac{\{k_{a,j+i,i} r_{j+i}\} n_{i,j+i}{}^s + \{D_{j,i}/\ln\,[A_j/(r_i + r_j)]\} n_i}{k_{b,j,i}(r_i + r_j) + D_{j,i}/\ln\,[A_j/(r_i + r_j)]}, \qquad (19a)$$

or if $j \gg i$

$$= \frac{\left\{\dfrac{\ln[A_j/(r_i+r_j)]}{D_{j,i}}\right\} n_{i,j}{}^s + \left\{\dfrac{1}{k_{b,j,i}(r_i+r_j)}\right\} n_i}{\dfrac{\ln[A_j/(r_i+r_j)]}{D_{j,i}} + \dfrac{1}{k_{b,j,i}(r_i+r_j)}}. \tag{19b}$$

Equation (19) reduces to the two special cases $n_{i,j}{}^0 \simeq n_i$ when the kinetics at the interface controls the process (fast diffusion), and $n_{i,j}{}^0 \simeq n_{i,j}{}^s$ when diffusion controls.

Substituting Eq. (19a) into Eq. (13a) yields

$$\beta_{j,i} \sim 2\pi k_{b,j,i}(r_i + r_j)n_i, \tag{20a}$$

when the kinetics at the interface control the capture process. Now, if the activation energy for emission, $E_{a,j,i}$ in Eq. (15), is such that multiatom emission is not possible and if n_i is not very much larger than $n_{i,j+i}{}^s$ then, from microscopic reversibility [Eq. (18c)] and Eq. (20a), there can be no capture of multiatom particles when the interface kinetics control the capture process. Hence, there exists only single atom emission and capture in these circumstances (Ostwald ripening if the system is supersaturated). When diffusion controls the capture process, i.e., when

$$D_{j,i}/\ln[A_j/(r_i + r_j)] \ll k_{b,j,i}(r_i + r_j), \tag{20b}$$

the capture rate is given by

$$\beta_{j,i} \sim \frac{2\pi D_{j,i}}{\ln[A_j/(r_i + r_j)]} n_i + k_{a,j+i,i} 2\pi r_{j+i} n_{i,j+i}{}^s. \tag{20c}$$

Further, if the system is highly supersaturated, i.e., if $n_i \ggg n_{i,j+i}{}^s$, then in spite of inequality (20b) and microscopic reversibility, Eq. (18c), the capture rate can be given by

$$\beta_{j,i} \sim \frac{2\pi D_{j,i}}{\ln[A_j/(r_i + r_j)]} n_i.$$

The emission rates are negligible due to the small values of $n_{i,j+i}{}^s$. In such circumstances we have only the migration and capture of atoms and particles, i.e., the model of Ref. (*1*).

In many cases we may have the single atom concentration, n_1, of the same order of magnitude, or smaller, than the saturation, although n_i is still much greater than $n_{i,j+i}{}^s$ for $i \geq 2$. In such circumstances we have the occurrence of single and multiatom capture and single atom emission.

4. ILLUSTRATIVE EXAMPLE

The differential-algebraic equations (9) and (10) can be solved numerically for given initial conditions to obtain concentrations $n_j(t)$ of j-atom particles at various times t. Since the surface area of all particles containing j atoms is proportional to $n_j j^{\frac{2}{3}}$, the total surface area at time t can be written as a fraction of the initial surface area

$$\frac{S(t)}{S_0} = \sum_j j^{\frac{2}{3}} n_j(t) / \sum_j j^{\frac{2}{3}} n_j(0), \tag{21}$$

from a knowledge of the size distribution. This fractional surface area is of interest here, rather than the size distribution, since the former affects the catalytic activity more directly and can be more easily measured.

For our example we consider the behavior of a system consisting initially of particles containing 50 atoms each. Such a system may be unrealistic both because of the smallness of the particles and the fact that they are all of the same size. However, we intend here to demonstrate only the inter-

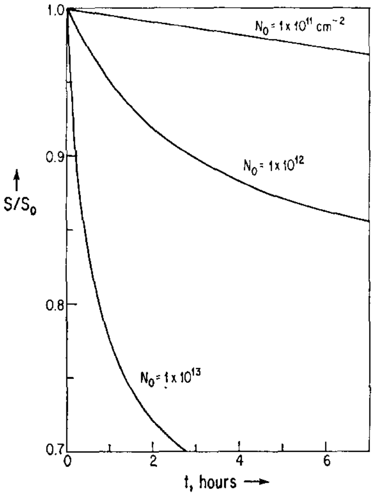

FIG. 1. Sintering curves for various values of N_0 (atom/cm^2) of metal crystallites on a substrate. The initial system contains only 50-atom particles of metal. Capture of all sized particles is allowed but only single atoms are emitted. The capture process is controlled by diffusion, $D_{j,i} = D_j + D_i$, where $D_k \alpha r_k^{-2}$. Particles are hemispherical, $r_j \alpha j^{\frac{1}{3}}$. The parameters used are $D_{16} = 2 \times 10^{-15}$ cm^2/sec, $\delta = 12$ Å, $V_m = 9$ cm^3, $n_{1_\infty}{}^s = 10^3$ cm^{-2}, $T = 10^3$°K, $A_0 = 10^4$ cm/sec, $E_{\mathrm{mm}} = 130$ kcal/mole, $E_{\mathrm{ms}} = 90$ kcal/mole. It is not clear whether the curves will follow the trends shown here at very large times.

relationships between terms in Sec. 3, and these are perhaps better shown on a simple system. The nature of Eqs. (9) and (10) is such that every size (i.e., every value of j) must be accounted for; hence, small enough particles are essential for a reasonable amount of computer time. No significant differences are expected if a larger particle size is used initially. Further, the formulation of Eq. (10) is stochastic, differing from those in Refs. (*16*, *18*). For a system of particles initially of one size, the latter formulations yield changes in particle sizes with time, but at any one time the systems always contain identical particles. In contrast, Eq. (10) allows us to start with a system of identical particles and to obtain a spectrum of sizes after a period of time. Since our formulation does not lead to singular results when starting with a system containing particles of only one size, it is advantageous to use such a system for the sake of simplicity and ease in analyzing the results.

All particles in the model system are assumed to be perfect hemispheres. In this way the radius of a j-atom particle is proportional to $j^{\frac{1}{3}}$.

The effective diffusion coefficient for two particles $D_{j,i}$ is the sum of the coefficients for each particle, $D_i + D_j$. It is reasonable to expect that the diffusion coefficient D_i is inversely proportional to the base area of a particle of i atoms, hence $D_{j,i}$ is set proportional to $r_i^{-2} + r_j^{-2}$.

The parameters A_j may be obtained by assuming that the area πA_j^2 of the substrate associated with each particle of j atoms is proportional to the area of the base of the particle. Then A_j is the equivalent radius of the corresponding subdivision so that

$$A_j^2 = r^2{}_j/\pi \sum_k n_k r_k^2. \tag{22}$$

Figure 1 illustrates the behavior of our sample system as plots of the fractional change in surface area of crystallites, S/S_0, against time, t, at a temperature of 1000°K. If the metal–metal bond energy can be related to the heat of sublimation, then E_{mm} is of the order of 100 kcal/gmole. The values used in Fig. 1 are 130 kcal/gmole for E_{mm} and 90 kcal/gmole for E_{ms}. The value of δ was taken as 12 Å, consistent with values for the Pt/Al$_2$O$_3$ system. The diffusion coefficients $D_{j,i}$ were obtained from the earlier size dependence assuming that $D_i = 2 \times 10^{-15}$ cm^2/sec for i corresponding to a particle of 10 Å diameter. The pre-exponential terms A_0 in Eqs. (15) and (17) were taken to be 1×10^4 cm/sec. The equilibrium concentration of single atoms at the interface of an infinitely large particle, $n_{1_\infty}{}^s$, was taken as 10^3 cm^{-2}. The molar volume, V_m, of Pt metal is 9 cm^3 (*25*), so that $r_1 = 2$ Å. These values yield diffusion as the controlling step in the overall diffusion and capture process. Single and multiatom particles are captured but there is emission of only single atoms.

In Fig. 1 the sintering is relatively small for smaller values of N_0, the metal loading, but increases with larger values of N_0. The values of the sintering index p [Eq. (1)], obtained by the best fit of the curves of Fig. 1 to the form of Eq. (1), changes with time. The initial value of p and the values after approximately 3 and 5 hr are shown in Table 1 for the three curves. Interestingly, though the curves of Fig. 1 are so disparate, the initial values of p are approximately the same in two cases. This shows that N_0 affects K, the rate constant of Eq. (1), to a significantly greater extent than it affects p.

Consider now the process of Ref. (*1*), which entails only migration and capture and does not involve any form of emission. Under these conditions, and with diffusion controlling the overall process, a relationship was derived between p and m, the exponent of the size dependence of the diffusion coefficient

$$p = 4 - 3m. \tag{23}$$

If m is set equal to $-\frac{2}{3}$, the value used in the present computations, the value of p is 6. The increase in the value of p between this value and those of Table 1 demonstrates the improvement that may be expected in the fitting of experimental data when the emission of single atoms is added to the model of migration and capture of single atoms and multiatom particles.

TABLE 1

Value of the Sintering Index p from Fig. 1[a]

N_0 (atoms/cm²)	p		
	$t = 0$	$t = 3$	$t = 5$
1×10^{11}	10.5	10.3	10.3
1×10^{12}	10.6	18.3	24.5
1×10^{13}	7.6		

[a] The time t is in hours.

DISCUSSION

At least initially, the sign of the change of surface area depends upon the relative rates of two processes. The first is the formation of 100-atom particles by collision of two 50-atom particles. The second is the splitting of 50-atom particles into monoatoms and 49-atom particles. Small enough values of N_0 result in large average distances between the initial particles and small probabilities that one particle approaches another. Since diffusion controls the capture process, there will be only a small rate of formation of the 100-atom particles so that there is a lesser decrease of surface area by capture. On the other hand, N_0 and the $D_{j,i}$ have virtually no effect on the initial emission of single atoms. The net result is an increase in the total surface area with time. Larger values of N_0 or the $D_{j,i}$ may increase the rate of the capture process sufficiently to lead to a decrease in the total surface area with time.

The present model and those models involving only monoatomic transfer differ in the paths available to the final (equilibrium) states. If $N_0 > n_{1\infty}^s$, the final state consists of a single large particle of radius r surrounded by single atoms having a concentration $n_1^s(r)$ as given in Eq. (5); if $N_0 < n_{1\infty}^s$, the final state consists of only single atoms. If only single atoms are transferred, and if the initial distribution contains no single atoms, the case of Flynn and Wanke (*18*), the possible paths correspond in Fig. 2 to curves A ($N_0 < n_{1\infty}^s$) and C ($N_0 > n_{1\infty}^s$).

In contrast, if multiple atom transfer is allowed, an additional element is considered in the overall process. In this case, assuming diffusion controls the capture process, the relative magnitudes of the diffusion coefficients and the emission coefficients determine the path followed by the system, although of course only $n_{1\infty}^s$ and N_0 determine the final state. Thus, curves A and C correspond to the paths if the

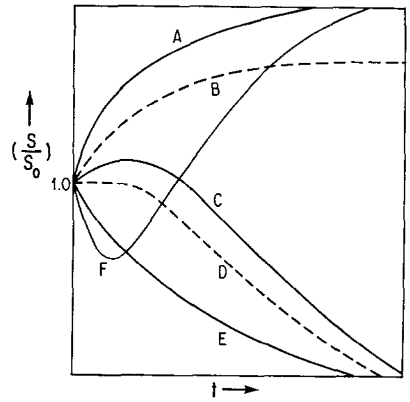

FIG. 2. Possible paths for sintering or splitting supported metal crystallites depend at small times upon the relative magnitudes of emission, migration and capture of metal species, and at large times upon the relative magnitudes of loading and saturation concentration of metal species. (A) The initial increase in surface area by emission is greater than the initial decrease by migration and capture, metal loading is less than saturation concentration. (B) Emission overrides capture initially, metal loading equals saturation concentration. (C) Emission overrides capture initially, metal loading is greater than saturation concentration. (D) Emission balances capture initially, metal loading is greater than saturation concentration. (E) Capture overrides emission initially, metal loading is greater than saturation concentration. (F) Capture overrides emission initially, metal loading is less than saturation concentration.

decrease in surface area by diffusion of particles and their coalescence is overshadowed by the increase in surface area by emission of particles. For the case of metal loading less than saturation concentration, this situation continues until finally only single atoms are left on the substrate (curve A). For larger metal loadings, emission causes an initial increase in surface area. This is followed by a decrease as concentrations of smaller particles increase, leading to an increase in the diffusion process and hence an increase in the capture rate, as shown in curve C. Curves E and F correspond to the paths for large diffusion coefficients. In curve E, where the metal loading is greater than the saturation, the large diffusion rates cause rapid agglomeration and the final state consists of one large particle and the equilibrium concentration of single atoms. If, however, the metal loading is small, the diffusion and capture process eventually slows down as particles grow larger and are further apart. Emission will gradually take over, as in curve F, and the final state should consist of only single atoms on the substrate.

Even though the final state is dictated by the metal loadings, the time required for this state to be approached may be very large. Hence, a supported metal catalyst corresponding to curve F may only sinter during its effective life. Similarly the catalyst of curve C may effectively not sinter at all.

CONCLUSIONS

This work presents a general model for the behavior of supported metal crystallites on a substrate in terms of the emission, migration and capture of single atoms and groups of atoms. It was possible to define conditions under which only single atoms are emitted and captured; there is no emission and particles of all sizes are captured; or single atom emission and multiatom capture takes place. The latter case was discussed here in detail.

We assumed that the process for the emission of a multiatom particle is analogous to the evaporation of a single particle. However, consideration of the number of bonds that need to be broken for multiatom emission leads to rates of particle emission that are many orders of magnitude smaller than rates of emission of single atoms. To account satisfactorily for emission of particles, rate equations for particle fracture must be developed.

In all the present calculations, diffusion controlled the overall migration and capture process. Depending upon the relative magnitudes of the diffusion and emission coefficients of all particles, the overall metal loading, and the saturation concentration, the model predicts a continuous increase in available surface area of the metal, an increase followed by a decrease, a decrease followed by an increase, or a continuous decrease. Hence, the present model enables us to treat both sintering and splitting in a unitary manner.

APPENDIX

Derivation of a Modified Lifshitz–Slyosov Continuity Equation

We start with the continuity equation for the j-mers, Eq. (4),

$$\frac{dn_j}{dt} = (\alpha_{j+1,1}n_{j+1} - \beta_{j,1}n_j) - (\alpha_{j,1}n_j - \beta_{j-1,1}n_{j-1}). \quad \text{(A1)}$$

If we consider n to vary continuously with j, Eq. (A1) can be rewritten for n a function of two variables, j and t, as

$$\frac{\partial n(j,t)}{\partial t} = \frac{\partial}{\partial j}[\{\alpha(j) - \beta(j)\}n(j,t) + \beta(j)n(j,t) - \beta(j-1)n(j-1,t)]. \quad \text{(A2)}$$

Substituting the first two terms of the Taylor series of $\beta(j-1)n(j-1,t)$ around $\beta(j)n(j,t)$ for the last term in brackets yields

$$\frac{\partial n(j,t)}{\partial t} = \frac{\partial}{\partial j}[\{\alpha(j) - \beta(j)\}n(j,t)] + \frac{\partial^2}{\partial j^2}[\beta(j)n(j,t)]. \quad \text{(A3)}$$

Of course this is not the only continuous variable approximation that can be made to Eq. (A1). Expanding α around $(j + \frac{1}{2})$ and β around $(j - \frac{1}{2})$, then expanding the result around j we obtain

$$\frac{\partial n(j,t)}{\partial t} = \frac{\partial}{\partial j}[\{\alpha(j) - \beta(j)\}n(j,t)] + \frac{1}{2}\frac{\partial^2}{\partial j^2}[\{\alpha(j) + \beta(j)\}n(j,t)]. \quad \text{(A4)}$$

The quantitative treatment of Ostwald ripening is based on the Lifshitz–Slyosov equation which is, in the present notation (*20*)

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial j}[n\{\beta(j) - \alpha(j)\}] = 0. \quad \text{(A5)}$$

Comparing Eqs. (A3) and (A4) we see that both contain a second derivative. However, Eq. (A5) does not. We suggest therefore, that either of the Eqs. (A3) or (A4) be used in the treatment of Ostwald ripening in supersaturated solutions. Which of these is a better choice depends upon the forms postulated for α and β. For example, if $\alpha = \beta$ Eqs. (A3) and (A4) are trivially identical.

ACKNOWLEDGMENT

We gratefully acknowledge the useful comments of Dr. S. E. Wanke.

REFERENCES

1. Ruckenstein, E., and Pulvermacher, B., *J. Catal.* **29**, 224 (1973).

2. Pulvermacher, B., and Ruckenstein, E., *J. Catal.* **35**, 115 (1974).

3. Wynblatt, P., and Gjostein, N. A., *Progr. Solid State Chem.* **9**, (1975).

4. Ruckenstein, E., and Malhotra, M. L., *J. Catal.* **41**, 303 (1976).

5. Basset, G. A. *in* "Proceedings of the European Regional Conference on Electron Microscopy" (A. L. Houwink and B. J Spit, Eds.), I. De Nederlandse Vereniging voor Electronen Microscopie, Delft, 1960.

6. Skofronick, J. G., and Phillips, W. B., *J. Appl. Phys.* **38**, 4791 (1967).

7. Masson, A., Métois, J. J., and Kern, R., *Surface Sci.* **27**, 463 (1971).

8. Kern, R., Masson, A., and Métois, J. J., *Surface Sci.* **27**, 483 (1971).

9. Chu, Y. F., and Ruckenstein, E. *Surface Sci.*, in press 1977.

10. Baker, R. T. K., Thomas, C., and Thomas, R. B., *J. Catal.* **38**, 510 (1975).

11. Baker, R. T. K., and France, J. A., *J. Catal.* **39**, 481 (1975).

12. Hughes, T. R., Houston, R. J., and Sieg, R. P., *Ind. Eng. Chem. Proc. Des. Develop.* **1**, 96 (1962).

13. Maat, H. J., and Moscou, L., *Proc. Int. Congr. Catal., 3rd, 1964* **2**, 1277 (1965).

14. Gruber, H. L., *J. Phys. Chem.* **66**, 48 (1962).

15. Hermann, R. A., Adler, S. F., Goldstein, M. S., and DeBaum, R. M., *J. Phys. Chem.* **65**, 2189 (1961).

16. Wynblatt, P., and Gjostein, N. A., *Scripta Met.* **7**, 969 (1973).

17. Wynblatt, P., and Gjostein, N. A., *Acta Met.* **24**, 1165 (1976).

18. Flynn, P. C., and Wanke, S. E., *J. Catal.* **34**, 390 (1974); **34**, 400 (1974).

19. Geus, J. W., *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, Ed.), Vol. 1. Academic Press, New York, 1971.

20. Lifshitz, I. M., and Slyosov, V. V., *J. Phys. Chem. Solids* **19**, 35 (1961).

21. Chakraverty, B. K., *J. Phys. Chem. Solids* **28**, 2401 (1967).

22. Jackson, K. A., *J. Crystal Growth* **5**, 13 (1969).

23. Hirth, J. P., and Pound, G. M., *in* "Progress in Materials Science" (B. Chalmers, Ed.), Vol. 11. Macmillan, New York, 1963.

24. Chen, J., personal communication.

25. "Handbook of Chemistry and Physics" (R. C. Weast, Ed.), 51st ed., p. B198. Chem. Rubber Co., Cleveland, Ohio 1970.