JOURNAL OF CATALYSIS 34, 390–399 (1974)

A Model of Supported Metal Catalyst Sintering

I. Development of Model

PETER C. FLYNN* AND SIEGHARD E. WANKE†

Department of Chemical Engineering, The University of Alberta,
Edmonton, Canada

Received February 6, 1974

An interparticle transport model for the sintering of supported metal catalysts is developed. The model postulates escape of atoms from crystallites to the support surface, rapid migration of these atoms along the surface, and their recapture by crystallites upon collision. A reduction in surface energy provides the driving force for transfer of metal from small to large particles.

The model can account for redispersion, for an effect of gas atmosphere on sintering behavior, and for considerable variation in order for a power law fit of sintering. It predicts that the character of the particle size distribution affects the rate of sintering.

NOMENCLATURE

A' and B	Constants in Eq. (2)
A	Pre-exponential factor in rate of loss equation [Eq. (3)]
D_i	Effective collision size of crystallite i
E_a	Activation energy for atom moving from crystallite to support
E_s	Activation energy for metal atom migration over support surface
F_s	Number of metal atoms migrating on support surface
G_i	Atoms gained by crystallite i
H_a	Heat of adsorption of single metal atoms on support
K	Rate constant in Eq. (1)
k_B	Boltzmann's constant
L_i	Atoms lost by crystallite i
M	Total number of crystallites (function of time)
m	Mass of metal atom
N_i	Number of atoms in crystallite
N_t	Total number of metal atoms in all crystallites
n	Order in the power-law model [Eq. (1)]
r	Particle radius [Eq. (2)]
S	Metal surface area [Eq. (1)]
S_0	Support surface area per metal atom (N_tS_0 = total support surface area)
T	Temperature
t	Time
V	Molar volume of metal
v	Velocity of atoms on support surface
α	Sticking probability of atoms colliding with crystallite
β	Defined by Eq. (3)
ν	Frequency factor ($\sim 10^{13}$ sec^{-1})
ϕ	Spreading pressure of metal on support surface.

INTRODUCTION

The overall process resulting in a change in metal dispersion of supported metal catalysts during use or treatment at elevated temperatures is called sintering. Since, in general, sintering results in a loss of catalytic activity, an understanding of the processes occurring during sintering is of importance in the design of catalysts with improved stability. Unfortunately,

---

* Present address: Syncrude Canada, Ltd., Edmonton, Alberta, Canada.

† To whom inquires concerning this paper should be addressed.

there is insufficient direct evidence to establish the mechanism of supported metal catalyst sintering.

Ruckenstein and Pulvermacher (*1, 2*) have carried out a detailed analysis of the sintering process by means of a model which envisages the sintering process as a migration of metal particles over the support surface, followed by the fusion of metal crystallites upon collision. Their results showed that the rate of metal surface area change is given by an equation of the form

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

where the value of n varies between 2 and 8, depending on whether the rate of fusion (particle sintering) or the rate of surface diffusion of metal crystallites is rate controlling. Recently, Wynblatt and Gjostein (*3*) in their sintering studies of supported Pt found the value of n to be ≈ 13. They proposed an equation, based on the concept of a nucleation barrier, to explain this large value of n. In their formulation, the resulting equation being somewhat similar to that of Somorjai (*4*), the constant K in Eq. (1) decreases exponentially with increasing average particle radius r, i.e.,

$$K = B \exp(-A'r/RT). \tag{2}$$

Wynblatt and Gjostein did not compare the predictions with experiment, but planned to pursue this in the future.

The model of Ruckenstein and Pulvermacher (*1, 2*), besides being unable to account for the above mentioned large value of n, encounters other difficulties in being unable to explain some of the experimental observations made during sintering studies. These include:

1. Under certain conditions, generally in an oxidizing atmosphere, metal dispersion increases during high temperature treatment (*5–8*). A simple crystallite diffusion model of sintering process cannot account for increases in metal surface area, although Ruckenstein and Pulvermacher propose to discuss crystallite separation in a future work.

2. The high activation energies observed for the sintering process, up to 70 kcal/g mole for Pt on Al_2O_3 (*9*), are difficult to account for on the basis of the fusion of two adjacent metal crystallites. (Ruckenstein and Pulvermacher do not quantitatively discuss the activation energies of crystallite surface diffusion and particle sintering).

3. The continued growth of metal particles to the extent that the metal particle size is of the order of the support particle size is difficult to explain on the basis of metal crystallite migration. Figure 1 illustrates this from electron micrographs of catalyst treated in this laboratory. The specimen is an impregnated 4.76% Pt on Alon (Registered trademark of the Cabot Corp.) alumina catalyst. The support consists of 10 to 30 nm discrete alumina particles which agglomerate upon wetting. The various micrographs show platinum particle sizes after impregnation, after reduction in hydrogen in mild conditions (250°C), and after 16 hr treatment in an O_2 atmosphere with temperatures ranging from 500 to 700°C.

It is evident that the platinum continues to grow in size on the Alon support even when it reaches 30 nm particle sizes, exceeding the average size of the particles in the support. The occurrence of this growth by crystallite transport over long distances of the irregular support, by diffusion from one Alon particle to the next, seems highly unlikely. A transfer of atomic or molecular metal species, either across the bridge where the support particles contact or through desorption, vapor phase transport, and readsorption, seems a far more plausible hypothesis for the formation of these large particles.

4. Despite the frequent citing of crystallite migration as a sintering mechanism [e.g., (*1, 2, 10–12*)], there is little concrete evidence of motion over the appreciable distances needed to account for sintering of supported metal catalysts. For example, in *in situ* film growth studies by transmission electron microscopy Pashley *et al.* (*13*) observed small reorientations, such as rotations of the order of 1°, when par-

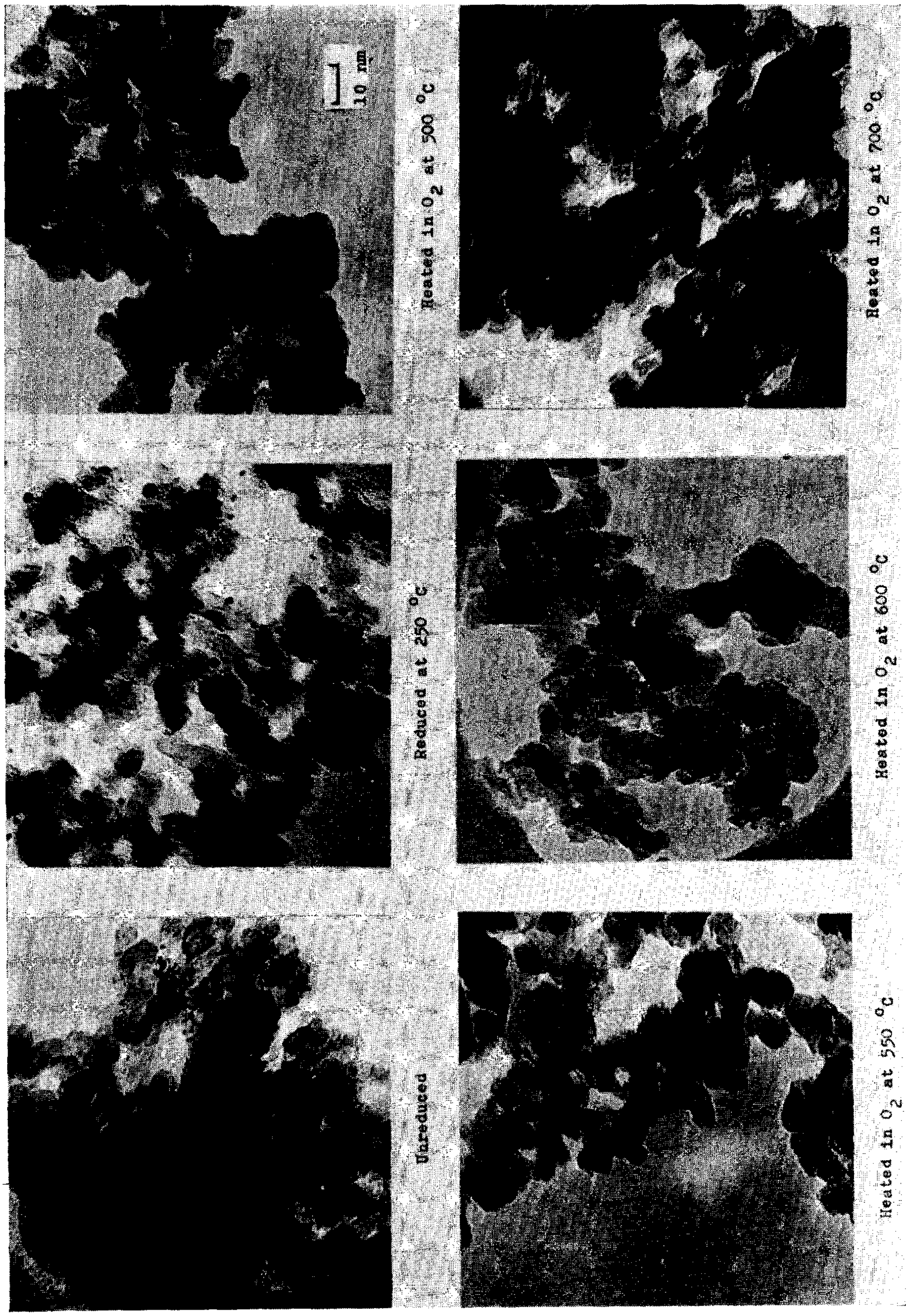

FIG. 1. Electron micrographs of 4.76% Pt on Alon alumina after various pretreatments, showing formation of large Pt crystallites.

ticles merged. However, they did not report significant crystallite motion. Phillips, Deslodge and Skofronick (*12*) cited crystallite diffusion in interpreting their electron micrographs. However, the authors were not able to describe their observations by their proposed model. In particular, Figs. 1 and 2 of Ref. (*12*) are odd in that larger particles (~100 nm) appear to move more rapidly than smaller particles (~5 nm).

Wynblatt and Gjostein (*14*) observed minimal migration, less than 10 nm in 16 hr at 1000°C in a hydrogen atmosphere, for Pt particles of an average size of 7.5 nm on an Al_2O_3 substrate. They conclude that particle migration is too slow a process for particle sizes greater than 5 nm to account for observed sintering rates. Geus' review (*10*) makes it evident that most evidence of substantial crystallite motion is inferential.

It should be noted that the conditions in which crystallite diffusion is cited as a mechanism in film growth are drastically different from those in typical supported metal catalyst sintering studies: first, temperatures are generally 200 to 500°C lower in film growth studies; second, coverage of the support is typically about 0.1 to 0.5 in film growth studies, while typical catalysts have about 10^{-3} times that coverage of support by metal; and finally, typical film growth supports are smooth, often cleaved planes, while typical catalyst supports are polycrystalline and highly irregular. Thus even if definitive evidence of crystallite diffusion at film growth conditions is obtained, the translation of this mechanism to supported metal catalyst sintering would not necessarily follow.

In light of these difficulties in interpreting experimental evidence of sintering via the model of diffusing crystallites, we have looked to alternate mechanisms to account for the sintering phenomenon. In this paper we develop a model for the sintering of supported metal catalysts based on individual metal atoms leaving the metal crystallites, migrating over the support and being captured by metal crystallites upon collision. This approach is by no means devoid of conceptual difficulties, but it can account for a variety of experimental observations of sintering.

A discussion of the individual steps in this process and possible experiments to discriminate between the particle versus atom migration model is presented below. In a subsequent paper (*25*) we present numerical calculations for specific cases for the model described below.

PROPOSED MODEL

The mechanism of supported metal catalyst sintering in the proposed model is postulated to consist of three steps: one, individual metal atoms (or molecules such as PtO in an oxygen atmosphere) move from the metal crystallite to the surface of the support; two, the metal atoms migrate over the support surface; and three, the migrating atoms are either captured by collision with a metal crystallite or are immobilized by a drop in temperature or by encountering an energy well on the support surface. Each of these three steps is discussed in detail.

1. Escape of Metal Atoms from Crystallites

Previous workers considering metal migration and particle agglomeration have generally discounted the possibility of loss of individual atoms, due to the large activation energy, E_a, that this step would require. The heat of sublimation of platinum, for example, is 135 kcal/g mole (*15*). Arguing by extension from measurements on other metals, Geus (*10*) estimated the dissociation of a pair of Pt atoms to be about 65 kcal/g mole. Thus most investigators of nucleation effects [e.g., Refs. (*10–13, 16–19*)] have concluded that for metals such as Bi, Au, Ag, Pt, etc., the dissociation of atoms from clusters of larger than a few atoms is negligibly small. Similarly, the forces between particle and support are presumed to be van der Waals type only, so that heat of adsorption, H_a, of single metal atoms is taken to be less than 20 kcal/g mole.

Supported metal catalyst sintering is generally observed at temperatures of 800–1000°K, which is higher than typical nucleation study temperatures of 500–600°K. At these temperatures, an activation energy of less than 60 to 75 kcal/g mole is necessary if a process is to occur with a significant rate. Thus the large sublimation energy and presumed low interaction of metal with support appear on first glance to rule out escape of metal atoms to the support surface from metal crystallites as a plausible mechanism.

However, Geus' extensive review (*10*) of data observed in metal film formation studies indicates that several factors may substantially increase the interaction between metal and support surface. In advancing this model we suggest that localized metal–support interactions are sufficiently large to reduce the net energy difference between an atom in the crystallite and an atom on the surface to the required value less than 75 kcal/g mole.

The presence of oxygen has been reported by many authors to significantly increase the interaction of metal crystals and oxide supports (*10*). Formation of a metal oxide layer at the support surface is believed to result in a strong chemical interaction, thought to involve metal incorporation in the support structure. For nickel, iron, chromium and titanium aging in air at room temperature has been observed to substantially increase the adherence of metal particles on films. This type of strong interaction between metal and support, not necessarily reversible by reduction, could readily enhance removal of a metal atom from the particle to the surface. (In certain atmospheres the escaping metal species would presumably be molecular rather than atomic.)

A second factor explored by Geus (*10*) which increases localized metal–support interaction is the presence of defects in the support structure. The well-known decorating effect, where crystals are seen to nucleate in the region around defects, is attributed to the favorable energetics of adatom adsorption in these regions. Thus again metal escape from particle to support surface can be enhanced in localized regions by the presence of defects.

Finally, Geus (*10*) reviewed evidence that impurities on the support surface increase the interaction of metal and support. The presence of cracking products of hydrocarbons or of carbon has been found to increase the localized adatom population. The role of such inpurities in serving as a bridge for the "spillover" of adsorbed gases from metal to surface has been discussed (*20*). By increasing metal–support interaction, such impurities may also help to bridge the spillover of metal atoms to the support.

These arguments for loss of metal atoms to the support surface are admittedly tenuous. However, they point to an interaction far more complex than the van der Waals forces cited in ruling out the possibility of particle dissociation. Because of the large heat of condensation of metals, and their ready mobility on support surfaces, no direct measurement of the heat of adsorption of Pt on typical supports is possible (*10*). Phillips, Deslodge and Skofronick (*12*) found that an H_a of 35 kcal/g mole for Au on SiO was required to explain their results in terms of their particle migration model. Tabatadze, Myasnikov and Evstigneeva (*21*) measured the conductance of metal oxides during the adsorption of noble metals. They observed large changes in conductance as long as metal atoms were supplied to the oxide surface. Their results indicate a strong electronic interaction of single metal atoms with the oxide surfaces which disappears once these atoms aggregate to form metal crystallites. This indirect evidence supports conclusions from nucleation and film growth that forces other than van der Waals are involved in the adsorption of metal atoms on oxide surfaces.

The reduction in surface energy is the driving force for the transfer of metal from smaller to larger crystallites. We are interested in obtaining an approximate relationship for the rate of loss of metal atoms from a crystallite to the support as a function of crystallite size. The Kelvin equation relates the spreading pressure, ϕ, to the crystallite radius, r, by

$$\phi = \phi_0 \exp(\beta/r), \qquad (3)$$

where the value of β depends on the shape of the crystallite, the metal–support contact angle, the metal–support and metal–vapor interfacial energies, the metal molar volume, and the temperature. For a specific support/metal system, at a constant temperature, the value of β should be relatively constant.

For a single crystallite in equilibrium with free atoms on a support surface, the rate at which the crystallite would capture atoms is proportional to $r\phi$, and therefore the rate of atom loss, dL_i/dt, is also proportional to $r\phi$. The rate of loss is independent of whether or not the system is in equilibrium if energy transfer is not controlling. Hence the ratio of the rates of loss for two crystallites of different size is given by

$$\left(\frac{dL_1}{dt}\bigg/\frac{dL_2}{dt}\right) = \frac{r_1\phi_1}{r_2\phi_2} = \frac{r_1}{r_2}\exp\left[\beta\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\right]. \qquad (4)$$

The Pt/Al_2O_3 contact angle is ~90°, and therefore the crystallites were taken to be hemispheres. For this case the value of β is defined by

$$\beta = \frac{(\gamma_1 + 2\gamma_2)V}{RT}, \qquad (5)$$

where γ_1 and γ_2 are the $Pt–Al_2O_3$ and Pt–atmosphere interfacial energies, V is the molar volume of Pt, and T was taken as 1000°K. In order to assess the range in reported values of γ [e.g., (*22*, *23*)] and the variation of Pt species (such as metallic Pt, PtO, etc.), three values of β, ranging from 4 to 6 nm, were employed in calculating relative rates of loss by Eq. (4). In Table 1 the rates of atom loss relative to a crystallite with a diameter of 25 nm are reported for the three cases over the size range 2 to 50 nm.

TABLE 1

Relative Rate of Loss of Atoms per Crystallite as a Function of Crystallite Size as Estimated by the Kelvin Equation (Normalized to 25 nm Diameter Crystallites)

Crystallite diam (nm)	Case I β = 4.0 nm	Case II β = 5.0 nm	Case III β = 6.0 nm
2	3.17	7.96	19.97
4	0.86	1.31	1.99
6	0.66	0.85	1.10
8	0.63	0.75	0.89
10	0.65	0.73	0.82
12	0.68	0.74	0.81
15	0.74	0.78	0.83
18	0.82	0.84	0.87
20	0.87	0.88	0.90
25	1.00	1.00	1.00
30	1.14	1.12	1.11
40	1.42	1.38	1.34
50	1.70	1.64	1.57
100	3.15	2.96	2.79

From the values reported in Table 1, it is evident that in the size range of interest in sintering studies the rate of loss of atoms from a crystallite may reasonably be approximated as independent of the crystallite size. The variation in loss is less than 30% up to 30 nm, except for very small particles where Eq. (3) predicts questionably high values of ϕ/ϕ_0. Accordingly, we have modeled the rate of loss of atoms from the *i*th particle as

$$\frac{dL_i}{dt} = Ae^{-E_a/RT}, \qquad (6)$$

where dL_i/dt is the rate of transfer of atoms to the surface, A is an arbitrary constant, and E_a is the activation energy required to move from a particle to the surface. For particle sizes above 30 nm the surface energy and size variance of the rate of loss do not compensate for each other, and the assumption of a constant loss rate, Eq. (6), becomes increasingly subject to error.

2. Migration of Metal Atoms Over Support Surfaces

The extensive work on nucleation and film growth leaves little doubt about the mobility of atoms on supports, even at temperatures much lower than those encountered during supported metal catalyst sintering (*10–13*, *16–19*). The atoms may be considered as a two-dimensional gas, in which case their speed is given by

$$v = \left(\frac{\pi k_B T}{2m}\right)^{1/2}, \tag{7}$$

or the motion may be described by the jumping from one surface site to next which is described by

$$v = a\nu \exp(-E_s/RT). \tag{8}$$

It should be noted that E_s, the activation energy for surface diffusion, is not necessarily equal to E_a, but is generally considerably smaller than E_a.

In the present model it is immaterial whether Eq. (7) or (8) is used, but Eq. (8) illustrates that a drop in temperature could readily immobilize surface atoms if certain sites on the support surface have large values of E_s. We presume a surface velocity rapid enough, at sintering temperatures, to lead to a uniform concentration of free surface metal atoms on the support surface.

3. Capture of Atoms by Metal Crystallites

Upon collision of a migrating atom with a metal crystallite, the atom may become incorporated in the crystallite. The rate at which a crystallite gains metal atoms by this process depends on the concentration of metal atoms on the support surface, the velocity of these atoms, and the effective diameter of the crystallite, D_i, i.e.,

$$\frac{dG_i}{dt} = \alpha \frac{v}{N_t} \frac{F_s}{S_0} D_i, \tag{9}$$

where α	sticking probability of an atom colliding with a crystallite (assumed to be independent of D)
N_t	total metal atoms
S_0	support area per metal atom
F_s	number of atoms migrating on support with an area N_tS_0 (i.e., F_s/N_tS_0 is the concentration of atoms on support surface).

Once the atom has become attached to the periphery of the particle it can migrate over the metal surface and become part of the crystal. The surface self diffusion rates of metals are generally quite large, the activation energy for Pt only being 26 kcal/g mole (*24*), and the resulting crystals should be three-dimensional rather than metal islands on the support.

4. A Summary of the Model

The net rate of change of the number of atoms in the *i*th particle is given by

$$\frac{dN_i}{dt} = \frac{dG_i}{dt} - \frac{dL_i}{dt}, \tag{10}$$

which, according to Eqs. (3) and (6) may be written as

$$\frac{dN_i}{dt} = \alpha v \frac{F_s}{N_tS_0} D_i - Ae^{-E_a/RT}. \tag{11}$$

The rate of change of the number of migrating surface atoms is given by the material balance

$$\frac{dF_s}{dt} = \sum_{i=1}^{M} \left(\frac{dL_i}{dt} - \frac{dG_i}{dt}\right)$$

$$= -MAe^{-E_a/RT} + \alpha v \frac{F_s}{N_tS_0} \sum_{i=1}^{M} D_i, \tag{12}$$

where M is the number of metal crystallites on the support of area N_tS_0.

This model of supported metal catalyst sintering may be likened to an evaporation condensation process among multisized droplets. In that case the variation in vapor pressure among drops of different size leads to a transfer of liquid from smaller to larger droplets. By our sintering model a single particle on a support surface would establish an equilibrium concentration of metal atoms migrating along the surface. With several particles of different size, however, the surface concentration is not equilibrated with each particle, and thus growth or decay in individual particle sizes occurs. Because smaller crystallites would equilibrate with higher concentrations of migrating surface atoms than larger crystallites, the larger crystallites grow at the expense of the smaller.

In a subsequent paper (*25*) we present solutions to Eqs. (11) and (12) for a variety of initial particle size distributions and parameter values. In this paper we restrict ourselves to some general predictions by these equations of changes in particle size distributions with respect to time.

DISCUSSION

1. Changes in Particle Sizes

Equation (11) predicts that large particles will grow while small ones will decrease in size as sintering progresses. At any time, for the specific particle size distribution present at that time, there exists a critical size; particles that are larger than this size will grow while smaller ones will diminish. This implies that as sintering progresses the initial particle size will broaden, resulting in particles smaller than the original minimum size. This broadening of the distribution is quite different than that predicted by the particle migration model, which predicts that as sintering progresses all particles have to be as large as or larger than the initial ones. Some experimental evidence exists that even in heavily sintered samples small crystallites are still present. For example, Matt and Moscu (*26*) sintered a catalyst whose initial particle size ranged from 1 to 5 nm. Even after severe sintering leading to 50 nm particles, they still reported the presence of particles in the 1 nm size range. While the sintered sample does not show smaller sizes than the initial sample, the 1 nm size probably represents the lower detection limit from their electron micrographs. Further experiments that follow the nature of the particle-size-distribution broadening would be useful in elucidating the mechanism of sintering.

2. The Effect of Initial Distribution

The proposed model also predicts that broad or multimodal distributions sinter more rapidly than narrow ones. This occurs because large particles effectively capture surface atoms, reducing the concentration of surface free atoms and thus lowering the uptake by smaller particles. In narrow distributions the driving force for transfer is small; unisized distributions (practically unattainable) are predicted not to sinter at all. This is quite different than the crystallite diffusion model of Ruckenstein and Pulvermacher (*2*), which predicts sintering among unisized particles. Experimental studies to investigate the effect of initial particle size distribution on the rate of sintering are presently being carried out.

3. The Possibility of Redispersion

Because of reduction in surface energy, this model predicts an ultimate transfer of mass from smaller to larger particles, and hence a reduction in metal surface area. However, in the initial stages of sintering some number of metal atoms accumulate on the support surface as migrating surface species. The presence of these free atoms increases the dispersion of the catalyst during the early stages of treatment.

The extent of initial dispersion rise is extremely sensitive to the model parameters, particularly $\alpha v/S_0$ and E_a, and can be shifted from negligible increase to complete redispersion of all metal. Figure 2 shows a typical dispersion history computed for a particle distribution, in which the dispersion rises 24% during formation of the free surface atoms. If during this time the catalyst were cooled and the surface atoms remained as individual atoms or formed small clusters, then a surface area measurement would show redispersion.

4. The Effect of Atmosphere

In this model, sintering behavior is sensitive to the ease of escape of an atom

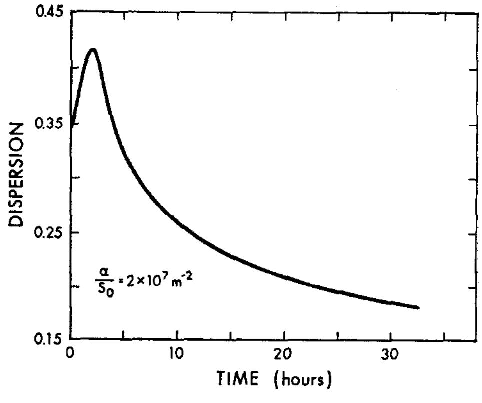

FIG. 2. A typical sintering history predicted by interparticle transport model, showing initial redispersion.

from the particles (E_a) and the rapidity of migration along the surface (v). Different atmospheres would affect both of these values, by changing the interaction of the metal and the support, and by changing the character of the migrating particle. For example, in an oxygen atmosphere a molecular species, such as PtO, would probably be formed. This species would have a different loss rate from the particle to the surface, as well as a different surface velocity, than atomic metal. Any reduction in escape energy (E_a) or surface velocity would increase the concentration of migrating surface atoms, and hence the potential for redispersion.

5. *Order of Sintering Rate with Respect to Metal Surface Area*

Fitting the metal surface area as a function of time as predicted by the model to Eq. (1) yields values of n that are less than zero, for the cases where redispersion is occurring, to values of n as large as 15. Other factors being equal, it is generally found that the values of n get larger as the average particle size increases. This is in agreement with the observation of Wynblatt and Gjostein (*3*), who proposed Eq. (2) to account for this occurrence. The value of n is also very sensitive to the width of the particle size distribution and other parameters in this model, suggesting that the power law description of sintering is a poor choice if this model is employed. This point is detailed further in a subsequent work (*25*).

6. *The Possibility of Multiple Mechanisms*

Sintering behavior occurs over at least two orders of magnitude of particle size, from 0.5 to 50 nm, and over a range of atmospheres, temperatures, supports, and metal loadings. While this work has postulated interparticle atomic or molecular migration as an alternate to particle motion, the two mechanisms are not exclusive. Wynblatt and Gjostein (*14*) suggest particle migration may be prevalent for particles under 5 nm, but that some form of interparticle transport must take place at larger sizes to account for observed rates of sintering.

CONCLUSION

A model for the sintering of supported metal catalysts, based on the dissociation of individual atoms from the metal crystallites, has been developed. The model postulates that large interactions between the support and metal atoms may potentiate the escape of metal to the surface. Evidence of high interaction between metal and a support is found for oxygen atmospheres (on oxide supports), in defect regions, and in the presence of contaminants.

The model predicts the transfer of metal from small to large particles, and hence an ultimate increase in the average particle size. However, transient increases in dispersion are associated with the formation of single metal atoms on the surface, which could remain as single atoms or form small clusters upon cooling. The atmosphere of sintering and the initial character of the particle size distribution are predicted to be important in determining the rate of sintering.

ACKNOWLEDGMENTS

One of us (P.C.F.) gratefully acknowledges the support of an International Nickel Co. Graduate Fellowship. We also appreciate the support of this research by the National Research Council of Canada.

REFERENCES

1. RUCKENSTEIN, E., AND PULVERMACHER, B., *AIChE J.* **19**, 356 (1973).

2. RUCKENSTEIN, E., AND PULVERMACHER, B., *J. Catal.* **29**, 224 (1973).

3. WYNBLATT, P., AND GJOSTEIN, N. A., *Scr. Met.* **7**, 969 (1973).

4. SOMORJAI, G. A. *in* "X-Ray and Electron Methods of Analysis" (H. van Olphen and W. Parrish, Eds.), Chap. 6. Plenum, New York, 1968.

5. WELLER, S. W., AND MONTAGNA, A. A., *J. Catal.* **20**, 394 (1971).

6. JOHNSON, M. F. L., AND KEITH, C. D., *J. Phys. Chem.* **67**, 200 (1963).

7. *Chem. Abstr.* **76**, 145405q (patent, Ger. Offen. 2, 137, 554).

8. *Chem. Abstr.* **68**, 31814b (patent, Neth. Appl. 6, 614, 074).

9. Herrmann, R. A., Adler, S. F., Goldstein, M. S., and De Baun, R. M., *J. Phys. Chem.* **65**, 2184 (1961).

10. Geus, J. W. *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, Ed.), Chap. 3. Academic Press, London, 1971.

11. Lewis, B., *Surface Sci.* **21**, 289 (1970).

12. Phillips, W. B., Deslodge, E. A., and Skofronick, J. G., *J. Appl. Phys.* **39**, 3210 (1968).

13. Pashley, D. M., Stowell, M. J., Jacobs, M. H., and Law, T. J., *Phil. Mag.* **10**, 127 (1964).

14. Wynblatt, P., and Gjostein, N. A., *Progr. Solid State Chem.* **9**, in press.

15. Plante, E. R., Sessoms, A. B., and Fitch, K. R., *J. Res. Nat. Bur. Stand., Sec. A* **74**, 647 (1970).

16. Zinsmeister, G., "Proceedings of the International Symposium on Basic Problems in Thin Film Physics" (R. N. Mayer and H. Mayer, Eds.), p. 33. 2nd ed., Vandenhoeck Ruprecht, Gottingen, 1966.

17. Lewis, B., *Surface Sci.* **21**, 273 (1970).

18. Poppa, H., *J. Appl. Phys.* **38**, 3883 (1967).

19. Halpern, V., *J. Appl. Phys.* **40**, 4627 (1969).

20. Neikam, W. C., and Vannice, M. A., *Proc. Int. Congr. Catal. 5th* p. 609 (1973).

21. Tabatadze, D. G., Myasnikov, I. A., and Evstigneeva, L. A., *Russ. J. Phys. Chem.* **46**, 1488 (1972).

22. McLean, M., and Hondros, E. D., *J. Mater. Sci.* **6**, 19 (1971).

23. "Handbook of Chemistry and Physics," 51st ed., p. F-23. Chem. Rubber Co., Cleveland, 1970.

24. Gjostein, N. A., "Metal Surfaces," Chap. 4, Amer. Soc. for Metals, Metals Park, OH, 1963.

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

26. Matt, H. J. and Moscou, L., *Proc. Int. Congr. Catal. 3rd, 1964* p. 1277 (1965).