

LETTERS TO THE EDITORS

Comments on the Sintering Mechanism of Supported Metal Catalysts

The term sintering, used in conjunction with supported metal catalysts, refers to the process(es) which results in changes in the metal crystallite size distribution (MCSD). Sintering can occur by at least two different mechanisms: one, the migration of entire crystallites over the support surface followed by coalescence of crystallites upon collision (this mechanism will be referred to as the crystallite migration mechanism); and two, the detachment of metal atoms (or molecular species) from crystallites followed by the migration of these atoms over the support surface and capture of the migrating atoms upon collision with stationary metal crystallites (this mechanism will be referred to as the atomic migration mechanism). The atomic migration mechanism is often called Ostwald ripening. These two mechanisms and various mathematical models based on these mechanisms have been described in detail (1-3). Although these two mechanisms predict considerably different behavior during the sintering process, it has not been possible to discriminate between these two models of the sintering process on the basis of experimental data (4).

In a recent article Granqvist and Buhrman (5) state that "accumulated evidence points almost unequivocally in favor of coalescence growth as distinct from Ostwald Ripening." Their conclusion is based on MCSD measured by several investigators (6-10) and the assumptions that the crystallite migration mechanism results in log-normal MCSD while the atomic migra-

tion mechanism results in MCSD with a substantial tail on the small-diameter side of the MCSD [see inset in Fig. 1 of Ref. (5)]. The conclusion of Granqvist and Buhrman (5) is incorrect for several reasons:

i. The atomic migration mechanism does not have to result in MCSD with a substantial tail on the small-diameter side of the distribution (shown below).

ii. The MCSD after sintering as predicted by the atomic migration mechanism is a strong function of the initial MCSD (11) and if the initial distribution is log-normal, then the distributions after sintering also tend to be log-normal. Granqvist and Buhrman (5) apparently do not distinguish between initial MCSD and MCSD after sintering. The sample MCSD they show in Fig. 1 of Ref. (5) in support of their conclusion is for a *freshly* reduced catalyst and not a sintered catalyst. The MCSD for freshly reduced catalysts is not only a function of reduction conditions but is a very strong function of the preparation conditions, e.g., impregnation versus ion exchange (8).

iii. There are examples in the literature which show MCSD, before and after thermal treatment, which are not log-normal distributions, e.g., Renouprez *et al.* (12) obtained multimodal MCSD, and Pope *et al.* (6) and Plank *et al.* (13) obtained bimodal MCSD (although Granqvist and Buhrman claim that the MCSD reported by Pope *et al.* (7) support their log-normal MCSD).

To substantiate the claim that an atomic migration mechanism does not have to result in MCSD with a substantial tail on the small-diameter side, we fitted the data presented by Bett *et al.* (9) and Nakamura *et al.* (10) by the atomic migration model described by Flynn and Wanke (2, 11). The simplest form of this model assumes that the concentration of migrating atoms on the support approaches zero. For this case the rate of change of atoms in the i th crystallite is given by:

$$\frac{dN_i}{dt} = \left(\frac{MD_i}{\sum_{j=1}^M D_j} - 1 \right) A \exp(-E/RT), \quad (1)$$

where N_i is the number of metal atoms in the i th crystallite, M is the total number of crystallites in the distribution, D_i is the effective diameter of the i th crystallite for the capture of migrating atoms, T is the absolute temperature, and A and E are adjustable parameters. [For the application of Eq. (1) to specific cases Ref. (11) should be consulted.] The results of the fit of this model, along with the values of $A \exp(E/RT)$ used, to the experimental data are shown in Fig. 1. The reported MCSD for the fresh catalysts were used as the starting distributions in the computations. The comparison between measured MCSD and those obtained from the atomic migration model are in good agreement. It should be noted that the calculated MCSD do not have a tail on the small-diameter side.

The data of Wilson and Hall (6) were also examined by the above atomic migration model using the MCSD after the treatment at 475°C as the initial MCSD [Fig. 1, Ref. (6)]. The MCSD given by Wilson and Hall (6) are in terms of the fraction of Pt surface area in a given crystallite size range. These distributions were converted to fraction of the number of metal crystallites in a given size range. The converted

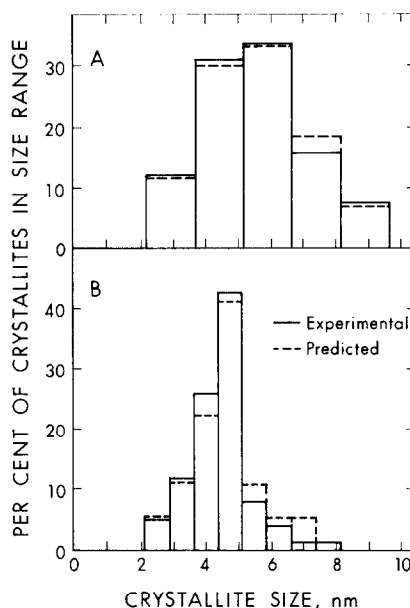


Fig. 1. Comparisons of experimental and predicted MCSD. (A) Results of Bett *et al.* (9) for a 20% Pt/carbon catalyst sintered in nitrogen at 600°C for 16 hr [$A \exp(-E/RT) = 0.325 \text{ sec}^{-1}$ for the predicted MCSD]. (B) Results of Nakamura *et al.* (10) for a 0.5% Pt/carbon catalyst sintered in hydrogen at 650°C for 72 hr [$A \exp(-E/RT) = 0.112 \text{ sec}^{-1}$ for the predicted MCSD].

MCSD are the experimental distributions shown in Fig. 2. Since MCSD for various treatment temperatures were given, a unique set of A and E values should be able to fit the data at all three sintering temperatures. Unfortunately, this was not the case. In Fig. 2 the experimental MCSD and the predicted MCSD for $A = 2.0 \times 10^2 \text{ sec}^{-1}$ and $E/R = 10,000 \text{ K}$ are compared.

There are several possible reasons, other than the possibility that the atomic migration mechanism is incorrect, that can explain the discrepancies apparent in Fig. 2. In the calculations it was assumed that the crystallites are cubes and that once the number of atoms in the crystallite become less than 14 the crystallite disappears. This is not a serious limitation if the average crystallite size is $> 2 \text{ nm}$, but if the initial average crystallite size is only 1 nm, as in

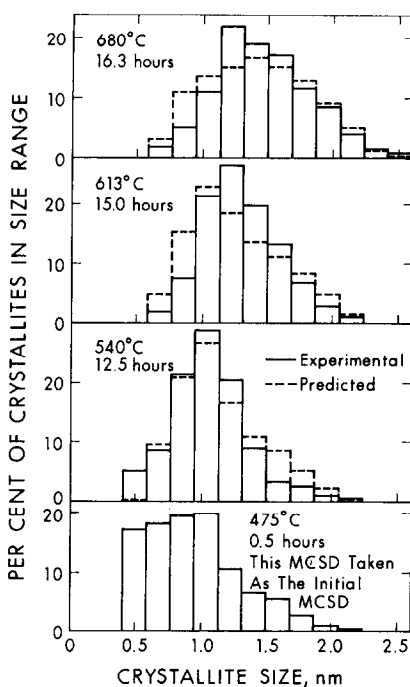


Fig. 2. Comparison of experimental and predicted MCD based on the results of Wilson and Hall (6) for a 2.85% Pt/Al₂O₃ catalyst sintered in hydrogen at the indicated temperatures and times. ($A = 200 \text{ sec}^{-1}$ and $E/R = 10,000 \text{ K}$ for the predicted MCD).

the above case, this assumption is very questionable. Another assumption inherent in Eq. (1) is that the gross rate of loss of atoms from a crystallite is independent of crystalline size [see Ref. (2)]. Again, this is a questionable assumption for very small crystallites. According to the Kelvin equation higher rates of loss would be expected for smaller crystallites. Modifications of the model can be made to take this into account (14), but such refinement of the model is probably not justifiable since the reliable determination of MCD in supported metal catalyst by transmission electron microscopy for size $< 1.5 \text{ nm}$ is questionable (12, 15). This difficulty in obtaining reliable MCD is apparent, upon close examination, in the results of Wilson and Hall (6). The experimentally

determined histograms shown in Fig. 2 [taken from Fig. 1 of Ref. (6)] show that $\sim 9\%$ of the crystallites have a diameter $> 1.5 \text{ nm}$ after treatment at 475°C but only $\sim 7\%$ of the crystallites are larger than 1.5 nm after treatment at 450°C .

The above arguments and fitting of experimental data of Bett *et al.* (9) and Nakamura *et al.* (10) have shown that the sintering of supported metal catalyst can be described by an atomic migration mechanism. This does not lead to the conclusion that sintering occurs by an atomic transport mechanism, because the fitting of experimental data by a mechanistic model does not constitute proof of the mechanism. Nevertheless, the ability of the atomic migration model to fit experimental data, and the observation by Baker *et al.* (16) that Pt crystallites on alumina are immobile at temperatures up to 900°C , gives strong support to the postulate that the sintering of supported metal catalysts occurs via atomic rather than crystallite transport.

REFERENCES

1. Ruckenstein, E., and Pulvermacher, B., *J. Catal.* **29**, 224 (1973).
2. Flynn, P. C., and Wanke, S. E., *J. Catal.* **34**, 390 (1974).
3. Wynblatt, P., and Gjostein, N. A., *Progr. Solid State Chem.* **9**, 21 (1975).
4. Wanke, S. E., and Flynn, P. C., *Catal. Rev. Sci. Eng.* **12**, 93 (1975).
5. Granqvist, C. G., and Buhman, R. A., *J. Catal.* **42**, 477 (1976).
6. Wilson, G. R., and Hall, W. K., *J. Catal.* **17**, 190 (1970).
7. Pope, D., Smith, W. L., Eastlake, M. J., and Moss, R. L., *J. Catal.* **22**, 72 (1971).
8. Wilson, G. R., and Hall, W. K., *J. Catal.* **24**, 306 (1972).
9. Bett, J. A., Kinoshita, K., and Stonehart, P., *J. Catal.* **35**, 307 (1974).
10. Nakamura, M., Yamada, M., and Amano, A., *J. Catal.* **39**, 125 (1975).
11. Flynn, P. C., and Wanke, S. E., *J. Catal.* **34**, 400 (1974).
12. Renouprez, A., Hoang-Van, C., and Compagnon, P. A., *J. Catal.* **34**, 411 (1974).

13. Plank, C. J., Kokotailo, G. T., and Drake, L. C., 140th Meet. Amer. Chem. Soc., Div. Colloid Chem., Chicago, Sept. 1961, Pap. 45.
14. Wanke, S. E., in "Sintering and Catalysis" (G. C. Kuczynski, ed.), p. 107. Plenum, New York, 1975.
15. Flynn, P. C., Wanke, S. E., and Turner, P. S., *J. Catal.* **33**, 233 (1974).
16. Baker, R. T. K., Thomas, C., and Thomas, R. B., *J. Catal.* **38**, 510 (1975).

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