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Size Distributions for Supported Metal Catalysts

Coalescence Growth versus Ostwald Ripening[1]

Several recent articles (*1–5*) in this journal have reported on size distributions for supported metal catalysts, which have been determined by standard techniques of electron microscopy. In this note we wish to point out that *the shape of such size distributions can be used as a means to determine by which mechanism the particles have grown* and that *the accumulated evidence points almost unequivocally in favour of coalescence growth* as distinct from Ostwald Ripening.

In principle the coarsening of a small particle on a substrate can occur via two fundamentally different mechanisms: (i) Whole islands can move over the substrate surface to take part in binary collisions accompanied by liquid-like *coalescence* of the particles; and (ii) growth can take place by interparticle transport of single atoms; this process is usually phrased *Ostwald Ripening.*

For coalescence growth we have previously (*6, 7*) formulated a simple statistical model where we regard the growth as a series of discrete events. We assume that only two particles coalesce at a time and that the change of volume at each step in the sequence is a random fraction of the particle volume after coalescence. These assumptions suffice to predict an asymptotic size distribution (i.e., in the limit of many coalescence events) where the *logarithm* of the particle volumes form a gaussian. This *log-normal distribution* then yields that the number of particles Δn per logarithmic size interval $\Delta(\ln x)$ is given by

$$\Delta n = f_{LN}(x)\Delta(\ln x), \tag{1}$$

with $f_{LN}(x)$ defined as

$$f_{LN}(x) = \frac{1}{(2\pi)^{\frac{1}{2}}\ln\sigma}\exp\left\{-\frac{1}{2}\left[\frac{\ln(x/\bar{x})}{\ln\sigma}\right]^2\right\}. \tag{2}$$

Here x denotes the diameter of a spherical or half-spherical particle, $\bar{x}$ is the statistical median for the diameters, and σ has the meaning of standard deviation. This model for particle growth has accounted satisfactorily for the observed size distributions of particles produced by inert gas evaporation (*8*) or by island growth in discontinuous noble metal deposits (*6, 7*) under experimental conditions such that coalescence was the dominant growth mechanism. Earlier theoretical treatments of coalescence growth of particles (*9*) have been based on rate equations for particle densities, which may be the appropriate approach to treat the detailed kinetics but which lack the conceptual simplicity of the present model.

Ostwald Ripening has been studied theoretically recently by Wynblatt and Gjostein (*10*) who improved an earlier treatment by Chakraverty (*11*). Time-independent size distributions were derived for growth limited by surface diffusion or by an interface reaction. The shapes of both the distributions are depicted in the inset in Fig. 1. One notices two characteristic features: the peaked curves have a

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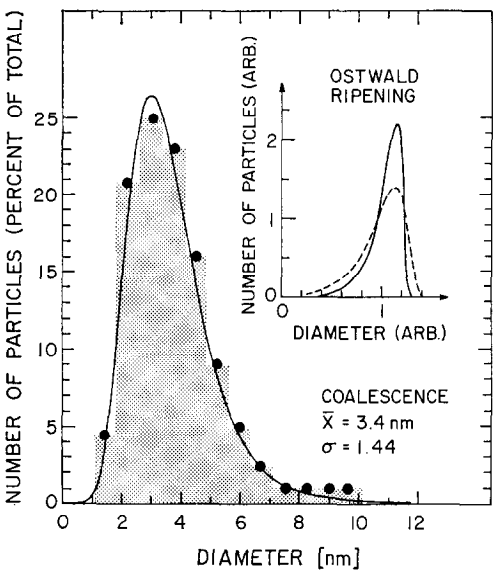

FIG. 1. The shaded region denotes a size histogram for Pt particles dispersed on chemically inactive charcoal as reproduced from Fig. 3b of Ref. (*5*). The mid-interval points are indicated by heavy dots. The fitted curve represents a log-normal size distribution obtained from Eqs. (1) and (2) with the shown values of $\bar{x}$ and σ. The inset depicts theoretical size distributions for particles growing by Ostwald Ripening as derived in Ref. (*10*). The solid-line curve denotes growth limited by surface diffusion, and the broken-line curve refers to interface reaction control.

substantial tail on the small-diameter side, and the distribution is identically zero above a certain finite diameter. None of these salient features is predicted by the log-normal distribution function for coalescence growth [Eqs. (1) and (2)] which gives a tail on the large-diameter side where the distribution approaches zero asymptotically.

Having established these important differences for growth by Ostwald Ripening or by coalescence we turn to the experimental size distributions of Ref. (*1*)–(*5*) and (*12*). For none of the published distributions is there any unambiguous tail at the small-diameter side or any sharp cut-off closely above the peak in the distribution! Instead a typical size histogram, as reproduced in the main part of Fig. 1, agrees very well with the log-normal distribution if $\bar{x}$ and σ are used as fitting parameters. This is equally true for almost all the published data on supported metal catalysts, albeit it should be pointed out that many of the size histograms are coarser than the one in Fig. 1. *The good correspondence with the log-normal distribution and the qualitative disagreement with the single-atom transport theories are strong evidence that particle growth for these cases is predominantly by liquid-like coalescence.* Of course, published size histograms for supported catalysts are relatively few in number and, until more extensive data are reported, it will remain somewhat unresolved whether coalescence is, in general, the predominant growth mechanism for supported catalysts.

As a secondary point, it is interesting to compare the widths of the size distributions (as given by σ) for the catalytic particles which were prepared by growth on an inert backing with those for particles grown under different experimental conditions. Excepting Ref. (*3*), we find that

$$\sigma = 1.32 \pm 0.12$$

for the catalysts, which compares well with discontinuous films of Cu, Ag, and Au where we found (*6*, *7*) $\sigma = 1.28 \pm 0.06$, when the growth was coalescence dominated. For particles which nucleate and grow in a noble gas atmosphere we obtained consistently (*7*, *8*) $\sigma = 1.48 \pm 0.12$, i.e., considerably wider distributions than for particles growing on a substrate. The result for the catalysts augments our earlier empirical finding (*7*) that the distribution width is a function of the kind of technique used to prepare the particles rather than the detailed conditions for particle coarsening within each specific method.

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