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# Reply to "Comments on the Sintering Mechanism of Supported Metal Catalysts"

The predominant mechanism by which a metal particle grows in a catalyst is a longstanding problem. In particular, two principally differing models have been discussed:

Coarsening by *single atom migration* between separate islands (usually phrased Ostwald ripening), and
Coarsening by collision of islands accompanied by their *coalescence.*

Theoretical analyses indicate that the particle size distributions resulting from these two models should be sufficiently different to permit a reasonably conclusive check of the growth mechanism. In our previous Letter (*1*) we scrutinized a number of published size distributions and advocated the view that, at least for many of the studied catalysts, coalescence growth provided the most plausible explanation. This conclusion was objected in the Comment to our work by Wanke (*2*) who argued that the available data should instead be taken as evidence for growth via single atom migration. We find his arguments far from convincing. In this Reply to Wanke's paper, we first discuss different theoretical models for Ostwald ripening and point out that the approach by Flynn and Wanke (*3*, *4*) contains several poorly known, and hence adjustable, parameters which make comparisons with any existing experimental results questionable. Furthermore, we do not find that the fit between theory and experiments, as given by Wanke (*2*), points clearly at the likelihood of Ostwald ripening over coalescence growth. Finally, we provide a new comparison between experimental results and the log-normal distribution function, which we found (*1*) to be the expected size distribution for particles growing by coalescence, which further augments our earlier conclusion that the catalyst particles generally grow by coalescence.

The phenomenon of Ostwald ripening was investigated extensively by Lifshitz and Slyozov (*5*) and by Wagner (*6*) who applied a hydrodynamic approach to describe particles growing in contact with a saturated solution. Chakraverty (*7*) extended their theory to particles growing on a planar surface and his formulation has been further developed and emended recently by Wynblatt and Gjostein (*8*). A common feature of these theories, which also constitutes their main virtue, is the derivation of time independent size distributions of well-defined shapes for growth governed by "surface diffusion control" or by "interface reaction control" [cf. Ref. (*8*) for the precise meanings of these expressions]. Irrespective of the rate determining mechanism, the size distributions were found to exhibit a unimodel curve with a tail towards the small diameter side and a cutoff, beyond which the distribution was identically zero, closely above the peak. An alternative and less elaborate model for the size distributions and their time evolution was formulated by Flynn and Wanke (*3*, *4*). Their most important relation is Eq. (1) of Ref. (*2*) for the time dependence of $N_i$ [notation as in Ref. (*2*)]. The expression contains two adjustable parameters, $A$ and $E$, and effective diameters $D_i$, whose

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definition includes some arbitrariness [cf. Eq. (9) of Ref. (*4*)]. Even more important is that the time evolution of the size distribution can be predicted only provided a starting distribution for an "unsintered" catalyst is given. As pointed out by Wanke (*2*) this implies that the $N_i$'s are a strong function of the initial size distribution. If this is confined to very small particles only, it cannot be regarded as accurately known and the whole approach by Flynn and Wanke (*3*, *4*) becomes unsatisfactory. An estimate of the limiting diameter at which the size determination becomes increasingly subject to error was given by Flynn *et al.* (*9*) who concluded that below 2.5 nm the particle detectability and apparent size were sensitive functions of the elevation of the particles within the catalyst due to defocusing effects. Furthermore, difficulties in preparing the catalysts for electron microscopy may affect the observed sizes (*10*) in particular for very small particles.

For coalescence growth we recently (*11*, *12*) formulated a simple statistical theory. From the two starting assumptions that only binary collisions are important and that the change of particle volume at each step in the growth sequence is a random fraction of the volume after coalescence we showed that the asymptotic size distribution should be log-normal [as defined in Eqs. (1) and (2) of Ref. (1)]. The entire distribution can hence be characterized in terms of a median diameter $\bar{x}$ and a geometric standard deviation $\sigma$. Provided the particles have undergone many coalescence events during the catalyst preparation, the log-normal distribution function (LNDF) should be obeyed for the initial distribution as well as after sintering. The main virtue of our approach is the prediction of a well-characterized size distribution; the main disadvantage is the simpleminded derivation which precludes treatment of the detailed kinetics. The LNDF yields a skew bell-shaped curve with a tail towards the large diameter side where the distribution goes asymptotically towards zero. This shape is in clear contradistinction with the predictions for Ostwald ripening from the theories by Chakraverty (*7*) and by Wynblatt and Gjostein (*8*), whereas the model by Flynn and Wanke (*3*, *4*) may predict features approaching those for the LNDF provided a suitable choice of their free parameters $A$ and $E$ and the initial distribution is made.

With the above discussion and comparison of growth via single atom migration and coalescence as a background, we now turn to the published size distributions for catalysts in order to elucidate whether coalescence provides the best explanation of the data, as argued in our previous Letter (*1*), or if Ostwald ripening gives a more appropriate description. Wanke (*2*) compared the experimental data by Bett *et al.* (*13*) Nakamura *et al.* (*14*) and Wilson and Hall (*15*) with the theory of Refs. (*3*) and (*4*) and, based on the approximate agreement for *two* size distributions, concluded that growth by single atom transport was strongly supported. None of the above experimental results can be reconciled with the theories of Refs. (*7*) and (*8*), which both pertain to Ostwald ripening. The results due to Bett *et al.* (*13*) were given in the form of one coarse histogram consisting of five staples covering the size range 3–10 nm. By adjusting the free parameter (which contains $A$ and $E$ as comparison is made at one temperature only) the predicted data agreed reasonably with the experimental ones. However, if the same data are instead compared with an LNDF we find an equally good agreement using $\bar{x} = 5.5$ nm and $\sigma = 1.32$. For an LNDF applied to the initial distribution for the catalyst studied by Bett *et al.* we get $x = 3$ nm and $\sigma = 1.4$. The data for a sintered catalyst given by Nakamura *et al.* (*14*) is shown as a histogram with eight staples in the interval 2 to 8 nm. By the results of Ref. (*9*) the staple for the smallest diameters should be regarded as uncertain. Again by fitting one parameter Wanke (*2*) arrived at a reasonable, though far from perfect, correspondence among theory and experiments. His fit to this set of data appears to be slightly better than what can be obtained by use of an LNDF. For Nakamura's size distributions pertaining to fresh catalysts, we find consistently an excellent agreement with LNDF's, although it should be kept in mind that some of the five distributions in their Figs. 2 and 3 are given in fairly coarse histograms. Wanke (*2*) also tried to fit the experimental data by Wilson and Hall (*15*) to his theory but discovered that "unfortunately" a unique set of *A* and *E* parameters did not give agreement as they should. As a solution Wanke offered several purely *ad hoc* explanations why this result might still be in accord with the theory of Refs. (*3*) and (*4*). The results for the sintered catalysts studied in Ref. (*15*), however, agree reasonably with the LNDF. The correspondence might be partly fortuitous, though, as the median diameters for the samples fall below 1.5 nm. In our previous Letter (*1*) we also found acceptable agreement between the LNDF and the experimental size distribution for initial and sintered catalysts in Refs. (*16–18*), which further supports our opinion that particle growth occurs predominantly by coalescence.

Wanke stated (*2*) that there are several examples in the literature (*16*, *19*, *20*) of size distributions which are not log-normal but rather bimodal or multimodal. This was taken as evidence for the inapplicability of coalescence growth; actually, such complex distributions—if observed unambiguously—cannot be reconciled with any presently existing theory. The claim that the size distribution of Pope *et al.* (*16*) is bimodal stems, we believe, from a close examination of the histogram in their Fig. 4b from which it is seen that the staple corresponding to sizes around 7 nm is somewhat lower than the ones for 6 and 8 nm. Whether or not this is a true effect rather than an artifact of the limited statistics for the sampling cannot be judged but, regarding the obvious difficulty to obtain size distributions which are accurate in minute detail, we would tend to disregard this tiny effect, and in our previous work (*1*) we fitted an LNDF to the distribution whose mode lies around 2 nm. Concerning the assertedly (*2*) multimodel distributions of Renouprez *et al.* (*19*), which were obtained by small angle X-ray scattering as well as by electron microscopy, we first quote directly from their conclusion: "The present work has shown that, for the most diluted catalyst . . . the distribution curves merely present one sharp maximum. . . . However, when the metal dispersion is less good, the distribution curves obtained by X-rays remains a satisfying representation of the reality, while the values obtained by electron microscopy are less reproducible." A glance at the X-ray data for their catalysts containing 2 and 3.7% Pt [Figs. 6–8 of Ref. (*19*)] shows one prominent maximum at a diameter of approximately 1.5 nm and, possibly, a second and much smaller peak at about 4 nm. It is by no means obvious that the second maximum represents a true effect. For no curve do we find the multimodal distributions alluded to by Wanke (*2*). For the third set of data, reproduced in a 15-year-old conference report by Planck *et al.* (*20*), we content ourselves with noticing that these results were obtained at a time when electron microscopy was an appreciably less well-developed and reliable technique than it is today. Hence, we find neither of Refs. (*16*), (*19*), and (*20*) to display unambiguous evidence for bimodal or multimodal size distributions and therefore they do not give strong evidence against the applicability of our model for growth via particle coalescence.

To conclude our discussion it is convenient to divide the studied samples into freshly prepared and sintered ones. For the *fresh catalysts* there is undoubtedly ample evidence that accurately determined size distributions agree nicely with the LNDF. One example of such a good fit was given in Fig. 1 of Ref. (*1*) where we used the data by Nakamura *et al.* (*14*). An even better example, which was not available to us when our previous article (*1*) was written, is provided by Bond (*21*) who depicts a detailed (14 diameter intervals over the range 3–30 nm) size histogram for a Pd–Au alloy catalyst with good statistical significance (439 particles evaluated). His data are reproduced in Fig. 1 where they are compared with an LNDF; the correspondence between theory and experiments is found to be virtually perfect if the shown values of $\bar{x}$ and $\sigma$ are used! The very accurate agreement, which hence is found in several cases, can hardly be coincidental but from our simple theory in Refs. (*11*) and (*12*) it must be regarded as a very strong evidence in favor of coalescence growth. For *sintered catalysts* the experimental situation is somewhat less clear-cut due to the very limited number of sufficiently accurate size distributions in the literature. As discussed above, we find consistently that an LNDF yields better agreement with experiments than do the theories for Ostwald ripening due to Chakraverty (*7*) and Wynblatt and Gjostein (*8*). Comparisons with the less elaborate model of Flynn and Wanke (*3, 4*) does not, to our mind, show that their theoretically predicted size distributions give a better fit than our LNDF. Consequently, we maintain our general conclusion from Ref. (*1*) that *the accumulated evidence points almost unequivocally in favor of coalescence growth* as distinct from single atom migration.

Finally, we would like to remark that there is still a serious lack of detailed and statistically significant size distributions, which adds a certain amount of uncertainty to any argument based on such. It is our hope that the discussion started by Wanke (*2*) will stimulate the needed accurate electron microscopy work.

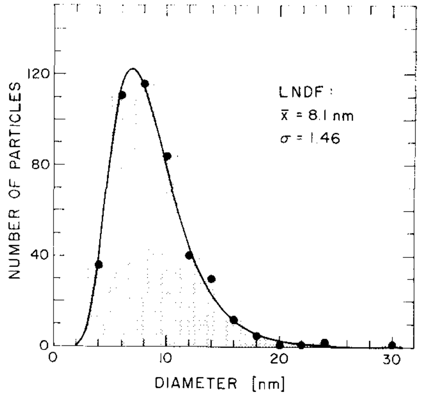

FIG. 1. The shaded region denotes a size histogram reproduced from Fig. 4.10 of Ref. (*21*); (●) the staple midpoints. The fitted curve represents an LNDF characterized by the shown values of $\bar{x}$ and $\sigma$. To ensure the correct normalization we have plotted $(\Delta x/s) \sum_i n_i f_{\mathrm{LN}}(x)$ versus $x$, where $\Delta x$ is the constant staple width in the histogram, $\sum_i n_i$ is the total number of particles in the evaluation and the function $f_{\mathrm{LN}}$ is defined by Eq. (2) of Ref. (*1*).

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