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# On the Determination of Particle Size Distributions in Supported Metal Catalysts

One basic problem in heterogeneous catalysis is the determination of the degree of metal dispersion in supported catalysts. From the knowledge of this parameter, information on the surface structure of the metal can be obtained and kinetic parameters can be calculated (*1, 2*). The structure of the metal surface is strongly modified by changes in the size of the metal crystallites. This is more dramatic in the size range under 40 Å, where there is an abrupt change of the mean coordination number of the atoms on the particles (*3–5*). For the primary demanding reactions (*6–8*), variations on the surface structure of the particles modify the activity and selectivity; this results in a dependence on the particle size and in general on the mode of preparation (*7*). It is then important to determine with good accuracy the mean diameter and the size distribution of the metal particles. A common practice consists in measuring the mean diameter and determining the size distributions by chemisorption and electron microscopy simultaneously (*10*). There are some examples in the literature in which correlations between the two techniques have been reported (*9–11*). The electron microscopy characterizations are normally made using standard bright-field images, i.e., images formed using the nondiffracted electrons. It is the purpose of this note to report that this type of image could be rather insensitive to the presence of very thin particles and important errors might result in the particle size determinations.

Let us consider a metal particle supported on a locally crystalline substrate such as Pt on $\gamma$-$Al_2O_3$ or graphite. The visibility of the particle in a transmission electron microscopy image will depend strongly on the orientation of both the particle and the substrate with respect to the incoming electron beam. Calculations

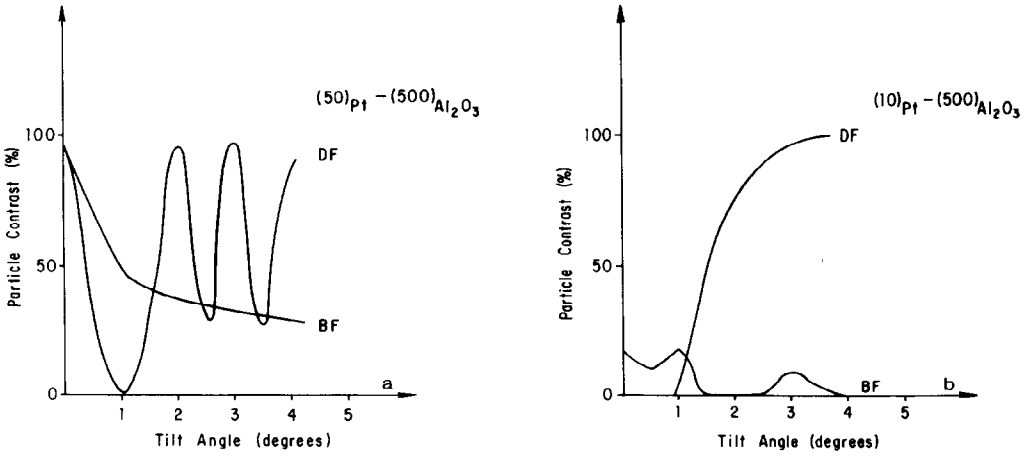


FIG. 1. Dynamical diffraction calculation of the contrast of platinum particles supported on $\gamma$-$Al_2O_3$. (a) The case of a 50-Å-thick particle on a 500-Å-thick $\gamma$-$Al_2O_3$ substrate; (b) the case of a 10-Å-thick particle on a 500-Å-thick $\gamma$-$Al_2O_3$ substrate.



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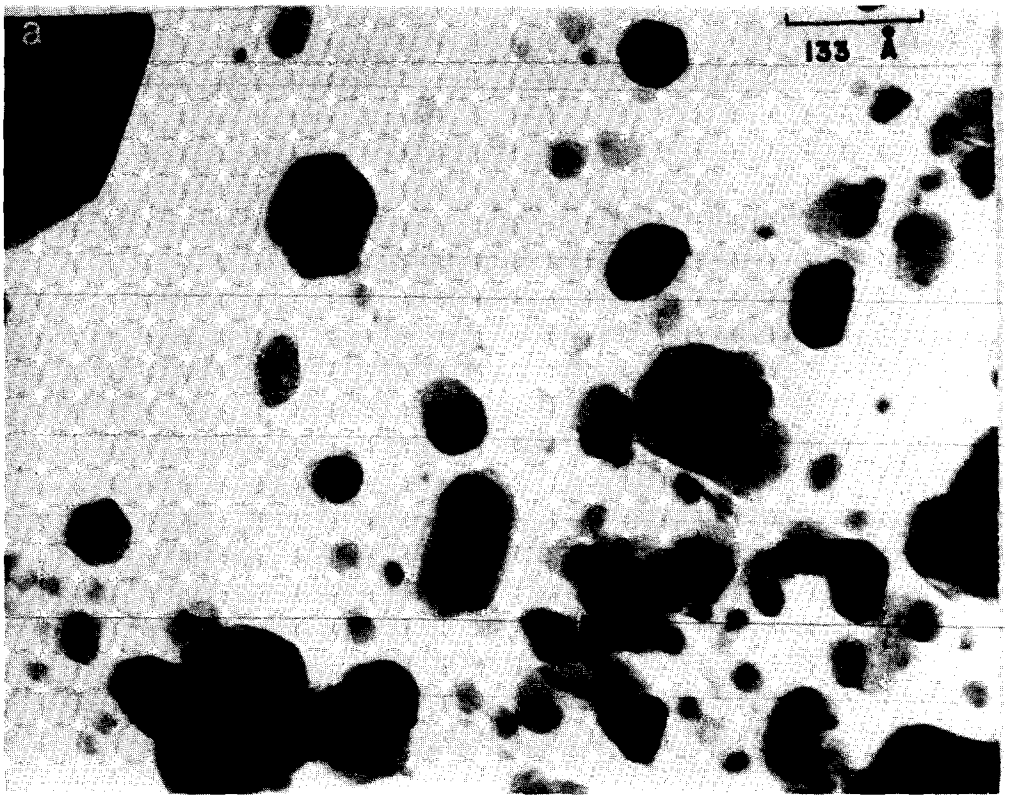
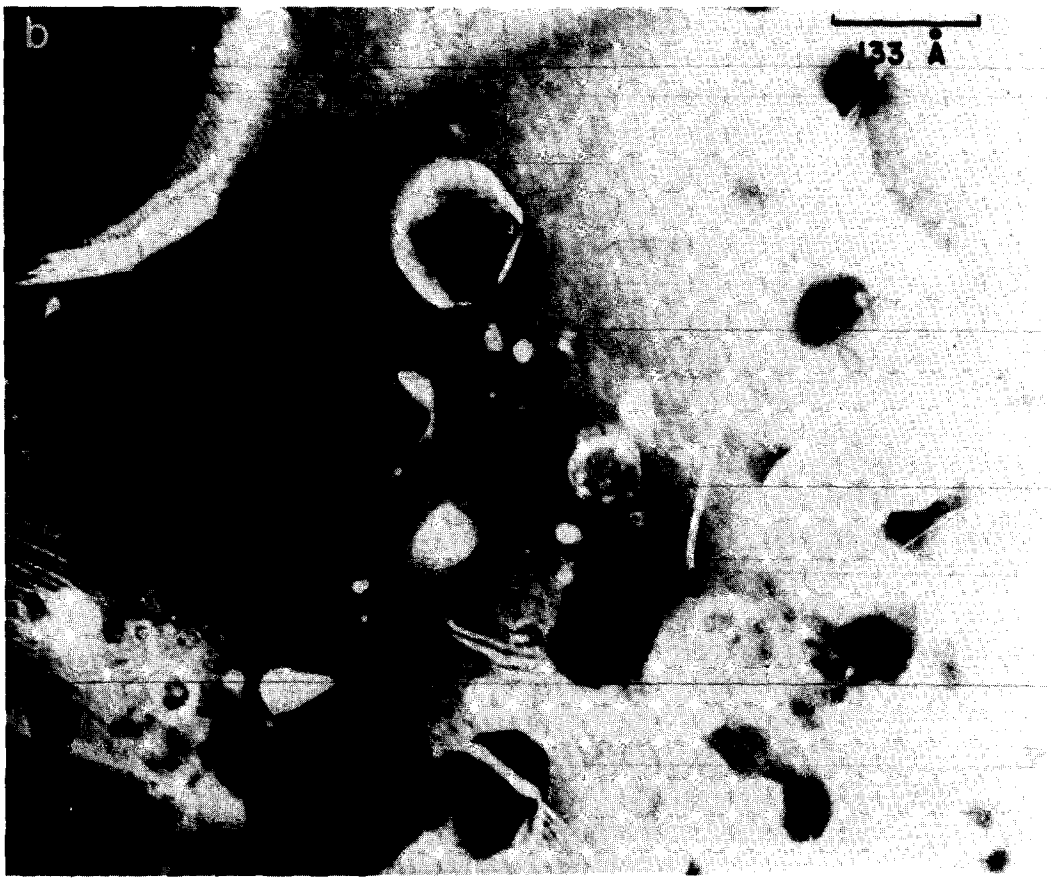

a
133 Å


b
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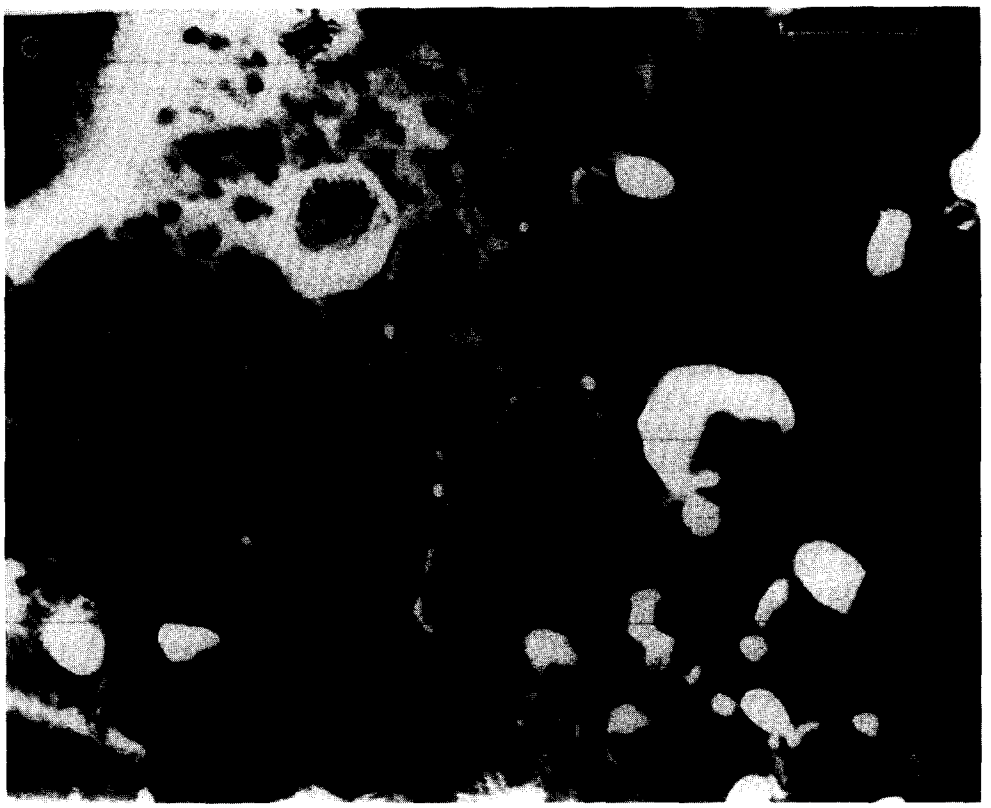

FIG. 2. Images of Pt supported on graphite. (a) Conventional bright field; (b) strong (220) Pt spot used to produce the dark-field image; (c) weak-beam image using the same (220) spot but now with the sample titled 1.5° away from the Bragg's angle. Note the particles that come into contrast in the weak-beam image.

of the particle contrast for the $Pt/\gamma$-$Al_2O_3$ system using the dynamical theory of electron diffraction for bicrystals developed by Gómez, Romeu, and Yacamán (*12*) are shown in Figs. 1a and b. In these figures the contrast of the particle was plotted with respect to the substrate (background) for dark-field and bright-field images. Particle thicknesses of 50 and 10 Å with substrate thickness of 500 Å were considered. The particle visibility was expressed as the percentage of contrast with respect to the background (zero will correspond to complete particle invisibility). The ordinate axis in the graphs represents the angle of deviation of the normal to the particle with respect to the incoming electron beam. An angle of half degree is close to the Bragg condition for Pt. As Fig. 1a shows, thicker particles are always visible in a bright field but their contrast is reduced with increasing deviation from the Bragg angle. On the other hand, the dark-field image has an oscillatory character and particles will not be visible in all the orientations. For 10-Å-thin particles the bright-field image always has a very low contrast and the particles will be almost invisible. The behavior of the dark-field image is quite different. When the deviation angle is less than 1°, the particles have no contrast. However, when the sample is tilted away 1°, the contrast becomes optimum. The intensity of the image is very low and this condition and long exposure times are required for optimum observation of extremely thin particles. During the experiment a tilting of the beam or the sample will be required to set this type of image.

The calculations were extended for Pt in other substrates such as graphite, $SiO_2$, and MgO. The results indicate that the type of behavior shown in Fig. 1 is maintained for those systems. The results can then be considered more general in nature.

Experimental examples of this contrast behavior are shown for a sample of Pt on graphite prepared by the methods described in an earlier publication (*13*). Figure 2 shows different types of images corresponding to the same sample region. Figure 2a corresponds to a conventional bright field; Fig. 2b is a dark-field image obtained by using a (220) Pt spot; and Fig. 2c is a weak-beam image formed by using the same metal spot. This last image was obtained following the techniques described by Yacamán (*14*). As is clear from Fig. 2, a large number of particles that were not visible in either the bright-field or the conventional dark-field images, become visible in the weak-beam image.

It is clear that if size distributions are obtained by using the conventional bright field, they will not always represent the true distribution of particle sizes, since the smallest particles could be out of contrast. In a real sample there are always variations in the local roughness and orientation of the support. This will lead to the result that many of the particles will not be visible unless a tilt is made. Further, the thinnest particles will be ignored in the standard analysis by TEM. It is well known that those particles might be the most active ones in some catalytic reactions (*15*). We do not wish to suggest that the correlations between electron microscopy and chemisorption methods reported in the literature are without merit, but we would like to point out that the lack of agreement frequently obtained might be the result of the use of bright-field electron microscopy techniques.

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M. JOSÉ YACAMÁN

*Instituto de Física, UNAM*
*Apartado Postal 20-364*
*Mexico City, Federal District 20, Mexico*

J. M. DOMÍNGUEZ

*Instituto Mexicano del Petróleo, IBP*
*Ave. de los Cien Metros 152*
*Mexico City, Federal District 14, Mexico*


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