The Relation between Dispersion and Particle Size on Supported Catalysts

The relation between catalyst dispersion and particle size is determined using computer calculations taking into account the particle roughness observed in weak beam thickness fringes. It is shown that a complex relationship exists between these parameters. Therefore the use of simple formulae to correlate chemisorption measurements with electron microscopy is questioned.

In the characterization of the state of dispersion (ϕ) of a catalyst chemisorption and electron microscopy are routinely used. In chemisorption measurements the amount of chemisorbed gas is determined and then the particle size (d) is calculated through a relation such as (1)

$$\phi = \frac{5 \times 10^{10} \, \rho_s W m}{N_a \rho_m d},\qquad (1)$$

where N_a is Avogadro's number, ρ_m and Wm are the atomic density and the molecular weight of the metal, respectively, ρ_s is the surface sites density, which is considered constant, and d is the diameter of the particle.

Equation (1) implies some simple assumptions on the particle shape (normally assumed to be spherical or cubical). When electron microscopy measurements of particle size yield the same average value then the stoichiometry assumed for the chemisorption is considered correct. However, disagreements between chemisorption and electron microscopy are commonly found in these type of measurements.

The purpose of this note is report that a very complex relation exists between dispersion and particle size and that simple formulas such as (1) cannot be used.

It has been reported that particles on Pt/ graphite have defined shapes such as cuboctahedra in various orientations (2, 3). This was determined using weak beam thickness fringes (4). However, further work using higher resolution has shown that the fringes are not straight, indicating a roughening of the surface of the cuboctahedral particles (5). The surface of the particle contains steps and complex arrays of atoms. This effect is due to the fact that the particles have in most cases an incomplete shell for the cubooctahedron structure. This is in turn a result of the rapid growth of the catalyst particles which prevents them from reaching equilibrium.

Calculations to study the structure of the particles surface using computer simulation have been carried out. The growth of a particle was simulated assuming that the arriving atoms will occupy positions on the surface corresponding to a minimum in the
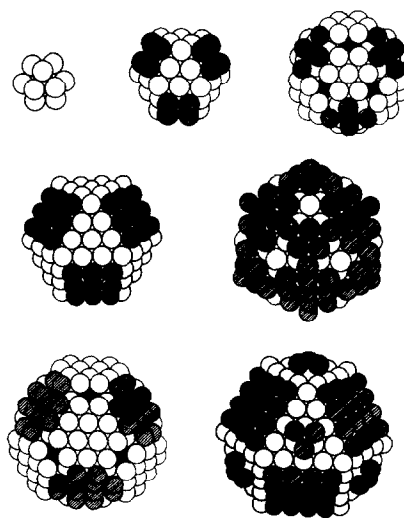

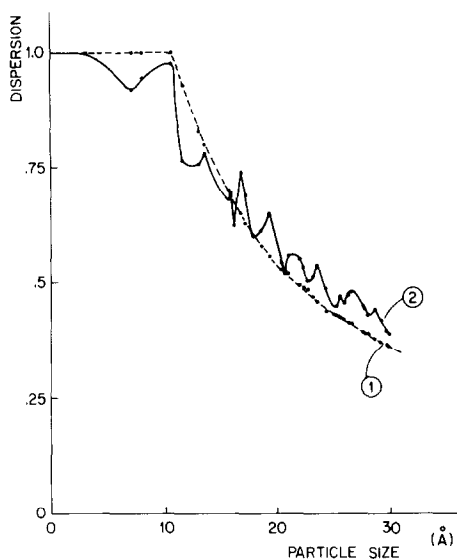Fig. 1. Typical sequence of the structure of a cuboctahedral particle.

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FIG. 2. Plot of the dispersion versus the particle size. (1) Dispersion is obtained with Eq. (1). (2) Dispersion calculated as N_s/N_T.

bonding energy. Those calculations have been described at length in another publication (5).

Figure 1 shows a typical sequence of the structure of the particle for a cuboctahedron of different sizes. The computer-calculated shapes showed excellent agreement with the thickness fringe profiles.

The dispersion of the particle can be calculated as the ratio of the surface atoms to total number of atoms in the particle. Figure 2 shows a plot of the dispersion so obtained versus the particle size for the case of Pt. The particle size was taken as the average radius of a sphere that circumscribes the particle. As can be seen the curve is very complex. For comparison purposes Eq. (1) is plotted in Fig. 2. It is clear that this equation yields a wrong particle size. It is interesting to note that the highest dispersion will be obtained for

about a 13-Å particle size. The more marked disagreement is obtained for sizes below 10 Å. Therefore disagreement between experimental data for particles below 10 Å is not necessarily due to a change in the stoichiometry of the adsorption (6).

More extended calculations are necessary for other particle shapes which are also observed in catalysts such as icosahedrons, platelets, single twinned particles, etc. However, the results are expected to follow the same trend. It is possible to conclude then that when interpreting chemisorption data curves simple geometrical formulas can lead to serious errors.

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