



**METAL CRYSTALLITE SIZE DETERMINATION:
COMPARISON OF CHEMICAL AND PHYSICAL METHODS**

Recent Altamira Notes have discussed the use of several different chemisorption techniques to determine crystallite sizes for supported metal catalysts. These techniques, temperature-programmed desorption, static chemisorption, and pulse chemisorption, can all be described as "chemical" methods because they rely on some way of monitoring the chemisorption or desorption of molecules on metal surfaces. A second general approach to the determination of metal crystallite sizes involves the use of techniques which may be described as "physical" methods. The objective of this Note is to compare the chemical methods described in earlier Notes to several physical methods discussed below.

Physical Methods

Physical methods of crystallite size determination rely not on the adsorptive capacity of supported metal catalysts but instead on phenomena associated with some physical property of the crystallites. Most often an observation is made using some form of energy to probe the sample. Two of the most commonly used physical methods are Transmission Electron Microscopy (TEM) and X-Ray Diffraction Line Broadening (XRD), employing as probes electron and x-ray beams, respectively. Other techniques are used less often due either to their expense (as in the case of Small-Angle X-Ray Diffraction (SAXS)), or because they apply specifically only to some metals (such as the use of Magnetic Measurements for ferromagnetic metals Fe, Ni, and Co).

Electron microscopy involves imaging a catalyst sample by directing a beam of electrons towards it. Metal crystallite sizes and shapes can be observed from the images obtained. Good contrast between the support and the metal crystallites is important. For TEM the electron beam must be transmitted through the sample, and hence techniques have been developed for preparation of very thin or dilute samples. The energy of the beam determines the resolution of the instrument and places a lower limit on the size of the crystallites which may be imaged. Resolution on the order of 2Å is easily achieved, so even samples with extremely small metal crystallites are good candidates for characterization by TEM.

TEM allows calculation of average crystallite size and size distribution through the careful, and often tedious, measurement of thousands of crystallites from numerous micrographs. An exhaustive investigation is the only way to ensure that the calculations are truly representative of the sample. Because crystallite size and shape can vary significantly in heterogeneous catalysts, different types of "average" crystallite size calculations may yield different results. The formulas below show how crystallite sizes are calculated using a) number-average diameter, d_n ; b) surface-average diameter, d_s ; and c) volume-average diameter, d_v :

$$a) \quad d_n = \sum n_i / \sum n_i$$

$$b) \quad d_s = \sum n_i d_i^3 / \sum n_i d_i^2$$

$$c) \quad d_v = \sum n_i d_i^4 / \sum n_i d_i^3$$

X-Ray diffraction is best known as a technique for finding out about the structure and composition of crystallite materials. X-rays diffracted through a crystalline material give diffraction lines for reflecting planes of different d-spacings. However, XRD may also provide information about the size of metal crystallites in powder samples down to about 4 nm, even though these systems lack the long-range order found in larger crystals of metal. A particular diffraction line is broadened as the crystallite size decreases. The average diameter determined by the Scherrer equation (see Klug and Alexander, "X-Ray Diffraction of Amorphous Materials", Wiley, New York, 1974) is a volume-average diameter:

$$d_v = K\lambda / (\beta - \cos \theta)$$

K is a constant related to the crystallite shape. B is the pure x-ray diffraction broadening which takes into account the broadening of the diffraction line due both to the size of the crystallites and to the instrument itself. λ and θ are the wavelength of the x-ray radiation employed and the Bragg angle, the angle between the radiation and the plane of the sample.

There are advantages and disadvantages to using both XRD and TEM. TEM requires high vacuum conditions and therefore sample pretreatment is more complicated. The cost of the electron beam and optics systems is often prohibitive for use as a routine characterization tool. TEM has the advantage of allowing the user to "see" the crystallites and thus make qualitative as well as quantitative assessments of the sample. Information about crystallite shape and heterogeneity, difficult to obtain with most methods, can also be found with TEM. When an exhaustive investigation is completed in which thousands of crystallites are measured; this technique is perhaps the most accurate of all crystallite size determinations.

XRD measures crystallites of 4 nm and greater, which in many important applications gives an unsatisfactory lower limit. The diameter determined from XRD is a volume-average diameter. For a sample with a wide distribution

of crystallite sizes or various crystallite shapes, this average may differ substantially from TEM number or surface averages. XRD is, however, more readily available than TEM and requires no controlled atmosphere.

Comparison of Physical and Chemical Methods

Chemical methods of crystallite size determination do not directly measure metal crystallite sizes, but instead infer a surface-average crystallite size from information about the interactions between adsorbates and surface metal atoms. All of these techniques involving chemisorption incorporate certain assumptions - either explicitly or implicitly - about the adsorbate/surface metal atom bonding stoichiometry as well as about the strength and kinetics of adsorbate/metal bonding. The advantage of using one chemisorption technique over another often depends on the experimental conditions employed and the adsorption properties of the particular catalyst system under investigation.

Because of this reliance on the nature of the interaction between adsorbate and metal surface, these chemical methods require more stringent controlled atmosphere conditions than, for example, XRD. The metal crystallites must be in the reduced metal state if assumptions made about chemisorption stoichiometries are to be valid. Poisoning of metal surface sites or otherwise rendering them inaccessible to adsorbate molecules will produce anomalous chemisorption uptakes and therefore inaccurate crystallite size measurements.

Even with these limitations, chemical methods of determining metal crystallite sizes offer in many cases the most straightforward approach. Experimental systems for performing chemisorption measurements are less expensive and easier to maintain than TEM or XRD. A large number of studies encompassing a wide variety of adsorbate/metal systems is documented in the literature and can be used for comparison with experimental results. For routine characterization of similar catalysts, or for ongoing quality control studies, chemisorption methods can provide easy and accurate metal crystallite determinations.

Each of the methods discussed above and in previous Altamira Notes has advantages and disadvantages in its use for metal crystallite size determinations. The most accurate, if not always viable, approach is to use multiple techniques, preferably combining both physical and chemical, to determine crystallite sizes.

SELECTED REFERENCES

1. "Particle Size, Particle Size Distribution, and Related Measurements of Supported Metal Catalysts," *Catalysis Reviews-Science and Engineering*, 29, 41 (1987).
2. "Metal Particle Size Determination of Supported Metal Catalysts," *Catalysis Reviews-Science and Engineering*, 8, 117 (1973).
3. "Influence of Metal Particle Size in Ni-on-Aerosil Catalysts in Surface Site Distribution, Catalytic Activity, and Selectivity," *Advances in Catalysis*, 22, 22 (1972).