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Particle Size Determination of Supported Catalytic Metals: Platinum on Silica Gel

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The applicability and limitations of the electron microscope, x-ray diffraction, and adsorption techniques for the determination of particle size of supported metals have been explored using platinum on silica gel as an illustration. The results obtained using the three techniques were found to be in reasonable agreement; thus any of the three methods would be suitable for the determination of particle size in this type of catalyst. It is concluded that the surfaces of platinum particles supported on silica gel are accessible for adsorption of hydrogen and that the "crystallite" size of platinum determined from x-ray line broadening is synonymous with "particle" size in this sample.

In the course of a study of supported catalytic metals, we found that a catalyst consisting of platinum supported on silica gel contained extremely small (10 to 40 Å) platinum particles having a rather narrow size distribution. The particle sizes were derived from the results of electron microscope, x-ray diffraction, and adsorption measurements. In the present study these results are used to illustrate the applicability and limitations of the above three techniques in the determination of the particle size of supported metals. Although such measurements have been reported before, (*4, 8, 9, 11, 12*) we will attempt to give a more integrated intercomparison of the three techniques than is elsewhere available. Making such a comparison using the above-mentioned sample of supported platinum was a particular challenge because its particle size range represents a lower limit to what can be "seen" by means of an electron microscope.

EXPERIMENTAL DETAILS

Sample Preparation

The platinum-silica gel catalyst used in the present study was prepared by an impregnation procedure. Enough 0.2 *M* chloroplatinic acid (19 ml) was added to 30 g of silica gel to give roughly 2.5 wt % platinum in the ultimate product. Enough distilled water was added to make a viscous slurry, the slurry was evaporated to near-dryness (with constant stirring) on a hot plate, and the product was dried 16 hr at 120°C. Two grams of the final product was reduced in a stream of hydrogen for 2 hr at 210°C. Portions of this reduced sample were used for electron microscope, x-ray diffraction and adsorption measurements as indicated in the following sections. Subsequent analysis showed that the reduced product contained less than 0.03% chlorine and did indeed contain 2.5 wt % platinum.

The support for the above catalyst is Davison Chemical Company's Grade 70 silica gel. Its aluminum content is 0.02 wt %, its surface area is 370 m^2/g and its pore volume is 0.97 cc/g. The average pore diameter calculated from the latter values is 104 Å.

Electron Microscope Technique

The platinum-silica gel catalyst was examined in the Siemens Elmiskop I at the Exploration and Production Division, Shell Development Company, Houston, Texas, through the courtesy of Dr. H. P. Studer. After a portion of the catalyst was lightly ground in a small mortar, the ground product was dispersed in butyl alcohol by ultrasonic treatment. A drop of this suspension was evaporated on a carbon film. Electron microscope pictures of the resulting specimen were taken at an enlargement of 40,000×. Subsequent photographic enlargement resulted in a total magnification of 200,000×. It is estimated that the probable error of this magnification is 5%.

x-*ray Technique*

Diffraction patterns for two samples of the platinum-silica gel catalyst were obtained with a General Electric XRD-3 x-ray diffractometer. To provide adequate count accumulation for recording the profile of the Pt reflections, the instrument was operated with a scanning speed of 2.4° per hour. Output was through a Tracerlab SC 34 ratemeter equipped with a 100-sec time constant. Patterns were obtained with nickel-filtered copper radiation using a pulse height analyzer set to pass the CuK_α radiation. A 1° beam slit, 0.2° detector slit and medium resolution Soller slit were used.

The two ½-gram samples, ground to pass 300 mesh, were prepared in the form of one-inch disks in an Applied Research Laboratories hydraulic press. This mode of preparation provides a sample of high density and smooth, flat surface and is ideal where preferred orientation of the crystallites is not a problem.

Corrections to the observed line breadths for instrumental broadening were made using the curves given by Klug and Alexander (*6*). The instrumental broadening itself was determined with a silica gel disk containing NaCl of size greater than 1000 Å and therefore effectively infinite with respect to the platinum samples.

Adsorption Technique

The apparatus used for adsorption measurements consisted of a constant volume glass system. Adsorption was determined from measurements of changes in pressure in the system; pressures were measured by means of a McLeod gage (for hydrogen adsorption) and a Bourdon gage manufactured by the Heise Company (for determination of dead space). The catalyst sample cell was connected to the apparatus through a stopcock and could be thermostated at any desirable temperature. A mercury diffusion pump, backed by a mechanical vacuum pump, was also connected to the system through a stopcock, as was a gas inlet train, thereby enabling the catalyst to be pretreated at various temperatures under various atmospheres.

Dead space was determined using helium. The hydrogen used in adsorption measurements was an electrolytic grade supplied by National Cylinder Gas Company. Remaining traces of oxygen had been removed by passage over platinum catalyst.

It was found in preliminary work that evacuating a hydrogen-reduced platinum-silica gel catalyst for 1 hr at 400–500°C was effective in obtaining a clean metal surface and yet resulted in little, if any, loss of metal surface area due to sintering. This pretreatment was adopted as standard for the platinum surface area measurements. In this preliminary work separate samples of a hydrogen-reduced platinum-silica gel catalyst were evacuated for 1 hr at temperatures increasing in 50° intervals from 0° to 900°C. Hydrogen chemisorption was then measured for each sample at 0°C. It was found that chemisorption increased with increasing temperature of evacuation up to 250°C, remained constant up to 800°C, and then decreased at 900°C, due, presumably, to sintering of the platinum or its support.

DATA AND DISCUSSION

Electron Microscope Technique

The greatest appeal of the electron microscope technique in the study of supported catalysts is that the investigator can "see" (under favorable conditions) the metal particles that are the seat of catalytic activity. Thus he can determine the

FIG. 1. 2.5% Pt on silica gel, reduced at 210°C. 150,000×.

distribution of particle sizes, calculate average particle size, and can even determine whether metal particles are randomly distributed or whether they are concentrated in piles or clusters. If the particles are large enough, their shape and crystalline form can also be determined. However, these kinds of observations are valid only if the minute quantity of sample "seen" in an electron microscope picture is truly representative of the original sample under study. The amount of sample examined in an electron microscope is exceedingly small. The observations reported below represent measurements on 10^{-17} g of platinum. The size of samples used in the adsorption or x-ray diffraction techniques described in this report is at least 10^{15} times this value. It is, therefore, extremely important that electron microscope pictures of several samples be taken. The reproducibility among pictures can then be used to gauge whether or not these samples are truly representative of the bulk material.

One of the electron microscope pictures of the sample under study is shown in Fig. 1. The small, black platinum particles are easily distinguished from the large, grey silica particles. It is apparent that much of the platinum has been dislodged from the silica support by the ultrasonic treatment. This is not always the case; a similar treatment of platinum supported on alumina does not dislodge the particles of platinum. Particle size measurements of platinum were made by use of lantern slide plates on which had been photographed a series of circles that increased regularly in diameter. The plate is placed on the photographic print and the circle found that most closely matches the size of the particle to be measured. This method is superior to that of using a linear scale in that a particle diameter averaged over several directions is easily and quickly obtained.

The results of measuring the diameters of 942 platinum particles in this sample of platinum on silica gel are shown in Table 1 and Fig. 2. Each diameter listed in Table 1 represents the midpoint of a 5 Å increment in particle diameter. Though these increments are very small, a series of careful intercomparisons of particle images

TABLE 1
SIZE DISTRIBUTION OF PLATINUM PARTICLES

Particle diameter (Å)	Number of particles	Percentage of particles
15	10	1.1
20	111	11.8
25	309	32.8
30	300	31.8
35	171	18.2
40	32	3.4
45	9	1.0

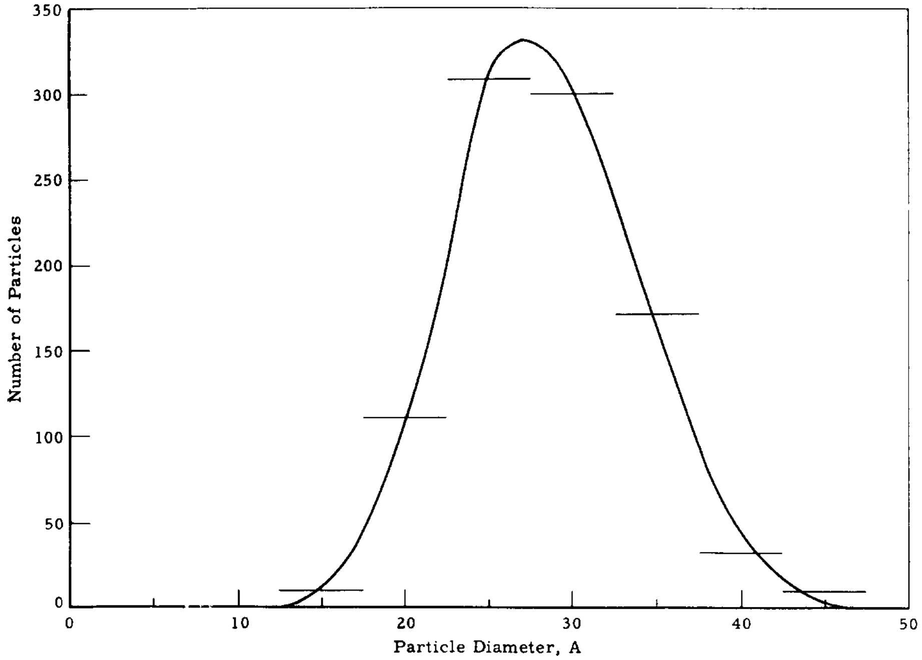

FIG. 2. Size distribution of platinum particles.

indicated that we could readily distinguish between particle sizes that differed by only 5 Å. This result demonstrates the high resolving power of the Siemens microscope.

Denoting the particle diameter by d_i and the number of particles in each diameter increment by n_i, the number average diameter for the above size distribution is given by

$$d_n = \frac{\Sigma n_i d_i}{\Sigma n_i} = 28.5\text{A}$$

the surface average diameter by

$$d_s = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} = 30.5\text{Å}$$

and the volume average diameter by

$$d_v = \frac{\Sigma n_i d_i^4}{\Sigma n_i d_i^3} = 31.5\text{Å}$$

The probable error of the above values is about 10%. The error is estimated to be this large because measurement of particle diameter varied to this extent among eight observers.

x-*ray Diffraction Technique*

The determination of particle size by means of the x-ray diffraction technique is based on the fact that the breadth of x-ray reflections, apart from an instrumental contribution, is inversely related to the dimensions of the crystals giving rise to these reflections. Thus this method of size determination entails the measurement of the breadth of one or more x-ray reflections. In the case of a supported metal it is therefore a minimum requirement that the metal reflection be intense enough to give a signal measurable above the background contributed by the support. The platinum on silica gel sample under study is an ideal system from this standpoint. Since the intensity of x-ray reflections is approximately proportional to the square of atomic number, platinum produces strong lines that are easily detectable above the relatively low background contributed by silica, even at a platinum content as low as 0.5 wt. %. Moreover, since silica gel is amorphous, it does not give rise to a diffraction pattern that could obscure reflections from platinum crystals.

It should be emphasized that line breadth is used to measure "crystallite" rather than "particle" size. Ordinarily, and especially for very small particles as is the case in the present study, these two terms are synonymous. Occasionally, however, particles are found to be aggregates of crystallites. In such cases "crystallite" size can be considerably smaller than "particle" size.

For crystallites of nonequal dimensions, such as needles or laths, measurements of line broadening can be used to determine crystallite shape as well. This is done by evaluating separate dimensions from breadths of lines that arise from different crystal planes. Extending this principle even further, it is possible under the most favorable circumstances to distinguish between spheres and simple polyhedra such as tetrahedra, cubes or octahedra. In any of these cases the size obtained is a volume weighted dimension which will therefore be somewhat larger than the surface average or number average dimension referred to in the previous section.

Theory

The crystallite size, δ, calculated from x-ray line broadening is determined from the formula (*6*)

$$\delta = \frac{k\lambda}{\beta \cos \theta}$$

In this equation λ is the x-ray wave length, θ is the Bragg angle, and β is the line breadth (in radians) after correction for instrumental broadening. The shape factor, k, is approximately unity; its exact value depends on the way β is measured (see below), the definition of δ, the shape of the crystallites, and on the particular reflection being measured.

The most satisfactory measure of β from a theoretical viewpoint is the integral breadth, β_a, defined as the integrated intensity divided by the maximum intensity. The crystallite size calculated with β_a has been shown (*7*) to be $\delta_a = (1/V)\int V_t dt$, the volume weighted thickness of the crystallite in a direction normal to the reflecting plane considered. In this case k is exactly unity. The integral involved in this expression for δ_a has been evaluated (*13*) for a number of common crystal forms, the usual practice being to consider δ_a as the cube root of the volume of the crystallite and to regard the numerical factor arising in the integration as part of the shape factor, k. Fortunately, the values of k thus derived still do not differ greatly from unity so that a good approximation to crystallite size is possible even though knowledge of the exact crystal shape is lacking.

The alternative measure of β is the breadth at half the maximum intensity, $\beta_{1/2}$, hereafter called "half-breadth." Values of the shape factor can be computed from theoretical profiles, when available, (*7*) for use with $\beta_{1/2}$. Although half-breadth measurements do not yield to the simple theoretical interpretation given for integral breadths, they are usually easier to obtain and often provide the more accurate size determination.

The definition of δ_a or $\delta_{1/2}$ as the cube root of the volume implies an isodimensional model. For a size distribution of such particles the x-ray measurements yield a volume weighted average given by

$$\delta = \frac{\Sigma n_i \delta_i^4}{\Sigma n_i \delta_i^3}$$

where there are n_i crystallites of volume δ_i^3.

Results: x-ray Technique

In Table 2 are given the integral breadth, β_a, and the half-breadth, $\beta_{1/2}$ corrected for instrumental broadening. Since platinum has a cubic close packed structure, the crystallites can be assumed to occur as regular polyhedra. Electron micrographs of larger platinum crystallites often reveal hexagonal outlines indicative of a cubic or octahedral form. Included in Table 2 are crystallite sizes calculated for cubes and spheres using reflections from the 111,200, and 200 planes.

TABLE 2
CRYSTALLITE SIZES FROM X-RAY LINE BROADENING

Reflection *hkl*	β_a	$\bar{\delta}_a$ in Å		$\beta_{1/2}$	$\bar{\delta}_{1/2}$ in Å	
		Sphere	Cube		Sphere	Cube
111	.0426	41.5	44.6	.0375	39.2	37.5
	.0441	39.8	42.9	.0382	38.4	36.7
200	.0463	38.9	36.2	.0389	38.6	38.2
	.0517	34.7	32.3	.0475	31.6	31.2
220	.0564	35.3	34.9	.0484	34.3	32.0
Average $\bar{\delta}$	—	38.8	39.9	—	37.2	35.8

It may be concluded from the results of Table 2 that the sizes calculated are insensitive within experimental error to choice of crystallite form or to type of line breadth measurement used. The volume average crystallite size is therefore taken as the over-all average of $\bar{\delta} = 37.9$ Å. For comparison with other sections of this report it is desirable to convert $\bar{\delta}$, which is the cube root of crystallite volume, to a diameter, d, previously defined. For spherical crystallites the volume average diameter is given by

$$\bar{d}_v = (6/\Pi)^{1/3}\bar{\delta} = 1.24\bar{\delta} = 47.0\text{Å}$$

For cubic crystals we obtain simply

$$\bar{d}_v = \bar{\delta} = 37.9\text{Å}$$

Adsorption Technique

The adsorption technique for the determination of metal particle size is based on the phenomenon that over an appropriate temperature range certain gases such as ethylene, carbon monoxide, oxygen, and hydrogen form a chemisorbed monolayer on the surface of transition metals. The surface area of such metals in supported catalysts can be determined from chemisorption measurements provided that a set of conditions can be realized wherein the chemisorbed gas does indeed form a complete monolayer on the metal surface, where adsorption on the support can be corrected for or is negligible, and where the area covered by a molecule of gas chemisorbed on the metal is known. This type of surface area determination entails a pretreatment sufficiently severe to free the surface of preadsorbed material and yet not so severe as to cause appreciable sintering or reaction with the substrate. The surface area so obtained in combination with the metal content of the supported catalyst can then be used to calculate a surface average particle size. Of course, if an appreciable fraction of the metal surface is inaccessible, the particle size so derived will be larger than the true particle size.

Consideration of the above-mentioned factors makes it evident that a great deal of background information is required before the adsorption technique can be used with confidence for the determination of metal particle size. Fortunately, there was considerable background information available on this subject (*1*, *4*, *8*, *11*, *12*). This information together with the results of earlier studies in this laboratory dictated our choice of hydrogen as the adsorbate.

The adsorption of hydrogen on the platinum-silica gel catalyst under study was measured at −78° and 0°C. The resulting isotherms are shown in Fig. 3. It can be seen that the catalyst becomes saturated with hydrogen at pressures above 0.1 mm Hg, even at 0°C. It is also evident that the amount of hydrogen required to reach saturation decreases with increasing temperature.

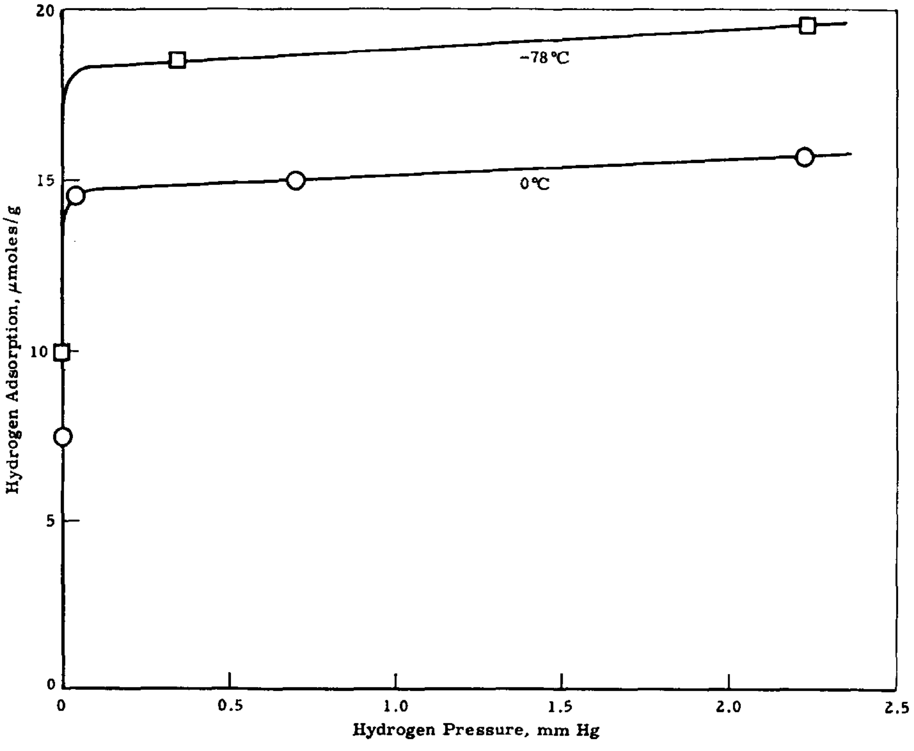

FIG. 3. Hydrogen adsorption by platinum supported on silica gel.

These results can be used to calculate the available platinum surface if the area covered by a chemisorbed hydrogen molecule is known. This area was found to be 22.4 Å^2 from the amount of hydrogen chemisorbed at 0°C by a sample of platinum black of known surface area.* From the above data, the platinum surface calculated for the catalyst under study is 2.04 m^2/g of catalyst. The average particle size of the platinum can be computed from this information in the following manner.

Consider a platinum particle whose volume, surface area, and diameter† are denoted by v, s, and d, respectively. It can easily be verified that

$$d = 6v/s$$

if the particle has the form of a sphere or of a regular polyhedron other than a tetrahedron. For a gram of catalyst that contains N such particles the total platinum volume is given by

$$V = \Sigma v_i$$

the total platinum surface by

$$S = \Sigma s_i$$

and the average particle diameter by

$$\bar{d}_s = 6\Sigma v_i/\Sigma s_i = 6V/S$$

where the subscript i denotes all particles from 1 to N. We denote the average diameter by d_s because it is identical with surface average diameter which, as already mentioned in a previous section, is given by

$$\bar{d}_s = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}$$

By assuming the particle density is that of bulk platinum we obtain

$$V = \frac{\text{Wt \% Pt}}{(21.4\text{g/cm}^3)(100)}$$
$$= 1.17 \times 10^{-3}\ \text{cm}^3\text{/g of catalyst}$$

Substituting the above values for S and V we obtain

$$\bar{d}_s = \frac{6(1.17 \times 10^{-3}\ \text{cm}^3\text{/g})}{2.04\ \text{m}^2\text{/g}} = 34.4\text{Å}$$

CONCLUSIONS

Results obtained using electron microscope, x-ray diffraction and adsorption techniques are summarized in Table 3. As has already been stated, the electron microscope technique yields a particle size distribution from which a number average, surface average, and volume average diameter can be calculated. Since the adsorption technique yields a surface average, and the x-ray technique, a volume average diameter, a direct comparison between these two results is not valid unless all platinum particles have the same size. In the case of the present sample, however, the size distribution is so narrow that the experimental error is larger than the difference between the two types of diameters. We conclude that the agreement among the results of the three techniques is reasonable particularly in view of the fact that the smallest platinum particles

TABLE 3
COMPARISON OF ELECTRON MICROSCOPE, X-RAY, AND ADSORPTION RESULTS

Type of diameter	Average particle diameter (Å)		
	Electron microscope	x-Ray	Adsorption
$\frac{\Sigma n_i d_i}{\Sigma n_i}$	28.5	—	—
$\frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}$	30.5	—	34.4
$\frac{\Sigma n_i d_i^4}{\Sigma n_i d_i^3}$	31.5	37.9[a]	—

[a] Calculated assuming that the crystallites are cubes.

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* Since the hydrogen molecule dissociates and covers two metal atoms upon chemisorption (*1*), a value of 11 Å^2 is obtained for the area occupied by a platinum atom. A comparison of this value with the area per platinum atom in the 100, 110, and 111 crystallographic planes (7.68, 10.85, and 6.65 Å^2, respectively) indicates that the 110 plane predominates in the surface of platinum black.

† Defined as the shortest distance between parallel faces.

can barely be "seen" by means of the electron microscope. Because of this agreement, it is evident that the surfaces of the platinum particles in the platinum-silica gel sample are accessible to hydrogen. It is also evident that "crystallite" size as measured by x-ray line broadening is synonymous with "particle" size in this case.

The applicability and limitations of the three techniques in the determination of particle size can now be summarized. The adsorption technique, in itself, does not furnish any details concerning the form of the supported metal. Its chief advantage is the relative ease and simplicity of the experimental measurement. The x-ray technique, though somewhat more time-consuming, furnishes more information. It can be used to determine, for example, whether the metal is deposited in a layer or whether the metal consists of separate crystallites. The electron microscope is capable of revealing the most information: particle shape, size, and size distribution. However, since the reliable measurement of particle size distribution is extremely tedious and time-consuming, the electron microscope technique is not suitable as a routine tool. Thus the applicability and limitations of each of the three techniques have to be assessed in the light of the individual problem. If the sample of supported metal to be examined represents an entirely new class of materials it would, of course, be worthwhile examining the sample using all three techniques. As more becomes known about such samples, more reliance could then be placed on adsorption measurements which could be checked occasionally by measurements of x-ray line broadening.

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