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The Structure and Activity of Supported Metal Catalysts

II. Crystallite Size and CO Chemisorption on Platinum/Silica Catalysts

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The structure of Pt/silica catalysts containing up to 11.5 wt % Pt was determined from X-ray line-broadening measurement of crystallite size, the proportion of platinum detectable by X-ray diffraction, and electron micrographs of ultramicrotome sections. Crystallite-size data and the proportionality of platinum area to (weight Pt)$^{2/3}$ suggests that a fixed number of crystallites increase in size with Pt content and this number is related to the pore structure of the silica support. The ratio (Pt atoms exposed)/(CO molecules adsorbed) varies from ~1 to ~2 with increasing platinum content. The experimental ratios are discussed in relation to previously predicted configurations for CO molecules on metal surfaces and infrared observations. It is suggested that the coverage of CO on platinum depends on the crystallite size, i.e., ratios of 2, which may be bridge bonding on larger crystallites and linear bonding on highly dispersed platinum. On this basis, numbers of CO molecules adsorbed calculated from crystallite-size distributions agree satisfactorily with experiment.

INTRODUCTION

It is usually said that CO is chemisorbed on metals either by a linear bond or by a bridge bond involving one or two surface metal atoms, respectively. Recently an extensive analysis (*1*) has been made of the configurations of CO molecules on the common planes of hcp, fcc, and bcc metals. On the (100), (110), and (111) planes of platinum, CO can be held by bridge bonds involving all the surface atoms in pairs, i.e., the ratio (platinum atoms exposed)/(CO molecules adsorbed) = 2. However, linearly bonded CO cannot pack to a ratio of unity on these planes. The repulsive energy would be prohibitive, by reason of its absolute value relative to the energy of the surface bond and because it would probably mean an activation energy of adsorption. The permitted configurations on the (100), (110), and (111) planes yield (Pt exposed)/(CO adsorbed) ratios of 2, 2, and 3, respectively.

Previous work on the chemisorption of CO on supported platinum suggests that effects due to small crystallite size and support may operate. Infrared studies (*2*) have shown that up to 15% of CO adsorbed on Cabosil-supported platinum is in the bridged structure. In Part I (*3*) it was shown that platinum areas calculated from CO adsorption on 2.75% Pt/silica catalysts on this basis agreed closely with areas calculated from X-ray data, implying that the ratio (Pt exposed)/(CO adsorbed) was 1.15. Further, the ratio of *total* number of platinum atoms to CO molecules adsorbed was found (*4*) to approach unity on high-area silicas (total Pt/CO adsorbed = 1.14 for a silica support of 780 m^2/g area).

In the present work, the effect of crystallite size on the mode of CO chemisorption was examined for a series of Pt/silica catalysts. At the lower platinum contents, most of the crystallites were <10 Å size while at the higher platinum contents, probably all the crystallites were sufficiently large to correspond to "bulk" platinum in surface properties. The "absolute" platinum areas were derived from X-ray measurements, cross-checked with crystallite-size distributions observed in electron micrographs of catalyst sections.

When the platinum content of a supported catalyst is increased, the platinum surface area may increase due to either an increase in the number of crystallites, or their mean size, or both. It has been suggested (*5*) from observations of the fraction of total platinum available for hydrogen chemisorption, that, for Pt/silica catalysts, changes in platinum content are reflected by the number of crystallites but not by their mean size.

In the present work, the observed crystallite sizes and the relation between platinum area and platinum content both suggest a different model for the increase in platinum area, dependent upon the pore structure of the silica support.

EXPERIMENTAL

A series of platinum/silica catalysts, containing up to 11.5% platinum was prepared by impregnating Davison grade 70 silica gel with chloroplatinic acid solution. The water was boiled off with continuous stirring and the catalyst dried at 120°C for 16 hr in an air oven. The catalyst was reduced at 210°C for 2 hr in a flow of hydrogen purified by diffusion through a silver-palladium membrane.

The area of platinum on the support was examined by chemisorbing carbon monoxide at 25°C. A conventional volumetric apparatus was used with a single-bulb burette of ~35-ml capacity and incorporating greaseless stopcocks with Viton A diaphragms, coated where necessary with polythene film. Pressures were measured with miniature Pirani gauges operated at constant filament temperature with self-balancing control units. The whole system was enclosed in a cabinet thermostated at 30°C. Carbon monoxide for adsorption, and helium for dead-space determinations were "spectrographically pure" gases (British Oxygen Co., Ltd.) supplied in Pyrex vessels.

The size of the platinum crystallites was determined from the broadening, B, of X-ray diffraction "lines," using a counter-diffractometer which provided a chart recording of the position, profile, and intensity of each diffraction maximum. Filtered copper radiation was used and the $K\alpha$ doublet was resolved by a graphical method (*6*); the correction for instrumental broadening, b, was made using Warren's expression: $\beta^2 = B^2 - b^2$. The mean crystallite size, L, can be obtained from the excess broadening, β, using the Scherrer equation

$$L = K\lambda/\beta \cos \theta$$

where λ is the radiation wavelength and θ is the Bragg angle. The value of the Scherrer constant, K, depends on the definitions of crystallite size and profile width, the shape of the crystallites, and the reflection being examined. Values of K lie between 1.0 and 1.16 for the lower index planes in a crystallite which is a sphere, octahedron, or cube, using the integral width, β_i (*7*). However, the broadening measured in terms of the profile width at one-half its maximum height, $\beta_{1/2}$, was considered more accurate, and was used in the present work. Crystallite sizes derived from $\beta_{1/2}$ using X-ray reflections from the (111), (200), and (220) planes in platinum/silica catalysts, assuming that the crystallites were present as cubes and using values of K between 0.84 and 0.89, agreed well with sizes based on β_i (*8*). For most platinum/silica catalysts usually the (111) diffraction profile was observed, but the classical Scherrer constant value, $K = 0.90$, was taken throughout as consistent with the experimental error.

Catalysts of the present type often contain substantial amounts of highly dispersed metal, i.e., crystallites of ~50 Å and less, which are not included in the X-ray measurement of mean crystallite size. The amount of platinum in this form was determined for each catalyst as follows: The amount of platinum detectable by X-ray diffraction, i.e., the area under the line profile, was measured relative to a catalyst where all the platinum had been grown

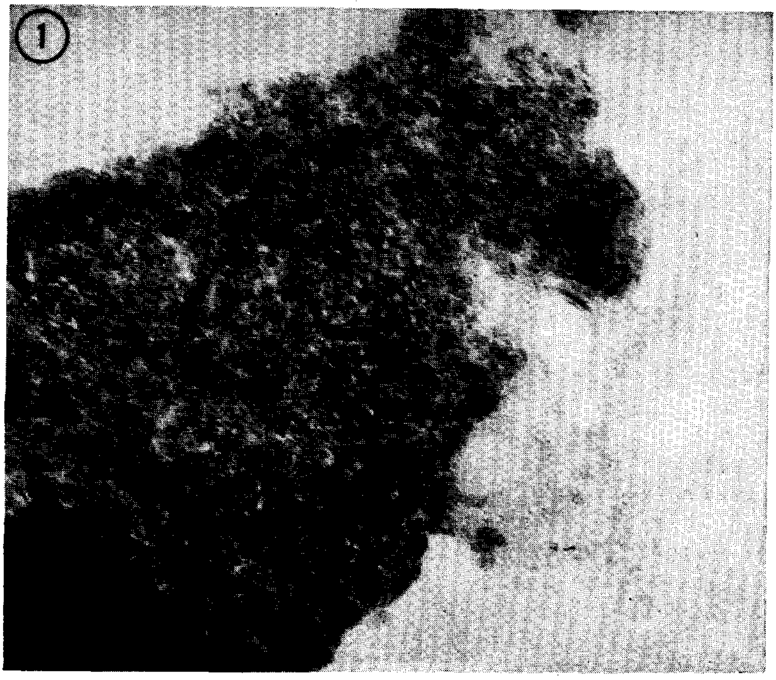


FIG. 1. Electron micrograph from ultramicrotome section of a 3% Pt/silica catalyst showing platinum crystallites dispersed in silica gel. Magnification, 100,000×.

to a detectable crystallite size by firing at 800°C. In each case magnesium oxide had been added as an internal standard. The total platinum content of each catalyst was determined by X-ray fluorescence analysis and hence the amount of platinum in the highly dispersed form could be calculated.

RESULTS AND DISCUSSION

The structure of Pt/silica catalysts, prepared as described above, is indicated by the electron micrograph (Fig. 1) of an ultramicrotome section. The platinum, showing up as dark spots, is evenly distributed as very small crystallites, <100 Å, throughout the pore system of the silica gel. About 1000 crystallites were sized in terms of their diameters, since they appear approximately spherical, in increments of 10 Å. Figure 2 shows the number of crystallites observed in each size range. The crystallites are predominantly in sizes below 50 Å, but the actual volume or weight of platinum in this size range is a very much smaller fraction of the total. As shown below, the main concern with the size distribution is the mean size of these crystallites below 50 Å, taken as our limit of crystallite-size measurement by X-ray

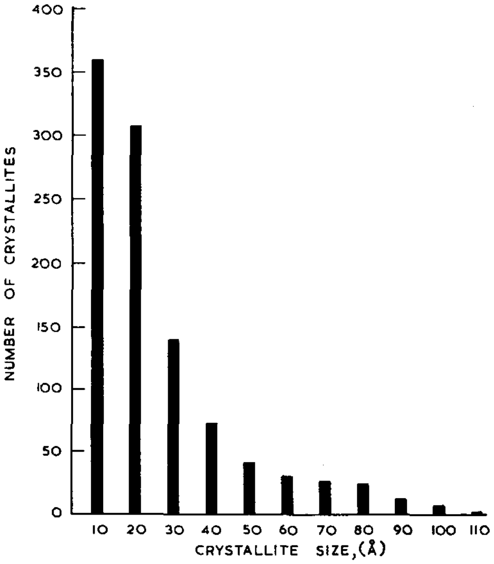


FIG. 2. Size distribution of platinum crystallites in 3% Pt/silica catalyst derived from Fig. 1.

line-broadening. The volume weighted mean diameter d_v, is derived as

$$d_v = \Sigma N_i d_i^4/\Sigma N_i d_i^3 = 31 \text{ Å for sizes} < 50 \text{ Å}$$

and

$$= 78 \text{ Å for sizes 50 Å and above}$$

where there are N_i crystallites of diameter d_i. If the crystallites are spherical, these sizes can be compared with sizes derived from X-ray data, which are taken as the cube root of the crystallite volume, V, implying an isodimensional model, thus,

$$V^{1/3} = (\pi/6)^{1/3} d_v = 0.806 d_v$$
$$= 25 \text{ Å for sizes} < 50 \text{ Å}$$

and

$$= 63 \text{ A for sizes 50 Å and above.}$$

Quantitative measurements of mean crystallite size by X-ray line-broadening in a series of catalysts containing up to 11.5% platinum are recorded in Table 1 together with the fraction of total platinum detected by X-ray diffraction, i.e., crystallites of 50 Å and above. The crystallite sizes reported refer to (111) diffraction "lines" but where others were observed, the calculated sizes were in agreement. For example, the crystallite sizes derived from the (111), (200), (220), and (311) planes in a 10.2% platinum/silica catalyst were 80, 75, 70, and 65 Å, respectively. Four diffraction lines were also observed in the catalyst with 8.5% platinum, then fewer lines as the platinum content fell and the crystallite size diminished. At 0.65% platinum, a very broad diffraction profile was recorded corresponding to crystallites of <50 Å size; below this platinum content, no diffraction from platinum was observed. Table 1 also shows that the amount of highly dispersed platinum (<50 Å) decreases as the platinum content increases, so that the 11.5% Pt/silica catalyst has over 90% platinum in the observed crystallite size.

TABLE 1
Crystallite-Size Data from X-Ray Line-Broadening

Pt content (%)	Pt detected by X-ray diffraction: Crystallite size (Å)	Fraction of total Pt detected	Pt area (m²/g catalyst)	Calc. area of undetected Pt (m²/g catalyst)	Total area of Pt (m²/g catalyst)
11.50	70	0.91	3.49	0.97	4.46
10.20	80	0.80	2.38	1.91	4.29
8.50	75	0.83	2.20	1.35	3.55
5.40	65	0.57	1.11	2.17	3.28
3.00	60	0.42	0.49	1.63	2.12
1.25	85	0.43	0.15	0.67	0.82
0.65	<50	—	—	—	—
0.30	No diffraction lines observed from Pt				
0.15	No diffraction lines observed from Pt				

The platinum surface areas in this series of catalysts were then calculated from the information on metal content, crystallite size, and fraction detected by X-ray diffraction. The platinum crystallites were envisaged as being cubes with five faces exposed to adsorbing gases, the sixth contacting the support, although electron micrographs suggest a roughly spherical crystallite shape. However, the volume/surface ratio is constant for spheres, cubes, or regular polyhedra other than a tetrahedron and presumably the silica is wetted by the platinum crystallites. Hence, the metal area of an amount of catalyst containing 1 g of platinum is given by $5 \times 10^4/l\rho$, where l is the edge length of the cube in angstrom units and ρ is the density of platinum. The area of platinum as crystalllites detectable by X-ray diffraction is shown in column 4, Table 1, but it is clear that the presence of finely divided platinum which is not detected leads to an underestimation of metal area. It was shown previously (*3*) for catalysts containing ~3% Pt, that agreement could be obtained between metal areas calculated from X-ray data and areas derived from CO chemisorption, if a mean crystallite size of 25 Å was taken for this finely divided platinum and the additional metal area thus calculated included in the result. The assumed mean size of 25 Å is now confirmed by the electron microscope results reported above for a similar catalyst. Hence column 5 of Table 1 shows the calculated area of the platinum undetected by X-ray diffraction and column 6 shows the total platinum area.

It is evident from Table 1 that the platinum surface area, which reflects the number and size of the platinum crystallites, is not a linear function of the platinum content. Poltorak and Boronin (*5*) found that the fraction of platinum atoms available for hydrogen chemisorption, γ, was approximately constant in a series of Pt/silica catalysts prepared from platinum "ammine," obtained by adding an excess of ammonia to a solution of H_2PtCl_6 at 70–80°C. Reduction in <1 torr hydrogen produced catalysts where all the platinum was accessible to hydrogen chemisorption, i.e., $\gamma = 1$. It was proposed that, once the preparative conditions have been specified, then changes in the weight percentage of platinum are reflected by the number of crystallites but not by their mean size. However, the observed crystallite size in the present series of catalysts shows an upward trend as the platinum content increases, i.e., the mean observed size and especially the fraction >50 Å both increase. Further, the platinum area is proportional to (platinum content)$^{2/3}$, which is the relation expected for the change in area associated with the growth of a *fixed number* of crystallites of regular shape, e.g., sphere or cube.

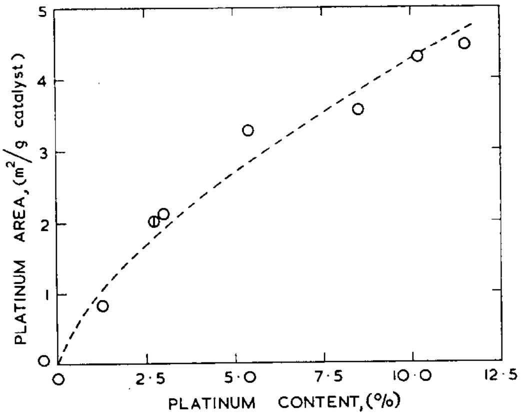


FIG. 3. Platinum surface areas derived from X-ray data as a function of platinum content in Pt/silica catalysts: ○, present experimental results; ⦶ , previous result, ref. (*3*); ---, line of best fit computed for Pt area $= K$ (weight Pt)$^{2/3}$.

Figure 3 shows experimental points for the platinum area as a function of platinum content; a curve (broken line) is fitted to these points on the basis of the above proportionality. The line of best fit was computed as

$$A = 19.83W^{2/3}$$

where A is the platinum area (m^2/g catalyst) and W is the weight of platinum per g catalyst. For a fixed number of crystallites, again envisaged as cubes exposing five faces, increasing in size

$$10^4A = 5N^{1/3}\rho^{-2/3}W^{2/3}$$

where ρ is the crystalline density and N is the number of crystallites. Hence, N can be evaluated

$$N = 3 \times 10^{16} \text{ crystallites/g catalyst}$$

The following model for the deposition of platinum crystallites in Pt/silica catalysts by the impregnation method is proposed. In preparing the catalysts the calculated volume of 0.1 *M* chloroplatinic acid solution, to produce the required platinum content, was diluted with water so that there was sufficient liquid to wet all the silica and fill its pores with dilute platinum salt solution. When the water is removed, platinum salt will be deposited in each pore, the amount depending on the volume of standard solution taken. If drying in air at 120°C does not produce significant movement and growth of the platinum salt "particles," there should be a constant number of platinum crystallites throughout the series. Further, this number of crystallites and the porosity of the silica support might be expected to correspond.

It has been shown previously (*9, 10*) that silica gel consists of aggregates of elementary particles which are roughly spherical and diameters of ~100 Å have been reported. For a random packing of such silica particles of varying size, the number of pores capable of nucleating a platinum crystallite is unknown, but an estimate of magnitude is possible. The total surface area, S, of these catalysts, determined by nitrogen adsorption, was ~200 m^2/g catalyst. Assuming no loss of area when uniform spherical silica gel particles contact, then from $S = 6 \times 10^4/\sigma d_s$, where σ is the crystalline density of silica, 2.3 g/cm^3, and the diameter, d_s, of the silica particles is ~130 Å. The corresponding number of elementary silica particles is 4×10^{17}/g catalyst.

The pore volume, determined by the absorption of carbon tetrachloride vapor (*11*), was ~1 cc/g catalyst. Well-packed samples of catalyst had a bulk density of 0.34 g/cc and hence taking the void space between granules as 40% of the total volume, the granules have 57% porosity. Not unexpectedly, this value lies outside the porosity range for closest packing (*12*), i.e., from rhombohedral (25.95% porosity) to the "most open" cubic packing (47.64% porosity). In, for example, the latter case, where each layer of spheres lies immediately above another on a rectangular base, the number of pores envisaged is equal to the number of elementary silica particles. Applied to the present series of catalysts this suggests that the maximum number of pores is 4×10^{17}/g catalyst, setting an upper limit to the number of platinum crystallites. However, the increased porosity observed experimentally suggests a certain amount of "voidage" within the granules, reducing the number of pores in keeping with the observed number of platinum crystallites, 3×10^{16}/g catalyst.

Carbon Monoxide Adsorption

Carbon monoxide was adsorbed at 25°C on samples of the catalyst which after preparation had been reduced in the adsorption apparatus at 210°C for 2 hr, then evacuated at 480–500°C overnight. Almost identical isotherms were obtained for repeat runs with the same sample but at least two separate samples at each platinum content were separately reduced and CO adsorption measured, again showing good agreement. Figure 4 shows CO adsorption on 8.5% and 11.5% Pt/silica catalysts; the minimal adsorption of CO on silica alone is also shown. On the basis of the platinum areas derived from X-ray data, monolayer coverage of CO for the weights of catalyst used containing 8.5% and 11.5% Pt is 0.89 and 0.78 cc (NTP), respectively. It is evident from Fig. 4 that many of the CO molecules are associated with more than one platinum atom.

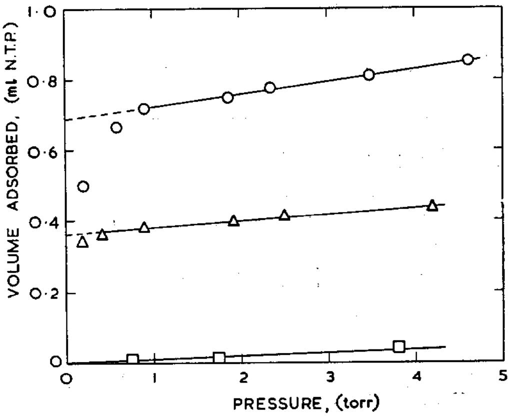


FIG. 4. CO adsorption at 25°C on Pt/silica catalyst: ○, 0.6 g 8.5% Pt catalyst; △, 0.42 g 11.5% Pt catalyst; □, silica support.

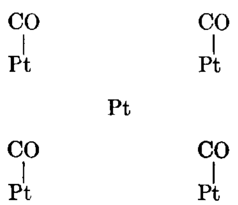
Table 2 shows the number of CO molecules at monolayer coverage for catalysts with platinum contents ranging from 0.15% to 11.5% and that, rather unexpectedly, the number adsorbed passed through a maximum at 8.5% Pt/silica. The number of platinum atoms exposed on the surfaces of crystallites in sizes detectable by X-ray diffraction and on the surfaces of crystallites <50 Å size is also shown. In calculating the exposed atoms it has been assumed that the three common planes, (100), (110), and (111) were present in equal amounts. The ratio, (total Pt atoms exposed)/(number of CO molecules

TABLE 2
CARBON MONOXIDE CHEMISORPTION

Pt content (%)	CO monolayer coverage (molecules/g catalyst)	Exposed Pt atoms from X-ray data		Total Pt atoms exposed/No. CO molecules adsorbed
		Crystallites >50 Å	<50 Å	
11.50	2.38×10^{19}	3.92×10^{19}	1.09×10^{19}	2.10
10.20	2.87×10^{19}	2.67×10^{19}	2.18×10^{19}	1.69
8.50	3.09×10^{19}	2.46×10^{19}	1.52×10^{19}	1.29
5.40	3.00×10^{19}	1.24×10^{19}	2.43×10^{19}	1.22
3.00	2.15×10^{19}	6.2×10^{18}	1.66×10^{19}	1.06
1.25	7.7×10^{18}	1.7×10^{18}	7.5×10^{18}	1.18
0.65	4.6×10^{18}	—	—	—
0.30	2.0×10^{18}	—	—	—
0.15	9×10^{17}	—	—	—

adsorbed), varies from ~1 to ~2 as the platinum content increases.

From the infrared evidence (*2*), it seems clear that most of the CO molecules are linearly bonded on the small platinum crystallites in supported catalysts. This does not necessarily mean a (Pt exposed)/(CO adsorbed) ratio of unity, since, as discussed above, linearly bonded CO should pack on *extended* surfaces (*1*) only to ratios between 2 and 3. The present evidence, however, indicates a near correspondence between the number of platinum atoms exposed and CO molecules adsorbed at low platinum contents. It would appear that where the total platinum area derives in large part from extremely small, irregular crystallites, the "flat" areas of platinum exposed are insufficient for the packing "rules" to apply. For example, on the (100) face of a unit cell of platinum, a ratio of 1.25 is possible



At the highest platinum contents, the observed ratio (Pt exposed)/(CO adsorbed) was ~2, implying either linear or bridge bonding if only the "permitted" CO configurations (*1*) are adopted [the ratio is 3 for linearly bonded CO on the (111) plane]. There is evidence favoring bridge bonding where the uninterrupted area of platinum has attained a reasonable size. On evaporated platinum films (*1*), the observed ratio (CO adsorbed)/(Kr adsorbed) could only be accounted for on the basis that the (111) face was present practically to the exclusion of the (100) and (110), and that it was covered with bridge-bonded CO molecules. Crystallites of 180 Å were observed in much lighter platinum films (*13*), deposited at the same substrate temperature and in a vessel of comparable geometry.

Spectra of CO chemisorbed on platinum films (*14*) prepared by flash evaporation of the metal in the presence of CO showed bands in the 1800–2100 cm^{-1} region in agreement with those found with supported samples. However, electron micrographs of the films showed small aggregates of particles with diameters of 45 ± 10 Å and therefore these platinum films had a considerable similarity to supported catalysts of low platinum content.

On the evidence of the present results, the ratio (Pt exposed)/(CO adsorbed) is dependent on the crystallite size and previous observations tend to associate this with bridge bonding on large crystallites and linear bonding on the highly dispersed platinum. It is interesting to attempt to calculate on this basis the number of CO molecules adsorbed from the simple crystallite-size distribution available from X-ray diffraction, i.e., proportions of crystallites >50 Å and <50 Å. It also seems reasonable to assume that as the highly dispersed platinum, <50 Å size, grows with increasing platinum content, then the ratio (Pt exposed)/(CO adsorbed) will change from unity through, say, 1.5 to 2. Obviously there is no reason why the 50-Å division, deriving from the sensitivity of the X-ray diffraction measurements, should limit the ratio to unity. Table 3 shows that the calculated number of CO molecules adsorbed/g catalyst agrees satisfactorily with the number observed experimentally.

TABLE 3
CO ADSORPTION CALCULATED FROM X-RAY DATA

Pt content (%)	Assumed ratio (Pt exposed)/(CO adsorbed)		No. CO molecules adsorbed/g catalyst	
	Crystallites		Calculated (10^{19})	Observed (10^{19})
	>50 Å	<50 Å		
11.50	2	2	2.51	2.38
10.20	2	1.5	2.79	2.87
8.50	2	1	2.75	3.09
5.40	2	1	3.05	3.00
3.00	2	1	1.97	2.15
1.25	2	1	0.84	0.77

The above results refer to the situation where the crystallite size was changed by varying the platinum content. It should also be possible to alter the ratio (Pt exposed)/(CO adsorbed) when the crystallite size is changed by other methods. Previously (*3*) crystallites were grown by firing in air before reduction which produced rather large crystallites, >300-Å size, at the higher temperatures. The platinum areas were correspondingly small, 0.03–0.06 m^2/g catalyst, limiting the accuracy of the adsorption measurements, but nevertheless an increased ratio was found. In the present work, a 5% Pt/silica catalyst was reduced under conditions such that the fraction of platinum detected by X-ray diffraction was 0.91, identical with that in the 11.5% Pt catalyst in Table 1, but with a larger mean size, 120 Å compared with 70 Å. The number of exposed platinum atoms derived from the X-ray data was 1.57×10^{19}; 0.78×10^{19}·CO molecules were adsorbed; and the ratio 2.01 confirmed the effect of crystallite size on CO adsorption.

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