Preparation of Highly Dispersed Catalytic Metals

Platinum Supported on Silica Gel

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Supported platinum consisting of 15-Å crystallites has been prepared by reduction of platinum ammine ions adsorbed on the surface of silica gel. Platinum is more highly dispersed in silica gel preparations made by ion exchange than that in similar catalysts made by impregnation with aqueous chloroplatinic acid. Characterization of platinum in both types of preparations has been carried out by hydrogen chemisorption, X-ray diffraction, and electron microscope techniques.

To make the most efficient use of a catalytic metal, it is desirable to obtain the highest possible degree of metal dispersion. This incentive is particularly strong in the case of a costly noble metal such as platinum. The present study illustrates a mode of preparation that should, in principle, accomplish the above aim. The key step consists of fixing metal cations through exchange with ions in the surface of a rigid support; subsequent reduction in hydrogen produces the supported free metal. Thus, by the very nature of the process by which it is made, the initial preparation should contain metal ions that —because of their like electric charge— are distributed uniformly over the surface of the support. As a result, individual metal atoms are probably formed during subsequent reduction, thereby making it possible to obtain the ultimate degree of dispersion. The above principle of preparation should be applicable for any reducible metal ion emplaced on any support that has appreciable ion exchange capacity. The platinum–silica gel system is the one examined in the present study.

Numerous studies have been made of supported platinum–silica gel catalysts;

reference is made only to the more recent work in this field (*1–3*). Our study most closely resembles that carried out by Poltorak and Boronin (*3*), though our approach and conclusions differ in several important respects from those of the former study. The most important difference in our finding that the metal formed by reduction of adsorbed platinum ammine ions is not subcrystalline, as was concluded by Poltorak and Boronin, but consists instead of tiny crystallites with diameters ranging from 5 to 30 Å. This difference may reflect the extreme difficulty in characterizing metal particles when their diameters approach atomic dimensions. In the present study, the degree of dispersion of supported platinum has been carefully determined by the hydrogen chemisorption, X-ray line-broadening, and electron microscope techniques that have been previously described (*4*).

EXPERIMENTAL DETAILS

Exchange between NH_4^+ from solution and H^+ from the hydrous oxide support was measured by immersing a given weight (usually 2 g) of the support in 50 ml of 0.1 M ammonium nitrate, noting the initial

pH with a calibrated pH meter, and quickly adjusting the pH of the suspension to the desired value (5, 6, 7, or 8) by addition from a burette of a standardized solution $0.1 M$ with respect both to ammonium hydroxide and ammonium nitrate. The amount of ammonium hydroxide required to maintain a given pH over a period of 20 min was found to be equivalent to the adsorbed ammonium ion obtained from subsequent analysis of the solid. Ion exchange had therefore taken place according to the reaction

$$H^+A + NH_4^+ = NH_4^+A + H^+$$
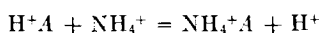
where A denotes the anion that forms part of the support.

Adsorption of $Pt(NH_3)_4^{2+}$ on alumina and silica gel was also measured by the above procedure. In this case, the salt solution was $0.001 M$ tetrammine platinous chloride and the standardized basic reagent was a solution $0.01 M$ with respect to tetrammine platinous hydroxide and $0.001 M$ with respect to tetrammine platinous chloride.

Tetrammine platinous chloride monohydrate is supplied by Engelhard Industries and J. Bishop and Company. The chloride can be converted to the hydroxide by passing a solution of $[Pt(NH_3)_4]Cl_2$ through the hydroxyl form of an anion exchange resin such as Amberlite IRA-400 made by Rohm and Haas Co.

The "ion-exchanged" platinum–silica gel series was prepared by dropwise addition of an appropriate volume of the above-described basic platinum reagent to a stirred suspension of silica gel in $0.001 M$ $[Pt(NH_3)_4]Cl_2$. Each product was filtered, dried at least 2 hr at 120°C, then heated in flowing hydrogen at 500°C for 1 hr.

The "impregnated" platinum–silica gel series was prepared by adding the appropriate volume of $0.2 M$ chloroplatinic acid to 30 g of silica gel, adding enough distilled water to make a slurry, and then evaporating the stirred slurry to near-dryness on a hot plate. Each product was dried at least 2 hr at 120°C, then heated in flowing hydrogen at 500°C for 1 hr.

The silica gel support was Davison

Chemical Company's Grade 70 material (60-200 mesh). It had an aluminum content of 0.02 wt %, a specific surface area of 370 m²/g, and a pore volume of 0.97 cc/g. The alumina was Alcoa's F-20 product which had been washed with $0.1 M$ NH_4NO_3 to remove the sodium (0.9 wt %) originally present. The purified product contained 0.1 wt % sodium, and had a specific surface area of 204 m²/g, and a pore volume of 0.23 cc/g.

Hydrogen chemisorption by each platinum sample was measured at 0°C from a flowing argon-hydrogen mixture which contained enough hydrogen (0.13 mole %) to give a hydrogen partial pressure of 1 torr. Previous work (4) had shown that a platinum surface is covered by a monolayer of chemisorbed hydrogen at this temperature and hydrogen pressure. Hydrogen adsorption on the metal-free support was negligible under these conditions.

Electron microscope examinations of the "ion-exchanged" catalysts which contained 0.7 and 4.5 wt % of platinum were made by means of the Siemens Elmiskop I. The catalyst was prepared for examination as follows:

A small amount of the catalyst is thoroughly washed in hexane or chlorothene (1,1,1-trichloroethane) and then ground in an agate mortar. The fine powder is suspended in Cellosolve (2-ethoxyethanol) and the coarser part allowed to sediment for 1 min. Specimen mounts for the electron microscope are prepared with the supernatant fine fraction in the usual manner by applying a small drop of the suspension with a wire loop to a carbon supporting membrane. In order to withstand the subsequent acid treatment, palladium specimen grids are used for mounting the carbon-supporting membranes. The dried specimens are enveloped evenly with a carbon film by rotating the specimen mounts during the carbon evaporation. Thus, the catalyst particles become sandwiched between two membranes of carbon. The specimen grids are then placed, face down, on 25% HF for 30 to 60 min. The silica is dissolved and removed, whereas the platinum particles are retained within the porous carbon
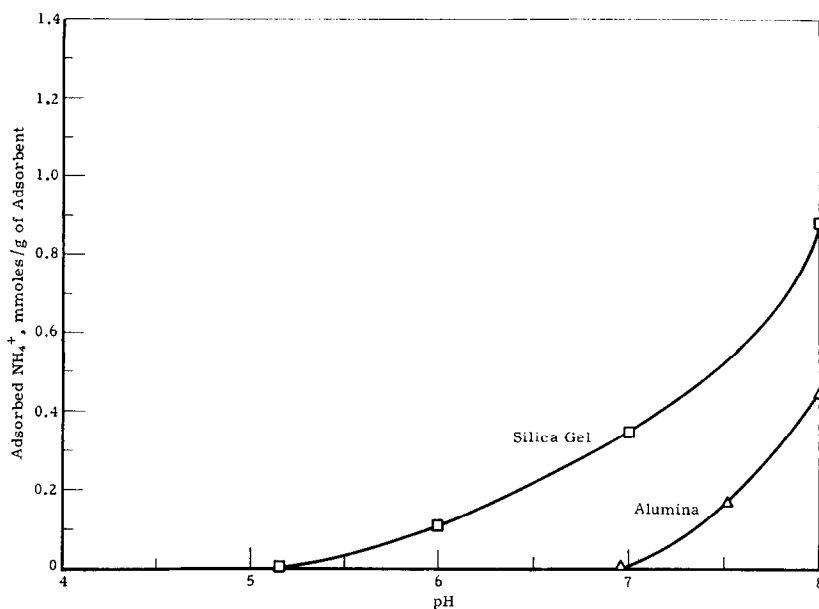
FIG. 1. NH_4^+ adsorption by hydrous oxides as a function of pH.

replica of the silica carrier. The specimen grid is finally transferred to water for rinsing. In order to avoid distortion and collapsing of the carbon envelopes, drying is preferably made from a liquid with a low surface tension, such as Freon-11 (CCl_3F, b.p. 23.8°C), instead of water. The water-washed specimens are carried through water-alcohol mixtures into iso-propyl alcohol and then into Freon-11. The specimens dry instantly upon removal from Freon-11.

To assure that the acid leaching step did not attack the platinum, a "blank" specimen consisting of 10 to 20 Å platinum particles (prepared by evaporation of platinum on a carbon film) was leached in 25% HF for 16 hr. Electron microscope examination showed that the platinum particles were unaffected by this acid treatment.

X-Ray diffraction measurements were obtained with a General Electric XRD-3 diffractometer as described in a previous report (4), but with two modifications intended to improve stability. Power for the X-ray tube was supplied from a constant potential source regulated within 0.1% in current and 0.3% in voltage. Output to the recorder was provided by a locally constructed rate meter designed for extreme stability and freedom from drift at relatively low counting rates. In the present case, instrumental broadening effects on line profiles are trivial and the problem is primarily that of detecting a significant diffraction effect from the platinum over that of the silica gel substrate. At the scan rate used (2.4°/hr), about 20 hr were required for recording both sample and silica gel blank patterns over the full range of the (111) and (200) reflections. This relatively long time interval dictated the instrumental stability requirements. The diffractometer could operate either with or without a direct beam curved quartz monochrometer. Scans under both conditions were obtained and there was no clear advantage of one method over the other in the present study. Improvements that might be expected with a monochrometer were offset by very low intensities, but the two methods did yield the same final results.

RESULTS AND DISCUSSION

Preparation

The preparation of supported metals by ion exchange is an outgrowth of previous
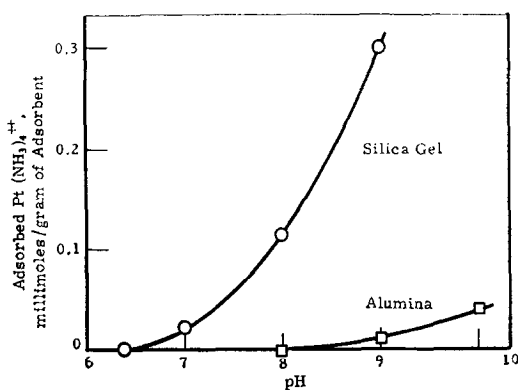
FIG. 2. Adsorption of $Pt(NH_3)_4^{2+}$ on silica gel and alumina.

work both in these laboratories and in the published literature which showed that hydrous oxides such as silica gel (5) and alumina (7) undergo exchange reactions with metal ions from aqueous solution. Data obtained by us that illustrate ion exchange of these oxides with ammonium nitrate are shown in Fig. 1. It can be seen that adsorption of NH_4^+ rises smoothly as the pH of NH_4NO_3 increases, and that silica gel takes up NH_4^+ in a pH range lower than that for alumina. This shows that silica gel is more acidic than alumina in an aqueous environment. Since NO_3^- is not taken up by these solids under these conditions, it is concluded that NH_4^+ undergoes exchange with H^+ in the surface of the support.

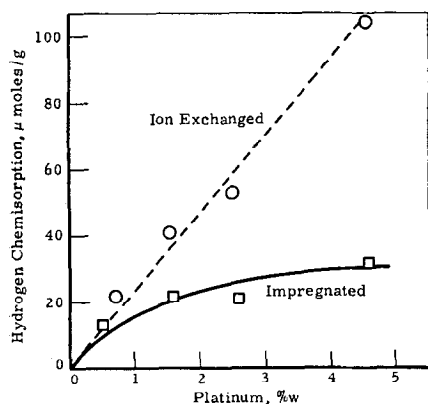Similar metal uptake is observed in the case of transition metals. However, a

FIG. 3. Hydrogen chemisorption by platinum–silica gel catalysts.

practical difficulty arises since cations of such metals precipitate as insoluble oxides or hydroxides at the high pH's required to bring about ion exchange. Precipitation can be prevented, however, if enough ammonia or amine is added to reduce the metal ion concentration to a level lower than that set by the solubility product of the oxide or hydroxide. In the case of platinum, the formation of the stable ammine complex, $Pt(NH_3)_4^{2+}$, fulfills this function.

Figure 2 shows that adsorption of $Pt(NH_3)_4^{2+}$ from dilute $[Pt(NH_3)_4]Cl_2$ solution by silica gel and alumina increases as pH is increased in a manner similar to that shown in Fig. 1. The amount of platinum taken up by these solids can therefore be controlled through appropriate adjustment of the pH of the aqueous suspension. The "ion-exchanged" series of platinum–silica gel preparations were prepared in this manner.

To provide a frame of reference, another platinum–silica gel series was prepared by conventional means: impregnation of the support with aqueous chloroplatinic acid. Since $PtCl_6^{2-}$ is not adsorbed or ion-exchanged by silica gel, the initial product obtained by this procedure presumably consists of H_2PtCl_6 crystals comparable in size with the pores in which they are deposited.

Degree of Platinum Dispersion

Since each surface atom of platinum chemisorbs one hydrogen atom, specific adsorption of hydrogen is an index of platinum dispersion. Platinum contents and hydrogen chemisorption values for the "ion exchanged" and "impregnated" series of platinum–silica gel preparations are listed in Table 1 and are plotted in Fig. 3. In the case of the impregnated preparations, the atomic ratio of adsorbed hydrogen to platinum decreases at higher platinum contents. The sample impregnated with 2.5 wt % platinum had been completely characterized in a previous study (4), which showed that the platinum consists of particles ranging from 15 to 45 Å in diameter.
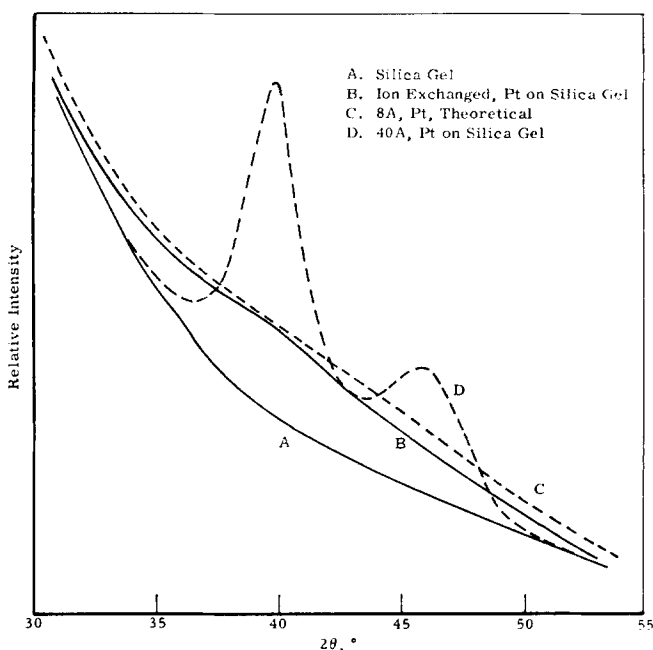
A. Silica Gel
B. Ion Exchanged, Pt on Silica Gel
C. 8A, Pt, Theoretical
D. 40A, Pt on Silica Gel

FIG. 4. X-Ray diffraction patterns of platinum supported on silica gel.

In the case of the ion-exchanged preparations, a 1:1 hydrogen–platinum ratio was obtained for each member of the series (Table 1). This finding suggested the intriguing possibility that the platinum in such samples might exist as atoms. However, the X-ray line-broadening and electron microscope measurements reported below show that most—perhaps all—of the platinum must consist of crystallites having an average diameter of 15 Å. The 1:1

TABLE 1

HYDROGEN CHEMISORPTION BY PLATINUM–
SILICA GEL PREPARATIONS

Platinum content (wt%)	Hydrogen chemisorption (μmoles/g)	Hydrogen-platinum atom ratio	Platinum surface (m²/g of catalyst)
Ion-exchanged catalysts			
0.7	22	1.2	2.9
1.5	41	1.0	5.4
2.5	53	0.8	7.0
4.5	105	0.9	13.9
		Avg. 1.0	
Impregnated catalysts			
0.5	13	1.0	1.7
1.6	22	0.5	2.9
2.5	21	0.3	2.7
4.6	32	0.3	4.2

hydrogen–platinum ratio can be rationalized when one realizes that essentially all the atoms in a 15-Å particle of platinum are exposed. Within the experimental error entailed in the chemisorption measurement, a 1:1 hydrogen–platinum ratio is therefore obtained.

The X-ray diffraction pattern for one of the "ion-exchanged" preparations (2.5 wt % Pt) and its silica gel support are shown as solid curves in Fig. 4. The platinum pattern is extremely broad—so broad that it would be difficult to distinguish without comparison with the support. Such a broad diffraction band is frequently attributed to an amorphous or poorly ordered phase, but this is unlikely in the present case because the presence of a maximum (2θ Cu $K\alpha$ ~40°) near the position of the strongest (111) platinum reflection indicates a repeat distance agreeing with that in the bulk metal. The breadth at half-maximum intensity of curve B, with correction for the (200) reflection, indicates a crystallite size of 10 ± 4 Å. The same size has been observed with somewhat greater certainty in the case of samples with 5% Pt.
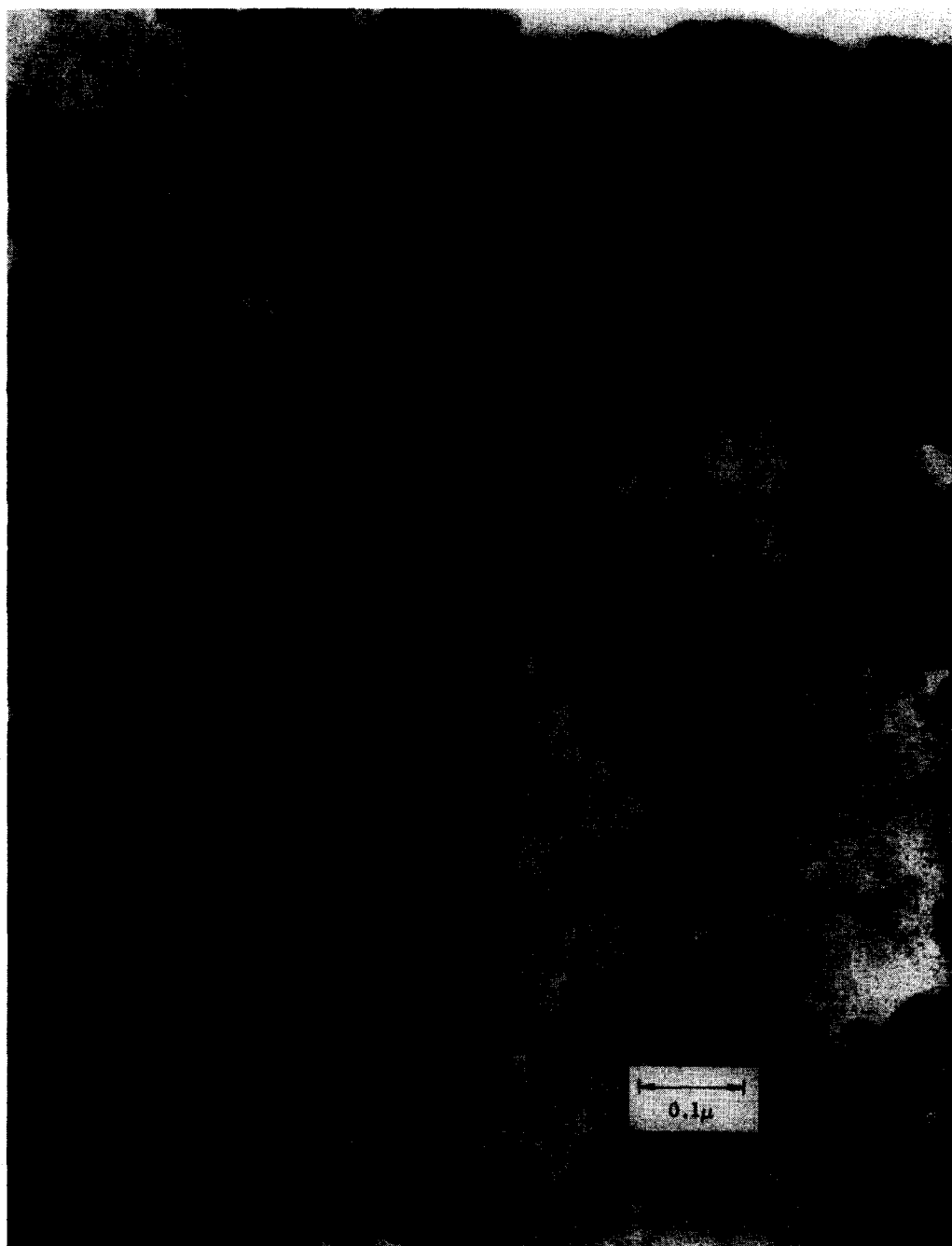
To substantiate our interpretation, the

Fig. 5. 4.5% Platinum on silica gel; carbon envelope; magnification 200 000×.

theoretical scattering curve for platinum cubes 8 Å on a side is included as the dashed curve C in Fig. 4. It is based on the calculation for a cube of 55 atoms given by Germer and White (8), multiplied by the square of the atomic scattering factor for platinum, roughly scaled, and added to the silica gel curve A. The resemblance to the experimental curve B is sufficient to verify our conclusions in that the somewhat greater breadth agrees with the slightly smaller crystal size. The amount of plat-
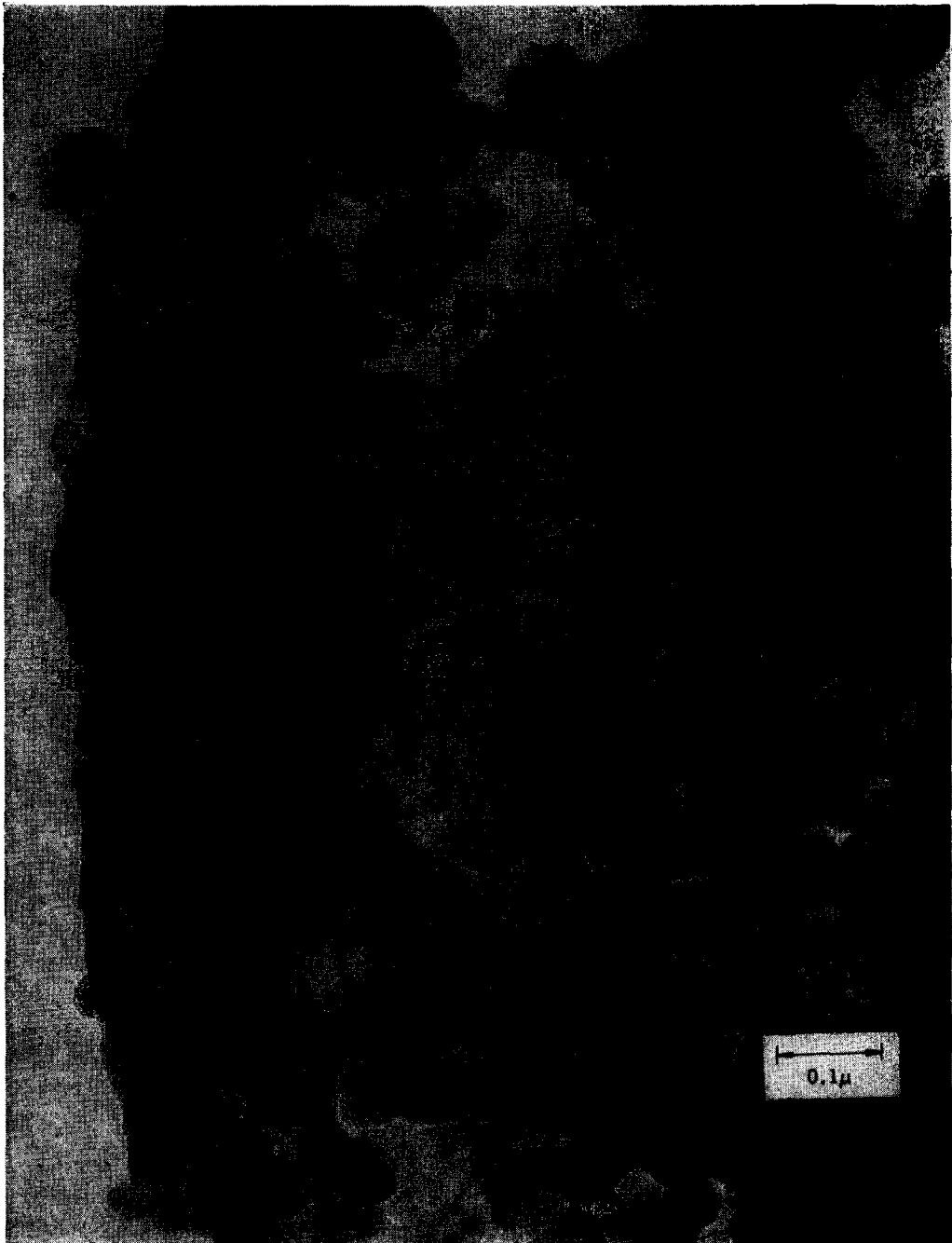
FIG. 6. 0.7% Platinum on silica gel; carbon envelope; magnification 200 000×.

inum present as 10-Å crystallites (70%) can be estimated from a comparison of the area under the diffraction peak with the area in a similar sample where the bulk of the metal is known to be in the form of larger crystallites as in curve D (2.5 wt % Pt, 40-Å crystals). The estimate of 70% is rather uncertain, but sustains our conclusion that most of the metal is present in crystalline form.

Electron micrographs of two platinum samples taken by a carbon replica tech-

nique (Figs. 5 and 6) show that the platinum in "ion-exchanged" preparations does indeed consist of particles whose diameters range from 30 Å down to the limit of resolution (5 Å).

To compare sintering of platinum in the two types of preparation at high temperatures, an ion-exchanged and an impregnated platinum–silica gel sample, each containing 1.6 wt % platinum, were heated in a stream of hydrogen at 500°, 700°, and 800°C for 2 hr at each temperature. The surface area of the platinum in the resulting samples was calculated from hydrogen chemisorption measurements. The results listed in Table 2 show that there is little difference in the loss in platinum area at 800°C between the two catalysts. Since the silica gel support itself undergoes a 20%

loss in surface area upon being heated to 800°C, it seems likely that, for both catalysts, a major part of the loss in platinum area has occurred through occlusion of platinum crystallites situated in the regions of the silica gel structure that have undergone collapse. If this is so, little sintering of platinum has occurred. The above stability towards sintering is in remarkable contrast to the behavior of unsupported platinum black, which undergoes a 99% loss in surface area in a stream of hydrogen at 125°C.

TABLE 2
SINTERING OF PLATINUM IN HYDROGEN
AT HIGH TEMPERATURES

Temperature (°C)	Impregnated catalyst (1.6 wt % Pt)		Ion-exchanged catalyst (1.6 wt % Pt)	
	Pt area (m²/g)	% Loss in area	Pt area (m²/g)	% Loss in area
500°	3.6	0	6.7	0
700°	2.8	22	5.8	13
800°	2.2	39	4.6	31

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