

## State of Dispersion of Platinum in Alumina-Supported Catalysts

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A study of the effects of various heat treatments on the state of dispersion of platinum in alumina-supported catalysts has shown that during heat treatments in hydrogen and air the hydrogen-chemisorption capacity (expressed as the H/Pt ratio) of the catalysts decreases. The mechanism by which this occurs, however, is not the same in the two cases. During heat treatment in an oxygen-containing atmosphere above 500°C agglomeration of platinum takes place. This results in a bimodal size distribution of Pt crystallites: Besides well-dispersed platinum (crystallites below 3 nm), a fraction of particles of about 10–15 nm is formed. There are practically no particles of intermediate size. A carefully controlled oxidation at low temperature (below 500°C) is not capable of redispersing the "big" crystallites. During heat treatment in hydrogen hardly any agglomeration of platinum takes place. However, a certain amount of platinum becomes "inaccessible" and causes the observed decrease in the H/Pt ratio. The actual mechanism by which this occurs still needs further investigation. Oxidation at a carefully controlled, low temperature (below about 500°C) restores the original contribution to the H/Pt value of the platinum fraction which has become "inaccessible" as a result of heat treatment in a hydrogen atmosphere. These results suggest that it is generally incorrect to derive the average platinum crystallite size solely from H<sub>2</sub>-chemisorption data: the existence of a direct link between "decrease in H/Pt ratio" and "sintering" is often highly debatable. For this reason the conclusions of various published studies are suspect.

### INTRODUCTION

Alumina-supported platinum catalysts are frequently used in industrial processes involving, for instance, oxidation (1), hydrogenation and dehydrogenation, and naphtha reforming (2). The performance of such catalysts is greatly dependent on the degree of exposure of the metal, since it is well known that the dispersion of the platinum may affect both the activity and the selectivity of the catalyst.

Changes in metal dispersion, deactivation, and aging of the catalyst, frequently observed after prolonged treatment at high temperatures or use under industrial conditions, are often ascribed not only to such obvious causes as coke formation, but

also to loss of available platinum surface area, presumably as a result of agglomeration of platinum crystallites. From the various papers published on the subject, however, only a qualitative picture can be derived. With respect to the sintering of platinum, for instance (3–5), no definite quantitative conclusions have been drawn so far since the many data available are often contradictory, which, considering the relatively large experimental error and the statistical nature of some of the analyses, is quite understandable. Relating the variables which influence the metal dispersion and thus affect the catalytic properties is therefore of vital importance for gaining an insight into catalysis by metals in general.

TABLE 1  
Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts Tested in This Study

Catalyst	Emplaced amount of platinum (% by weight)	Origin of the Al <sub>2</sub> O <sub>3</sub> support	Compound used during impregnation	Remark
A	0.4	Pseudoboehmite <sup>a</sup>	Pt(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	—
B	0.8	Pseudoboehmite	Pt(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	—
C	2.0	Pseudoboehmite	Pt(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	3 different preparations
D	0.4	UOP <sup>b</sup>	H <sub>2</sub> PtCl <sub>6</sub>	—
E	0.8	UOP <sup>b</sup>	H <sub>2</sub> PtCl <sub>6</sub>	—
F	0.5	Péchiney, type A	Pt(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	—
G	0.5	Steamed UOP <sup>b</sup>	Pt(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>	—

<sup>a</sup> This alumina was prepared as follows: 1764 g of Al(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O was dissolved in 18 liters of distilled water. A concentrated (25%) NH<sub>4</sub>OH solution (8 liters) was made up with distilled water to a total volume of 20 liters. The two solutions were mixed with vigorous stirring; the final pH of the mixture was 10.5. The precipitated alumina hydrogel was filtered off and washed with distilled water until the filtrate was free of nitrate ions. The precipitate was dried at 120°C and calcined at 650°C for 3 h. After calcination it was broken to 14–35 mesh particles.

<sup>b</sup> Universal Oil Products.

In this context we thought it worthwhile to study the effects of various heat treatments in air and hydrogen on the dispersion of platinum in alumina-supported catalysts. Since careful characterization of such catalysts is essential to a proper understanding of the observed differences of opinion, we examined all samples using H<sub>2</sub> chemisorption, X-ray diffraction, and electron microscopy as analytical techniques. Although this investigation has a partly exploratory character, we hope that its results will help to shed some light on the factors that influence the behavior of this interesting catalyst system.

#### EXPERIMENTAL

(A) *Catalysts and catalyst treatments.* The various Pt/Al<sub>2</sub>O<sub>3</sub> catalysts tested in this study are listed in Table 1. Four different alumina supports were used as carrier materials. Catalysts A, B, and C were deposited on a very pure pseudoboehmite-type alumina<sup>1</sup> to minimize interference

during X-ray diffraction analyses. Catalysts D and E were prepared with a commercial UOP<sup>2</sup> alumina as carrier, and catalyst F with a Péchiney type-A alumina as carrier. The UOP alumina used for catalyst G was freed from chlorine by steaming at 500°C.

The seven catalysts were prepared by the "dry pore volume" impregnation method after precalcination of the alumina supports at 500°C. The freshly precalcined materials were impregnated with the appropriate volume of an aqueous solution of Pt(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> or H<sub>2</sub>PtCl<sub>6</sub>, as indicated in Table 1. Unless stated otherwise, the impregnated aluminas were dried for 15 min at 100–120°C and subsequently calcined in a ventilated muffle furnace for 1 h at 280°C, followed by 3 h at 500°C.

To investigate the effects of various heat treatments we subjected the alumina-supported Pt samples to heat treatments in either air or hydrogen (5000 Nl. liter<sup>-1</sup>. h<sup>-1</sup>) in the same apparatus as that used for the hydrogen-chemisorption measurements (*vide infra*).

<sup>1</sup> For method of preparation see Table 1.

<sup>2</sup> UOP, Universal Oil Products.

(B) *Hydrogen-chemisorption measurements.* The degree of exposure of the platinum was determined by hydrogen chemisorption (H/Pt atomic ratio). The measurements were carried out in a conventional static sorption apparatus (6) at  $-78^{\circ}\text{C}$  and 0.1 Torr  $\text{H}_2$  (7). These conditions were chosen to minimize adsorption on the support and maximize adsorption on the metal. Since under these conditions the "net adsorption" on the supported Pt has to be found by subtracting the adsorption on the nonmetalized support from the total adsorption on the catalysts, we have taken great care to determine adsorption isobars for hydrogen on our aluminas in order to obtain reliable correction values. To eliminate a possibly low coverage of Pt by oxygen, all samples were reduced in hydrogen prior to the adsorption proper. This reduction was carried out at  $400^{\circ}\text{C}$  and atmospheric pressure for 1 h, followed by heating under vacuum ( $10^{-6}$  Torr) at  $400^{\circ}\text{C}$  for 16 h.

(C) *X-ray diffraction analysis (8).* From X-ray diffraction photographs of the various Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalysts we determined the average particle size of the Pt crystallites contributing to the diffraction pattern. Apart from this, we also determined the amount of Pt which these crystallites represented.

All the catalyst samples were powdered and mounted in a rotating specimen holder of a diffractometer equipped with a proportional counter. The slit system was slightly modified to ensure a high counting rate. With  $\text{CuK}\alpha$  radiation and a 2-kW generator the diffracted intensity was recorded as a function of the scanning angle (step scanning from  $2\theta = 76^{\circ}$  to  $2\theta = 86^{\circ}$  in about 6 h). From the recorded intensity curve the intensity of the (311) platinum reflection was obtained after subtraction of the background caused by the  $\gamma\text{-Al}_2\text{O}_3$  carrier.

The average particle size  $D$  of the Pt crystallites was calculated from the line-

width  $\beta$  of the (311) reflection according to the equation:

$$D = k[\lambda/(\beta \cos \theta)],$$

in which  $\theta$  is the Bragg angle and  $\lambda$  is the wavelength of the  $\text{CuK}\alpha$  radiation. Using the integral linewidth ( $\beta = \text{peak area/peak height}$ ), the proportionality constant  $k$  was found to be about 1. The linewidth was corrected for contributions originating from the experimental set-up.

To obtain quantitative information about the amount of platinum detected, we prepared a number of calibration mixtures by very carefully homogenizing platinum black powder and the  $\gamma\text{-Al}_2\text{O}_3$  carrier materials. The platinum content of these calibration mixtures ranged from 0.28 to 1.14% by weight. The various calibration mixtures were heated in air at  $450^{\circ}\text{C}$  to obtain (311) Pt linewidths comparable to the values found with the actual catalyst samples used in this investigation. After correction for background caused by the  $\gamma\text{-Al}_2\text{O}_3$  carrier the ratios of the observed Pt intensities agreed very well with the ratios of the Pt contents in the calibration mixtures. Throughout this investigation the resulting calibration curve was used to determine the amount of the platinum detected in the actual catalyst samples.

(D) *Electron-microscopic analysis (9).* To determine the particle-size distributions of the Pt crystallites in the various catalysts, we studied the samples by electron microscopy, using the ultramicrotome as well as the carbon replica technique.

In a number of experiments the specimens were prepared as follows. Mixtures of catalyst powder and methyl methacrylate were heated under 5 atm nitrogen at  $50\text{--}60^{\circ}\text{C}$  for 5 h. The polymerized material was subsequently cut on an ultramicrotome with a diamond knife into ultrathin sections (15–35 nm). To check the thickness graduation some samples comprising sections as well as latex spheres of known



FIG. 1. Electron micrograph of  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst (C - 1;  $\text{H}/\text{Pt} = 0.23$ ). The platinum particles are approximately 12.5 nm. 82% of the platinum present is detected. 250,000 $\times$ .

diameter (100 nm) were shadow casted. According to this method the indicated section thickness proved to be quite good. The major part of the specimens was prepared by spraying a dilute aqueous suspension of catalyst powder onto carbon supports of about 5-nm thickness. For each catalyst sample we investigated 100-200 observations which had fields of the

size of Fig. 1. From these we selected three or four representative photographs for further analyses.

In the samples heat treated in hydrogen we roughly estimated the amount of platinum detected by electron microscopy. This was done by measuring the amount of catalyst and the amount of platinum per unit area of the electron microscope

TABLE 2

Heat Treatment in Air: Influence of Calcining Severity on Dispersion of Alumina-Supported Platinum<sup>a</sup>

Sample	C-1	C-2	C-3
First calcination (°C) (for 1 h)	550 (3 h)	280	280
Second calcination (°C) (for 3 h)	None	500	500
Sintering conditions			
Atmosphere			Air
Time (h)			6
Temperature (°C)			550
X-ray diffraction results			
Fraction of total Pt content detected (in large particles)	0.82	None	0.42
Average size of detectable particles (nm)	12.5	—	8
Electron microscopic results			
Fraction of total Pt content detected (in large particles)	0.70	None	0.20
Average size of detectable particles (nm)	12.5	—	12.5
H <sub>2</sub> chemisorption results			
H/Pt overall	0.23	0.98	0.62
Calculated H/Pt values (basis X-ray analysis)			
Of large particles	0.09	—	0.07
Of fine particles	0.95	—	1.03

<sup>a</sup> Support: pseudoboehmite alumina, see Table 1.

images. Using three of four photographs per catalyst sample, we visually estimated the photographic density per unit area of photograph. The average photographic density of a number of individual  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystals was taken as a standard. The thickness of these crystals was taken equal to their lateral dimensions.

## RESULTS

### (A) Heat Treatments in Air

Table 2 lists some results obtained on three samples, all consisting of 2% by weight Pt on alumina (samples C-1 to C-3), but differing in the way in which they had been heated in air, either during or after the preparation proper.

Samples C-1 and C-2 show the effect of the calcining conditions during the preparation. The sample calcined at 550°C (C-1) had a low H/Pt value (0.23). A

much better catalyst (C-2, H/Pt = 0.98) was obtained when we applied a careful, staged calcination below 500°C during its preparation. This calcination procedure proved particularly suitable for the catalysts prepared with the platinum-ammonia complexes. Owing to the rapid oxidation of ammonia, strong exothermic effects (10) occurred during calcination. The third sample, C-3, was obtained by subjecting sample C-2 to a post-treatment in air at 550°C for 6 h. This treatment lowered the H/Pt ratio from 0.98 to 0.62.

In the sample of the highest H/Pt value (C-2), no Pt crystallites could be detected by either electron microscopy or X-ray analysis. The electron micrographs (see, e.g., Fig. 1) of the samples calcined at 550°C (C-1 and C-3) showed platinum particles of nearly uniform size (10–15 nm). About the same average particle size was calculated from the X-ray diffraction data. The amounts of platinum found by X-ray analysis (expressed as a percentage of the total amount of platinum present in the catalyst) were 82 and 42 for C-1 and C-3, respectively. The remaining, undetected amount of platinum must have consisted of platinum particles smaller than 3 nm, which is the detection limit of the applied X-ray analysis technique.

From the particle size of the coarse particles we can calculate an H/Pt value belonging to this fraction of platinum. For this calculation we used a relationship between average particle size  $d$  (in nm) and H/Pt, which we derived from the work of Spenadel and Boudart (11):

$$\text{H/Pt} = 0.885/d.$$

This conversion of chemisorption data to metal particle size and vice versa requires a number of assumptions as discussed in detail by e.g., Spenadel and Boudart (11) and Adler and Keavney (12). Apart from the assumption that all particles are present as cubes with one face in contact with the support and the remaining five faces

exposed, the most essential assumption is that each platinum surface atom adsorbs one hydrogen atom. The results published by Spenadel and Boudart (11) convincingly show that for platinum crystal sizes larger than 5 nm but smaller than 100 nm hydrogen chemisorption gives values identical with those obtained from X-ray line broadening. Since in our case the detected particles are 10–15 nm, we think it is justified to calculate their contribution to the overall H/Pt value. The H/Pt values of the coarse fraction thus obtained are given in Table 2. From a simple H/Pt balance the H/Pt value of the nondetectable (i.e., <3 nm) particles can be calculated. From the results shown in Table 2 we conclude that after sintering in air the nondetectable part of the platinum must be still very well dispersed (H/Pt is practically 1.0), while the majority of the detectable part is present as 10 to 15-nm particles. To substantiate this conclusion we prepared a number of samples by subjecting catalyst E (0.8% by weight Pt/UOP alumina) to different heat treatments in air. The duration of the treatments was varied from 6 to 70 h and the temperatures from 500 to 650°C. Hydrogen chemisorption measurements carried out on this series of samples gave H/Pt values between approximately 0.9 and 0.2. From X-ray diffraction measurements we calculated the mean crystallite size as well as the weight fraction of platinum detected.

In agreement with the results obtained for the 2% by weight Pt/Al<sub>2</sub>O<sub>3</sub> samples (C-1 to C-3), we found that, irrespective of the H/Pt value of the air-sintered samples E, the mean crystallite size of the detectable amount of the platinum was about the same for all samples, viz., 15 ± 2.5 nm. The half-width values of the (311) reflections of platinum were found to be the same for all samples, in spite of differences in H/Pt value.

Examination of the electron micrographs of some 100 Pt crystallites per sample con-

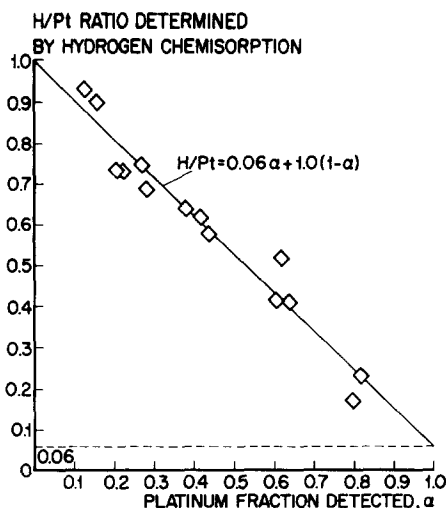


FIG. 2. Relation between the overall H/Pt ratio and the extent of Pt agglomeration for various Pt/Al<sub>2</sub>O<sub>3</sub> samples sintered in air ( $\alpha$  = fraction of metal detected as particles of 15.0 ± 2.5 nm).

firmed that in the air-sintered samples of low H/Pt value Pt particles of 10 nm and larger were present. No particles between 1 and 10 nm were observed. The average H/Pt value for the detected Pt was calculated and found to be 0.063.

The above results show that during heat treatment in air above 500°C sintering of Pt takes place, which results in a bimodal distribution of crystallite sizes (13). Besides well-dispersed Pt, a fraction is present with particles of around 15 nm (with an H/Pt value of about 0.06). To check whether this mode of sintering can account for the observed H/Pt losses, we have plotted in Fig. 2 the H/Pt values measured by hydrogen chemisorption versus the weight fraction ( $\alpha$ ) of the platinum detected by X-ray diffraction. A correlation was found that can be described by:

$$\text{H/Pt} = 0.06\alpha + 1.0(1 - \alpha),$$

where the H/Pt value of the detectable platinum is taken 0.06, based on the analysis described above; the H/Pt value of the nondetectable platinum is assumed to be 1.0.

It is worth noting that in the experi-

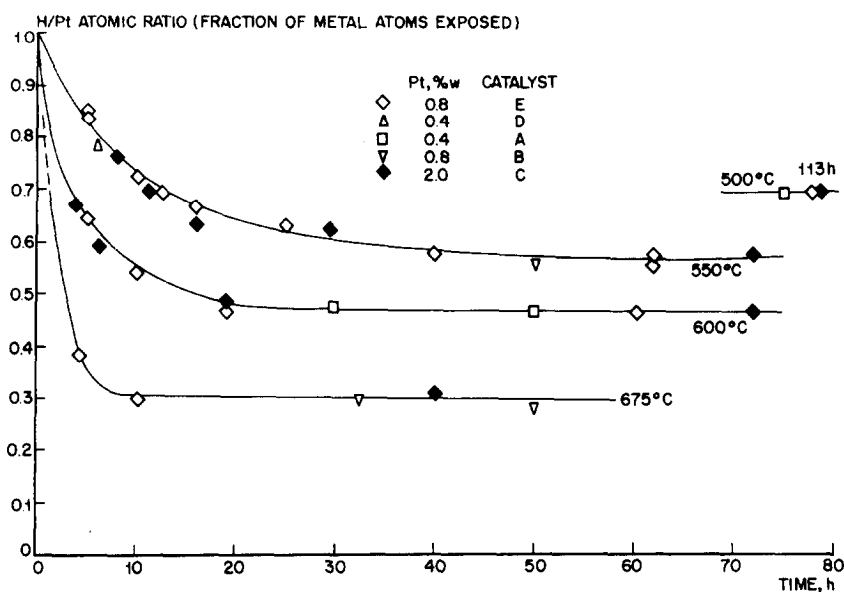


Fig. 3. Decrease of H/Pt value during heat treatment in hydrogen.

ments reported by Baker *et al.* (13b) the platinum particles once formed remained immobile on the surface. This indicates that particle growth probably occurs via the movement of very small particles (<3.0 nm in size).

### (B) Heat Treatments in Hydrogen

(1) *Hydrogen-chemisorption data.* Five different Pt/Al<sub>2</sub>O<sub>3</sub> samples (catalysts A-E with Pt contents ranging from 0.4 to 2.0% by weight) were heated in pure hydrogen

TABLE 3

Heat Treatment in Hydrogen: Influence of Temperature on H/Pt Loss of Alumina-Supported Platinum (Catalysts: See Fig. 3)

Temperature (°C)	Isothermal steady-state H/Pt ratio	Rate constant of H/Pt loss $k$ (h <sup>-1</sup> )
500	0.70	0.045 <sup>a</sup>
550	0.58	0.103
600	0.48	0.214
675	0.30	0.540

<sup>a</sup> Calculated from Arrhenius plot of the rates determined at 550, 600, and 675°C.

at temperatures ranging from 500 to 675°C. Hydrogen-chemisorption measurements were carried out on the fresh and heat-treated samples. The H/Pt ratio of the fresh samples was found to be practically 1.0 in all cases. The results presented in Fig. 3 show that the decrease of the H/Pt ratio during heating in hydrogen is independent of the metal load and origin of the alumina. At a given temperature the H/Pt ratio of all samples decreases at the same rate, reaching a more or less stable level within the 100 h of our experiments. The approach to this stable level [the "isothermal steady-state H/Pt," H/Pt<sub>(iss)</sub> (14)] was found to follow first-order kinetics quite well and can be described by the equation:

$$-d(\text{H/Pt})/dt = k\{\text{H/Pt}_{(t)} - \text{H/Pt}_{(iss)}\},$$

where the symbol  $t$  stands for time (h). Data on the decline rate constants  $k$  and "isothermal steady-state H/Pt" have been collected in Table 3.

Assuming that the temperature dependence of the rate constant obeys the Arrhenius equation, the activation energy for the loss in available surface area of

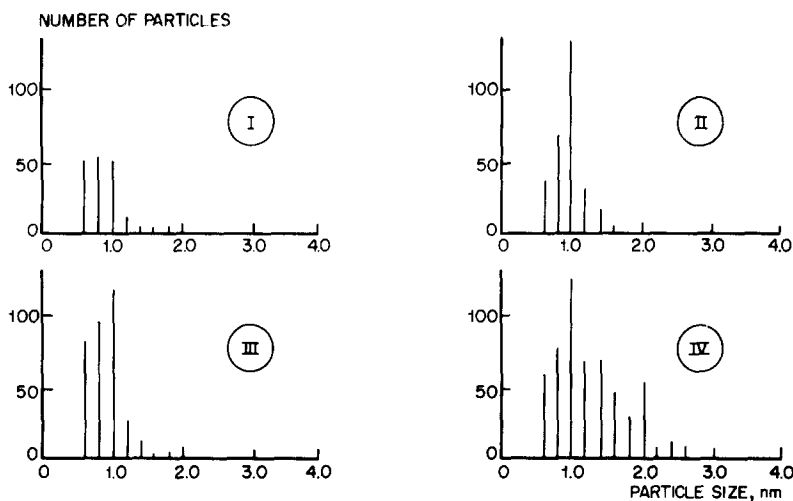


Fig. 4. Particle-size distributions of Pt/Al<sub>2</sub>O<sub>3</sub> samples obtained by heat treating catalyst E in hydrogen at different severities.

supported platinum in hydrogen is found to be 20.9 kcal/g. at Pt, a value very close to the 18.4 kcal/g. at Pt reported by Khassan *et al.* (14) for the sintering of platinum black in vacuum.

(2) *X-ray and electron-microscopic results.* Further studies were carried out on a number of samples which had been obtained by heating catalyst E in hydrogen at different temperatures. Heating times were such that in all cases the "isothermal steady-state H/Pt" had been reached. After determining the H/Pt atomic ratio by hydrogen chemisorption, these samples were investigated by X-ray diffraction and electron microscopy.

In none of the samples was platinum detected by X-ray diffraction. For H/Pt values down to about 0.3 this result is not surprising, since the size limit of the particles that can be detected with X-ray diffraction in these samples is about 3 nm. This corresponds to a calculated H/Pt value of 0.28. However, with the sample heated in hydrogen at 850°C (H/Pt < 0.2, corresponding theoretically to platinum particles > 4 nm) the absence of a clear X-ray pattern is rather puzzling. With this sample only a very small hump at the (311) platinum position was observed, too

small to fit in with the low H/Pt value. Apparently, under the prevailing conditions no, or hardly any, agglomeration of platinum crystallites takes place. Additional evidence for the latter conclusion was obtained from electron-microscopic analyses, the results of which are shown in Fig. 4. Although the average size of the detectable particles increases slightly with decreasing H/Pt ratio, it is obvious that in all cases this average particle size is too small to explain the measured H/Pt values. Moreover, the number of detected platinum particles was much smaller than expected. A quantitative determination of the amount of platinum detected by electron microscopy revealed that this amount is only a small fraction of the Pt present in the samples.

From the known amounts and the particle-size distribution of the detectable fraction of platinum we calculated its contribution to the overall H/Pt value (see Table 4). The remaining, nondetectable fraction of the platinum should comprise particles smaller than about 0.6 nm, the detection limit of our electron microscope (Siemens Elmiscop 101). Assuming that the latter fractions have H/Pt values very close to 1.0, we calculated the overall H/Pt



TABLE 4  
Distribution of Alumina-Supported Platinum (Catalyst E) after a Heat Treatment in Hydrogen

Sample	I <sup>a</sup>	II	III <sup>b</sup>	IV
Overall H/Pt ratio determined by H <sub>2</sub> chemisorption	0.70	0.58	0.48	0.30
Fraction of Pt detected by electron microscopy, % by weight	4.5	9.6	12.2	39.2
Calculated average H/Pt ratio of the detected particles	0.94	0.92	0.90	0.75
Contribution of the detected Pt particles to the overall H/Pt ratio	0.042	0.088	0.110	0.294
Fraction of Pt present in particles <0.6 nm required to give the overall H/Pt ratio (particles with H/Pt = 1.00), % by weight	65.8	49.2	37.0	0.6
Fraction of Pt "inaccessible" to H <sub>2</sub> (Pt with H/Pt = 0.00), % by weight	29.7	41.2	40.8	60.2

<sup>a</sup> I, 110 h, 500°C; II, 60 h, 550°C; III, 60 h, 600°C; IV, 10 h, 675°C.

<sup>b</sup> Example of H/Pt balance (sample III):  $0.48 = (12.2/100) \times 0.90 + (37.0/100) \times 1.00 + (40.8/100) \times 0.00$ .

ratios for the various samples. The calculated values, which were all between 0.9 and 1.0, are much higher than the actual values measured by hydrogen chemisorption.

This striking discrepancy between calculated and measured H/Pt values can be accounted for only by assuming that the platinum fraction not detected by electron microscopy contributes only in part to the measured overall H/Pt value (see Table 4). This means that after heat treatment in hydrogen a certain amount of platinum is no longer available for hydrogen chemisorption. This "inaccessible" fraction of the platinum is presented in Table 4.

Upon treatment in hydrogen no significant changes could be detected in the alumina support, such as a collapse of the pore structure, which could result in part of the metal being trapped within the support. We therefore assume that all of the platinum is still physically accessible to hydrogen, but part of it has lost its ability to chemisorb hydrogen.

Essential for the results mentioned in Table 4 is the fact the adsorption stoichiometry does not depend on metal particle

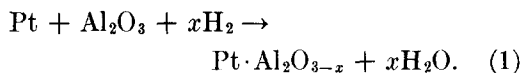
size. For all our calculations we assumed that each surface platinum atom chemisorbs one hydrogen atom. Consequently, the data obtained on the amounts of "inaccessible" platinum are at least correct on a relative basis.

It will be clear that the estimate of the platinum fraction detected by electron microscopy has to be regarded as rather rough, because for highly dispersed supported metal catalysts this technique gives qualitative rather than quantitative results. If, however, we accept that the quantitative determination of the amount of platinum present in these samples as particles of 0.6 to 3.0 nm is accurate within a factor of two to three, the amount of platinum present as "inaccessible" platinum will not change dramatically.

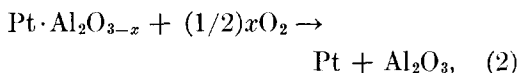
(C) *Effect of Air Treatments on the H/Pt Value of Catalysts Severely Pretreated in Hydrogen*

To explain why part of the platinum can lose its ability to chemisorb hydrogen one could conceive that during heat treatment in hydrogen part of the platinum

reacts with the alumina surface of the carrier:



According to this hypothesis the "inaccessible" amount of platinum is the platinum converted into Pt·Al<sub>2</sub>O<sub>3-x</sub>. Owing to the interaction with the support it has lost its ability to chemisorb hydrogen. This interpretation is consistent with the surface reduction of alumina occurring at high temperature as proposed previously (15). Since the energetics for surface compounds are unknown and considerably different from those for bulk compounds, thermodynamic data cannot be used in predicting the possibility of the proposed reaction. We therefore looked for other qualitative arguments. Since it can be expected that the Pt·Al<sub>2</sub>O<sub>3-x</sub> surface compound will be sensitive to oxygen:



we wondered what would happen if a hydrogen-pretreated Pt/Al<sub>2</sub>O<sub>3</sub> catalyst were exposed to an oxidative atmosphere. We investigated this matter more closely using Cl-free samples to rule out a possible interaction by halogen (13b). The H/Pt values of the freshly calcined samples and

TABLE 5

Increase of the H/Pt Value of Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts Previously Heated in Hydrogen by Repeated Oxidation-Reduction

Catalyst	H/Pt atomic ratio		
	Original	After heat treatment in hydrogen	After five oxidation/reduction cycles
G	0.72	0.47	0.70
F	0.60	0.43	0.60
F	0.60	0.24	0.60
C	1.00	0.64	0.97

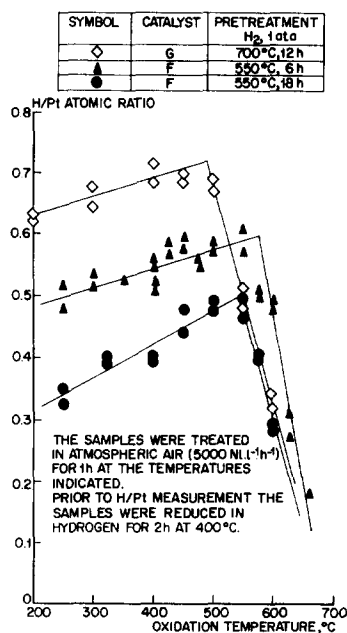


FIG. 5. Effect of oxidation treatment on the H/Pt value of Pt/Al<sub>2</sub>O<sub>3</sub> samples previously heated in hydrogen.

the H/Pt values upon hydrogen pretreatment have been collected in Table 5.

As can be seen from the results presented in Fig. 5 and Table 5 we succeeded in increasing the H/Pt value of the catalyst samples which had been purposely maltreated in a hydrogen atmosphere.

Figure 5 clearly shows that the results are greatly affected by the temperature of the air treatments. With Cl-free UOP alumina the best results were obtained between 400 and 500°C, with Péchiney alumina between 450–550°C.

The increase in H/Pt value obtained at a given oxidation temperature is independent of the length of the oxidation period (which was varied from 15 min to 6 h) and of the oxygen partial pressure (both atmospheric air and oxygen were used). However, on repeated oxidation-reduction a further increase of the H/Pt atomic ratio was observed. We found that the H/Pt value increased with every additional air treatment, although the increase became progressively smaller. The

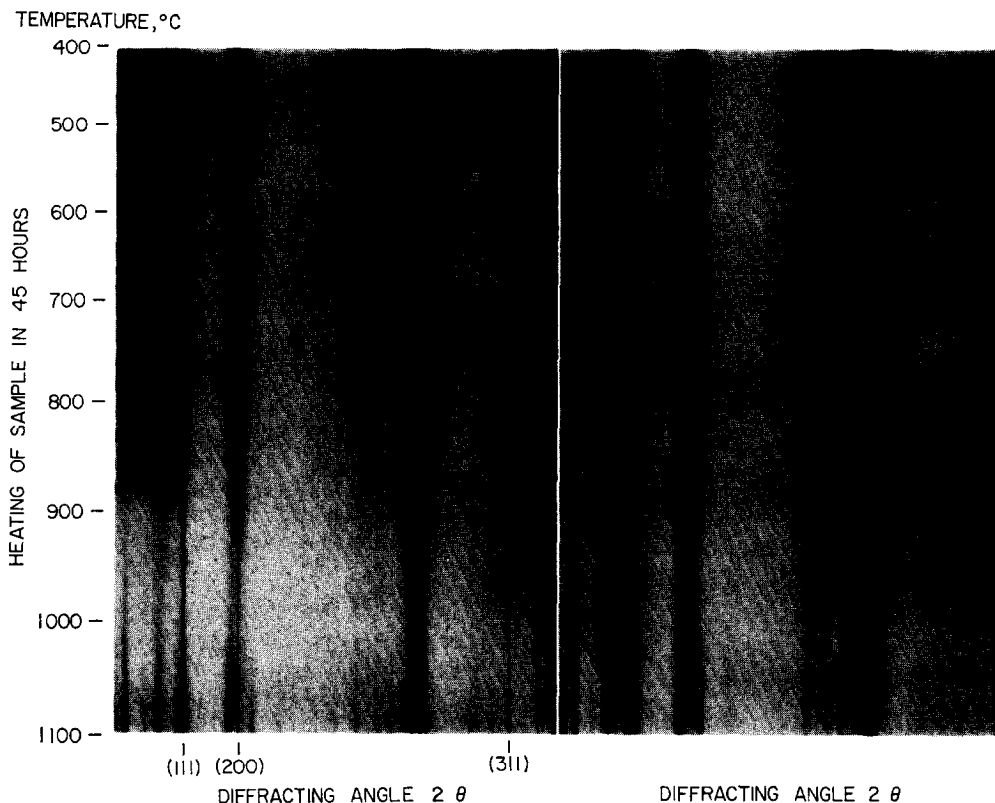


FIG. 6. Guinier photographs of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (sample E). (A) Heat treatment in air. The pattern contains three distinct Pt lines superimposed on the alumina pattern (see Fig. 6B). (B) Heat treatment in hydrogen. The pattern consists of alumina lines only.

best results which we obtained by repeated oxidation/reduction are given in Table 5.

*(D) Effect of the Heating Atmosphere; Comparison of Air and Hydrogen*

When we compare the results presented in the two foregoing sections, it is obvious that the mechanisms of H/Pt loss by heat treatment in air and in hydrogen must be completely different, in line with many other observations reported in the literature [e.g., Refs. (5, 16-20)]. Our results demonstrate that calcining in air leads to partial (and ultimately complete) transformation of the well-dispersed Pt into large crystallites (10 nm and larger, with no crystallites of intermediate size), whereas crystallite growth does not occur to any

significant extent in an H<sub>2</sub> atmosphere. In H<sub>2</sub> the loss of H/Pt is mainly caused by part of the Pt becoming "inaccessible."

A straightforward illustration of the different responses of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts to heat treatments in hydrogen and air is given by two X-ray diffraction photographs made with a high-temperature Guinier camera (Fig. 6). The left photograph was made while the catalyst sample was being heated up in air from about 300 to 1100°C during 45 h. Up to about 575°C, only the diffraction pattern of the Al<sub>2</sub>O<sub>3</sub> support is recorded, which is in line with the highly dispersed nature of the platinum being maintained. At about 575°C, Pt lines appear (the 111, 200, and 311 lines are clearly visible, superimposed on the alumina diffraction pattern). This demonstrates the sintering of part of the well-

dispersed Pt into X-ray detectable crystallites. This photograph also shows that the intensity of the Pt lines gradually increases, whereas the line width stays practically constant. This means that after reaching a certain size the Pt crystallites do not grow any further, but gradually increase in number [see also Baker *et al.* (13b)]. The right photograph, taken from catalyst sample E heated up in hydrogen, does not show any Pt lines at all, even at temperatures where the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is transformed into  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. This demonstrates that in an H<sub>2</sub> atmosphere sintering of Pt does not occur to any significant extent.

#### DISCUSSION

Our results clearly show that care should be taken in predicting the average size of the platinum particles from hydrogen-chemisorption data alone, even if one restricts oneself to samples treated in oxygen. By the same token it is not correct to predict a H/Pt value from an average particle size determined by either X-ray analysis or electron microscopy if one does not have the additional information about the extent to which the detected amount of platinum represents the total amount of Pt in the sample. Consequently, the H/Pt ratio cannot be used as a yardstick of crystallite size under all circumstances. This should be kept in mind in, for example, studies related to the question of whether or not there occur Pt-catalyzed structure-insensitive reactions, which is still an important controversial issue in the literature [see e.g. Refs. (21-24)].

Various authors [e.g. Refs. (3, 29-31)] have fitted their data to a simple power equation of the form:

$$dS/dt = -k \cdot S^n,$$

where  $S$  is the metal surface area,  $n$  is generally reported as an integer, and the activation energy is incorporated into the constant  $k$ . Even if we restrict ourselves to the results obtained upon sintering in

air, we find that the processes occurring are too complicated to justify the application of such a simple power law equation. With respect to the sintering mechanism, we feel that the results obtained so far are insufficiently conclusive to allow a distinction to be made between crystallite migration (32) and atomic or molecular interparticle transport (33) as possible alternatives describing the reported phenomena. Further experiments will be necessary to establish which factors lead to loss of exposed platinum surface area.

Previously reported data (25-28) on the catalytic activity of Pt/Al<sub>2</sub>O<sub>3</sub> are consistent with the concept that part of the platinum may lose its ability to chemisorb hydrogen through a chemical reaction with the support. In these studies Pt/Al<sub>2</sub>O<sub>3</sub> samples, prepared along the lines which we followed to make catalysts E and F, were subjected to treatments in hydrogen to obtain H/Pt values ranging from 1.0 down to 0.22. High-temperature treatment in hydrogen always caused the activities to decrease, both for benzene hydrogenation (25) and for *n*-hexane dehydrocyclization and isomerization (28). The observed activity decrease was found to be proportional to the reduction in H/Pt ratio. These activity data together with our observations justify our assumption as regards the existence of "inaccessible" platinum. It will be clear, however, that more experiments are needed to explain in detail the intriguing phenomena occurring in reducing atmospheres. We intend to report on such results in a subsequent paper (34).

Various investigators [e.g. Refs. (12, 35-39)] have reported increases in Pt dispersion during treatments of Pt catalysts in oxygen-containing atmospheres, a phenomenon which has been attributed to redispersion of the metal. It is interesting to note, however, that the ultimate level of H/Pt to which we were able to restore the H/Pt value never exceeded the H/Pt

level of the fresh sample (i.e., prior to the treatment in hydrogen). Part of the platinum present in our freshly prepared, non-optimal samples (H/Pt lower than 1.0) had presumably been sintered during catalyst preparation into "big" crystallites, before we started the pretreatments in hydrogen. The fact that we could not raise the H/Pt ratio above the original value by successive oxidation/reduction treatments strongly suggests that the beneficial effect of an oxidation treatment is limited to recovery of that portion of the platinum which had become "inaccessible" during maltreatment in hydrogen and that by oxidation one does not actually redisperse sintered platinum.

Figure 5 shows that beyond a certain temperature the beneficial action of the air is counteracted by sintering of the platinum, which then causes a steep drop in the ultimate H/Pt value with increasing temperature. After a treatment at 650°C, for instance, the resulting H/Pt values are lower than those of the starting material (see Fig. 5). The H/Pt ratio of a catalyst maltreated in this way could not be restored by air treatment at the preferred lower temperatures. This again shows that an oxidative treatment can only recover the fraction of platinum lost by severe heat treatment in a hydrogen atmosphere, and that it is incapable of actually redispersing big crystallites.

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