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Surface Interactions in the Pt/γ-Al_2O_3 System

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Using temperature-programmed reduction, Pt oxide deposited on γ-Al_2O_3 was found to be present in two phases: a particulate phase in which the Pt oxide is aggregated and has little interaction with the support, and a dispersed phase in which Pt oxide has a larger interaction with the support. The lower the concentration of Pt oxide in the dispersed phase, the stronger is the Pt oxide–support interaction. Using selective chemisorption of H_2 and CO on Pt/γ-Al_2O_3 samples, the Pt oxide concentration in the dispersed phase was found to increase proportionally with Pt loading until a saturation concentration of 2.2 μmol Pt/m^2 (BET) is reached. Beyond this concentration, the excess Pt oxide aggregates to form a particulate phase. At 500°C in O_2 a quasi-equilibrium between Pt oxide in the dispersed phase and that in the particulate phase is reached. The behavior of Pt oxide on γ-Al_2O_3 during other various heat treatments was found, using transmission electron microscopy, to depend on Pt loading as well as temperature and chemical atmosphere.

INTRODUCTION

A number of previous studies (*1–6*) of platinum oxide deposited on a γ-alumina support have shown the presence of two platinum oxide phases: a two-dimensional dispersed phase, in which Pt oxide is present in Pt–Al_2O_3–Cl or PtO_2–Al_2O_3 complexes (*1–3*) and is soluble in acids and acetylacetone, and a three-dimensional particulate phase in which Pt oxide is present in crystallites and is insoluble in acids. The existence of two phases in other supported transition metals and metal oxides has also been reported (*7–16*). It has been demonstrated that at low concentration, transition metal oxides on oxide supports can be dispersed into a two-dimensional phase by heat treatment in air or vacuum at about 500°C (*12–15*). At high metal concentration, a saturated dispersed phase is in equilibrium with a particulate phase after this treatment. The saturation concentration of the dispersed phase varies with the metal oxide and also with the composition of the support.

This work continues the investigation of the two phases of Pt oxide on γ-alumina with the following objectives: (i) to give further evidence of the existence of two phases, aside from the solubility differences, (ii) to determine the saturation concentration of the dispersed phase, and (iii) to describe the behavior of Pt on γ-alumina during heat treatment in oxidizing and reducing atmospheres with reference to the two phases.

EXPERIMENTAL

I. Materials

A granular γ-Al_2O_3 support was made by agglomerating Dispal-M γ-Al_2O_3 powder (Conoco Chemicals) by wetting with water, drying, and calcining at 600°C. The result-

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TABLE 1

Hydrogen and Carbon Monoxide Adsorption on Pt/γ-Al_2O_3[a] at 25°C

Sample	Pt loading		H uptake (μmol/m^2)	H/Pt	CO uptake (μmol/m^2)	CO/Pt
	(wt%)	(μmol/m^2)				
1	0.78	0.25	0.31	1.24	0.21	0.85
2	1.64	0.48	0.57	1.18	0.40	0.83
3	3.30	1.17	1.47	1.26	0.97	0.83
4	7.39	2.82	2.42	0.86	1.63	0.58
5	13.8	4.60	2.86	0.62	1.88	0.41
6	23.1	12.3	7.63	0.62	5.41	0.44

[a] Fresh Pt/γ-Al_2O_3 samples were calcined at 400°C in air and reduced at 300°C by H_2 before adsorption.

ing solid mass was crushed and sieved and the 0.5- to 1.0-mm-diameter fraction was chosen for the support. An adsorption-impregnation method was used to prepare the samples (Table 1). The support for each sample was immersed in distilled water into which aqueous H_2PtCl_6 of a desired concentration was added. The samples were evaporated and dried in air at 120°C. Samples with high Pt loading were rewetted with water and redried to distribute the Pt ions uniformly. Each sample was calcined in air at 400°C for 2 hr. The Pt content of each sample was determined by X-ray fluorescence. The chloride content of some selected samples was determined by the same method.

Research grade N_2 and CO were used without further purification. Hydrogen was purified by passage over an Engelhard Deoxo Pd catalyst and a 4-Å molecular sieve at 78° K. PtO_2 (40 mesh, Ventron Corp.) was used without further purification. This PtO_2 was found to be insoluble in an HF solution. An analysis by X-ray diffraction indicated the presence of a small amount of metallic Pt.

II. Adsorption Measurements

The apparatus and procedure for measuring BET area, and hydrogen and carbon monoxide adsorptions of supported platinum samples, are described in previous papers (*14*, *15*). All samples were pretreated in H_2 at 300°C (in some cases at 500°C) for 2 hr and outgassed at the same temperature for another hour.

III. Temperature-Programmed Reduction (TPR)

TPR measurements were made in a flow system similar to that described by Robertson *et al.* (*17*). A small amount of PtO_2 or Pt/γ-Al_2O_3 was precalcined in air at 500°C and placed in a TPR cell at −75°C through which H_2-Ar(15:85) gas flowed. The temperature of the sample was programmed to rise at a constant rate of 8°C/min and the amount of H_2 uptake during the reduction was measured by a thermal conductivity detector.

IV. Transmission Electron Microscope (TEM)

TEM micrographs were obtained using a Siemens Elmiskop I TEM. The selected area electron diffraction patterns and energy dispersive X-ray analyses were obtained using a Philips 300 TEM. The extraction replication procedure used in making these measurements is similar to that described by Benesi *et al.* (*18*) and Dalmai-Imelik *et al.* (*19*). A small amount of ground sample was spread on a microscope slide and was coated with a layer of evaporated carbon. The carbon film containing sample particles was separated from the slide by floating it first on the surface of a 10% HF solution to dissolve the alumina completely, and then on the surface of distilled water to wash away the HF. The replica film was then picked up from the water surface using microscope grids and allowed to dry on bibulous paper before observation in the TEM.

RESULTS

I. Chemisorption Measurements

A. Fresh samples. Adsorption isotherms of H_2 and CO on six fresh Pt/γ-Al_2O_3 samples of varying Pt loading were measured at 25°C. H_2 and CO uptakes of each sample were determined from these measurements by extrapolating the isotherms to zero pressure of the adsorbate. These uptakes along with H/Pt and CO/Pt for each sample, the ratios of H and CO adsorbed at 25°C to the total number of Pt atoms in the sample, are summarized in Table 1.

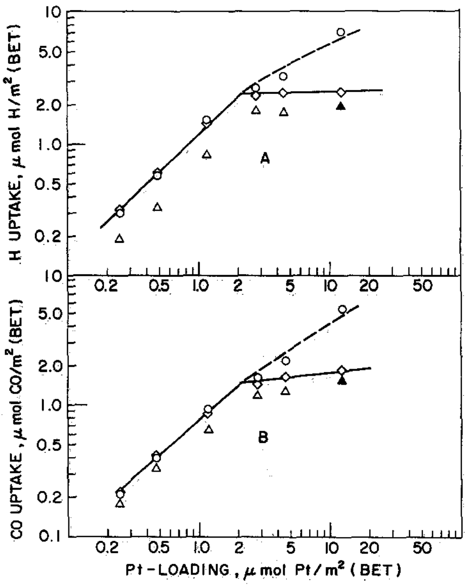


FIG. 1. Chemisorption of H (A) and CO (B) on Pt/γ-Al_2O_3 samples as a function of Pt loading: (○) heated 2 hr in H_2 at 300°C; (△) heated 2 hr in H_2 at 500°C; (▲) heated 2 hr in H_2 at 750°C; (◇) heated 5 hr in O_2 at 500°C.

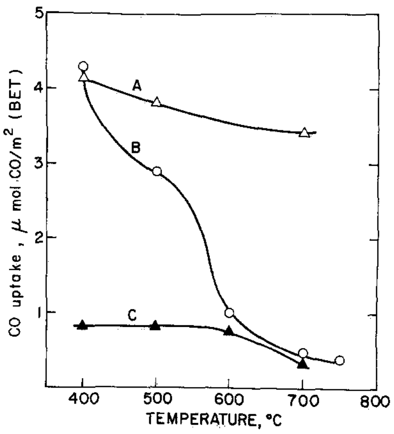


FIG. 2. CO chemisorption on Pt/γ-Al_2O_3 samples after 3-hr heat treatments at various temperatures: (A) sample 6 *in vacuo;* (B) sample 6 in dried air; (C) sample 3 in dried air.

It has been suggested that the stoichiometric H/Pt and CO/Pt ratios for a completely dispersed sample are unity (*20*) and 0.87 (*21*), respectively. So the high ratios of H/Pt (1.18–1.26) and CO/Pt (0.83–0.85) in the samples of low Pt loading (samples 1, 2, and 3) probably indicate complete dispersion of Pt in these samples. H/Pt ratios higher than unity have been found previously on well-dispersed supported Pt samples (*6*, *22–25*) and were attributed to multiple adsorption (*23*, *25*) and adsorption on the interstices of monolayer Pt atoms (*6*). On the other hand, the H/Pt and CO/Pt ratios in the samples of high Pt loading (samples 4, 5, and 6) are much lower than unity and 0.87, respectively. These ratios decrease sharply with increasing Pt loading.

B. Heat treatments in oxidizing and reducing atmospheres. A comparison was made in Fig. 1 of H and CO uptake on samples 1 to 6 after each step in the following sequence of heat treatments: (i) H_2 at 300°C for 2 hr (points 0), (ii) H_2 at 500 or 750°C (points △ or ▲) for 2 hr, and (iii) O_2 at 500°C for 5 hr (points ◇). The decrease in accessible Pt area in all samples following heat treatment in H_2 at 500 or 750°C indicates sintering. The general in-

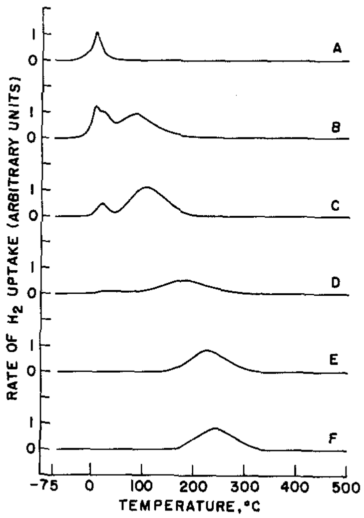


FIG. 3. Temperature-programmed reduction of PtO_2 and Pt/γ-Al_2O_3 samples: (A) PtO_2 powder; (B) sample 6; (C) sample 5; (D) sample 4; (E) sample 2; (F) sample 1 (see Table 2).

crease in accessible area following heat treatment in O_2 at 500°C indicates redispersion of these H_2-sintered samples.

Another comparison was made in Fig. 2 of the degree of sintering in flowing dried air of samples 3 (curve C) and 6 (curve B) in the temperature range 400 to 750°C. Sintering data for sample 6 in vacuum (curve A) was included as a reference. Sample 6 sinters substantially between 400 and 600°C unlike sample 3 which sinters negligibly. At temperatures higher than 600°C, sintering in the two samples is almost identical.

II. Temperature-Programmed Reduction

In this study a nonsupported PtO_2 sample and five γ-alumina-supported samples of varying Pt loading were reduced at temperatures ranging from -75 to 500°C. The results shown in Fig. 3 and Table 2 indicate that the nonsupported PtO_2 was reduced below 25°C with a maximum rate at ~5°C (curve A). The 10% difference between calculated and observed values of H_2 uptake (Table 2) for this sample is probably due to the presence of the small amount of metallic Pt mentioned previously. In the samples of high Pt loading (curves B, C, and D), reduction occurs in two temperature ranges: 5 to 20°C and ~90°C. In the samples of low Pt loading (curves E and F), only the high temperature reduction was found.

III. Particle Size Measurements

TEM can be used to directly measure the particle size of Pt supported on a very thin alumina film (*26*). When granular silica or alumina is used as support material, interference from support particles may make it impossible for direct TEM measurement and very difficult for measurement with extraction replicas (*27*, *28*). However, a carbon replica in which the support particles were dissolved with a dilute HF solution allowed Pt/silica and Pt/alumina samples to be successfully measured by Benesi *et al.* (*18*) and Dalmai-Imelik *et al.* (*19*). A similar method is used in this study to measure alumina-supported Pt oxide particles which are insoluble in HF solution.

Four sets of transmission electron micrographs were made in which four samples of varying Pt loading were subjected to different sequential heat treatments. Pt particle sizes were measured directly from the micrographs at a magnification of

TABLE 2

Temperature-Programmed Reduction of Platinum Oxide on γ-Al_2O_3

Sample	Pt in sample (μmol)	Observed H_2 uptake (μmol)	Calculated[a] H_2 uptake (μmol)	$T_{\text{max rate}}$ (°C)
PtO_2 powder	17.5	32.6	35.0	5
6	73.0	36.4	146.0	10 90
5	22.9	38.5	45.8	20 100
4	11.5	21.0	23.0	175
2	13.9	27.6	27.8	220
1	14.1	24.4	28.2	245

[a] Based on the assumption that all Pt is present as PtO_2.

TABLE 3

The TEM Data on Particle Size

Sample	Heat treatment sequences	Particle size range (TEM) (Å)	Average particle size (TEM) (Å)	Average particle size (electron diffraction line broadening) (Å)
1	500°C, 3 hr, O_2	—	—[a]	
1	300°C, 3 hr, H_2	—	—[a]	
1	500°C, 3 hr, H_2	10–30	15	
1	750°C, 3 hr, H_2	10–30	15	
3	500°C, 3 hr, H_2	10–35	20	
3	500°C, 5 hr, O_2	10–35	20[b]	
3	600°C, 4 hr, O_2	10–75	35	
3	750°C, 4 hr, O_2	200–800	300	
6	500°C, 3 hr, O_2	10–30	15	13
6	300°C, 3 hr, H_2	10–55	30	
6	500°C, 3 hr, H_2	10–55	30	
6	750°C, 3 hr, H_2	10–30	20	18
		55–150	70	
6	750°C, 5 hr, H_2	10–30	20	
		60–300	130	
6	500°C, 16 hr, O_2	60–300	130[c]	

[a] No particles observed.

[b] Less than 5% of the particles were left after this heat treatment.

[c] Used as standard for line broadening in electron diffraction.

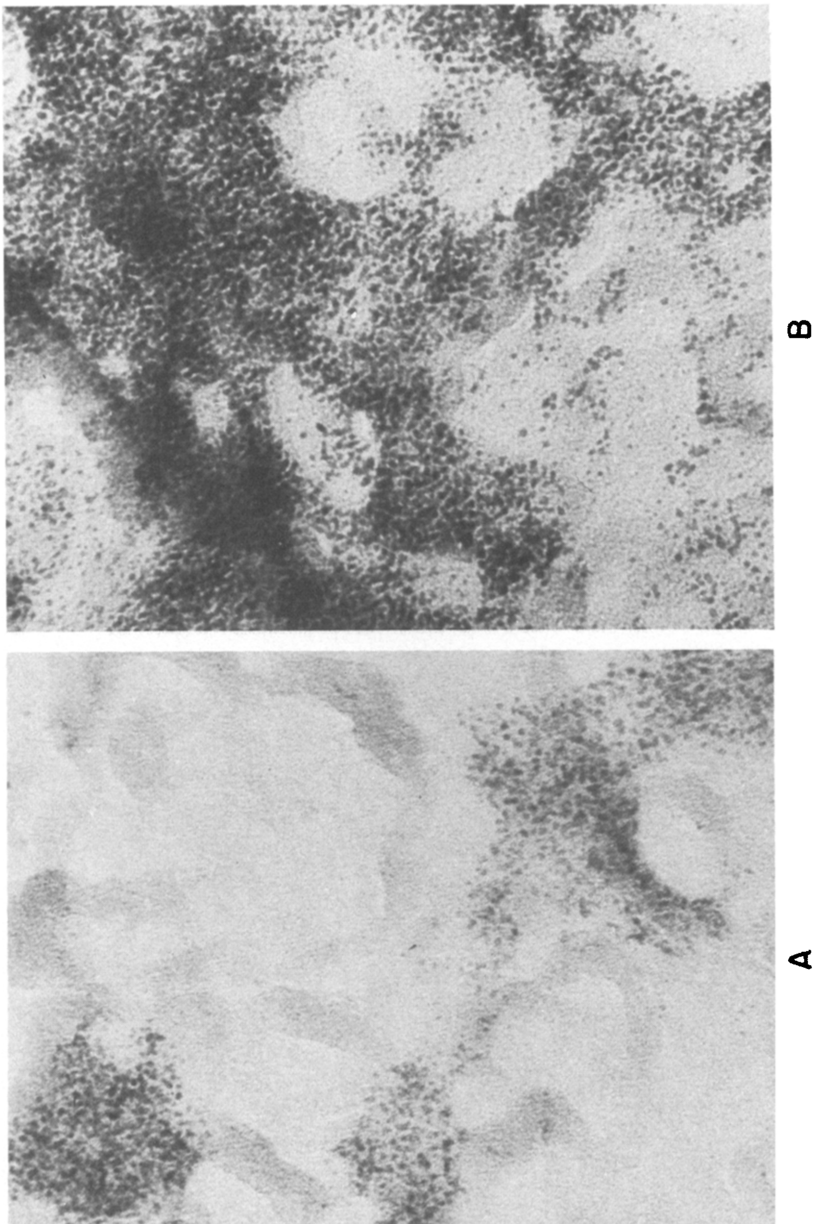
550,000× or 350,000×. For some of the samples, electron diffraction patterns were also taken and particle sizes were calculated from measurements obtained from microdensitometer traces of the diffraction patterns using the Sherrer line broadening equation. These data are summarized in Table 3. Figure 4 shows representative areas of selected micrographs.

After heating sample 1 in O_2 at 500°C and after heating in H_2 at 300°C, no particles were found in the micrographs (Table 3) and no Pt was detected on the extraction replicas, indicating that this Pt was soluble in the HF solution. Only after heat treatment of sample 6 in H_2 or sample 3 in air at 750°C was a large increase in particle size found. It is interesting to note that heat treatment in H_2 at 750°C can produce a bimodal size distribution (Fig. 4C and Table 3). Only the small particles are redispersed during the subsequent heat treatment in O_2; the larger crystallites remain intact (Fig. 4D).

DISCUSSION

I. The Existence of Two Phases and the Dispersion Limit

The temperature-programmed reduction gives evidence of two phases of Pt oxide on a γ-Al_2O_3 support, in addition to evidence from solubility differences mentioned previously. Samples 4 to 6 (curves B, C, and D, Fig. 3) show both phases: a particulate phase where the Pt oxide has little interaction with the alumina support as seen by the reduction at ~10°C, resembling the reduction of unsupported bulk PtO_2; and a dispersed phase where the Pt oxide interacts more strongly with the support, and thus is reduced at higher temperatures.


B
A

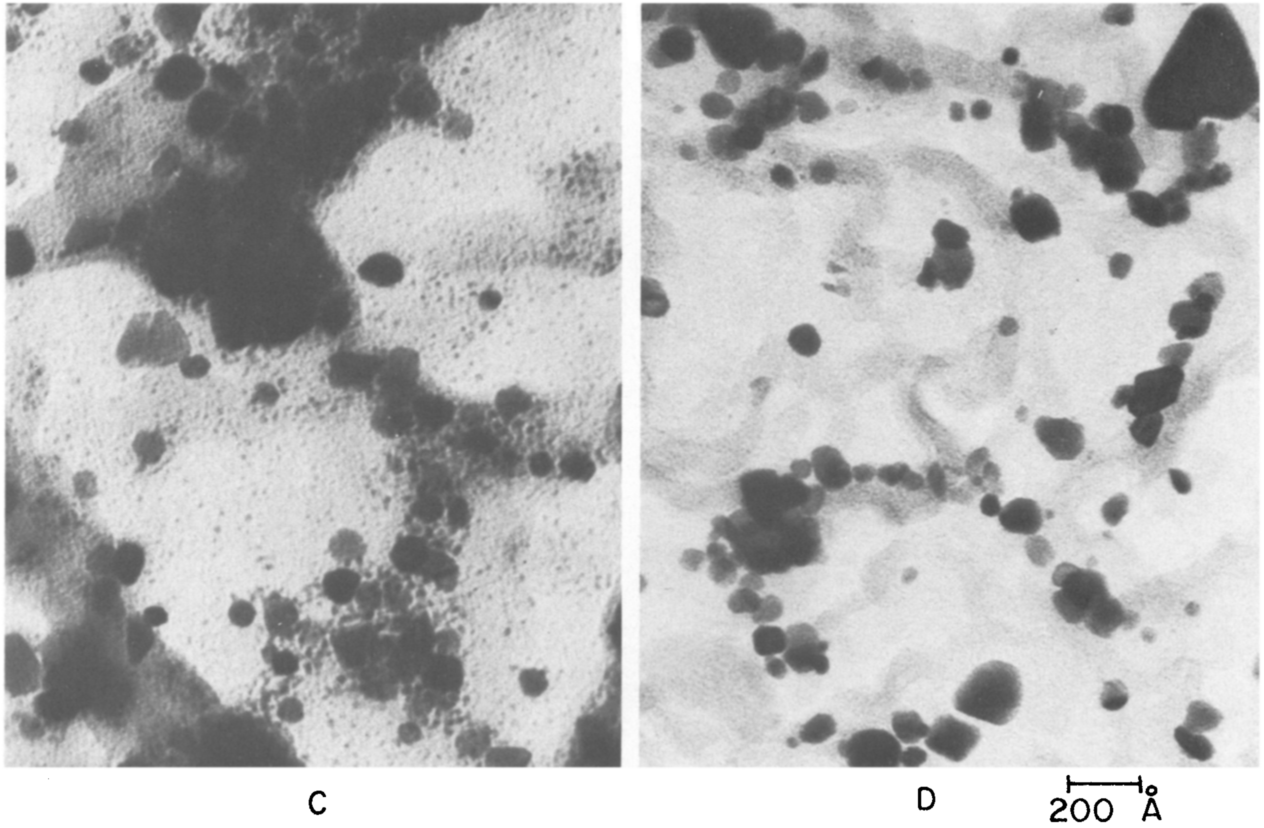


FIG. 4. Transmission electron micrographs of Pt/γ-Al_2O_3 samples: (A) sample 1, 750°C, 3 hr, H_2; (B) sample 6, 500°C, 3 hr, O_2; (C) sample 6, 750°C, 5 hr, H_2; (D) sample 6 [same sample as in (C)], 500°C, 16 hr, O_2 (see Table 3).

TABLE 4

Chloride Content in Sample 4 after Sequential Treatments

Sequential treatments	Cl^- content (mg/g)
Dried at 110°C, 5 hr, air	58.0
400°C, 5 hr, flowing air	24.5
300°C, 3 hr, flowing H_2	11.5
500°C, 5 hr, flowing H_2	6.5
500°C, 20 hr, flowing air	<1.0

In the samples of low Pt loading (curves E and F), only dispersed phase Pt oxide is found. The H_2 uptake measurements during these reductions (Table 2) indicate that Pt oxide in the dispersed phase is PtO_2 while Pt in the particulate phase is probably mixed PtO_2, PtO, and metallic Pt. The large increase of the reduction temperature with dilution of PtO_2 in the dispersed phase indicates that all the dispersed PtO_2 molecules are in close contact with the support and they are probably separated from each other. The larger this separation, the stronger is the PtO_2–Al_2O_3 interaction. This interaction may result in a dissolution of PtO_2 into the surface layer of Al_2O_3 or in the formation of a $PtO_2 \cdot Al_2O_3$ complex as previously suggested (*1–3*). The PtO_2 in the dispersed phase would consequently be soluble in the acetylacetone and dilute HF solution. As pointed out previously (*3*, *29*) chloride is not required for the formation of this soluble stable complex. The chloride ions in the support of the samples used in this study (Table 4) may stabilize Pt ions on alumina (*1*) and thereby increase their dispersibility.

Although the two phases are strictly defined only for Pt oxide on alumina, the chemisorption data (Table 1) shows that after reduction in H_2 at 300°C, samples 1 to 3 remain completely dispersed. In these samples of low Pt loading, Pt area increases proportionally with Pt loading (Fig. 1) until it reaches a dispersion limit of about 2.2 μmol Pt/m^2 (BET). Beyond this limit the excess Pt oxide aggregates to form particles or crystallites.

II. The Quasi-equilibrium of Pt Oxide on γ-Al_2O_3 in O_2 at 500°C

The surface concentration of exposed Pt atoms in fresh samples of high Pt loading (reduced at 300°C in H_2) can exceed the dispersion limit of 2.2 μmol Pt/m^2 (BET). However, heat treatment in O_2 at 500°C decreases this surface concentration to the dispersion limit (Figs. 1 and 2). Heat treatment of these samples in flowing H_2 at 500°C decreases the exposed Pt surface concentration below the dispersion limit, but heat treatment in O_2 at 500°C increases it back to the dispersion limit (Fig. 1). These results indicate a saturation concentration of Pt oxide in the dispersed phase and a quasi-equilibrium between Pt oxide in the dispersed phase and that in the particulate phase at 500°C in O_2. The saturation concentration of dispersed phase Pt oxide is ~2.2 μmol/m^2 (BET). Pt oxide at this concentration, if closely packed in a monolayer, can cover only about 15% of the surface area of the alumina support. The crystallite size of Pt oxide in the particulate phase at equilibrium is ~15 Å (Table 3, sample 6 after 500°C heat treatment in O_2).

A similar quasi-equilibrium was also found in other supported transition metal oxide systems (*13–15*). Saturation concentration was found to vary mainly with support material and to a lesser extent with transition metal. For example, the saturation concentration of cobalt oxide on zirconia was found to be ~8 μmol Co/m^2 (BET) (*13*) while in Re and Rh oxide on γ-Al_2O_3 it was 2 to 2.5 μmol/m^2 (BET) (*14*, *15*).

III. Behavior of the Two Phases in Oxidizing and Reducing Atmospheres

The behavior of supported Pt samples during heat treatment in oxidizing and reducing atmospheres depends on (i) Pt loading, (ii) state of dispersion, and (iii) temperature of heat treatment. Behavior in O_2 at 500°C (Figs. 1 and 2 and Table 3) can be interpreted with reference to the equilibrium of Pt oxide in the two phases. For samples of Pt loading below the saturation concentration (samples 1–3), all the Pt oxide can be dispersed during heat treatment at 500°C in O_2. Fresh samples of Pt loading above the saturation concentration sinter during heat treatment at 500°C in O_2 to reach the saturation concentration of the dispersed phase so the two Pt oxide phases will be in equilibrium.

Heat treatment in hydrogen at various temperatures and in O_2 or air at ≥ 600°C reduces or decomposes Pt oxide to form metallic Pt which aggregates (Table 3). In H_2 at 300°C, Pt atoms formed from the dispersed phase PtO_2 remain completely dispersed. It is uncertain whether these Pt atoms are aggregated to form discontinuous monolayer patches (*6*) or small clusters of about 6 atoms (*30*), or remain atomically dispersed (*31*). On the other hand these same Pt atoms after reduction at 500 or 750°C by H_2 aggregate to form particles of 10 to 35 Å and their accessibility to H_2 and CO adsorption decreases. Particulate phase PtO_2 crystallites grow somewhat larger in H_2 even at 300°C. At 750°C Pt particles in two size ranges are produced in samples of Pt loading above the saturation concentration. Only the small particles of 10 to 30 Å, similar to those formed from dispersed phase PtO_2 under these conditions, are redispersed in O_2 at 500°C. Large particles also form in O_2 at ≥ 600°C, even in samples with Pt loading below the saturation concentration. At 750°C, the aggregation of Pt particles in O_2 is much faster than it is in H_2.

Loss of Pt area during heat treatment in H_2 at 500°C and its subsequent recovery after heat treatment in O_2 at 500°C were observed previously (*32–34*). Dautzenberg *et al.* attributed the loss to the reduction of the alumina support during heat treatment in H_2 at 500°C to form a $Pt\text{–}Al_2O_{3-x}$ complex or a Pt_3Al alloy which does not adsorb hydrogen and from which Pt can be regenerated by heat treatment in O_2 at 500°C. The above TPR results do not support this interpretation. Reduction of Pt oxide on alumina is complete at 300°C and no further reduction is found at 500°C in H_2 (Fig. 3).

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