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Pt/Al_2O_3

I. Percentage Exposed and Its Effect upon the Reactivity of Adsorbed Oxygen

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A set of platinum catalysts on γ-alumina was prepared by impregnation with $Pt(NH_3)_2(NO_2)_2$ aq and $Pt(NH_3)_4(NO_3)_2$ aq. Calcination at 200–400°C followed by reduction at 300–500°C gave percentages exposed of platinum as measured by hydrogen chemisorption at 25°C (D_h) $\simeq$ 100%. Direct reduction of incompletely dried material led to lower values of D_h. The ratio D_t/D_h (D_t is the percentage exposed by hydrogen–oxygen titration at 25°C) was unity for $D_h < 45\%$, but it fell progressively below unity at larger values of D_h. At $D_h > 90\%$, not all oxygen adsorbed at 25°C reacted with pulses of hydrogen at 25°C. The ratio O/Pt_s increased with increasing temperature of adsorption of oxygen and at large enough O/Pt_s, reaction with hydrogen at 25°C became incomplete for all catalysts. The value of O/Pt_s at which reaction became incomplete was structure sensitive and decreased with increasing D_h, from about 1.15 for $D_h = 36\%$ to 0.5 for $D_h = 94\%$. At smaller D_h, O/Pt_s became about 2 after exposure to oxygen at 300°C; at D_h near 100%, O/Pt was about 1.15. Properties of Pt/SiO_2 and Pt/Al_2O_3 for these reactions are compared.

INTRODUCTION

Previous papers (*1–7*) have reported the preparation of a set of Pt/SiO_2 catalysts (*1*), the measurement of the percentage exposed of the platinum crystallites (*1, 2*), the measurement of the crystallite size and shape (*2, 3*), the adsorption of oxygen on the catalysts and the reactivity of adsorbed oxygen with hydrogen (*1*), and the effect of percentage exposed of the platinum crystallites upon various catalytic reactions (*4–7*). To provide some information on the effect of the support, a series of Pt/Al_2O_3 catalysts has been prepared and characterized. A study of the hydrogenolysis of methylcyclopropane and of isotopic exchange between deuterium and cyclopentane on these catalysts appears in the following paper (*8*).

In the preparation of the Pt/SiO_2 catalysts, recipes in the literature led immediately to the desired wide range of percentages exposed (6.2–81%). In the present work, we wished to avoid the presence of any added chloride which could generate strongly acidic sites. Further, in our standard pretreatment, the one which preceded measurement of percentage exposed by hydrogen chemisorption (O_2,300°,0.5;H_2,300°,1;Ar,450°,1 where O_2,300°,0.5 indicates treatment in oxygen at 300°C for 0.5 hr, etc.), the highest temperature employed is 450°C. As in the preparation of the Pt/SiO_2 catalysts, we wished to avoid temperatures much in excess of 450°C during preparation so that, after the standard pretreatment, the nature of the alumina surface of all catalysts would be nearly the same. Further, exposure of Pt/Al_2O_3 catalysts to hydrogen at high temperatures (~600°C) has been reported to result in anomalous behavior and the formation of particles whose distribution in diameter is bimodal (*9*) and it is known that *bulk* platinum and alumina react

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with hydrogen at still higher temperatures (~1000°C) to form Pt,Al alloys (*10*). We elected to prepare the catalysts by impregnation with $Pt(NH_3)_2(NO_2)_2$ or $Pt(NH_3)_4(NO_3)_2$ followed by reduction with hydrogen. It was easy to prepare catalysts of percentages exposed of ~100% by this procedure, but we encountered difficulty in preparing catalysts with percentages exposed of 15–70%. The desiderata given above precluded the use of sintering at high temperatures to achieve percentages exposed in this range. Development of a method to prepare such catalysts led to the preparation of many more Pt/Al_2O_3 catalysts than the 10 catalysts made in the Pt/SiO_2 set.

Since a substantial effect of structure sensitivity was observed in the adsorption of oxygen on the Pt/SiO_2 catalysts and in the reaction of hydrogen with the adsorbed oxygen, this paper reports a study of this matter for Pt/Al_2O_3 catlaysts and a comparison of the behavior of platinum on the two supports with respect to these reactions. Rather a large number of papers have been published on such subjects, but agreement among them is poor.

TABLE 1

The Preparation of Al_2O_3–PtNN Catalysts

D_h[a] (%)	Pt (wt%)	T_{calcd}[b] (°C)	Time (hr)	T_{red}[c] (°C)	Time (hr)
106	0.212	200	0.33	300	2
103.8	0.293	400	1.0	500	2
100.9	0.293	400	1.0	300	25
96.7	0.293	400	1.0	300	2
94.2	0.301	400	3.0	400	3
88.4	0.293	400	1.0	500	49
84.5	0.269	500	10	500	9
74.0	0.297	400	1.0	500	10.5
72.4	0.282	85[b]	12	200	2.5
66.7	0.274	220	3	300	2
47.6	0.307	400	1	500	26
43.6	0.330	400	2.5	500	239[e]
39.4	0.212	90[b]	18	300	2
36.1	0.289	85[b]	12	300	2
26.1[f]	0.823	85[b]	12	300	2
4.2	0.212	85	12	300	2
4.1[d]	0.300	400	2	500	18

[a] The percentage exposed D_h is given to higher accuracy than warranted so that it may serve as part of the catalyst code.

[b] The calcinations at the temperature listed were in flowing oxygen or in flowing purified air except those marked by superscript *b*, which were effected by heating in air in an oven.

[c] Temperature of reduction in hydrogen.

[d] Between calcination and reduction, the catalyst was heated in N_2 for 1.5 hr at 600°C.

[e] The catalyst was successively calcined and reduced three times for the total times shown.

[f] After reduction, 36.1–Al_2O_3–PtNN was reimpreganted and treated as shown.

EXPERIMENTAL RESULTS

Catalysts

Most catalysts were prepared by impregnating alumina to incipient wetness with an aqueous solution of $Pt(NH_3)_2(NO_2)_2$ which was converted to a solution of the more soluble $[Pt(NH_3)_3(NO_2)]NO_2$ by the addition of ammonia. Some preliminary catalysts were made without the addition of ammonia. Techniques of impregnation were the same as those employed with Pt/SiO_2 (1). Table 1 lists the conditions of preparation of some of the Pt/Al_2O_3 catalysts.

The γ-Al_2O_3, Aerocat 1000 extrudate which was kindly supplied by the American Cyanamid Company, was reported to be about 99.99% pure. By neutron activation analysis at the Triga Mark I nuclear reactor at Reed College, Portland, Oregon, the iron content was 30 ± 10 ppm. The alumina was crushed by hand and sieved to 80–100 mesh. The specific surface area was 160 m^2/g, the specific pore volume was 0.5 cm^3/g, and the average pore diameter was about 12 nm. The sieved alumina was washed in a fluidizing up-flow of redistilled water to remove fines, washed once with 0.1 *M* nitric acid, then washed with water to neutrality, and dried at 85°C in an oven. It was then heated to 600°C in flowing tank air at 3° min^{-1}, rehydrated by exposure to water vapor in a desiccator for 150 hr at

25°C, and dried in flowing nitrogen for 6 hr at 125°C.

When the impregnated alumina was dried under two infrared lamps, calcined in flowing tank air, and reduced in H_2–N_2(1:1) at 300°C or for 2 hr at 500°C, D_h (the percentage exposed of platinum measured by chemisorption of hydrogen) was ~100%. Protracted reduction at 500°C led to D_h = 85–88%. Drying the catalyst in flowing argon followed by reduction at 300°C led to D_h = 103.7%, but if the catalyst was reduced directly without preliminary drying, D_h was only about 3%. Even when drying was extended to leave only 4–6% water, D_h was 4–5%.

The water content of the catalyst at the beginning of the reduction is a major variable in determining the value of D_h. When incompletely dried catalyst was treated in hydrogen at slowly rising temperatures (0.5° min^{-1}) substantial drying may have preceded the start of reduction. In such cases values of D_h of 40–70% were found. Values were variable and D_h may have varied through the catalyst bed. Reduction in these instances would be better effected in a fluidized unit such as we have since used in the preparation of Pd/SiO_2 catalysts.

Very similar results were obtained with catalysts prepared by impregnation with $Pt(NH_3)_4(NO_3)_2$ aq. Reduction at 300°C preceded by heating in argon at 200°C gave D_h = 98.1% and at 300°C, 136%. Argon at 80°C gave only 48.6%. If argon treatment was omitted and the catalyst was heated rapidly to 400°C in hydrogen, D_h was only 4.4%. Conditions which should have led to intermediate levels of water gave D_h of 59.3 and 56.8%. Preparation via $Pt(NH_3)_4(NO_3)_2$ is easier than that with $Pt(NH_3)_2(NO_2)_2$ because of the much larger solubility of the former compound. Results appear to be nearly the same.

Two catalysts were prepared on an alumina derived from Catapal (Continental Oil Co.) by impregnation with $[Pt(NH_3)_3(NO_2)]NO_2$. Calcination at 400°C followed by reduction at 300°C for 2 hr gave D_h = 80.6%. When reduction was at 500°C for 2 hr D_h was 81.3%.

The identity of catalysts is indicated by D_h–Al_2O_3–PtN for catalysts made from $Pt(NH_3)_2(NO_2)_2$; –PtNN is substituted for catalysts made from $[Pt(NH_3)_3(NO_2)]NO_2$; and –$PtNO_3$ for catalysts made from $[Pt(NH_3)_4](NO_3)_2$.

Physical Characterization of Catalysts

As with Pt/SiO_2 (*1*), measurement of D_h was effected at 25°C by a pulse technique using very pure argon as the carrier gas. About 0.25 g of the stored catalyst was first given our standard pretreatment, O_2,300°, 0.5;H_2,300°,1; Ar,450°,1 and cooled in argon. A short argon flush separated the exposures to oxygen and hydrogen. The surface of platinum was then believed to be clean. The following sequence of measurements was run: hydrogen chemisorption at 25°C; desorption of hydrogen at 450°C; hydrogen chemisorption at 25°C; desorption of hydrogen at 450°C; exposure to oxygen at 25°C for 0.25 hr followed by passage of five pulses of hydrogen in argon to effect the hydrogen–oxygen titration; desorption of hydrogen at 450°C. The average of the two hydrogen chemisorptions is taken as the percentage exposed D_h on the assumption that H/Pt_s = 1. In fact, the value of D_h depends upon the temperature employed for hydrogen chemisorption. Thus, in a set of continuous experiments with 106–Al_2O_3–PtNN, the temperatures and measured values of D_h were: 0°C, 110%; 25°C, 105%; 75°C, 86%; and 135°C, 60%.

In the hydrogen–oxygen titration, the percentage exposed, D_t, is taken as $\frac{2}{3}$(moles H_2 consumed)/(total Pt). Figure 1 shows the relation between D_h and D_t. In three instances a "D_t" was measured by trapping a pulse of hydrogen in the catalyst zone rather than by passing pulses of hydrogen. After about 1000 min, the flow of argon through the catalyst bed was restored and the amount of unconsumed hydrogen was

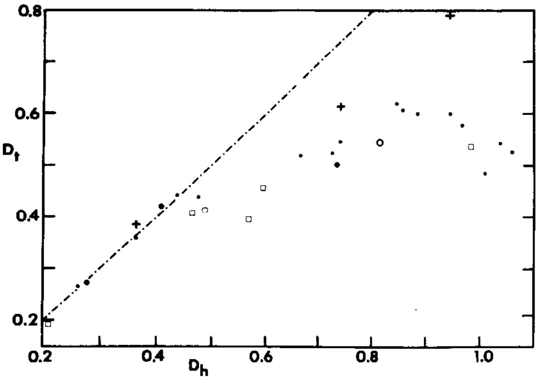

FIG. 1. Percentage exposed by hydrogen–oxygen titration, D_t, vs percentage exposed by hydrogen chemisorption, D_h, both as fractions. Small disks, Al_2O_3–PtNN. Large disks, preliminary Al_2O_3–PtN catalysts in which calcination was in a muffle furnace. Squares, Al_2O_3–$PtNO_3$. Circle, Al_2O_3–PtNN on Catapal. Crosses, hydrogen consumption measured by trapping a pulse of hydrogen for 1000 min.

measured. "D_t" was calculated in the same way as D_t.

As tested on the two catalysts on Catapal, measurement of hydrogen chemisorption first and then the hydrogen–oxygen titration gave the same results as running the measurements in inverted order. Further, three successive hydrogen–oxygen titrations followed by desorption at 450°C led to the same D_t. A second hydrogen–oxygen titration on three other Al_2O_3–PtNN catalysts also gave reasonable checks. Although trapping hydrogen on 94.2– and 74.0–Al_2O_3–PtNN for 1000 min at 25°C led to a somewhat increased value of D_t (Fig. 1), both catalysts on Catapal gave essentially the same value for the usual hydrogen–oxygen titration and for experiments in which hydrogen was trapped with the catalyst at 100°C for 1–2 hr, then heated to 450°C and the released hydrogen measured.

For $D_h < 70\%$, the amount of hydrogen desorbed at 450°C after the usual hydrogen–oxygen titration was in reasonably good agreement with that desorbed after measurement of the adsorption of hydrogen. At $D_h > 90\%$, the amount desorbed was substantially smaller.

To investigate the origin of the low values of D_t/D_h at $D_h \geq 45\%$, measured amounts of oxygen were adsorbed on 94.2–, 66.7–, and 36.1–Al_2O_3–PtNN after they had received the standard pretreatment. The following procedures gave values of N_O/N_s (O_{ads}/Pt_s) which increased in the order listed: (1) Exposure of the catalyst to one small and fully adsorbed pulse of oxygen at 25°C; (2) passage of five pulses of oxygen at 25°C (this corresponds to an exposure to oxygen for about 30 sec), at 100°C, at 200°C (only for 94.2–Al_2O_3–PtNN), and at 300°C. Unadsorbed oxygen passing the catalyst was measured catharometrically. (3) A pulse of oxygen was trapped with the catalyst at 300°C for 1 hr and the amount of oxygen released upon restoring the flow of argon was measured.

Five pulses of hydrogen were passed over the catalysts at each N_O/N_s. If N_{O-r} is the number of atoms of oxygen which reacted with hydrogen and N_{H-r} is the number of atoms of hydrogen consumed,

$$N_{O-r} = (N_{H-r} - N_s + N_O)/3.$$

After the titration, it is assumed that hydrogen atoms occupy all sites not occupied by atoms of oxygen. For example, in

$$\begin{array}{l} \text{O O} \qquad\qquad\quad \text{H H O} \\ \text{PtPtPt} + 2\text{H}_2 \rightarrow \text{PtPtPt} \\ \qquad\qquad\qquad + \text{H}_2\text{O (adsorbed on Al}_2\text{O}_3\text{)} \end{array}$$

$N_s = 3$, $N_O = 2$, $N_{H-r} = 4$, and $N_{O-r} = 1$. N_{O-r}/N_O vs N_O/N_s is plotted in Fig. 2.

The adsorption of hydrogen and oxygen on the alumina alone was negligible.

These experiments were extended in studies with 20.9–Al_2O_3–$PtNO_3$ and 106–Al_2O_3–PtNN and compared with 27– and 81–SiO_2–IonX of Ref. (*1*). After the standard pretreatment, a catalyst was heated in oxygen at 50°C for 1 hr and then at progressively higher temperatures to 450°C. After each exposure to oxygen, the catalyst was flushed and cooled in argon, five pulses of hydrogen were passed at 25°C, and the loss

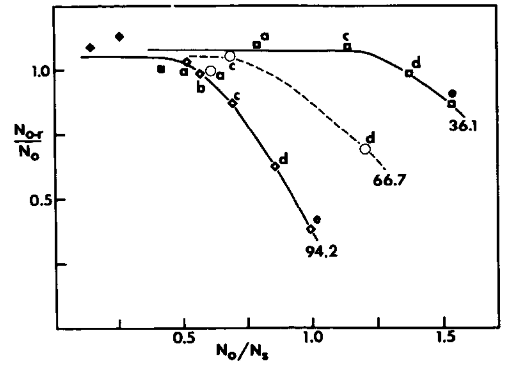

FIG. 2. Fraction of adsorbed oxygen, N_{O-r}/N_O, which reacted with five pulses of hydrogen at 25°C vs N_O/N_s, the ratio of the number of atoms of oxygen adsorbed to the number of surface atoms of platinum. Filled symbols involve oxygen put on as one small pulse. In the case of open symbols, oxygen was adsorbed by the passage of five pulses of oxygen at various temperatures: (a) at 25°C; (b) at 100°C; (c) 200°C; and (d) 300°C. In (e) oxygen was adsorbed from a large pulse of oxygen trapped with the catalyst for 1 hr at 300°C. Diamonds, 94.2–Al_2O_3–PtNN; circles 66.7–Al_2O_3–PtNN; and squares, 36.1–Al_2O_3–PtNN. One sample of catalyst was used in each case and a standard pretreatment was performed before each adsorption of oxygen.

of hydrogen was measured. The catalyst was then isolated, heated to 300°C, argon flow was reestablished, and the amount of released hydrogen was measured. Three pulses of hydrogen were then passed over the catalyst at 300°C. Negligible loss of hydrogen occurred from pulses 2 and 3. The total amount of oxygen originally on the platinum could be calculated assuming that all oxygen had reacted and that the surface of platinum was free of hydrogen after the titration at 300°C. This last assumption is not quite correct, but the error so introduced is of the order of magnitude of the experimental uncertainty. Results are shown in Tables 2 and 3. Titration with hydrogen of catalyst which had been exposed to five pulses of oxygen at 25°C followed by measurement of the amount of hydrogen released by 450°C led to coverages by oxygen in reasonable agreement with those measured directly.

DISCUSSION

Preparation and Percentage Exposed of the Catalysts

When γ-alumina was impregnated with aqueous solutions of $Pt(NH_3)_2(NO_2)_2$ or $Pt(NH_3)_4(NO_3)_2$ to about 0.3 wt% Pt, calcined at 200–400°C, and reduced at 300–500°C, catalysts resulted in which the percentage exposed of the platinum crystallites (D_h) was in the vicinity of 100% (see Table 1). Reduction at 500°C for protracted periods gave reduced values of D_h but the distribution in the platinum crystallite diameters of such catalysts may have been bimodal (*9*). If, however, the impregnated alumina was inadequately dried before reduction, smaller values of D_h resulted and, if only ~5 wt% of water was present, D_h was ~4%. The crystallite diameters in such materials were about 30 nm and the crystallites cannot have been in the normal mesopore structure of the alumina where the average pore diameter was about 12 nm. In addition to the effect of initial content in water, the rate of temperature rise appeared to have influenced D_h by affecting the water content at the time reduction commenced. As judged by the large lattice energy of solid platinum, reduction of the catalysts requires the formation of nuclei of Pt(0). These then grow by migration of Pt(II) to the nuclei (or perhaps vice versa). Migration appears to be facilitated by the presence of water on the surface of the alumina or, alternatively, water may inhibit nucleation. Similar effects of partial drying before reduction have been reported before: for H_2PtCl_6/SiO_2 but not for silica ion-exchanged with platinum ammine complexes (*11*) and for H_2PtCl_6/Al_2O_3 (*12*).

By suitable adjustment of the operating parameters, a number of catalysts of intermediate values of D_h were prepared (Table 1).

In the determination of percentage exposed by hydrogen chemisorption one assumes that $H/Pt_s = 1.00$, but there is no a priori reason why this should be true. On

TABLE 2

Reaction of Hydrogen with Oxygen Adsorbed on Pt/Al_2O_3 Given as H_2/Pt

T_{ox}[c] (°C)	106–Al_2O_3–PtNN[a]				20.9–Al_2O_3–PtNN[b]			
	Titration[d] 25°C	Desorption[e] 300°C	Titration[f] 300°C	Total[g]	Titration[d] 25°C	Desorption[e] 300°C	Titration[f] 300°C	Total[g]
25	—	—	—	0.52[h]		—	—	0.18[h]
25[i]	0.86	0.32	—	0.54	0.29	0.11	—	0.17
50	0.60	0	0.10	0.71	0.38	0.09	0	0.28
100	0.61	0	0.14	0.75	0.39	0.08	0	0.31
150	0.50	0	0.27	0.77	—	—	—	—
200	0.35	0	0.61	0.96	0.41	0.03	0	0.38
300	0.19	0	0.93	1.12	0.39	0	0.06	0.45
400	—	—	—	—	0.38	0	0.13	0.51
450	0.07	0	1.07	1.14	0.34	0	0.32	0.66

[a] The sequence of runs was 200, 100, 300, 50, 450, and 150°C.

[b] The sequence of runs was 100, 300, 50, 450, 200, and 400°C.

[c] Temperature of exposure to oxygen for 1 hr except at 25°C.

[d] H_2 consumed in the hydrogen titration at 25°C as H_2/Pt, i.e., H_2/total Pt.

[e] H_2 desorbed at 300°C as H_2/Pt.

[f] H_2 consumed from three pulses of H_2 at 300°C as H_2/Pt.

[g] Total H_2 consumed as H_2/Pt = sum of the titrations at 25 and 300°C less the desorption at 300°C. This quantity is taken as equal to initial O/Pt.

[h] Loss of O_2 from five pulses of O_2 at 25°C expressed at O/Pt.

[i] Calculated from hydrogen titration of Pt/Al_2O_3 previously exposed to oxygen at 25°C for 15 min. Desorptions were at 450°C rather than at 300°C.

TABLE 3

Reaction of Hydrogen with Oxygen Adsorbed on Pt/SiO_2 Given as H_2/Pt[a]

T_{ox} (°C)	81–SiO_2–IonX[b]				27–SiO_2–IonX[c]			
	Titration 25°C	Desorption 300°C	Titration 300°C	Total	Titration 25°C	Desorption 300°C	Titration 300°C	Total
25	—	—	—	0.50[d]	—	—	—	0.15[d]
25[e]	1.02	0.46	—	0.57	0.29	0.11	—	0.19
50	—	—	—	—	0.30	0.05	0	0.25
100	1.00	0.27	0	0.73	—	—	—	—
200[f]	1.00	0.12	0	0.88	0.32	0.01	0	0.31
250	0.96	0.04	0	0.92	0.32	0.005	0	0.32
300	0.84	0	0.13	0.97	0.35	0	0.019	0.37
350	0.84	0	0.26	1.10	0.33	0	0.023	0.36
450	0.84	0	0.26	1.10	0.29	0	0.025	0.31

[a] The significance of the column headings is the same as in Table 2. The catalysts were prepared by ion exchange of silica gel with $Pt(NH_3)_4^{2+}$ (*1*).

[b] The sequence of runs was 300, 100, 200, 250, 450, and 350°C.

[c] The sequence of runs was 185, 50, 300, 250, 350, and 450°C.

[d] Loss of O_2 from five pulses at 25°C.

[e] Calculated from the hydrogen–oxygen titration data of Ref. (*1*).

[f] 185°C for 27–SiO_2–IonX.

Pt/SiO_2, H/Pt_s decreased steadily with an increase in the temperature at which chemisorption was measured (1). Pt/Al_2O_3 behaved similarly: on 106–Al_2O_3–PtNN the apparent D_h was 110% at 0°C, 86% at 25°C, and 60% at 135°C. Indeed a value of D_h = 106% indicates that H/Pt_s was not exactly unity at 25°C on that catalyst. However, a number of previous studies have shown that D_h measured at 25°C agrees rather closely with percentage exposed calculated from data obtained by transmission electron microscopy and by X-ray techniques. The most detailed such intercomparison is probably that reported in Refs. (1–3) for Pt/SiO_2.

It was impossible to examine the Pt/Al_2O_3 catalysts of Table 1 by the full X-ray line profile analysis employed for Pt/SiO_2 (3). The loadings in platinum were too low and the coincidences with lines from the γ-alumina support permitted analysis only of the (311) line of platinum. A special catalyst containing 3.77 wt% Pt and D_h = 40% was examined by Dr. R. K. Nandi using only the (311) line. The calculated value of D_X (percentage exposed by X-ray (3)) was 27% for the catalyst as stored in air and after the pretreatments, standard, O_2,300°,0.5;H_2,25°,1, and O_2,300°,0.5;H_2, 450°,1. However, only about half of the total amount of platinum was detected and the catalyst probably contained significant amounts of more highly dispersed platinum.

Reaction of Platinum Crystallites with Oxygen and Then with Hydrogen

As shown in Fig. 1, up to D_h = 45%, D_h and D_t (a percentage exposed calculated by the conventional hydrogen–oxygen titration (13)) were in good agreement. Above D_h = 45%, the ratio D_t/D_h progressively declined. Further, at $D_h \geq 90\%$, the value of the final hydrogen desorption at 450°C (after the hydrogen–oxygen titration) fell below the amount corresponding to D_h. As will be shown, two structure-sensitive factors are involved. (1) The ratio O/Pt_s ((oxygen *atoms* adsorbed)/(surface atoms of Pt)) which results from O_2,25°,0.25 falls below unity for D_h greater than 45% and (2) the reactivity of hydrogen with O* decreases with increasing D_h with the result that at $D_h \geq 90\%$ not all O* resulting with O_2,25°,0.25 reacts with five pulses of hydrogen during the titration at 25°C. More O* would presumably react in a static volumetric hydrogen–oxygen titration (13).

The behavior of Pt/SiO_2 in the hydrogen–oxygen titration differed somewhat from that of Pt/Al_2O_3 shown in Fig. 1. For Pt/SiO_2, D_t/D_h was nearly a straight line with a slope of about 0.88 from D_h = 6.2 to 81% (1).

The three catalysts of Fig. 2 were first exposed to the standard pretreatment and then dosed with measured amounts of chemisorbed oxygen. The resulting ratio, N_O/N_s ($=O/Pt_s$), is given on the x-axis. After each loading by oxygen, five pulses of hydrogen were passed over the catalyst at 25°C and the consumption of hydrogen was measured. N_O/N_O resulting from exposure to five pulses of oxygen at 25°C was less than unity and decreased with increasing D_h. The fraction of adsorbed oxygen which reacted with the hydrogen pulses, N_{O-r}/N_O, was calculated as described in the experimental section and is plotted on the y-axis. For D_h = 36.1%, all adsorbed oxygen was removed up to N_O/N_s = 1.15. At larger N_O/N_s, not all was removed, but even at N_O/N_s = 1.5 most was removed. For D_h = 94.2%, even at N_O/N_s = 0.5, barely all O* reacted and, as N_O/N_s increased, the fraction of O* which reacted dropped rapdily. At N_O/N_s = 1.0, less than 40% of the adsorbed oxygen was removed. The behavior of 66.7–Al_2O_3–PtNN was intermediate.

It is clear, then, that the rate of reaction of O* with hydrogen decreases as D_h increases and, at $D_h \geq 90\%$, even the amount of adsorbed oxygen which results from O_2,25°,0.25 is too large to be fully removed by five pulses of hydrogen at 25°C. A similar trend was observed with Pt/SiO_2 (1). On 81–SiO_2–IonX, the treatment O_2,25°,0.25 gave an amount of adsorbed oxygen which could just barely be removed by hydrogen pulses at 25°C.

Inspection of Fig. 2 suggests that it would be difficult to choose a set of operating conditions which would lead to O/Pt_s equal to unity at all D_h and which would permit the adsorbed oxygen to be fully removable by hydrogen at any temperature at which one can assume that N_H/N_s was unity after the treatment with hydrogen, i.e., at which one could assume that D_t = (consumed H)/3.

In the experiments of Table 2, increasing amounts of oxygen were adsorbed on two Pt/Al_2O_3 catalysts which had been exposed to the standard pretreatment. This oxygen was then removed by hydrogen in three stages in each of which consumption of hydrogen was measured: (1) reaction with five pulses of hydrogen at 25°C, (2) reaction between residual O* and *H from stage 1 upon heating to 300°C, and (3) reaction of any remaining *O with pulses of hydrogen at 300°C. This last reaction was always fast.

On 106–Al_2O_3–PtNN, only part of the original adsorbed oxygen reacted in stage 1 and the actual amount reacted declined monotonically with increasing O/Pt (where O/Pt represents the ratio of oxygen *atoms* adsorbed to *total* platinum atoms and is given by the column labeled "Total"). At $O/Pt \geq \sim 0.6$, insufficient *H remained from stage 1 fully to react with residual *O in stage 2 and the remaining *O was removed in stage 3.

On 20.9–Al_2O_3–PtNN, all adsorbed oxygen was removed in stage 1 when O/Pt_s was about unity since O/Pt_s and (H desorbed in stage 2)/Pt_s were nearly equal. At O/Pt_s much above unity, reaction in stage 1 became incomplete. Consumption of hydrogen in stage 1 increased to $O/Pt_s \simeq 2$, beyond which *H formed in stage 1 became insufficient fully to react with residual adsorbed oxygen and consumption in stage 3 became detectable. Even a small stoichiometric excess of *H over residual adsorbed oxygen resulted in complete removal of adsorbed oxygen in stage 2 and zero consumption of hydrogen in stage 3.

As shown in Table 3, Pt/SiO_2 catalysts behaved rather like Pt/Al_2O_3. However, adsorbed oxygen on 81–SiO_2–IonX reacted more readily with hydrogen in stage 1 than did that on 106–Al_2O_3–PtNN and there was insufficient *H fully to reduce adsorbed oxygen only at $O/P \geq \sim 0.93$ rather than at ~0.6. On the other hand, as shown prevously (*1*), stored (and oxygen covered) 81–SiO_2–IonX adsorbed oxygen at 300°C to give larger O/Pt than did clean 81–SiO_2–IonX and this oxygen was less reactive with hydrogen than was that formed on the clean catalyst.

27–SiO_2–IonX reacted with oxygen to give lower values of O/Pt_s than did 20.9–Al_2O_3–PtNN at the same temperature. Further, O/Pt_s maximized at a temperature of exposure to oxygen of about 300°C and then declined at higher temperatures, whereas O/Pt_s on 20.9–Al_2O_3–PtNN increase monotonically with increasing temperature of exposure to oxygen. As a result, after exposure to oxygen at 450°C, O/Pt_s is much larger on 20.9–Al_2O_3–PtNN than on 27–SiO_2–IonX, 3.15 vs 1.19. At 300°C also, platinum crystallites of lower D_h react with much more oxygen in the case of Pt/Al_2O_3 than in that of Pt/SiO_2. Thus, in the standard pretreatment, O_2, 300°,0.5;H_2,300°,1;(Ar or He),450°,1, the reduction stage starts with platinum which is more oxidized in the case of Pt/Al_2O_3. The greater reactivity of Pt/Al_2O_3 with oxygen may result from migration of a platinum oxide onto the surface of the alumina immediately adjacent to the platinum crystallite. Silica, however, does not stabilize a platinum oxide, or, at least, not to the same extent as alumina.

There are a number of reports dealing with the adsorption of oxygen on clean surfaces of bulk platinum by the techniques of surface chemical physics (*14*). Coverages much below unity were usually seen but, of course, exposures usually were in Langmuirs rather than in atm min. Oxygen adsorbs on platinum in multiple binding states, and, in the case of a (100)-oriented ribbon, four plus a molecular low temperature state were reported (*15*).

It is not easy to make straightforward comparisons between the results of this paper and those of previous studies on Pt/Al_2O_3 in which the catalysts were prepared by impregnation with H_2PtCl_6 aq. Further, where pulse techniques were employed, data were not provided which permit one to estimate the purity of the carrier gas at the catalyst.

Previous work in which T_{ox} was varied usually indicated that O/Pt increased with increasing T_{ox}. Maxima in O/Pt vs T_{ox} (a, b) like that noted with 27–SiO_2–IonX (Table 3) were observed or desorption of oxygen from oxygen-covered platinum (c, d) was observed in the following cases:

(a) at T_{ox} = 400°C in oxidation at P_{O_2} = 1.7 Torr of a Pt/SiO_2 made by ion exchange with $Pt(NH_3)_5Cl^{3+}$ (*16*, *17*),

(b) at 300°C for Pt/SiO_2 of D_h = 23% (*18*),

(c) at 325°C from platinum foil, but O/Pt_s was only about 0.4 (*19*),

(d) only above 575°C for platinum wire (*20*) but this had thick layers of oxide.

The work of Wilson and Hall (*21*) involved catalysts prepared from H_2PtCl_6/Al_2O_3 reduced at 500°C to give $D_h \simeq$ 100% and sintered at higher temperatures to prepare catalysts of lower D_h. Despite the different methods of preparation, at their T_{ox} (25°C) our ratios, (O/Pt)/H/Pt), accord well with their ratios; unity for catalysts of small D_h and about 0.5 for $D_h \simeq$ 100%. Freel (*22*) also observed values of near unity or about 0.5. He concluded that the first value was observed for catalysts given prolonged reduction at 500°C (15 hr or more) whereas less drastic conditions of reduction led to the lower value. This applied both to Pt/SiO_2 and Pt/Al_2O_3 catalysts. We see no sign of such a correlation for Pt/Al_2O_3 prepared by our methods.

Some previous work reported values of O/Pt_s on supported catalysts which rose to unity only at T_{ox} much higher than those found in the present work:

(a) only at T_{ox} = 400°C for a Pt/SiO_2 of D_h = 61% for which P_{O_2} was 1.7 Torr (*16*);

(b) only at $T_{ox} \simeq$ 300°C for a Pt/Al_2O_3 of D_h = 46% and O/Pt_s was only 0.7 at T_{ox} = 250°C for a Pt/SiO_2 of D_h = 100% (*23*);

(c) or, O/Pt_s was ~0.8 and relatively insensitive to T_{ox} at up to 300°C (*18*) on Pt/SiO_2 and Pt/Al_2O_3 with D_h = 20–30% (this work and that in (b) just above involved chromatographic techniques).

On the other hand, on platinum wire, oxide films were reported to grow very slowly at 450–600°C but to reach thicknesses of 90 nm at 600°C (*20*). The films consisted of β-PtO_2. There was no indication of any formation of crystalline PtO_2 under the milder conditions of the present paper. Further, a number of workers have reported that exposure to oxygen at about 500°C of Pt/Al_2O_3 of low D_h followed by reduction led to an increase in D_h (*24*). This has been interpreted as resulting from migration of some oxide of platinum onto and then over the surface of the alumina support. Our data indicate the redispersion does not result from O_2,300°,0.5;H_2,300°,1, at least not after the initial exposure to this treatment. However, one might worry about redispersion affecting the results of Tables 2 and 3 at the highest T_{ox}. This possibility cannot be fully excluded, but the results on 20.9–Al_2O_3–PtNN at T_{ox} = 200°C appear to fit smoothly into the results at 50, 100, and 300°C although results at the last three temperatures preceded the run at 450°C, whereas that at 200°C followed it.

The origin of the discrepancy between the present finding that O/Pt_s considerably exceeds 1.00 at higher T_{ox} and previous reports that it does not is not clear. Procedural factors may be involved and the length of exposure may be a factor. However, as shown in Fig. 2, even exposure to pulses of oxygen at 300°C led to values of O/Pt_s which exceeded unity for the two Pt/Al_2O_3 of lower D_h.

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