JOURNAL OF CATALYSIS **20**, 394–407 (1971)

O_2 Chemisorption at High Temperatures on Platinum–Alumina and Platinum–Zeolite

S. W. WELLER AND A. A. MONTAGNA*

Department of Chemical Engineering State University of New York at Buffalo,
Buffalo, New York 14214

Received June 23, 1970

As a contribution to the "surface thermodynamics" of supported platinum catalysts, the adsorption and desorption of oxygen on platinum–alumina and platinum–zeolite (Type Y) has been studied at 475 and 525°C. H_2 chemisorption at 200°C was used as a measure of Pt dispersion. The adsorption isotherms for O_2 on Pt–zeolite showed a semistep at partial pressures near the estimated dissociation pressures of bulk PtO; the limiting O:Pt atom ratio at higher pressures was about 0.86:1. No such steps were observed in the isotherms for O_2 on Pt–Al_2O_3, and the atom ratio of net O:total Pt reached the surprisingly high value of 3.7:1 at 525°. This is attributed to a partial reduction of the Al_2O_3 surface, catalyzed by the Pt, during the catalyst prereduction with H_2 at 550°C. Measurements of Pt dispersion by H_2 chemisorption showed that: (a) a limiting atom ratio of net H:total Pt of 1:1 was observed for Pt–Al_2O_3, but 2:1 for Pt–HY; (b) Pt–HY was more susceptible to sintering than was Pt–Al_2O_3; (c) "redispersion" of Pt in Pt–Al_2O_3 on cyclic exposure to O_2 and H_2 occurred during the reduction step; and (d) the "redispersed" Pt in Pt–Al_2O_3 was quite resistant to subsequent sintering in cyclic O_2–H_2 treatment.

INTRODUCTION

The deserved prominence of platinum as a hydrogenation–dehydrogenation catalyst tends to obscure the fact that it is one of the most active oxidation catalysts known. Since it is axiomatic that the chemical condition of a catalyst surface is shaped by the reaction environment, it is essential to consider the formation and stability of platinum oxides on the surface. Tretyakov, for example, has observed Pt_3O_4 (by electron diffraction) on the surface of Pt, and Pt_3O_8 (by X-ray diffraction) in the bulk, after the Pt was used as catalyst for the H_2–O_2 reaction (*1*).

Unfortunately, and surprisingly, not only the thermodynamics, but even the very existence of simple oxides such as PtO as *bulk* phases (much less surface) are not unequivocally established. It has been generally believed that PtO_2 (c) decomposes on heating to give O_2 and Pt_3O_4 (c), which in turn decomposes to give PtO (c). On the basis of Latimer's data for $Pt(OH)_2$, Brewer estimated that for PtO at 298°K, $\Delta G_f^0 = 11 \pm 4$ kcal/mole, $\Delta H_f^0 = -17 \pm 5$ kcal/mole, and $\Delta S_f^0 = 20$ eu (*2*). In 1951, one of us (S.W.W.) estimated $\Delta H_f^0 = -17$ kcal/mole and $\Delta S_f^0 = 19$ eu; values for other temperatures were computed on the assumption that $H_T - H_{298}$ and $S_T - S_{298}$ are the same for PtO and PbO (*3*). From these values we may compute for PtO the following free energies of formation and dissociation pressures:

T(°K)	ΔG_f^0 (kcal/mole)	p_{O_2}(atm)
298	−11	6.4×10^{-17}
600	−5	2.3×10^{-4}
800	−1	0.28

We may also note that the most recent

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* Present address: Gulf Research and Development Co., P.O. Drawer 2038, Pittsburgh, Pa. 15230.

survey of electrode potentials in the platinum/solution system also gives the value ΔG_f^0 (298) = -11.5 kcal/mole for PtO (*4*).

Ariya and co-workers (*5*) report a calorimetric value for ΔH_f^0 for Pt_3O_4 that is substantially lower than Brewer's value (-9.8 vs -16 kcal/g atom of O), as well as a tensiometric value (decomposition pressure vs temperature) which they claim to agree with their calorimetric value. However, our recalculation of ΔH_f^0 from the raw data given by Ariya *et al.* (*5*) for decomposition pressures shows that their ΔH_f^0 (tensiometric) is in fact -18.5 kcal/g atom of O, in reasonable agreement with Brewer's estimate but substantially different from Ariya's calorimetric value.

It is noteworthy that in a recent review of the thermochemistry of platinum (*6*), the platinum oxides are conspicuous by their almost total absence.

The very existence of both PtO (c) and Pt_3O_4 (c) have been seriously questioned. Grandadam (*7*) and Laffitte and Grandadam (*8*), on the basis of a careful chemical study, concluded that what had previously been called Pt_3O_4 was in fact a mixture of PtO and PtO_2, and he gave methods for synthesizing and characterizing PtO and PtO_2. This was promptly questioned by Baroni (*9*), who, on the basis of sketchy X-ray results, stated that Grandadam's PtO and PtO_2 were only surface compounds of undefined stoichiometry. Moore and Pauling (*10*) prepared "PtO" by fusing $PtCl_2$ with KNO_3 and concluded, from its X-ray diffraction pattern, that it was isomorphous with PdO. Galloni and Busch (*11*) claim that Moore and Pauling actually synthesized PtO_2, not PtO. In a recent investigation of the platinum–oxygen system at elevated temperature (400–900°C) and pressure (25–3500 atm), Muller and Roy (*12*) found Pt_3O_4 and *two* forms of PtO_2 (designated α and β), but *no* PtO. However: (1) Muller and Roy did not investigate the conditions quoted by Grandadam as appropriate for synthesizing PtO (in fact, Grandadam is not referred to by Muller and Roy); and (2) Muller and Roy report an unidentified phase whose diffraction pattern "bears a superficial resemblance" to that of PdO. It is difficult to imagine so confusing a situation for such a prosaic system.

A major objective of the present research was to obtain direct information on the surface thermodynamics of supported platinum catalysts by studying the reaction Pt (surf) + $\frac{1}{2}$ O_2 (g) = PtO (surf) in a temperature–pressure regime predicted from the estimated bulk thermodynamics. Two supports were studied, eta-alumina and a decationated type Y zeolite; these were found to give quite different results. Since each sample was subjected to a number of cyclic treatments at high temperature, the degree of platinum dispersion was characterized at each stage by the determination of hydrogen chemisorption at 200°C.

The most relevant previous research has been a series of papers by Gonzalez and Parravano (*13*) and Bortner and Parravano (*14*, *15*) on the equilibrium Me (surf) + H_2O (g) = Me–O (surf) + H_2 (g); we are very grateful to Professor Parravano for discussion of this work.

EXPERIMENTAL METHODS

Catalyst samples. The eta-alumina (Lot No. 110J91-3Z) was obtained through the courtesy of the Houdry Laboratories, Air Products and Chemicals. It had a surface area of 250 m^2/g, and it contained 0.16% SiO_2, 0.04% Na_2O as major impurities; the total content of transition metals (Mn, Fe, Cu, Ni, Cr) was less than 140 ppm. The 0.5 wt % Pt–Al_2O_3 was prepared by us by the "minimum excess solution" technique. The η-Al_2O_3, ground and sieved to a 35–45 mesh size, was impregnated with an appropriate volume of aqueous chloroplatinic acid. The 0.55 wt % Cl^-–Al_2O_3 used in the adsorption blanks was prepared by a similar technique with the use of aqueous HCl.

The 0.5 wt % Pt-decationated type Y zeolite was prepared by us by various treatments of a sample of Pt (ion-exchanged)–NH_4Y kindly furnished by the Linde Division (Lot No. 13357-9). A corresponding sample of NH_4Y used in adsorption blanks was Linde's Lot No. 13067-1. These both have a $SiO_2:Al_2O_3$ mole ratio of about 5 and a residual Na_2O content of about 1.6 wt %, corresponding to an 88% degree of decationation.

Gases. Matheson "ultrahigh purity" hydrogen was further purified by passage through Pd–Al_2O_3, a type 4A molecular sieve column, and a liquid N_2 trap. Matheson "extra dry oxygen" was purified by passage through a type 4A molecular sieve column and a Dry Ice trap. Liquid carbonic helium was purified through activated carbon at −195°, molecular sieve type 4A, and a liquid N_2 trap. Liquid carbonic "ultrahigh purity" nitrogen (>99.999%) was passed through a type 4A column and a liquid N_2 trap.

Apparatus. The volumetric adsorption studies were carried out in a glass high-vacuum system that was of conventional design except for one feature: an electromagnetically-actuated gas circulation pump and a cold trap were connected in series, in a closed loop, with the catalyst sample tube. During the high temperature adsorption measurements, it was thus possible to control the water partial pressure by continuous recirculation of the gas through the sample and the in-line cold trap. The sample was protected from mercury vapor by an in-line gold leaf trap.

The sample was contained in a Vycor bulb 1.75-in. high by 1-in. diameter, equipped with a central thermowell. Sample temperatures were measured by an iron–constantan couple, inserted in the well, and a millivolt potentiometer. Sample heating was by an 18-in. tube furnace controlled by a Bayley precision controller, model 76-15.

Procedures. The Al_2O_3 and Pt–Al_2O_3 samples were pretreated according to the following schedule: heat from 25 to 450° in 2 hr in H_2 flowing (through and out) at the rate of 200 ml/min; hold at 450° for 0.5 hr; heat from 450° to 550° in 0.5 hr; and hold at 550° for 1 hr, all in flowing H_2. The sample was then evacuated at 550° for 2 hr and cooled under vacuum either to 200°, in ca. 2 hr, for measurement of the degree of platinum dispersion, or to any other desired test temperature.

A different pretreatment schedule was found necessary for the ion-exchanged Pt–HY catalyst to avoid sintering of the Pt. This sample, and the corresponding NH_4Y control, were first calcined in flowing O_2 and then reduced in flowing H_2. The detailed schedule was: (1) heat in O_2 (flow rate 200 ml/min) to 250°C in 1 hr; hold at 250°C for 1 hr; heat to 550°C in 1 hr; hold at 550°C for 1 hr; evacuate for 1 hr at 550°C; cool to room temperature under vacuum; then (2) heat in H_2 (200 ml/min) to 300°C in 0.75 hr; hold in flowing H_2 at 300°C for 2 hr; evacuate and heat, while evacuating, to 550° in 1 hr; hold at 550°C for 1 hr; cool to 200°C for measurement of H_2 chemisorption; finally (3) evacuate while heating to 550°C in 1 hr; hold under vacuum at 550°C for 2 hr; and cool to the test temperature.

The degree of Pt dispersion was measured by H_2 chemisorption at 200°C and 5–20 cm Hg pressure. At least 1 hr was allowed for equilibration at each pressure in the case of the alumina-base catalysts, and at least 16 hr in the case of the HY-base materials. The net H_2 uptake by the Pt was obtained by subtracting from the gross uptake a blank, typically small, corresponding to uptake by the Pt-free support at the same pressure.

The in-line recirculation pump was not used during the determinations at 200°C of H_2 chemisorption or of He dead space. It was used, with the in-line trap kept at −78°C, during all measurements (including He dead space) at high temperature (450–550°C).

The points for oxygen uptake at high temperature were recorded, for both adsorption and desorption branches, only after a "steady-state" value of the pressure was reached in this fixed-volume experimental system. "Steady-state" was operationally defined as meaning no observable change in pressure over a period of several hours. In any experiment, adsorption points were first determined by incremental additions of oxygen to the system. Similarly, desorption points were measured after incremental removals of measured amounts of oxygen from the system.

RESULTS

Pt-Al_2O_3. Figure 1 shows oxygen adsorption isotherms obtained during a series of adsorption–desorption cycles at 525°C on a sample (Sample B-2) of 0.49% Pt on η-Al_2O_3 and on a control sample (Sample C-4) containing 0.55% HCl on the same η-Al_2O_3. The range of oxygen pressures studied was chosen to cover the computed value (see below) for the dissociation pressure of bulk PtO at 525°C.

The first adsorption run (Ads. I) over freshly reduced catalyst resulted in "steady-state" O_2 uptakes which increased linearly with pressure, from 0.56 ml (STP)/g at 8.5 cm Hg to 0.84 ml (STP)/g at 28.3 cm Hg. During the first desorption run (Des. I), the first point, at 20 cm Hg, agreed reasonably well with the adsorption branch. At lower pressures, however, Des. I was observed to diverge substantially from Ads. I. The tentative conclusions at this stage were: (1) O_2 adsorption is at least partially reversible at 525°C; and (2) some gradual sintering of the Pt may be occurring in O_2 at 525°C. To confirm the latter conclusion, Ads. II was performed immediately after Des. I. These adsorption data in Ads. II, shown in Fig. 1, were even lower than those in Des. I, consistent with the hypothesis of gradual sintering.

The circulating pump failed (because of accumulated glass dust from wear) after 3.5 hr at the highest pressure (25.8 cm Hg) of Ads. II. It became convenient, therefore, to determine directly at this point whether any decrease had occurred in the degree of dispersion of the Pt. The sample was given a standard reduction in flowing H_2 at 550°C (see Procedures above), followed by H_2 chemisorption at 200°C.

The results of H_2 chemisorption at 200°C [ml (STP)/g] are shown in Fig. 2. The same data, corrected for the (duplicate) blank runs (Samples C-1 and C-4) on Cl^-–Al_2O_3, and computed in terms of an atom ratio H:Pt (net H atoms adsorbed per [total] Pt atom in the sample), are shown in Fig. 3. The results were surprising.

The net H_2 uptake on the original sample, labeled "Before O_2 Ads. I" in Figs. 2 and 3, corresponded to a H:Pt ratio of 1:1 for $p_{H_2} > 6$ cm Hg. The net H_2 uptake after Ads. II, labeled "Before O_2 Ads. III" in Figs. 2 and 3, was indistinguishable from that on the freshly reduced sample; again a H:Pt ratio of 1:1 was observed. (Experimental scatter corresponds to an uncertainty of about ±0.05 in this ratio.) These measurements of Pt dispersion imply that either (a) the Pt was not sintered, in contradiction to the O_2 adsorption results; or (b) if sintering had occurred in O_2 at 525°C, the Pt was

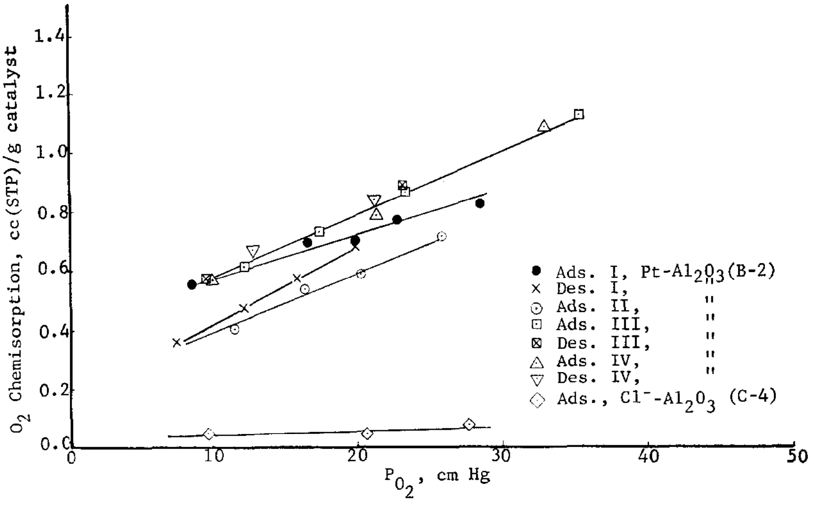

FIG. 1. O_2 chemisorption at 525°C on Pt-Al_2O_3 and Cl^-–Al_2O_3.

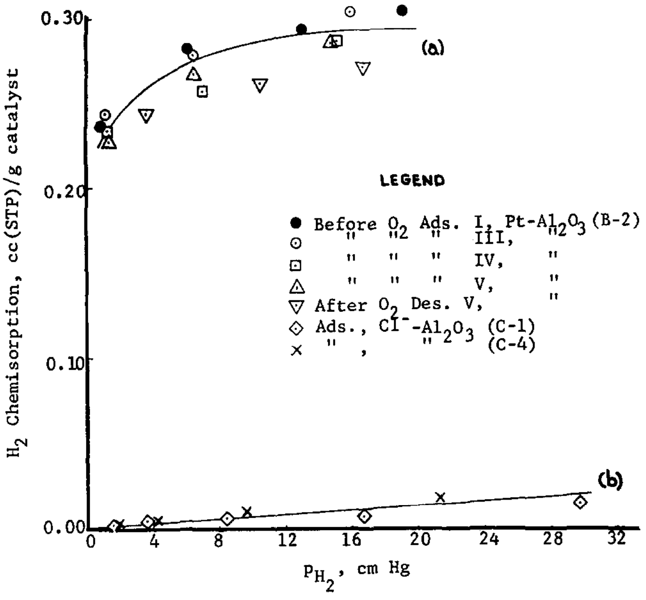

FIG. 2. H_2 chemisorption at 200°C on Pt-Al_2O_3 and Cl^--Al_2O_3.

redispersed during the 550°C reduction in H_2.

In either case, the H_2 chemisorption measurements indicated that essentially all of the Pt atoms were surface atoms at the time of the dispersion measurement. On this basis, the results of the next adsorption run, Ads. III in Fig. 1, were expected to be as high as those for Ads. I. As Fig. 1 shows, however, Ads. III was even *higher* than Ads. I. To add to the complication, Des. III (immediately following Ads. III) was identical to Ads. III, no sign of sintering being observed.

At this point the sample was again reduced at 550°C in order to study H_2 chemisorption at 200°C. Again the dispersion measurement (Fig. 3, "Before O_2 Ads. IV") showed the H:Pt ratio to be essentially 1:1.

One further adsorption–desorption cycle

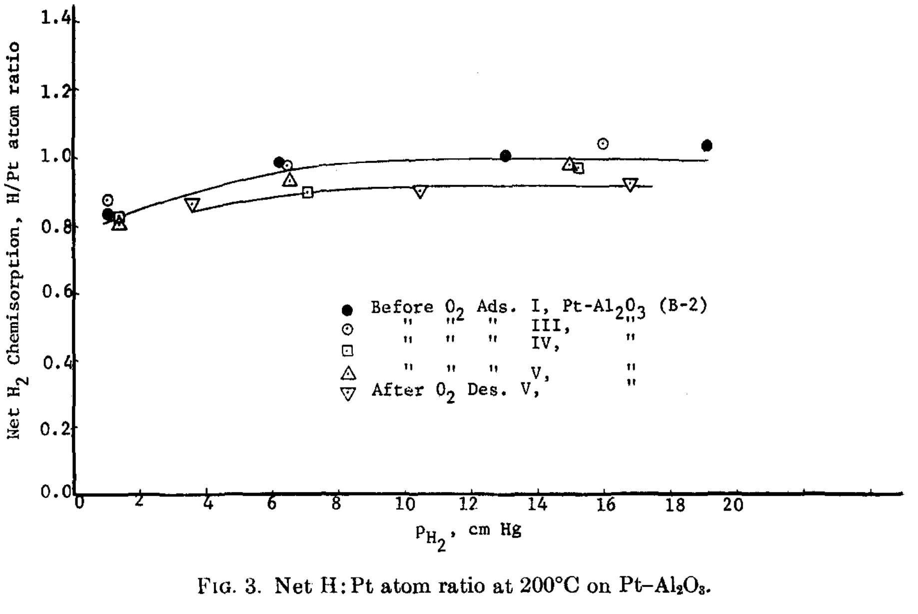

FIG. 3. Net H:Pt atom ratio at 200°C on Pt-Al_2O_3.

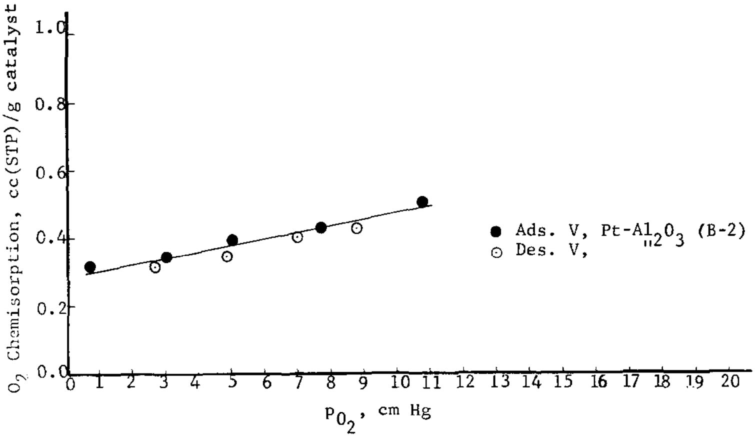

FIG. 4. O_2 chemisorption at 475°C on Pt-Al_2O_3.

at 525°C was carried out. The results, Ads. IV and Des. IV in Fig. 1, were indistinguishable from the reversible behavior shown by Ads. III and Des. III. The sample appears to have been stabilized by the 550°C reduction after Ads. II.

One O_2 adsorption–desorption cycle (Ads. V and Des. V) was run at 475°C. The results are shown in Fig. 4. The dispersion measurement by H_2 after Des. V (cf. Fig. 3) was slightly lower, the limiting H:Pt ratio being about 0.9:1.

The *net* uptakes of O_2 at both 525 and 475°C, obtained by correcting the total uptakes shown in Figs. 1 and 4 for the Al_2O_3 blank, are summarized in Fig. 5 for Runs III–V, where the sample was apparently stabilized. The O_2 chemisorption in Fig. 5 is expressed as the atom ratio of O:Pt (net O atoms adsorbed per [total] Pt atom in the sample). The O:Pt ratio ranged from about 1 to 1.7 at 475°C, and from about 1.9 to 3.7 at 525°C. The high values at 525°C are particularly striking (see Discussion, below).

Pt–Hy. H_2 chemisorption at 200°C, used to measure Pt dispersion, was relatively slow

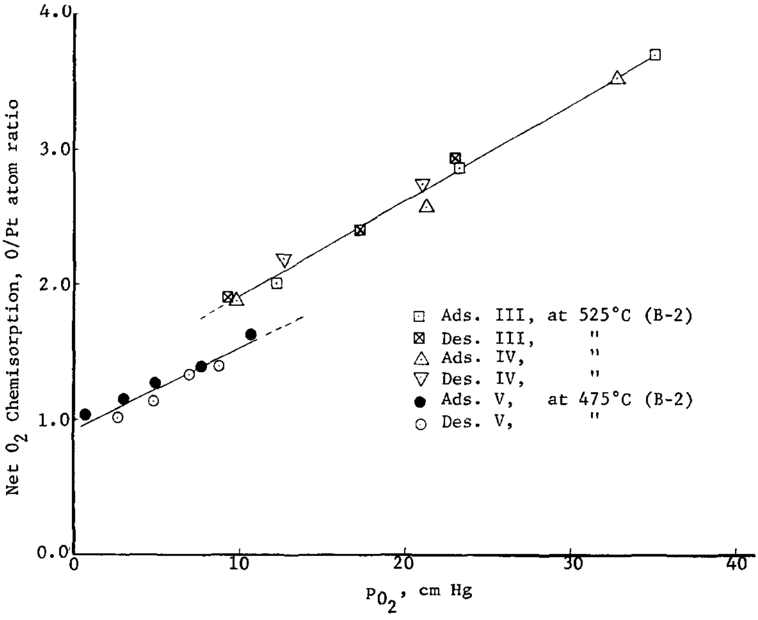

FIG. 5. Net O:Pt atom ratio at 475° and 525°C on Pt–Al_2O_3.

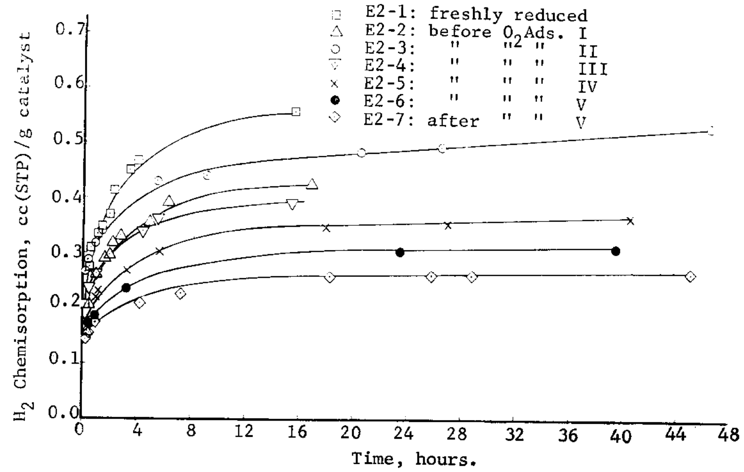

FIG. 6. Time dependence of H_2 chemisorption at 200°C on Pt–HY.

on Pt–HY. The time dependence of H_2 chemisorption is shown in Fig. 6 for a freshly reduced sample (E2) and at various stages during successive O_2 adsorption measurements at 475 or 525°C (see below). H_2 pressures of 10–17 cm Hg are represented in these curves. Although the rate of H_2 chemisorption becomes relatively low (and constant) after about 12 hr, the fact that it is nonzero introduces some ambiguity into the value for Pt dispersion. The H_2 adsorption Tests E2-1 to E2-7 are identified in the legend of Fig. 6; e.g., Test E2-1 was made on the freshly reduced Pt–HY, Test E2-7 on the sample after O_2 Ads. V.

Because of this time dependence, the value of H_2 chemisorption after 16 hr at 200°C was arbitrarily taken as the measure of Pt dispersion. These values for the total H_2 adsorption, as well as those for the net adsorption after subtraction of the "blank" value (0.017 ml/g) observed for HY without Pt, are listed in Table 1. Also listed are the atom ratios H:Pt (net H atoms adsorbed per [total] Pt atom in the sample).

Test No. E2-1, on the freshly reduced sample, gave a H:Pt ratio of 1.97:1 (Table 1). Although there is some uncertainty in this value because of the time factor, clearly the value for fresh Pt–HY is near to 2:1, in marked distinction to the value of 1:1 for Pt–Al_2O_3. This strongly suggests that Pt is in a different physical state in the HY support than in η-Al_2O_3.

After Test E2-1 the sample was again reduced in flowing H_2 at 300°C and evacuated at 550°C, as recommended by Lewis (*16*). Redetermination of the hydrogen chemisorption at 200°C (Test E2-2) resulted in the lower value of 1.50:1 for the H:Pt ratio, indicating some sintering on this additional H_2 treatment. The first attempt to determine O_2 adsorption on this sample at 525°C failed because of a system leak; however, the sample had been exposed to O_2 at the time of the leak. Another dispersion measurement (Test E2-3) was made, therefore, again after 300°C reduction and 550°C evacuation. As Table 1 indicates, a slightly *higher* H:Pt ratio of 1.68:1 was obtained. This is quite analogous to the apparent redispersion of sintered Pt observed in

TABLE 1

H_2 CHEMISORPTION ON Pt–HY

200°C, 16hr, ca. 15 cm Hg.

Sample	H_2 adsorbed, ml (STP)/g Total	Net	Net H:total Pt atom ratio
E2-1	0.56	0.543	1.97:1
2	0.43	0.413	1.50:1
3	0.48	0.463	1.68:1
4	0.40	0.383	1.39:1
5	0.35	0.333	1.21:1
6	0.30	0.283	1.03:1
7	0.26	0.243	0.88:1

$Pt\text{-}Al_2O_3$ during the reduction of an oxidized sample.

After this minor redispersion, the Pt on HY sintered gradually with each oxidation–reduction cycle (Table 1). The Pt–HY is considerably more prone to sintering under these conditions than is $Pt\text{–}Al_2O_3$.

The O_2 adsorption–desorption isotherms on Sample E2 of Pt–HY at 475 and 525°C are shown in Fig. 7. Steady-state values were achieved within 0.5 hr initially; however, for the high pressure points on the later runs with sintered catalyst (Ads. IV and Ads. V), establishment of "steady-state" required about 15 hr.

In terms of a generalized description, the O_2 adsorption increased gradually with increasing pressure and then tended to level off, up to an O_2 pressure of ca. 11 cm Hg at 475°C or ca. 20 cm Hg at 525°C. Above these pressures, the O_2 adsorption increased more rapidly and again leveled off when an asymptotic value of ca. 0.30 ml (STP)/g was reached for both temperatures. This asymptotic value was the same for all samples, implying that it is independent of Pt dispersion. By contrast, at pressures below the computed decomposition pressures for PtO (see Discussion, below) the uptake decreased with increased cycling of the sample (i.e., with decreasing H:Pt ratio).

A tentative interpretation of these adsorption isotherms is that at the lower O_2 pressures, surface oxidation of the platinum was occurring; at higher pressures, bulk oxidation was achieved.

O_2 chemisorption is largely irreversible on Pt–HY at 475 and 525°C, as evidenced by Des. II and Des. III, Fig. 7. "Steady-state" during desorption was usually reached within 1 hr. In some instances this was confirmed by noting the lack of any further change over an additional 20-hr period.

Determination of the "blank" O_2 uptake over the HY support showed that at pressures above 7 cm Hg, an almost constant value of 0.05–0.06 ml (STP)/g was observed at both 475 and 525°C. The data of Fig. 7 for Ads. II-Ads. V, corrected for this "blank" and expressed in terms of the atom ratios O:Pt (net O atoms adsorbed per [total] Pt atom in the sample), are plotted in Fig. 8. Several points are easily noted from Fig. 8: (a) the sensitivity of the O_2 uptake to cycle number in the low pressure region, which, along with the decreasing 200° H_2 chemisorption data (Table 1), strongly imply progressive sintering of the Pt; (b) the approach to a common asymptotic value of O:Pt for all samples in the high pressure region; and (c) the fact that this asymptotic value is roughly 0.85 ± 0.05, which is very much less than the corresponding values for the $Pt\text{–}Al_2O_3$ system (cf. Fig. 5).

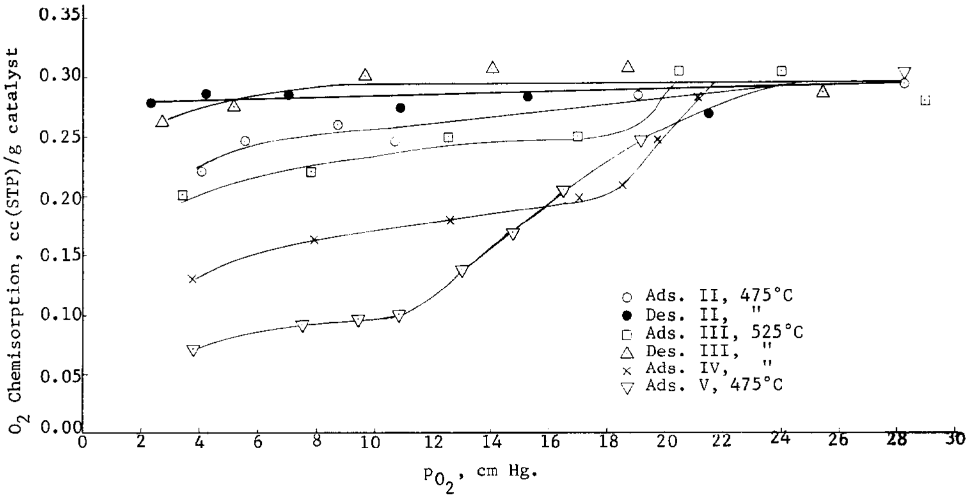

FIG. 7. O_2 chemisorption at 475 and 525°C on Pt–HY.

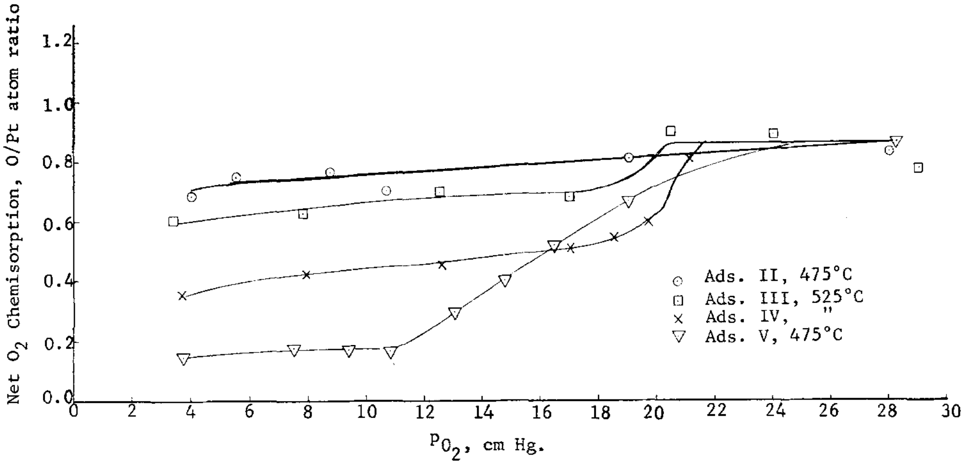

FIG. 8. Net O:Pt atom ratio at 475 and 525°C on Pt-HY.

To confirm the postulated sintering of Pt in the sample of cycled Pt-HY, X-ray diffraction patterns were obtained of (a) this sample after Test E2-7, Table I (curve B, Fig. 9); (b) Pt-NH_4Y as received (curve D); (c) HY treated in O_2 at 550°C and H_2 at 300°C and used in the determination of the "blanks" for H_2 and O_2 (curve A); (d) Pt-HY obtained by direct reduction of Pt-NH_4Y in H_2 at temperatures up to 550°C (curve C), a procedure previously shown to give a sample showing negligible H_2 chemisorption at 200°C; and (e) Pt-Al_2O_3 (Sample B2) after O_2 Ads. V. The patterns for the zeolite samples are shown in Fig. 9. The major conclusions are the following:

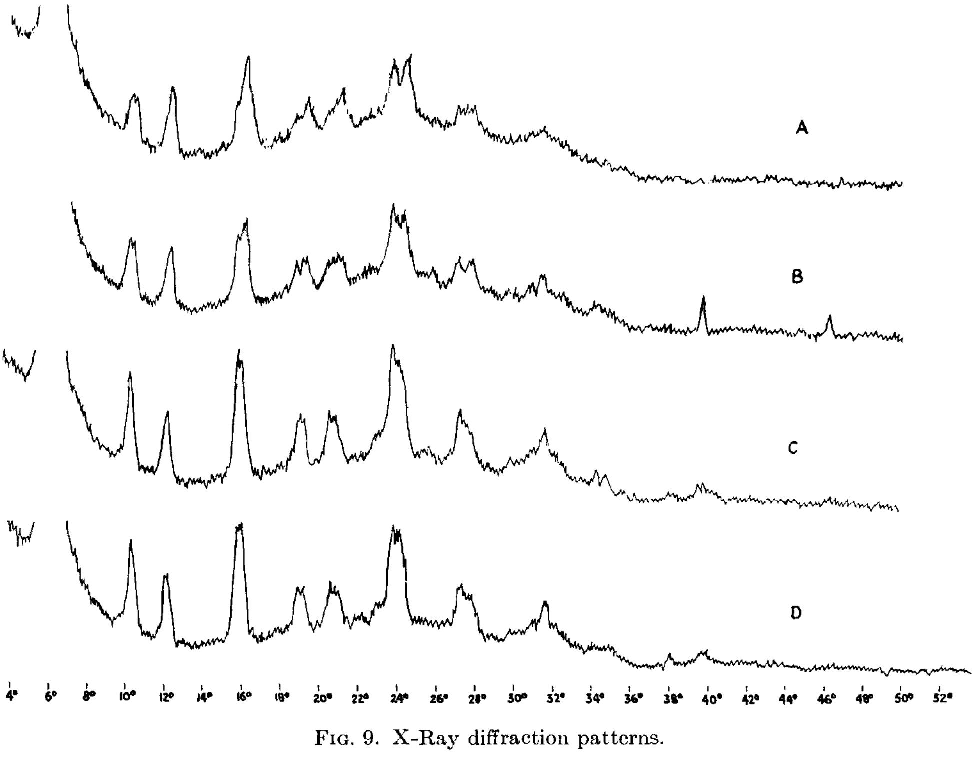

FIG. 9. X-Ray diffraction patterns.

1. Only the cycled Pt–HY sample (curve B) showed the lines for metallic Pt at 39.7 and 46.3°. This confirms the presence of Pt crystallites in this sample.

2. No Pt lines were observed in the cycled Pt–Al_2O_3, consistent with the observed H:Pt ratio of about 1 after the last O_2 chemisorption test.

3. No Pt lines were observed in the Pt–HY directly reduced by H_2 at 550°C, in spite of the fact that this sample showed no ability to chemisorb H_2 at 200°C. For this unexpected result we may suggest the following *ad hoc* interpretation: Pt ion-exchanged into NH_4Y migrates during the direct reduction in H_2 into positions not thereafter accessible to H_2 at 200°, but it is not "sintered" in the sense of having crystallized. Such a migration clearly does not occur when the Pt–NH_4Y is first treated in O_2 up to 550° prior to reduction in H_2.

4. If the sum of the peak heights between 14 and 37° is used as a measure of zeolite "crystallinity" (*17*), the directly-reduced Pt–HY and the as-received Pt–NH_4Y had about the same crystallinity. However, the cycled Pt–HY and the HY used in the chemisorption studies had both lost about 35% of the original crystallinity.

Discussion and Summary

Two effects of the support seem to be evident on the behavior of the platinum–oxygen system at high temperature:

1. Some chemical interaction between support and supported Pt that is responsible for (a) O:Pt ratios well in excess of unity and increasing with increasing p_{O_2}, for Pt–Al_2O_3; and (b) an essentially constant value of O:Pt = 0.85:1 at high p_{O_2}, for ion-exchanged Pt–HY.

2. Some greater tendency of Pt to sinter when ion-exchanged into HY than when impregnated on η-Al_2O_3.

The almost-step behavior of the O_2 adsorption isotherms on Pt–HY (cf. Fig. 8) suggests the possible occurrence of a bulk phase change. For this reason we consider first the reliability of the estimates of dissociation pressure of PtO at 475 and 525°C.

Dissociation pressures of bulk PtO and Pt_3O_4. As noted in the Introduction, few reliable data exist on the thermodynamic properties of the platinum oxides, and even the identity of the oxides is in question. The most direct experimental determination of the heat of formation of bulk Pt_3O_4 is the work of Ariya *et al.* (*5*), and the inconsistency between the calorimetric and tensiometric values has already been pointed out. Some observations are in order on the experimental methods employed by Ariya *et al.*:

1. The stoichiometry of the oxide and the extent of reduction are important in the calorimetric method. Ariya *et al.* reduced $PtO_{1.39}$ (not the theoretical $PtO_{1.33}$) at 25°C with H_2 saturated with H_2O vapor. The extent to which reduction was complete was apparently not studied.

2. Since only the equilibrium O_2 pressure and the temperature need be measured in the tensiometric method for the heat of formation per gram atom of oxygen, neither the stoichiometry nor extent of reaction need be known. However, it is essential that reversibility be demonstrated. Although this question is not discussed by Ariya *et al.* (*5*), we are inclined to treat the tensiometric data as probably more reliable than the calorimetric. The tensiometric method does *not* establish the stoichiometry of the solid phase being studied.

If we ignore the question of whether Ariya's tensiometric data relate to Pt_3O_4 (c) or PtO (c), there is good agreement between the calculated value of -18.5 kcal/g-atom of O for ΔH_f^0 in the temperature range studied by Ariya (923 to 973°K) and the earlier estimate (*3*) of -18 kcal/g-atom of O for ΔH_f^0 (800°K) based on the value of ΔH_f^0 (298) of -17 kcal/g-atom of O (*3*, *4*) and the heat capacity of PbO.

ΔS_f^0 (298°K) has been estimated as -20 eu/g-atom of O (2) and -18.8 eu/g-atom of O (*3*). The latter value, along with the assumption that C_p (PtO) = C_p (PbO), leads to the estimate ΔS_f^0 (800°K) = -21.2 eu/g-atom O; this is in reasonable agreement with the value ΔS_f^0 (953°K) = -22.7 eu/g-atom of O that may be calculated from the tensiometric data of Ariya *et al.* (*5*) with the use of $\Delta F_f{}^0 = -RT \ln p_{O_2}{}^{1/2} = \Delta H_f{}^0 - T\Delta S_f{}^0$.

The estimated values of $\Delta F_f{}^0$ (298°K) of -11 kcal/g-atom of O (*2*) and -11.4 kcal/g-atom of O (*3*) are in close agreement with the value -11.3 kcal/g-atom of O calculated for PtO more recently by Novak and Markovic from electrode potentials (*4*).

From these data were calculated the dissociation pressures, nominally for PtO (c), tabulated in the Introduction. Interpolation gives a calculated dissociation pressure of 5 cm Hg at 475°C and 21 cm Hg at 525°C. In attempting to interpret the isotherms of Fig. 8, however, it is important to observe that the calculated dissociation pressures are very sensitive to errors in the estimates of $\Delta F_f{}^0$. An uncertainty in $\Delta F_f{}^0$ of 1 kcal/g-atom of O results in a calculated range of 1 to 18 cm Hg for the dissociation pressure at 475°C, and a range of 6 to 76 cm Hg at 525°C. The arguments for bulk oxidation at the higher pressures in Fig. 8 therefore must be taken as instructive rather than rigorous. Clearly it would be useful to have more reliable thermodynamic data.

State of Pt on the support. Our results on H_2 chemisorption at 200°C add nothing new to current belief about the state of high Pt dispersion on freshly reduced Pt–Al_2O_3. However, the state of dispersion of Pt ion-exchanged into type Y zeolite is not so well established and requires further comment.

Rabo and co-workers (*18*) report a H:Pt ratio of 2:1 for a 0.5% Pt–CaY catalyst and deduce that the Pt is atomically dispersed. No correction was reported for a "hydrogen blank" on the CaY support, however. Our measurements indicate that a value of 1.97:1 is still obtained on Pt–HY even after the "blank" correction. Unfortunately, all such corrections for the adsorption by the support are based on the unproven assumption that no Pt–zeolite interaction exists that might cause a higher "blank" when Pt is present. In fact, this assumption is explicitly denied in the work of Lewis (*16*).

Lewis confirms a rather high ratio of H:Pt = 1.76:1 for a Pt–CaY sample. His prereduction was for 24 hr at 300°C rather than the 1 hr used by Rabo *et al.* (*18*) and ourselves, and some slight sintering could have occurred during this step. However, Lewis also studied X-ray absorption edge spectroscopy, X-ray line broadening, and acid solubility of his samples. His conclusions were that only the 0.5:1 H:Pt chemisorbed in 1 hr at 300°C changes the X-ray absorption edge, and that the additional 1.2:1 H:Pt slowly adsorbed over the next 20 or more hours ends up on the support. Moreover, he found that 60% of the Pt was soluble in acid, and that the undissolved 40% was present as crystallites of average size equal to 60 Å.

We observe only that Lewis' data on absorption edge show substantial spread, and that the effect on the edge spectrum may decrease with increasing H_2 adsorption. Nevertheless, Lewis' implicit questioning of the proper adsorption "blank" remains an important and unresolved one. Our own results on O_2 adsorption on Pt–Al_2O_3 lend credence to the notion that H_2 activated by Pt may move to, and react with, a refractory support (see Discussion below).

Effect of support on sintering of Pt. Since Pt ion-exchanged into HY is believed to be bonded to ionic sites in the zeolite framework, we had expected this catalyst to be more resistant to sintering than Pt–Al_2O_3. The reverse was true. Two factors seems to be responsible for this: (a) HY is relatively susceptible to thermal damage ("loss of crystallinity"), and (b) there is evidence for a Pt–alumina complex which stabilizes the Pt.

Such a complex was apparently first proposed by McHenry *et al.* (*19*) on the basis of solubility of some of the Pt, along with alumina, in aqueous HF or in acetylacetone. Johnson and Keith (*20*) subsequently invoked a Pt–alumina complex to explain Pt redispersion on sintered Pt–Al_2O_3 reforming catalysts. Both the extent of Pt solubility in H_2SO_4 and the Pt surface area on subsequent reduction were found to increase with increasing severity of the oxidation treatment. Interestingly, they observed sintering, not redispersion, if the oxidation was conducted under conditions that bulk oxidation of Pt could not occur.

Redispersion had been previously observed by Gruber (*21*), and a recent patent (*22*) claims a method for reactivating Pt–Al_2O_3 catalysts by treating with O_2 at a partial pressure of at least 5 psia at 900°F, followed by reduction with a H_2-containing gas.

Our own results on Pt–Al_2O_3 (Figs. 1 and 3) indicate that redispersion occurs not during the oxidation but during the subsequent reduction step. The gradual reduction in O_2 adsorption during Ads. I, Des. I, and Ads. II (Figure 1) indicates sintering. It is only after the subsequent 550°C reduction (after Ads. II) that redispersion of Pt into a more stable, highly dispersed configuration is observed; presumably it is this configuration that should be described as a "Pt–alumina complex." To our knowledge no satisfying chemical description, on the atomic scale, has been advanced for such a complex.

Effect of support on O:Pt ratio. Oxygen chemisorption around 500°C was quite different on η-Al_2O_3 and HY:

1. The net O:Pt ratio on Pt–Al_2O_3 was in the range of 1:1 to 3.7:1; on Pt–HY it was 0.85:1 or less at comparable conditions.
2. A step-like rise in O_2 uptake vs p_{O_2}, particularly at 525°C, was exhibited by Pt–HY but not Pt–Al_2O_3. The step was at pressures near the estimated dissociation pressures for PtO.
3. On Pt–HY the O:Pt ratio decreased steadily with increased cycle number, for p_{O_2} less than the estimated dissociation pressure; on Pt–Al_2O_3 the O:Pt remained at a high value once the "redispersion" of Pt had occurred.
4. The O_2 uptake appeared to be reversible, at 475 and 525°C, on Pt–Al_2O_3 but not on Pt–HY.

The following discussion is an attempt to rationalize these observations. We may first consider the predicted behavior of an idealized system of Pt crystallites on an inert support:

1. If PtO (c) exists and is immiscible with Pt (c), we expect bulk PtO to form whenever p_{O_2} exceeds the dissociation pressure of PtO (c) at the test temperature, provided diffusion through the solid phases is sufficiently rapid to permit equilibration.
2. If "surface thermodynamics" were identical with "bulk thermodynamics," no O_2 uptake would be observed for p_{O_2} less than the dissociation pressure of PtO (c). However, it is well known at least since the work of Almquist and Black (*23*) that the unique energetics of metal atoms in a surface results in some surface oxidation (in alternate language, oxygen chemisorption) even at pressures where the stable bulk phase is the metal. Such surface oxidation, as a function of increasing p_{O_2}, should cease when the surface is completely covered. Then, when $p_{O_2} \geq$ the dissociation pressure of PtO, bulk oxidation of all the Pt atoms should occur with a consequent step rise in oxygen uptake until the stoichiometry of PtO is reached.
3. If the Pt is very highly dispersed, it is conceivable that O:Pt ratios greater than unity can be reached, since the oxidation level of a surface or isolated Pt atom is not necessarily the same as for atoms in bulk. Mills *et al.* (*24*) have reported O:Pt ratios approaching two during the oxidation of a well-dispersed Pt–Al_2O_3 catalyst at 450°C.
4. In the region of p_{O_2} where only surface oxidation can occur, the O:Pt ratio at a given p_{O_2} should decrease as the temperature increases, and it should decrease if the Pt sinters. For higher values of p_{O_2}, where bulk PtO is stable, this ratio should equal unity for all samples, sintered or not.
5. When surface but not bulk oxidation can occur, the O:Pt ratio at a given p_{O_2}, corrected to unit Pt surface area, should be identical for all supports provided no chemical (i.e., electronic) interaction occurs between Pt crystallite and support.

The behavior of Pt–HY is roughly consistent with these predictions. The exceptions are (a) in the region of stability of bulk PtO, the O:Pt ratio was about 0.85:1 instead of unity; (b) at 475°C bulk oxidation appeared to set in at pressures higher than the estimated dissociation pressure; and (c) the O_2 uptake was essentially irreversible.

The somewhat low value for the O:Pt ratio can be reconciled either if the "blank" for O_2 uptake by the support is too high by a factor of two when Pt is present, or if some Pt atoms are inaccessible to O_2 because of migration into a zeolite cage with small pores. Both of these possibilities are plausible for ion-exchanged Pt–HY.

By contrast, the behavior of the Pt–Al_2O_3 sample was quite different than predicted. No sign was evident of a step rise in the isotherm as a function of p_{O_2}; at a given p_{O_2}, the O:Pt ratio was actually higher at 525°C than at 475°C; and the O:Pt ratio reached the unlikely value of 3.7:1 at 525°C and $p_{O_2} = 35$ cm Hg for a well-dispersed sample.

We believe that these results for Pt–Al_2O_3 arise for two reasons:

1. Our own data (*25*) on pure Al_2O_3 indicate that a slow reduction of the surface occurs in the presence of dry H_2 at 550°C, at a rate which may be limited by the rate of H_2 dissociation. In the presence of Pt the extent of reduction of the Al_2O_3 surface during the preliminary H_2 treatment at 550°C would then be more rapid, provided that H atoms are able to move from Pt to Al_2O_3.
2. The limiting value of O:Pt for highly dispersed Pt is greater than unity, even at temperatures near 500°C.

If incremental reduction of the Al_2O_3 surface occurs in the presence of Pt, the subsequent uptake of O_2 (in reoxidation of the Al_2O_3 surface) should be irreversible. The amount of O_2 consumed in this way should be measured by the extrapolation of the O_2 adsorption isotherm to zero pressure, provided that O_2 chemisorption on the Pt is reversible near 500°C. The extent of surface reduction would be determined by the H_2 pretreatment, which is identical for the 475 and 525°C O_2 studies, and we would expect the same intercept for both temperatures. As Fig. 5 indicates, the intercept is about 1.2:1 for 525°C and about 0.9:1 for 475°C. If we assume an average value of 1 (expressed in terms of O:Pt ratio) for the O_2 thus consumed in the irreversible reoxidation of the Al_2O_3 surface, the "true" O:Pt ratios for O_2 reacting with the Pt then fall in the range of about 0.9:1 to 2.7:1 at 525°C, and about 0 to 0.6:1 at 475°C. The ratios greater than unity at 525°C are attributed to the second factor mentioned above.

If this interpretation is correct, we are also led to the surprising conclusion that the O:Pt ratio for "surface" platinum oxides increases with increasing temperature. This question deserves separate study in a system free from the complication of possible surface reduction of the support.

ACKNOWLEDGMENT

It is a pleasure to acknowledge support of this research by the donors of The Petroleum Research Fund, administered by the American Chemical Society.

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