Metal-Support Interaction in Pt/Al$_2$O$_3$ Catalysts

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The aim of this study was to find out why in Pt/Al$_2$O$_3$ catalysts a large fraction of the Pt becomes "inaccessible" to hydrogen chemisorption upon treatment in hydrogen at high temperature (>500°C). To this end hydrogen-treated catalyst samples were investigated using hydrogen- and oxygen-chemisorption measurements, a catalytic characterization via *n*-hexane conversion reactions, and NMR measurements of the Pt Knight shift. The chemisorption capacity was found to decrease considerably for hydrogen but not for oxygen. The selectivity of *n*-hexane conversions changed and the Knight shift differed from that of samples reduced at low temperature. The results agree with the assumption that the highly dispersed particles form an alloy with the Al from the support.

INTRODUCTION

Alumina-supported platinum catalysts are used in several important industrial processes. For optimum efficiency, the metal surface area should be as large as possible. In the past, various highly dispersed catalysts were prepared and much attention was paid to changes in metal dispersion [see, e.g., Ref. (1)]. Several techniques were developed for the determination of the degree of metal dispersion and of metal surface areas. Initially hydrogen chemisorption was most often used, while later on X-ray diffraction and electron microscopy also found wide application (2). With these techniques the sintering behavior of Pt/Al$_2$O$_3$ catalysts was investigated in numerous studies [for a review see Ref. (1)]. The results of one of these studies (3), which dealt with the changes in metal dispersion resulting from treatments in either air or hydrogen at high temperature, initiated the work described here. It was reported that unlike air treatments which, according to the three above-mentioned techniques, gave mutually consistent results, treatments in hydrogen led to large discrepancies. Extensive sintering of the platinum was suggested by hydrogen-chemisorption measurements while a corresponding increase in particle size could not be detected by electron microscopy and X-ray diffraction. So, during treatments in hydrogen at high temperature some hitherto unclarified change in the catalyst system seems to render part of the platinum undetectable by hydrogen chemisorption and possibly inoperative in the catalytic process.

The aim of the present study is to explain this apparent platinum loss. An attempt is made to trace the "undetectable" platinum and to elucidate the mechanism that makes it undetectable. Our approach is based on the following observations (3):

(i) The hydrogen chemisorption capacity shows a decrease which is not reflected by an increase in particle size during electron microscopy and X-ray diffraction measurements; and

(ii) the original hydrogen chemisorption

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capacity is restored by repeated oxidation/reduction cycles under conditions which do not lead to redispersion of (air-)sintered platinum particles.

From these observations we conclude that after the high-temperature treatment in hydrogen the platinum is still present in a highly dispersed state at, or very close to, the surface, but, as a result of some change in environment, is no longer capable of chemisorbing hydrogen. Under the reaction conditions (high temperature, reducing atmosphere) a platinum-assisted reduction of the alumina support (4) seems conceivable. Therefore, we decided to test the hypothesis that the apparent platinum loss is caused by the (strongly exothermic) formation of a platinum–aluminum alloy. To this end we did the following experiments:

(i) Chemisorption measurements to investigate whether the platinum that is inaccessible to hydrogen can be detected by other adsorbates;

(ii) catalytic measurements to detect any changes in catalytic selectivity caused by chemical changes in the Pt/Al₂O₃ system; and

(iii) magnetic resonance experiments to obtain a direct indication of chemical changes.

EXPERIMENTAL METHODS

Catalysts and Catalyst Pretreatment

As a previous study (3) had shown that the apparent platinum loss is independent of the platinum load and the type of alumina support, most experiments were carried out with one of the catalysts (E) used in that study, viz. 0.8 Pt (prepared by impregnation with H₂PtCl₆) on γ-Al₂O₃. For the magnetic resonance experiments we used a home-made 5 wt% Pt/Al₂O₃ catalyst in order to obtain a measurable platinum signal.

Before being subjected to gas treatments at high temperature, all the samples were thoroughly dried *in situ*. Whenever chemisorption or magnetic resonance experiments had to be performed, this drying was accomplished by heating under vacuum (3 hr at 300°C); in the case of catalytic measurements we used a stream of ultra-dry hydrogen (16 hr at 200°C). The dried samples were treated at high temperature by passing either dry air or hydrogen from a palladium diffusion unit over them. Oxidized samples were reduced afterwards in flowing hydrogen (1 hr at 400°C).

Chemisorption Measurements

Platinum surface areas were determined by a chemisorption of hydrogen and oxygen. Use was made of a static sorption apparatus (see Fig. 1), which comprised a very accurate, thermostatted pressure transducer (Datametrics Inc.) allowing an easy determination of pressure differences of 10^{-3} Torr ($1 = 133.3$ N m⁻²). As the volume of the adsorption chamber was about 200 ml such a difference corresponds to gas consumptions of the order of 0.01 μmol.

Prior to the adsorption proper the reduced samples were heated under vacuum (10^{-6}–10^{-7} Torr) for at least 2 hr at 400°C until a mass spectrometer connected to the chemisorption cell indicated that no more hydrogen was evolved.

The measurements were carried out at 0°C and 0.1 Torr equilibrium pressure using 0.5 g of catalyst.

Catalytic Measurements

The catalytic behavior of the Pt/Al₂O₃ samples after various pretreatments was characterized by monitoring the conversion reactions of *n*-hexane as a function of temperature. These experiments were carried out in a quartz downflow microreactor connected to a gas–liquid chromatograph, at a flow of 2.5 Nl/g cat, a molar ratio of hydrogen to *n*-hexane of 10 and atmospheric pressure.

In order to minimize catalyst deactivation during the test the hexane was introduced as a H_2/C_6 pulse of 120 sec in a continuous H_2 stream. At the end of the pulse a sample of the effluent was injected into the glc. In this way the conversion was measured from 250 to 550°C at intervals of 25°C. In addition, some tests were carried out with a continuous H_2/C_6 feed.

RESULTS

Chemisorption Measurements

It appeared interesting to determine surface areas using adsorbates other than hydrogen. We chose oxygen because a titration of a hydrogen-covered platinum surface with this gas (5) would also permit a direct comparison of the two adsorbates.

In hydrogen chemisorption (HC) and oxygen chemisorption (OC) measurements the exposed metal surface area is determined from the amount of gas adsorbed on a clean surface. In hydrogen titration (HT) and oxygen titration (OT) measurements this surface area is derived from the gas consumption by surfaces covered with oxygen and hydrogen, respectively. As the literature is rather controversial about the best way to perform and interpret these HC, OC, HT, and OT measurements (5–7) we adopted the following approach. The stoichiometries of the various adsorption reactions under our experimental conditions (0.1 Torr, 0°C) were determined using a fresh catalyst reduced at a temperature where chemisorption, electron microscopy, and X-ray diffraction indicated the same degree of dispersion. These stoichiometries were then used to interpret the results of similar measurements on samples reduced at high temperatures. The underlying assumption that during high temperature treatments in hydrogen the adsorption stoichiometries remain unaltered seems to be reasonable because, according to the literature (8), these stoichiometries only change with changing particle size
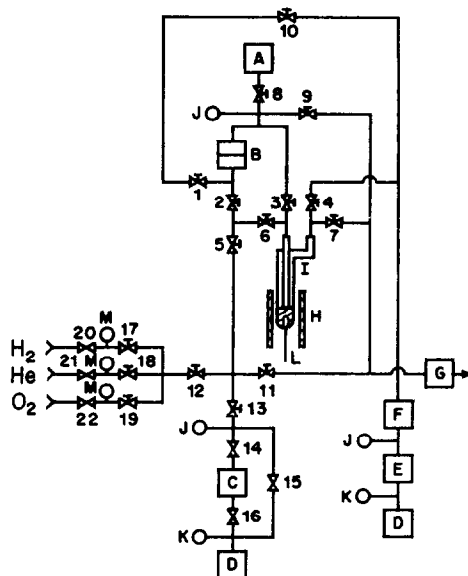

FIG. 1. Adsorption apparatus. A, ionization pump; B, pressure transducer; C, oil-diffusion pump; D, rotary vacuum pump; E, turbo-molecular pump; F, mass spectrometer; G, flowmeter; H, furnace; I, quartz reactor; J, ionization gauge; K, Pirani gauge; L, thermocouple; M, manometer; 1–10, high-vacuum bakeable valves; 11–22, Hoke vacuum valves.

and such a change was not observed in our samples.

Catalyst Reduced at 400°C

(a) HC and OC measurements. For our purposes the H/Pt ratio is conveniently defined as the amount of hydrogen that is irreversibly adsorbed at 0°C and 0.1 Torr divided by the total amount of Pt present in the sample (on an atom-to-atom basis). The amount of irreversibly adsorbed hydrogen is defined as the amount that is adsorbed after 40 min exposure to hydrogen at 0°C and 0.1 Torr minus the amount that is readsorbed in a second measurement after 10 min evacuation at 0°C. In terms of dispersion the values thus obtained may be slightly too low (H/Pt $\approx$ 0.85–0.95). The values obtained by adding the reversibly and irreversibly adsorbed amounts are certainly too high (H/Pt $\approx$ 1.1–1.2).

TABLE 1

Gas Consumptions in Adsorption Measurements after Reduction of Fresh Catalyst at 400°C

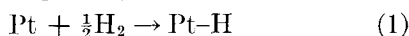|	HC	OT$_1$	HT$_1$	OT$_2$	HT$_2$	OC
N ml/g catalyst	0.39	0.39	0.78	0.39	0.79	0.20
Atoms gas/atom Pt	0.90	0.91	1.80	0.92	1.83	0.46

O/Pt ratios are defined in a similar way but can be determined by a single adsorption measurement because the amount of oxygen that is reversibly adsorbed at 0°C is negligible. The amount of chemisorbed oxygen equals about half the amount of chemisorbed hydrogen.

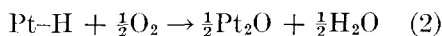Chemisorption of O$_2$ and H$_2$ on the support proved to be negligible under the experimental conditions.

(b) *HT and OT measurements.* For reasons to be discussed below it was convenient to titrate hydrogen-covered catalyst samples with oxygen. During the titration oxygen is consumed to remove the adsorbed hydrogen (which migrates as H$_2$O to the support (7)) and is also chemisorbed on the Pt. The resulting oxygen-covered Pt surface can be titrated in the same way with hydrogen. These H$_2$/O$_2$ cycles can be repeated several times on the same sample.

The results of these measurements are presented in Table 1. They can be interpreted using the following stoichiometries:
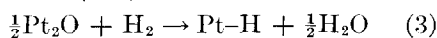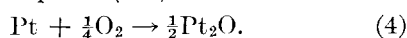
H$_2$ chemisorption (HC):

$$Pt + \tfrac{1}{2}H_2 \rightarrow Pt-H \qquad (1)$$

O$_2$ titration (OT):

$$Pt-H + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}Pt_2O + \tfrac{1}{2}H_2O \quad (2)$$

H$_2$ titration (HT):

$$\tfrac{1}{2}Pt_2O + H_2 \rightarrow Pt-H + \tfrac{1}{2}H_2O \quad (3)$$

O$_2$ chemisorption (OC):

$$Pt + \tfrac{1}{4}O_2 \rightarrow \tfrac{1}{2}Pt_2O. \qquad (4)$$

Thus, the relative gas consumptions for HC:OT:HT:OC are 2:2:4:1.

In the next section these stoichiometries will be used to interpret the results of

adsorption measurements on samples reduced at high temperatures.

Catalysts Reduced at High Temperatures

(a) *HC–OT–HT measurements.* Experimentally the most convenient way to compare H$_2$ and O$_2$ chemisorption behavior is to determine the H/Pt ratio from a HC measurement and then to titrate the hydrogen-covered surface with O$_2$. In this way time-consuming heating and evacuation between two adsorption measurements can be omitted. In addition, consecutive HT and OT measurements can show whether initial gas consumptions are reproduced in subsequent measurements.

Table 2 presents the results obtained with samples reduced at 550°C (row a) and 650°C (row b). For both samples they can be summarized as HC < OT$_1$ ≈ $\tfrac{1}{2}$HT$_1$ ≈ OT$_2$. Thus, initially the chemisorption capacity is much lower for hydrogen than for oxygen, indicating the presence of new sites which do accept oxygen but no hydrogen. At the end of the titration measurements the hydrogen chemisorption capacity, calculated according to the previous section as $\tfrac{1}{2}$HT, seems to be increased, suggesting that these new sites are reconverted (in oxygen at 0°C) into "normal" sites which adsorb both gases. Surprisingly, however, a direct determination of the hydrogen chemisorption capacity, after reduction and evacuation of the sample at 400°C, yields a value approximately equal to the initial value.

(b) *HC–OT–HC measurements.* In order to find out whether the hydrogen chemisorption capacity of the catalyst increases

upon exposure to O_2 at higher temperatures, we did some experiments in which the catalyst was subjected to an oxidation at 300°C after each OT measurement. Upon reduction and evacuation at 400°C, HC and OT were determined. In this way HC–OT–HC–etc. instead of HC–OT–HT–etc. sequences were obtained.

From the results in Table 3 (columns a and b) and Fig. 2 it can be seen that now, contrary to the observations mentioned under (a), the amount of hydrogen chemisorbed (HC) increases progressively, in agreement with earlier results (3). Apparently, at 300°C in O_2 reconversion into sites adsorbing both gases takes place. In addition, these results, just like those under (a), show that the gas consumption in subsequent OT measurements is constant. This implies that OT measurements do not discriminate between the two types of site. Table 3, column c, shows that after real sintering (in air) HC and OT remain approximately equal, as found in measurements on fresh catalysts reduced at low temperature. In this case, O_2 treatments at 300°C do not increase the hydrogen chemisorption capacity either.

(c) *HC and OC measurements.* As OT measurements do not discriminate between the two types of site, we repeated the previous experiments using oxygen chemisorption instead of oxygen titration upon cleaning the surface after each hydrogen chemisorption measurement. The results of such a HC–OC–HC sequence are presented in Table 4 and Fig. 2.

The OC measurements required decreasing amounts of oxygen as the hydrogen chemisorption increased after each treatment in O_2 at 300°C, whereas the corresponding OT measurements required a constant amount of oxygen. Furthermore, it should be noted that the first OC value was even higher than the one determined for a fresh catalyst reduced at 400°C.

Catalytic Conversion of n-Hexane

If after a hydrogen treatment at high temperature the platinum is, at least partly, present in a different form or chemical environment, this should be reflected by a different behavior in catalytic reactions. A convenient way to investigate this is to look at the conversion of *n*-hexane into cracking, isomerization, and (dehydro)-cyclization products as a function of temperature.

With a view to preventing changes due to exposure to air, the measurements were initially performed after *in situ* pretreatment of the catalyst. This implies that the platinum surface area at the start of the test is unknown. Figure 3 shows the distribution of the reaction products as a function of temperature after various pretreatments; the most important products are cracking products (C_1–C_5), isomers (2-methylpentane and 3-methylpentane), and benzene. Compared with the sample reduced at 400°C (I), the airsintered sample (IV) shows only minor changes. The selectivity for cracking is somewhat increased, which is probably a consequence of an increased particle size (9). The samples reduced at 550°C (II) and 700°C (III) show a drastically enhanced selectivity for the nonde-

TABLE 2

Gas Consumptions (in at/at) in Adsorption Measurements after
Treatment in H_2 at High Temperature

	HC	OT_1	HT_1	OT_2	HT_2	OT_3	HT_3
(a) 16 hr in H_2 at 500°C	0.49	0.71	1.34	0.71	1.35	—	—
(b) 16 hr in H_2 at 650°C	0.24	0.57	1.11	0.59	1.09	0.59	1.12

Hydrogen Chemisorption versus Oxygen Titration
Values (in at/at) of H$_2$ Treated Catalyst after
Repeated O$_2$/H$_2$ Treatments

n^a	(a)^b		(b)^b		(c)^b	
	HC	OT	HC	OT	HC	OT
0	0.36	0.66	0.25	0.59	0.38	0.42
1	0.46	0.66	0.37	0.56	0.41	0.44
2	0.52	0.67	0.40	0.59	0.41	0.43
3	0.56	0.68	0.41	0.59		

^{a} n, number of O$_2$/H$_2$ treatments.
^{b} Pretreatment: (a) 64 hr in H$_2$ at 550°C; (b)
16 hr in H$_2$ at 650°C; (c) 64 hr in air at 600°C.

structive reactions. These results con-
vincingly show that "sintering" in hydrogen
and in air leads to completely different
catalytic properties.

In order to find out whether these changes
are really due to a change in the state of
the platinum on the support, we did the
following experiments. The H/Pt ratio was
measured for a hydrogen- and an air-
treated sample and the n-hexane test was
performed with quantities of both samples
representing an equal hydrogen-detectable
platinum surface area. The underlying as-
sumption that this surface area does not
change upon exposure to air after the
chemisorption measurement is justified, as
was shown by the results in the section on
chemisorption. These tests yielded results
in agreement with those from Fig. 3.
Similar results were obtained after admix-
ture of chlorided alumina. Thus, the ob-
served differences are not due to a differ-
ence in hydrogen-detectable platinum sur-
face area or to a difference in acidic
properties.

To interpret the changes in catalytic
behavior caused by the high-temperature
hydrogen treatment, we compared the re-
sults with those of similar measurements
on an unsupported Pt$_3$Sn alloy sample
(10). Figure 4 shows the percentage con-
version of n-hexane into cracking products

and benzene as a function of temperature
for a sample reduced at 400°C, a similar
sample reduced at 700°C, and the unsup-
ported Pt$_3$Sn sample. These results were
obtained using a continuous H$_2$/C$_6$ feed.

Magnetic Resonance Experiments

Direct information about the (chemical)
changes in the Pt/Al$_2$O$_3$ system due to
high-temperature reduction can only be
obtained from a physical technique which
gives direct information about the state
of Pt on the support. In principle, nuclear
magnetic resonance spectroscopy would be
able to provide such information via the
Knight shift (11), which is related to the
electron density on the nucleus under in-
vestigation. To test this, we did some mea-
surements using the following samples:

(a) 10% Pt (black) with γ-Al$_2$O$_3$, as a
reference;
(b) 5% Pt/γ-Al$_2$O$_3$ reduced at 400°C;
and
(c) 5% Pt/γ-Al$_2$O$_3$ reduced at 675°C.

The low-temperature reduced sample proved
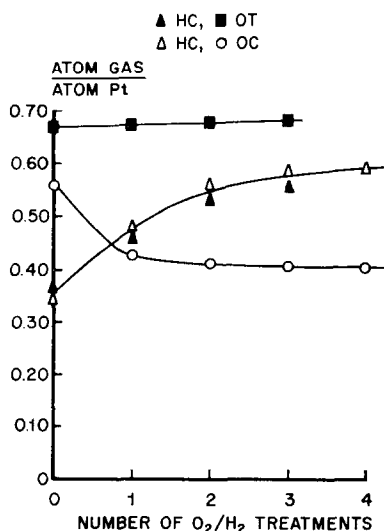to have nearly the same Knight shift as

FIG. 2. Changes in gas consumptions of samples
treated in H$_2$ at high temperature as a result of
O$_2$/H$_2$ treatments.

TABLE 4

Hydrogen Chemisorption versus Oxygen Chemisorption Values (in at/at) of H_2 Treated Catalyst after Repeated O_2/H_2 Treatments[a]

n^b	0	1	2	3	4
HC	0.34	0.48	0.55	0.58	0.58
OC	0.56	0.45	0.42	0.41	0.40

[a] Pretreatment: 64 hr in H_2 at 550°C.
[b] n, number of O_2/H_2 treatments.

the reference material. The sample reduced at 675°C, however, gave a down-field shift of -1.2%, suggesting an appreciable change in electron density on the platinum.

DISCUSSION

General Remarks

The results of this study once again show that high-temperature treatments in H_2 and in O_2 lead to completely different catalysts. It appears that samples with equal H/Pt ratios differ not only in particle size distribution, as shown in Ref. (3), but also in oxygen chemisorption and catalytic behavior. So, it is obviously incorrect to
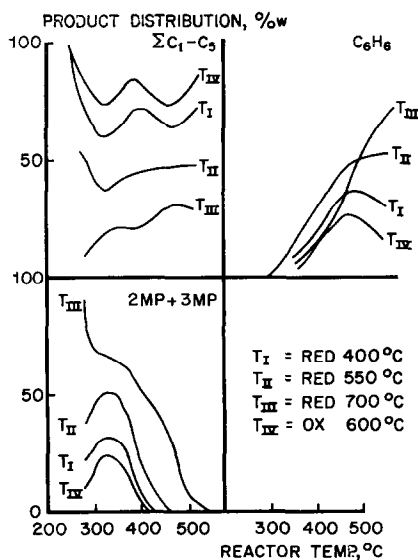

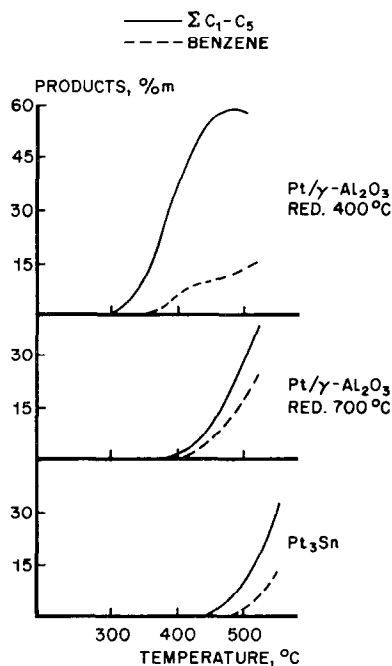FIG. 3. Product distribution in n-hexane conversions.

FIG. 4. Formation of benzene and cracking products from n-hexane as a function of temperature.

characterize such samples merely by their H/Pt ratio.

Weller and Montagna (4) reported that pure Al_2O_3 is not completely inert to dry H_2 at temperatures of about 500°C. Being well aware that bulk reduction of Al_2O_3 is thermodynamically impossible under these circumstances, they interpreted the observed H_2 consumption as being due to a reduction of the surface to an aluminum suboxide. Both the absence of thermodynamic data for the lower oxides and the fact that the energetics for surface species are unknown and may differ substantially from the bulk data make quantitative statements impossible. Weller and Montagna also found that the measured H_2 consumption increased with increasing treatment time. If the formation of H atoms is involved in this reaction, the presence of platinum on the Al_2O_3 may increase the reduction rate to a large extent. A similar kinetic phenomenon was observed in the reduction of oxides of base metals (12). It

seems that the temperature at which the reduction of these oxides starts can be decreased by several hundred degrees by adding small amounts of metals which are able to adsorb H_2 dissociatively. Hydrogen atoms then migrate from the metal center to the oxide region.

In the case of Al_2O_3 this decrease of the initial reduction temperature is probably insufficient to explain a partial reduction at about 600°C because at least bulk thermodynamics do not allow this at realistic H_2 and H_2O partial pressures. However, apart from the rate increase caused by dissociative adsorption there is in the Pt/Al_2O_3 system another driving force in the direction of surface reduction, namely, the (strongly exothermic) formation of a platinum–aluminum alloy. The large change in free energy is then reduced to a much smaller value corresponding to realistic $H_2:H_2O$ partial pressure ratios. In fact, Bronger and Klemm (13) reported a procedure for the preparation of Pt_nAl_m alloys by reduction of a physical mixture of Pt and Al_2O_3 in a stream of ultra-dry H_2. The composition of the alloy formed depends on the H_2O partial pressure and the Pt:Al atomic ratio. They found quantitative conversion above 900°C. The temperature at which the reduction starts may, however, be much lower for surface reduction and alloy formation in highly dispersed Pt/Al_2O_3 catalysts, where there is a strong metal-support interaction.

Other evidence of reactions between the two partners in this system was reported by de Bruin et al. (14), who observed a surface reaction in vacuum between a Pt film and Al_2O_3 at about 1000°C. Quite recently, Sprys and Mencik (15) observed a similar reaction under the electron microscope: Pt deposited on a thin $\gamma\text{-}Al_2O_3$ film was seen to consume the alumina when the Pt was heated by an intense electron beam. The reaction product was identified by electron diffraction as Pt_3Al.

From the above it is clear that the forma-

tion of a Pt–Al alloy from Pt and Al_2O_3 is well possible. Considering that in our experiments the H_2O/H_2 ratio is extremely low, that the heats of formation of these alloys are apparently (13, 16) rather high, and that in our highly dispersed systems thermodynamics do not preclude alloy formation under the reaction conditions, we assume that alloy formation actually takes place. In the light of this hypothesis we will now examine our results.

Interpretation of the Results in Terms of the Alloy Model

Chemisorption measurements. The chemisorption stoichiometries determined from measurements after reduction at low temperature [Eqs. (1)–(4)] are in good agreement with results of Wilson and Hall (7), who found HC:OC:HT ratios of 2:1:4 under similar conditions. We assume that after reduction at high-temperature chemisorption on unalloyed Pt can be described by these reaction equations.

The observed decrease of the hydrogen chemisorption capacity after reduction at high temperature can be easily rationalized in terms of the alloy model by assuming that hydrogen chemisorption, which does not take place on Al, is dissociative and needs two adjacent Pt sites. This decrease is in line with observations on PtSn (10) and PtAu (17) alloys, where hydrogen but not CO chemisorption is suppressed relative to Pt metal.

The observed difference between the HC and the successive OT measurement $(HC < OT_1)$ is also understood, as Al chemisorbs oxygen but no hydrogen. So, an amount of oxygen $(OT_1\text{–}HC)$ is consumed by the alloy sites in addition to the amount needed for normal oxygen titration according to Eq. (2) with $OT \approx HC$. As in subsequent OT measurements, even after heating in O_2, the overall oxygen consumption remains constant, the stoichiometry of the reaction with the alloy must be the

same as in Eq. (2), i.e., $\frac{1}{2}O_2$ per Pt atom. This can be represented schematically as

$$\text{Pt}_x\text{Al} + \tfrac{1}{2}x\text{O}_2 \rightarrow \text{Pt}_x\text{AlO}_x. \qquad (5)$$
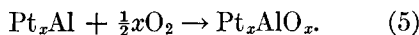
The interpretation of the HT measurements is more difficult. The observation that the hydrogen consumption HT is too large to correspond with the number of oxygen-covered Pt sites implies that oxygen must at least partly be removed from the Pt_xAlO_x sites.

One explanation which we have considered is that the alloy decomposes in an O_2 atmosphere at 0°C. Equation (5) must then be written with $x = 3$ as:

$$\text{Pt}_3\text{Al} + \tfrac{3}{2}O_2 \rightarrow \tfrac{3}{2}\text{Pt}_2\text{O} + \tfrac{1}{2}\text{Al}_2\text{O}_3. \quad (6)$$
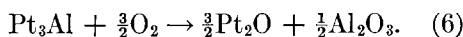
The number of oxygen-covered Pt sites thereby increases. From Eqs. (2), (3), and (6) it then follows that $OT_1 = \frac{1}{2}HT_1 = OT_2$ etc., as is indeed observed. However, this explanation had to be rejected because the HC measurement at the end of the titration measurements indicated that the amount of free Pt had not increased. Besides, considering bulk properties only, Pt–Al alloys are stable in air at room temperature (18).
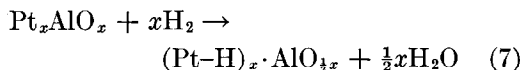
Another possibility considered in that oxygen is removed as H_2O from the alloy sites to the support, i.e., that Reaction (5) is reversed. Then OT also equals 0.5 HT. This is, however, rather unlikely because it requires oxygen to be removed from Al–O or
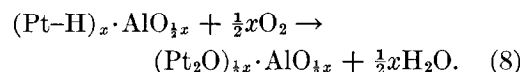
$$
\begin{array}{c}
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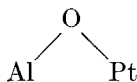
by hydrogen at 0°C. Unless Al in alloys behaves completely different from pure Al, the Al–O interaction must be considered to be too strong for that.

A remaining, rather tentative, explanation is that exposure to O_2 at 0°C modifies the alloy sites in such a way that the normal Pt behavior in chemisorption is restored without decomposing the alloy. Then the HT and OT measurements can be represented schematically as:

$$\text{Pt}_x\text{AlO}_x + x\text{H}_2 \rightarrow$$
$$(\text{Pt–H})_x \cdot \text{AlO}_{\frac{1}{2}x} + \tfrac{1}{2}x\text{H}_2\text{O} \quad (7)$$

and

$$(\text{Pt–H})_x \cdot \text{AlO}_{\frac{1}{2}x} + \tfrac{1}{2}x\text{O}_2 \rightarrow$$
$$(\text{Pt}_2\text{O})_{\frac{1}{2}x} \cdot \text{AlO}_{\frac{1}{2}x} + \tfrac{1}{2}x\text{H}_2\text{O}. \quad (8)$$

Only after reduction at 400°C, preceding the final HC measurement, is oxygen removed from the Al and the Pt_xAl restored, leading to the original low HC value.

The results obtained with catalysts reduced at high temperatures fit well in the alloy model: During heating in O_2 Reaction (6) takes place to a certain extent. The amount of free Pt and consequently HC increases. The increasing ratio of free to alloyed Pt does not influence OT [Reactions (2) + (5)] but leads to a decreasing OC value [Reactions (4) + (5)].

Catalytic measurements. A growing interest in bimetallic catalysts has initiated a large number of investigations into the catalytic behavior of platinum diluted with an inert second metal. It would seem that the function of the second component is mainly to isolate platinum atoms rather than to change the activities per atom. This dilution results on the average in smaller Pt sites, leading to the suppression of reactions requiring more than one Pt atom relative to reactions taking place on single atoms (19, 20). Although the literature about site requirements is not unequivocal, there is agreement about the fact that alloying, i.e., formation of small sites, enhances the selectivity for nondestructive reactions. As can be seen in Figs. 3 and 4, the behavior of the $\text{Pt/Al}_2\text{O}_3$ catalysts reduced at high temperature fits well in this picture.

Magnetic resonance experiments. The Knight shift measurements on Pt samples indicate that the state of Pt after reduction at 400°C is the same for a 5 wt% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ sample as for a mixture of Pt

(black) and Al$_2$O$_3$. This suggests that after reduction at 400°C the Pt is present as a zero-valent species on the catalyst and not as a surface complex. As the Knight shift of this sample changes upon reduction at higher temperatures, there must be a change in the Pt° species. Evidence in support of alloy formation was obtained from a reported measurement on bulk PtAl$_2$ (21), for which a (larger) shift (−4.2%) in the same direction was found.

Alternative Interpretations

Apart from alloy formation there are several other possible explanations for the observed decrease in H/Pt ratio. The most trivial one would be that the decrease is due to catalyst poisoning. However, the possibility of a contamination stemming from the H$_2$ feed can safely be ruled out, as can a possible poisoning by contaminants from the support because the same H/Pt decrease was observed (3) for catalysts prepared in different ways from different aluminas. Moreover, catalyst poisoning does not easily explain why the H/Pt and O/Pt values are influenced in different ways or why the effects are observed only after treatments at high temperature.

Another explanation would be that the platinum surface is reconstructed in such a way that H$_2$ is no longer adsorbed. Such a reconstruction is, however, difficult to envisage for particles beyond the detection limit of the electron microscope as the only literature data suggesting that some exposed faces do not adsorb hydrogen show that such a behavior is confined to perfect, stepless close-packed faces. Besides, this explanation fails to account for the observed change of the Pt Knight shift.

REFERENCES

1. Wancke, S. E., and Flynn, P. C., *Catal. Rev. Eng. Sci.* **12**, 93 (1975).
2. Spindler, H., *Int. Chem. Eng.* **14**, 725 (1974).
3. Dautzenberg, F. M., and Wolters, H. B. M., *J. Catal.* **51**, 26 (1978).
4. Weller, S. W., and Montagna, A. A., *J. Catal.* **21**, 303 (1971).
5. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
6. Mears, D. E., and Hansford, R. C., *J. Catal.* **9**, 125 (1967).
7. Wilson, G. R., and Hall, W. K., *J. Catal.* **17**, 190 (1970).
8. Freel, J., *J. Catal.* **25**, 149 (1972).
9. Anderson, J. R., Macdonald, R. J., and Shimoyama, Y., *J. Catal.* **20**, 147 (1971).
10. Verbeek, H., and Sachtler, W. M. H., *J. Catal.* **42**, 257 (1976).
11. Clogston, A. M., Jaccarino, V., and Yafet, Y., *Phys. Rev.* **134A**, 650 (1964).
12. Il'Chenko, N. I., *Russ. Chem. Rev.* **41**, 47 (1972).
13. Bronger, W., and Klemm, W., *Z. Anorg. Allgem. Chem.* **319**, 58 (1962).
14. De Bruin, H. J., Moodie, A. F., and Warble, C. E., *J. Mater. Sci.* **7**, 909 (1972).
15. Sprys, J. W., and Mencik, Z., *J. Catal.* **40**, 290 (1975).
16. Wengert, P. R., and Spanoudis, L., *J. Amer. Ceramic Soc.* **57**, 94 (1974).
17. Biloen, P., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **50**, 77 (1977).
18. Klemm, W., Dorn, F., and Huch, R., *Naturwissenschaften* **45**, 490 (1958).
19. Sachtler, W. M. H., and Van Santen, R. A., *Advan. Catal.*, **26**, 69 (1976).
20. Hagen, D. I., and Somorjai, G. A., *J. Catal.* **41**, 466 (1976).
21. Jaccarino, V., Blumberg, W. E., and Wernick, J. H., *Bull. Amer. Phys. Soc.* **6**, 104 (1964).