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Studies of the Hydrogen Held by Solids V. Investigation of Platinum Supported on Alumina Catalysts by Exchange with Deuterium Gas

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The number of exposed Pt atoms (Pt surface area) and of alumina hydroxyl groups were determined, in the same experiment, by exchange with D_2 as the temperature was raised. In agreement with earlier work, H/Pt ratios of 0.7 to 0.9 were found, indicating that most of the metal atoms were accessible for the chemisorption of hydrogen. Part of this metal-associated hydrogen could be exchanged at −195° and all of it at −80° whereas the alumina hydroxyl groups did not exchange at an appreciable rate below 100°. The concentration of the latter was not lowered appreciably by impregnation with H_2PtCl_4, but was decreased by treatment with HF. It was concluded, therefore, that surface OH may be replaced by F, but that Pt^{2+} does not "base-exchange" with the catalyst hydrogen. The most satisfactory picture is that the Pt is present as submicroscopic crystallites.

Evidence was obtained that alumina supports contain more than one species of hydrogen. The hydroxyl groups of the catalyst containing reduced Pt exchanged with D_2 in a higher temperature range than those of the control. When oxygen was initially present on the metal surface, however, the reverse was true, suggesting that the D_2O formed by its reduction provided an auxiliary path for exchange of the support hydrogen. Fluoriding also increased the temperature interval of the exchange. Chloride, put onto the catalyst with Pt, may have been responsible for the upward shift in exchange temperature of the $Pt\text{-}Al_2O_3$ catalyst.

INTRODUCTION

Platinum supported on various aluminas, with varying amounts of halide promoter, is an important industrial catalyst, and is thought to possess both a hydrogenation–dehydrogenation and an acid function. Various attempts have been made to characterize these functions separately. In particular, several workers (*1–5*) have tried to measure the average size of the platinum aggregates and the available metal surface area by the chemisorption of H_2 or CO at low pressures and elevated temperatures. This work was complicated by the difficulty of separating the adsorption on the metal from that on the much larger oxide surface. Although the authors do not concur in all particulars, there is now general agreement on some of the more important points. For example, when the catalyst is freshly reduced and evacuated at about 500°, almost every platinum atom is available for the chemisorption of hydrogen. At levels of about 1% Pt, the metal atoms cover only a small fraction of the total surface. Nevertheless, they are probably not monodispersed; otherwise, it would be difficult to understand how hydrogen can be chemisorbed as atoms with no appreciable activation energy. On the other hand, Spenadel and Boudart (*1*) have calculated that if the platinum is aggregated, the aggregates on the average can be no larger than several unit cells. These workers also indicated the possibility that the support cooperates in the cleavage of the hydrogen molecule.

So far, few studies have been devoted to the hydrogen held on the surface of the support, and none to the way in which it may be modified by the presence of the platinum. The present work was undertaken to provide such information and to see what could be learned concerning the nature and distribution of platinum on the catalyst surface from studies of the exchange of the catalyst hydrogen with pure D_2. The effect of fluoriding the catalyst was also examined in a preliminary way.

A method of analysis of the hydrogen held by solids has been developed based on its exchange with D_2 as the temperature is slowly, but continuously, raised. This method, together with a simple theoretical treatment, has afforded a means of separating forms of hydrogen which have widely different reactivity with D_2, e.g., those held by silica, alumina, and silica-alumina catalysts. This work has been reported in a series of papers (*6*), where we have dubbed the method a differential hydrogen analysis (DHA), by analogy with differential thermal analysis. It was used in the present work to assess differences in behavior of alumina and fluorinated alumina, with or without added Pt, as well as to compare the area and distribution of Pt found by this method with data obtained in earlier studies.

EXPERIMENTAL

Five catalysts were studied; all were made from the same mother batch of alumina. This was prepared by the neutral hydrolysis of redistilled aluminum isopropoxide using a threefold excess of deionized, distilled H_2O. The gel was dehydrated by heating over a steam bath for several days, followed by oven drying at 105° for 100 hr. The preparation was calcined at 640° for 15 hr in N_2 atmosphere, cooled *in situ*, and bottled. Samples A and B were controls. Aliquots of the mother alumina were soaked in purified H_2O for 90 hr, dried at 105° and calcined at 640° for 12 hr; Samples A and B were calcined in streaming high purity N_2 and O_2, respectively. Spark spectra analysis revealed that these preparations had total metallic impurity levels of less than 50 ppm. X-ray measurements of the alumina hydrate and of samples removed on heating it in steps to 650° indicated that the final products were probably mixtures of *eta* and *gamma* alumina.

The fluorided alumina was prepared in the same way by soaking in 0.035 *M* transistor grade H_2F_2 instead of pure H_2O. Acid, equivalent to 1.5% F, was present; 1.22% was found by quantitative analysis. The Pt-Al_2O_3 and Pt-F-Al_2O_3 catalysts were prepared in similar fashion from the mother alumina and from the fluorided alumina using solutions of H_2PtCl_6 containing reagent equivalent to 0.75% Pt. The finished catalysts analyzed 0.75% and 0.66% Pt, respectively; 0.62% Cl was found in the Pt-Al_2O_3 catalyst. A determination of the amount of Cl in the fluorided catalyst was not attempted. These catalysts were made to our specifications by the MK Research & Development Company, Pittsburgh, Pa.

The catalysts were weighed into small glass reactors which could be attached to an all-glass circulating system using 10/30 standard taper joints. They were all pretreated in the same way. Evacuation was started and continued for 1 hr at room temperature. The catalyst was then surrounded by a cold furnace and heated to 250°; evacuation was continued at this temperature until 1 hr had elapsed. The furnace temperature was then raised *in vacuo* to 550° (3 hr) where the catalyst was treated with flowing oxygen for 2 hr. The catalyst was evacuated overnight at this temperature. According to Gruber (*5*), this leaves the platinum about half covered with oxygen.

When several experiments were made with the same catalyst, it was back-exchanged overnight in flowing H_2 at 550°. This left the platinum in the reduced state. The Pt surface could be freed of hydrogen by evacuation at 550° or it could be left fully covered with hydrogen by outgassing at the temperature of liquid nitrogen. Since the hydrogen held on the platinum surface exchanged completely and virtually instantaneously at room temperature (rapidly even at −80°), whereas the surface hydroxyl groups exchanged at a negligible rate below 100°, the amount of hydrogen adsorbed on platinum could be readily determined. The Pt could be reoxidized by treatment with O_2 at 550° following back-exchange of the hydroxyl groups.

The D_2 had a nominal purity of 99.95%; it was further purified by passing through a Pd thimble; H_2 (nominal purity 99.8%) was passed through a purification train (*6*), terminating with a charcoal trap thermostated at −195°. The O_2 was passed through anhydrous $Mg(ClO_4)_2$ before use.

The equipment used in the exchange experiments and the method for treatment of the data have been detailed elsewhere (*6*). It will suffice to say here that the catalyst was contacted with a measured amount of D_2 at room temperature and the gas was circulated over the catalyst as the temperature was raised about 2° per minute. The composition of the gas phase was monitored by a set of thermal conductivity cells which constituted two legs of a Wheatstone bridge. The bridge output was continuously recorded on the same chart as the temperature (the emf from a thermocouple in contact with the catalyst tube). These data were converted into plots of reaction rate, dx/dt, vs. the reactor temperature, where x is the atom fraction H in the gas phase. Different types of hydrogen, corresponding to decidedly different activation energies for exchange, form separate DHA peaks on such plots. In the present experiments, the rising temperature program was stopped at 550° to avoid alteration of the catalyst properties at higher temperature; no fluorine was lost from the catalysts under these conditions.

The sample tube was connected to a conventional BET system, which made up part of the circulating loop. Thus, *in situ* measurements of hydrogen chemisorption and nitrogen surface areas could be made. As preliminary work revealed that the catalysts could be put through a series of experiments without appreciable loss in total surface area, this property was generally measured only in the last step in the present experiments.

RESULTS

The experiments carried out in this work are listed in Table 1, along with the numerical data calculated from the isotope dilutions. The first two rows of data are for samples of the two control aluminas following overnight evacuation at 550°. Sample B was found to have the higher hydrogen content. This may have been due, in part, to structural differences stemming from the preparation procedures, but the larger sample size was also a factor. This has been found to be a general feature of our results obtained with alumina and silica-alumina catalysts, i.e., the larger the sample, the less effective is the dehydration under a given set of conditions. Further dehydration took place as the catalyst was back-exchanged with flowing hydrogen (Expt. 3). The effects of added-back water were tested (Expt. 4) by releasing 3.6 cc (NTP) of H_2O into the catalyst as the exchange reached about 100°. The total amount of hydrogen found at equilibrium (Expt. 4) was increased accordingly.

The DHA patterns obtained in this series of experiments are contained in Figs. 1 and 2. Two forms of hydrogen held by the control alumina are clearly resolved. The principal peak at about 240–260° has been observed with all of the aluminas that we have tested. The weaker peak near 180° does not always appear and in some cases, a band in the neighborhood of 360° has been observed (*6*). Reducing the catalyst during the back-exchange appeared to move the front edge of the principal peak to somewhat higher temperatures. Release of H_2O into the gas in the temperature range where the exchange rate is becoming appreciable moved the front edge back to its original position.

The supported platinum catalyst is compared with its control in Fig. 2. In the oxidized state (Expt. 5), the front edge of the exchange curve was at lower temperatures than when the catalyst was back-exchanged (reduced) in hydrogen (Expts. 6 and 7). In all of these cases, the partially split DHA curves indicated at least two

TABLE 1

HYDROGEN CONTENT AND HYDROXYL EXCHANGE STUDIES OF ALUMINA, FLUORINATED ALUMINA, AND PT SUPPORTED ALUMINAS

Experiment number	Catalyst and pretreatment	Weight (g)	H_2 content [cc(NTP)/g]		Surface area (m^2/g)	$OH^-/cm^2 \times 10^{-14}$
			H_2 on Pt	Hydroxyl hydrogen		
	Control Alumina					
1	Sample A, standard pretreatment[a]	4.004	—	6.4	136	2.5
2	Sample B, standard pretreatment[a]	4.939	—	9.0	—	3.1
3	B, back-exchanged;[b] evacuated 1 hr at 550°	4.939	—	8.0	—	2.7
4	B, back-exchanged; cooled to ~25° and evac. ½ hr; 3.6 cc H_2O[c] added-back during exchange at 100°	4.939	—	8.4	158	2.8
	Pt on Alumina					
5	Standard pretreatment	4.309	—	6.3	138	2.5
6	Back-exchanged; H_2 cooled (−195°); evac. 1 hr at −195°	4.309	0.38	6.3	—	2.4
7	Back-exchanged; evac. 1 hr at 550°	4.309	—	6.2	—	2.4
8	Back-exchanged; H_2 cooled (−195°); evac. 1 hr at −195°	4.309	0.36	6.0	—	2.3
9	Back-exchanged; oxidized 2 hr at 550°; evac. 16 hr at 550°	4.309	—	6.2	—	2.4
10	Back-exchanged; oxidized 2 hr at 550°; evac. 16 hr at 550°; H_2 chemisorption at 250°; cooled to room temp. and evac. 1 hr	4.309	0.36	7.1	—	2.8
11	Back-exchanged; evac. 1 hr at 550°	4.309	—	6.3	135	2.5
	Fluorinated Alumina					
12	Standard pretreatment	4.154	—	4.6	143	1.7
	Pt on Fluorinated Alumina					
13	Standard pretreatment	4.735	—	4.4	—	1.8
14	Back-exchanged; evac. 1 hr at 550°	4.735	—	3.6	—	1.4
15	Back-exchanged; H_2 cooled (−195°); evac. 1 hr at −195°	4.735	0.24	3.5	—	1.4
16	Back-exchanged; evac. 1 hr at 550°	4.735	—	3.5	—	1.4
17	Back-exchanged; oxidized 2 hr at 550°; evac. 16 hr at 550°	4.735	—	3.5	134	1.4

[a] For details of standard pretreatment see text.

[b] Back-exchange consisted of treatment in flowing H_2 for 16 hr at 550°.

[c] This amount was calculated on the basis of the Pt content of catalyst used in Experiments 5–11; calculations were based on the assumption that H_2O is released from oxidized catalysts in the ratio Pt:O of 1.5.

different forms of hydrogen on the alumina surface. A similar splitting may be observed in the curves in Fig. 3, where it is also shown that the front edge of the exchange curve can be reproducibly moved 80–100° to lower temperatures (compare with Fig. 2) by reoxidizing the catalyst after the back-exchange.

The hydrogen content of the platinum-alumina catalyst, when evacuated at 550° (Expts. 5–11), was about the same, per unit area, as that of the control samples.

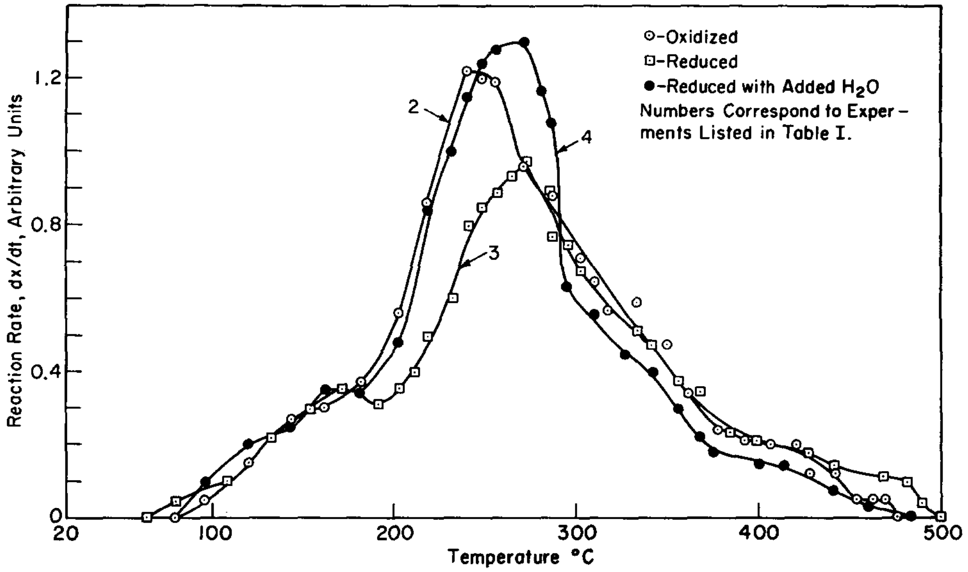

Fig. 1. Rising temperature deuterium experiments on the control alumina catalyst.

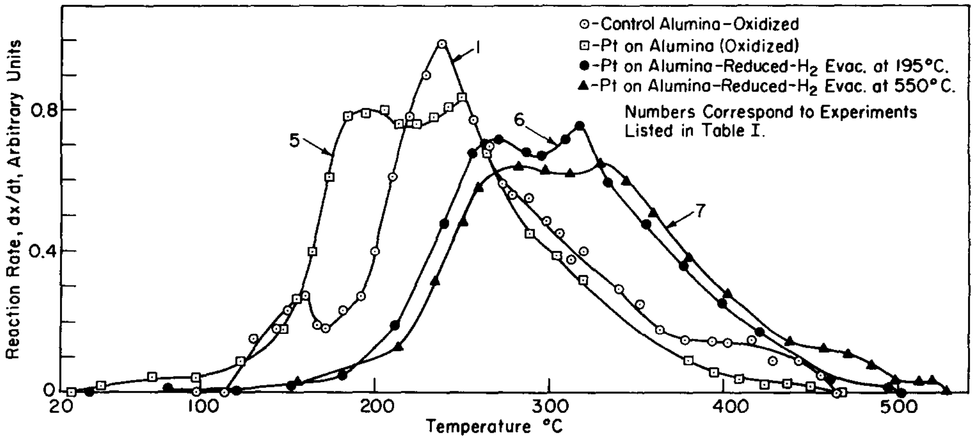

Fig. 2. Rising temperature deuterium exchange experiments comparing Pt on alumina with its control.

The rate plots were different, however; this was most evident when the platinum was reduced. Following back-exchange at 550°, the catalyst was cooled in hydrogen and then evacuated for 1 hr at —195°, leaving the surface of the platinum covered with chemisorbed hydrogen. This equilibrated readily with deuterium at room temperature, where exchange of the alumina hydroxyls was negligible (Expt. 6); the 0.38 cc/g, determined in this way, corresponded to an atom ratio, H/Pt, of 0.9, indicating high dispersion of Pt. This figure was checked several times (Expts. 8 and 10) with fair reproducibility. In an auxiliary experiment following No. 11, the back-exchanged catalyst was cooled in hydrogen to —195° and outgassed for 1 hr at this temperature. On contact with D_2, an immediate exchange leading to pseudoequilibrium occurred; from this, it was calculated that 0.17 cc/g had exchanged. When the temperature was raised to —80°, an additional 0.22 cc/g was found. Raising the

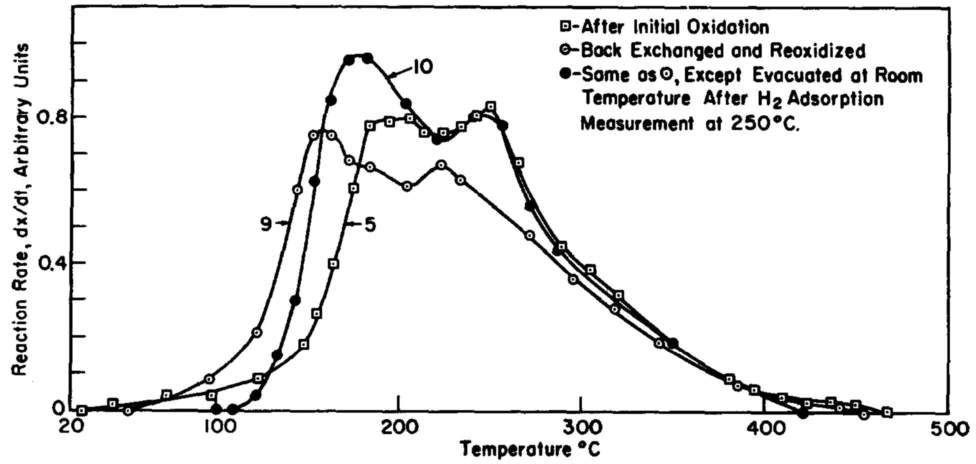

FIG. 3. Rising temperature deuterium exchange experiments with the Pt-alumina catalyst in the oxidized state.

temperature to 27° or to 85° gave no further detectable increase. The sum, 0.39 cc/g, is in excellent agreement with data shown in Table 1. Thus, about 45% of the hydrogen held by Pt may be readily exchanged at —195° and all of it at —80°. This behavior is typical of a metal surface, as revealed by previously reported work (*6–8*). It is indicative of a multicomponent exchange system and implies a heterogeneity of adsorption sites, e.g., different crystal planes. The low temperature range of the exchange is also as expected for the surface of a transition metal. Thus, in agreement with Spenadel and Boudart (1), we are led to conclude that most of the Pt is present as submicroscopic crystals, i.e., so small that 70–90% of all the atoms are exposed.

The alumina hydrogen decreased slightly from Expt. 5 to Expt. 8, until the catalyst was reoxidized. After two successive reoxidations, however, this value increased to above its initial level, but fell again at the end of this series (Expt. 11) where it was also demonstrated that the DHA curve could be moved back to higher temperatures in good agreement with that for Expt. 6. Presumably the alumina is slightly rehydrated during the oxidation of the hydrogen covered Pt surface and by H_2O formed when H_2 is "chemisorbed" on the oxidized Pt. Following the exchange carried out in Expt. 5, the water held in the liquid nitrogen trap was regenerated and measured volumetrically. The 0.29 cc/g found may be compared to Gruber's result (*5*) for an oxidized Pt surface evacuated at high temperature, i.e., the ratio: $H_2O/Pt = 0.4$, may be compared with Pt_2O. This should be regarded as a lower limit, however, as the recovery of H_2O from the catalyst probably was not quantitative under the conditions used.

Following Expt. 8, the catalyst was contacted with hydrogen at 240 mm Hg for 2 hr at 250°. The measured uptake (0.31 cc/g) indicated an H/Pt of 0.7 in fair agreement with the value obtained by exchange in this experiment. Similarly, prior to carrying out the exchange in Expt. 10, the hydrogen adsorption was measured directly on the reoxidized catalyst. The 1.08 cc/g uptake was not altered by pumping the residual hydrogen through a liquid nitrogen trap. This uptake corresponds to an H/Pt of 2.5 indicating, in agreement with Gruber (*5*), that hydrogen was consumed to form water from the oxygen remaining adsorbed on the platinum following the 16 hr evacuation at 550°. This water does not appear to be removed from the catalyst under the conditions used in the adsorption experiment.

The effect of fluoriding the mother alumina is shown in Fig. 4; the hydrogen

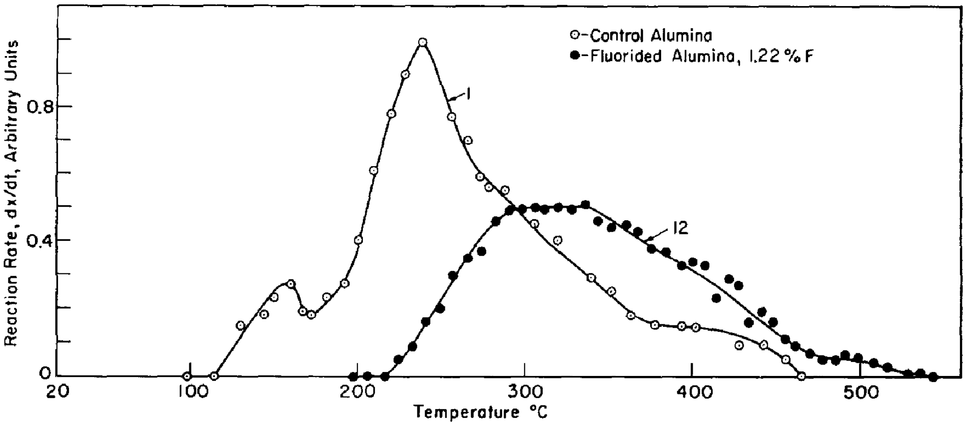

FIG. 4. Rising temperature deuterium exchange experiments on pure and fluorided aluminas.

content was lowered (Expt. 12) and the temperature of the exchange was increased nearly 100°. Experiments corresponding to those discussed in earlier paragraphs for the unfluorided systems were carried out. The behavior of the Pt-F-Al_2O_3 catalyst was similar to that of the Pt-Al_2O_3 except that the regions of exchange were moved to higher temperatures. In the oxidized state, the Pt-F-Al_2O_3 catalyst exchanged at lower temperatures (ca. 80°) than when reduced; however, the DHA pattern of the reduced Pt-F-Al_2O_3 and its control were closely similar. This may be contrasted with the unfluorided system; the reduced Pt-Al_2O_3 exchanged in a higher temperature range than its control.

It is readily apparent (Table 1) that fluoriding alumina reduced its hydrogen content by about 35%. Specifically, the incorporation of 6.4 meq/g of fluorine into the alumina surface lowered its hydrogen content by about 3 meq/g. The addition of Pt (and Cl) had no appreciable effect on this property.

In Expt. 15 it was found that 75% of the H adsorbed on Pt exchanged rapidly at —195° and the remainder at —80°; the H/Pt was 0.7. A still lower value (0.5) was found with another sample, suggesting that Pt is more easily sintered on fluorided, than on unfluorided, alumina. In the oxidized state, the H/Pt of the latter catalyst was 1.1; these values were closely checked by direct chemisorption measurements.

CONCLUSIONS AND DISCUSSION

The principal findings of the present work may be summarized as follows:

(1) The extent of the platinum surface and the surface hydroxyl content of the alumina support can be simultaneously determined by the DHA method described herein.

(2) The values obtained for the amounts of hydrogen associated with platinum were generally a little higher than those for the hydrogen chemisorption at 250° and 240 mm Hg (conditions frequently used to estimate Pt surface area).

(3) By either technique, and in agreement with earlier work (*1–5*), the Pt was found to be highly dispersed; nearly one H atom was chemisorbed for each Pt atom in the catalyst.

(4) In all cases, evidence was obtained that several types of hydrogen are associated with the alumina or fluorided alumina support.

(5) Promotion with F apparently increased the activation energy for exchange of the catalyst hydrogen with D_2 gas, i.e., the DHA pattern moved to higher temperatures. Cl, put onto the alumina during impregnation with H_2PtCl_6, may act in the same way.

(6) With the supported platinum catalysts, the exchange took place at lower temperatures when the catalyst was treated in oxygen and evacuated than when the Pt

surface was freed from oxygen by reduction with hydrogen. The reducible oxygen provides an additional exchange mechanism by introducing D_2O into the system; this is formed by reaction with D_2 in the temperature range below that where exchange of hydroxyl groups takes place.

(7) Supporting platinum on the catalyst surface did not materially lower the concentration of surface hydroxyl groups. This is of interest as the platinum dispersion is very high. It is evident that Pt^{2+} did not simply substitute for surface hydrogen by base exchange.

(8) On the other hand, the fluorine promoter lowered the hydrogen content, presumably by substituting for surface hydroxyl groups.

Although the authors' conclusions differ somewhat in detail, the several reports (*1–5*) of studies of the distribution of platinum atoms on the surface of alumina are all in general agreement with the picture recently presented by Gruber (*5*). For catalysts which have been prepared by impregnation with H_2PtCl_6, nearly all of the Pt atoms are accessible to the gas phase initially, so that after the catalyst has been reduced in H_2 and evacuated at 550°, CO/Pt and H/Pt ratios near unity are obtained. Higher values are found if the reduction is omitted, because water formed by reaction of H_2 with chemisorbed oxygen is not pumped off at 250°.

Spenadel and Boudart (*1*) calculated the surface area of a Pt black from its capacity to chemisorb hydrogen by making the assumption that each surface metal atom held one chemisorbed hydrogen atom; this value agreed with that obtained by the BET method from the physical adsorption of argon within 2%. There is, then, strong support for the view that H/Pt ratios near unity demonstrate that the platinum is nearly atomically dispersed. The catalyst studied in the present work contained 0.75% Pt. If this were uniformly monodispersed, the individual Pt atoms would be separated by approximately 25 Å. However, such isolated Pt atoms could not be expected to dissociate H_2 on chemisorption nor to behave as a metal in the exchange with D_2. Our finding that D_2 exchanges rapidly at —195° with a large portion of the catalyst hydrogen strengthens the view that the Pt is present in metallic clusters, e.g., as microcrystals of one or two unit cells in size.

Spenadel and Boudart pointed out that the amount of hydrogen chemisorbed on Pt might be overestimated if the act of adsorption involved passing hydrogen atoms onto adjacent alumina sites which were not able to chemisorb hydrogen in the absence of platinum, and reasons were cited why this mechanism is unlikely. The present work substantiates this view. If the Pt and alumina acted cooperatively, it could reasonably be expected that the presence of Pt would enhance the exchange of the surface hydroxyl groups with D_2. This does not occur. The rate plots of the reduced $Pt\text{-}F\text{-}Al_2O_3$ catalyst and the $F\text{-}Al_2O_3$ are virtually identical, whereas the reduced $Pt\text{-}Al_2O_3$ actually exchanges at higher temperature than its control. The effect with the latter system is probably due to Cl incorporated into the catalyst with the Pt rather than to the Pt itself.

As pointed out by Gruber, one of the difficulties encountered in measuring the chemisorption of H_2 on Pt is that correction must be made for hydrogen adsorbed on the support under the experimental conditions. Although this correction is relatively small, it is difficult to properly evaluate because it is not known how the metal may modify the support. The present work provides an independent means of measuring the capacity of the Pt to hold hydrogen. It is of interest to note (Table 1) that the amount of hydrogen associated with Pt is the same regardless of whether the catalyst is outgassed at room temperature or at liquid nitrogen temperature and that fair agreement exists among the several methods used to estimate the Pt area.

Pliskin and Eischens (*9*) characterized two types of hydrogen covalently bound to Pt surfaces, the one being much more strongly held than the other. They suggested that the more loosely held form corresponded to the chemisorption of a second hydrogen atom onto Pt atoms already holding the more strongly bound form. This assignment appears inconsistent with the interpretation that the number of surface Pt atoms is measured by the chemisorption of hydrogen; H/Pt ratios greater than unity are not found in the literature when the system is free of chemisorbed oxygen. The highest ratio in the present work was 1.17; this was from the total hydrogen adsorption at 25° and 482 mm Hg, uncorrected for adsorption on the alumina base. The corrected value was 0.8, in fair agreement with our observations at lower pressure and higher temperature. It must be concluded, therefore, that either there are not many surface Pt atoms bonded to two H atoms, or that the criterion used in this and earlier work (*1–5*) for estimating the extent of Pt surface is in error. At present, it seems more reasonable to suppose that the reversible form revealed in the infrared work (*9*) corresponds to a change in hybridization as H/Pt approaches unity. The correct explanation must take into account the rapid development of a second band at shorter wavelength as the surface population density approaches unity. Within the precision of the available data, this can be accomplished by assuming that (below half coverage) the hydrogen is bonded to more than one surface Pt atom, but that this is no longer possible as the coverage approaches unity. An alternative explanation might be that the weaker adsorption takes place on crystal faces not covered at lower pressures.

Experiments of the type described herein provide no detailed information regarding the kinetics of the exchange processes. They do, however, provide certain limitations which may be helpful in future work. For example, the exchange processes on reduced platinum and on the alumina surfaces appear to be independent. When cooled in hydrogen and evacuated at —195° or at room temperature, a monolayer of chemisorbed hydrogen is held on the platinum surface. This portion exchanges completely and independently below room temperature, behaving like a transition metal. Moreover, the increased temperature range required to exchange the hydroxyl groups after the alumina has been fluorided may be explained if it is assumed that D_2 is adsorbed at a few active centers and mixes with the OH by migrating from oxygen to oxygen. In this case, the presence of F would interfere with the surface transport processes; Cl may act in the same way. This picture is consistent with the lack of a similar effect with the Pt-F-Al_2O_3 vs. F-Al_2O_3 system where the surface has already responded to fluorination.

According to Gruber (*5*), approximately half a monolayer of adsorbed oxygen can be removed from Pt on evacuation to 550°; the surface composition is then roughly Pt_2O. In the present work (Expt. 10), this was tested by the direct measurement of hydrogen chemisorption at 250°. The result (1.08 cc/g) was just about three times the value obtained for the reduced catalyst, indicating that the Pt surface was still nearly covered with chemisorbed oxygen following a 16 hr evacuation at 550°.

The supports used in this work evidently contained at least three different types of hydrogen of varying reactivities with D_2. Peri (*10*) found infrared bands attributable to hydroxyls having three different force constants. Semiquantitative estimates of the amounts of the several forms, and how they vary with pretreatment, could be made by combining the two methods. Several forms of hydrogen are also clearly indicated for the platinum-supported catalysts, but in different relative amounts than present in the mother catalyst. Fluoriding the catalyst, with or without the addition of Pt, appears to broaden the distribution somewhat (Fig. 4).

In Part IV (*6*), of this series of papers, a considerable body of information was marshaled to demonstrate that the hydroxyl groups of silica-alumina and silica gel are chemically similar and resemble more closely alcoholic hydrogen than the protons of a strong acid. It was concluded that these were the hydroxyl groups required to terminate the lattice and that any acidic hydrogen present could only amount to a small fraction of the total. The surface hydroxyl concentration found in the present work for the alumina supports ($\sim 2.8 \times 10^{14}/\text{cm}^2$) is closely similar to values found for silica and silica-alumina pretreated in the same way ($\sim 2 \times 10^{14}/\text{cm}^2$). It is therefore reasonable to suppose that these hydrogen atoms do not contribute to the acidity of alumina; this view is supported by the fact that fluoriding the catalyst reduces its hydrogen content whereas this promotor is generally thought to increase its acidic properties. Thus, the acid function of the alumina supports may be Lewis in nature, e.g., incipient AlF_3 with the fluorided catalysts, or may involve dual cationic-anionic sites formed by condensation of surface hydroxyl groups.

Attention should be called to the results of Expts. 2, 3, and 5 to 10 in Table 1. The hydroxyl hydrogen content fell slowly with continued heat treatment at elevated temperature. However, when H_2O was added back, either directly or by reoxidizing the platinum surface, the hydroxyl content again increased. It is evident, therefore, that the results described herein are for a static, nonequilibrium state existing after prolonged evacuation at 550°.

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