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Hydrogen Adsorption by Alumina-Supported Platinum

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Isotherms at 295 and 77°K for hydrogen adsorbed on wet or dry samples of alumina-supported platinum are used to deduce the existence of five kinds of hydrogen adsorption. Type I is reversible at 77°K, includes both physical and weakly bound chemical adsorption, and most is accounted for by adsorption on the alumina support. Type II is irreversibly bound at 77°K on a surface not previously exposed to H_2. Type III is an activated chemisorption with an infrared band at 2060 cm^{-1}. It is not adsorbed at 77°K and can be pumped off at room temperature. Type IV has an infrared band at 2120 cm^{-1} and is adsorbed at 77°K only if the sample contains adsorbed hydrogen which is irreversibly bound at 295°K. The binding energy for this species is lower than that for type III. Type V hydrogen is irreversibly bound at room temperature and is necessary for the adsorption of type IV at 77°K. The quantities of the various kinds of adsorption vary with the nature of the surface and can be used to determine whether two samples differ merely in exposed area or in the nature of the surface. This technique is used to show that aged dry samples which have experienced many H_2–O_2 titrations and reactivations differ from freshly prepared dry samples only in active surface area, while water changes the relative amounts of different forms of adsorption.

INTRODUCTION

The preceding paper (*10*) reported evidence indicating the existence of two infrared active species of adsorbed hydrogen on alumina-supported platinum. The intensities of the bands responsible for these species depend upon the presence of water, either added or formed *in situ* by reaction of hydrogen with adsorbed oxygen. Tsuchiya *et al.* (*1*) have reported four forms of chemisorbed hydrogen on platinum black from evidence obtained by temperature programmed desorption.

The work reported here is designed to parallel the infrared studies so that a correlation of results might yield a fuller understanding of hydrogen adsorbed on platinum.

EXPERIMENTAL PROCEDURES

The alumina-supported platinum containing 10% by weight of platinum was prepared and pressed in 0.1 g quantities by the procedure given in the preceding paper (*10*). A 2 g sample was placed in a U-shaped Pyrex reactor and installed in a conventional gas handling system equipped with a gas burette, a mercury manometer, and a recirculation loop. The system was capable of maintaining a vacuum of 2×10^{-6} Torr measured by an ion gauge.

The sample was degassed for 4 hr at 393°K, for 4 hr at 573°K, and then cooled to 473°K. Unpurified tank hydrogen was passed over the sample at a flow rate of 10 $cm^3\ sec^{-1}$ at 473°K for 18 hr. After the sample was degassed for 30 min, purified hydrogen was circulated at 573°K via a liq-

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[2] This study was initiated before the sudden death of Professor Richard J. Kokes. Any imperfections in this report are the responsibility of the other authors. We are saddened by the loss of a good friend and colleague.

uid nitrogen trap for 5 hr at 10 cm^3 sec^{-1}. The sample was cooled in helium or in flowing hydrogen, depending upon the experiment to be performed.

A sample of aluminum oxide was subjected to a similar treatment after impregnation with 10% HCl. This sample was used as a blank to determine the effect of the support.

Temperatures were measured with a Chromel–Alumel thermocouple in contact with the outside of the reactor. Dead space volumes were measured with helium. Purification procedures used for gases are given in the preceding paper (*10*). Water was distilled under vacuum and pumped for several minutes.

The surface area of the sample was 113 m^2 g^{-1} determined by the BET method using nitrogen at 77°K.

RESULTS

Hydrogen adsorption isotherms were measured volumetrically at pressures ranging from 25 to 475 Torr for samples at 295 and 77°K and with various pretreatments. Figure 1 shows a typical set of isotherms measured at 77°K for a freshly prepared sample. All isotherms at this temperature were similar to those shown in Fig. 1. Isotherms at room temperature were almost straight lines with very small slope. Checks for reversibility were made as each isotherm was run. Points at lower pressure taken before and after points at higher pressure always coincided.

Table 1 summarizes the data extracted from the isotherms at 100 Torr under varying pretreatments and temperatures for a freshly prepared dry sample, a dry

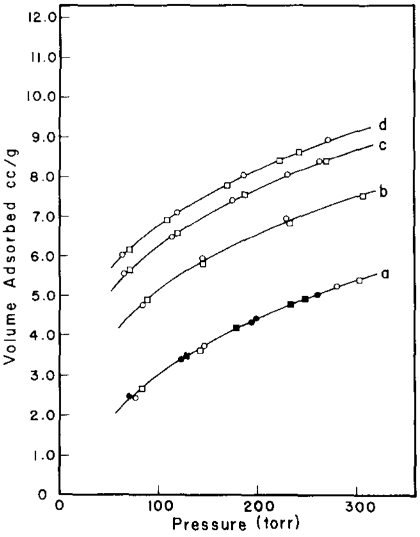

FIG. 1. Isotherms at 77°K for hydrogen on freshly prepared alumina-supported platinum. The different symbols on each curve represent different runs. (a) After evacuation of any isotherm at 77°K (line F Table 1); (b) after reactivation and evacuation at 573°K and cooling to 77°K in helium (line C); (c) after exposure to and evacuation of hydrogen at room temperature, and cooling in helium to 77°K (lines D + G); (d) after cooling to 77°K in hydrogen (lines E + G).

TABLE 1

ADSORPTION DATA FROM ISOTHERMS AT 100 TORR

	H_2 adsorbed (μmoles g^{-1} sample)				
	Dry				
Characterization	Fresh	Aged	Wet aged	Fresh dry/ aged dry	Dry/ wet
A. 295°K after cooling in He from 573°K	145	115	115	1.26	1.00
B. 295°K after evacuation and reexposure to H_2	31	28	38	1.11	0.74
C. 77°K after cooling in He from 573°K	229	184	42	1.24	4.38
D. 77°K after exposure to H_2 at 295°K, evacuation, and cooling in He	166	137	50	1.21	2.74
E. 77°K after exposure to H_2 at 295°K, evacuation, and cooling in H_2	188	152	91	1.24	1.67
F. 77°K after evacuation of C, D, or E at 77°K and reexposure to H_2	134	103	31	1.30	3.32
G. Irreversibly bound at 295°K (A–B)	114	87	77	1.31	1.13
H. Irreversibly bound at 77°K after cooling in He from 573°K (C–F)	95	81	11	1.17	7.36
I. Irreversibly bound at 77°K after exposure to H_2 at 295°K, evacuation, and cooling in He (D+G–F)	146	121	96	1.21	1.26
J. Irreversibly bound at 77°K after exposure to H_2 at 295°K, evacuation, and cooling in H_2 (E+G–F)	168	136	137	1.24	.99

sample aged for several months with many reactivation cycles, and the same aged sample to which water has been added by exposing the surface to 21–23 Torr of water vapor at room temperature for 20 min and evacuating for 30 min.

The entries in lines A, B, and C of Table 1 are self-explanatory. It should be noted that the entries for lines D and E are for hydrogen adsorption in addition to that left on the surface after evacuation at 295°K. The entries for line F are for hydrogen adsorption for samples previously exposed to H_2 at 77°K, pumped at 77°K and reexposed to H_2. The values are independent of the hydrogen pretreatment. The entries for lines G and H are for the amount of hydrogen which cannot be pumped off in 15 min after adsorption on a surface cooled in helium. Lines I and J are for total hydrogen which cannot be pumped off at 77°K for samples exposed to hydrogen at 295°K, evacuated at 295°K, and cooled in He or H_2, respectively. Note that for lines I and J the amount of hydrogen irreversibly bound at room temperature is included by adding line G to the values in lines D and E. It should be emphasized that, although the data are given for 100 Torr, the entries for lines G through J inclusive are independent of the pressure because, as shown in Fig. 1, the various isotherms differ from one another only by an additive constant at all pressures studied.

No significant adsorption was observed at room temperature on a sample of aluminum oxide without platinum. At 77°K all adsorption was reversible on both a wet and dry sample surface. The amounts adsorbed on cooling in hydrogen to 77°K are 111 μmoles/g for a dry surface and 26 μmoles/g for a wet surface.

Table 1 also gives the ratios of the entries in each line for the fresh and aged dry samples and for the aged dry and wet samples. Within experimental error the ratios for the two dry samples are constant, with a mean value of 1.23 and a standard deviation of 0.06. We conclude that aging has decreased the surface area by 19% but has not changed its character. On the other hand, the ratios for the dry to wet sample vary by a factor of 10 and, therefore, the nature of the surface has been drastically changed.

Comparison of lines H, I, and J leads to the conclusion that some of the hydrogen adsorption has a sufficiently high energy of activation to prevent adsorption at 77°K. The existence of activated adsorption is clearly confirmed by the isobar at 100 Torr shown in Fig. 2 for a freshly prepared dry sample. The solid line indicates the adsorption values for a sample evacuated at 573°K, cooled in helium to 77°K, exposed to H_2, and observed as the temperature is increased to 373°K. The broken line indicates the adsorption as the temperature is lowered from 373°K. The time between points was 15 min except for an overnight period between the end of the increasing temperature run and the beginning of the decreasing temperature run. During this overnight period, 0.19 cm^3 g^{-1} was ad-

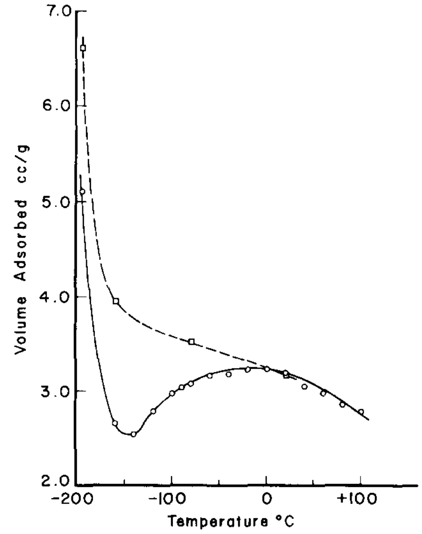

FIG. 2. Isobar at 100 mm pressure for hydrogen on alumina-supported platinum. (○) Points obtained on initial exposure at 77°K and with increasing temperature; (□) points with decreasing temperature.

sorbed. In order to provide continuity in the graph, this amount was subtracted from the decreasing temperature curve. The additional amount adsorbed when approaching 77°K from higher temperatures over that adsorbed at 77°K indicates 75 μmoles g^{-1} of activated adsorption. This value is in excellent agreement with that of 73 μmoles g^{-1} calculated for the fresh dry sample from the difference between line J and H in Table 1.

Many methods have been suggested for determining the fraction of surface of platinum to total platinum from data for hydrogen adsorbed on a clean surface (H_c), oxygen adsorbed on a clean surface (O_c), and total hydrogen uptake on a surface containing chemisorbed oxygen (H_t) (*2–6*). Varying assumed stoichiometries yield predicted ratios of $H_c:O_c:H_t$ ranging from 1:1:2 to 2:1:4. For our freshly prepared dry sample the observed ratios are 1.58:1:3.68 using values taken from room temperature isotherms extrapolated to zero pressure. These values are very similar to those reported by Wilson and Hall (*5*) of 1.52:1:3.64 for a sample containing 2.8% Pt supported on silica. Approximating the ratio of surface platinum to total platinum by O_c:Pt yields a value of 0.35 and by H_c:Pt yields a value of 0.56 for the fresh dry sample, 0.42 for the aged dry sample, and 0.44 for the aged wet sample.

DISCUSSION

The results presented above indicate that five kinds of adsorbed hydrogen can be present on alumina-supported platinum at 77°K. We shall describe briefly the properties of each of these forms of hydrogen and indicate the quantity of each type found for our aged dry and wet samples. Since the ratios of adsorbed hydrogen on the fresh dry sample to that on the aged dry sample are constant to within experimental error and equal to 1.23 ± 0.06 (Table 1), the quantity of each type of hydrogen is 23% higher on the freshly prepared sample than it is on the aged sample.

Type I: This form is characterized by reversible adsorption at 77°K. It includes physically adsorbed hydrogen and any chemisorbed hydrogen with extremely low binding energy and energy of activation for adsorption. It is infrared inactive. The quantity of type I hydrogen present on a surface at 77°K and 100 Torr is independent of previous exposure to hydrogen and is similar to the amount of hydrogen adsorbed on alumina alone. The quantity of this form of hydrogen is given by line F of Table 1 and accounts for 103 μmoles g^{-1} of H_2 on the dry sample but only 31 μmoles g^{-1} on the wet sample. This type was decreased by 23% on aging, which is much more than would be expected for sintering of alumina under the mild conditions of this project. We are therefore led to believe that a significant portion of type I hydrogen is chemisorbed and may be responsible for H_2/D_2 exchange at low temperature.

Type II: This species is formed by rapid irreversible adsorption at 77°K on a surface free of hydrogen. It must therefore have a very low energy of activation. It is infrared inactive. The quantity is given by line H Table 1 and is 81 μmoles g^{-1} for the dry sample and 11 μmoles g^{-1} for the wet sample.

Type III: This form of hydrogen has an energy of activation too high to permit adsorption at 77°K, but has a low enough binding energy to become reversibly bound at room temperature. Its properties correspond to those observed for the species responsible for the 2060 cm^{-1} infrared band reported in the preceding paper (*10*). The quantity can be estimated by subtracting line I from line J in Table 1. We find 15 μmoles g^{-1} for the dry sample and 41 μmoles g^{-1} for the wet sample. This increase of almost a factor of 3 between wet and dry samples is in agreement with the marked enhancement of the 2060 cm^{-1} band on wet samples compared to dry samples.

Type IV: This species is responsible for the 2120 cm^{-1} infrared band. Since, as determined in the preceding paper, this band is absent when a sample is exposed to hydrogen at 295°K, evacuated, and cooled to 77°K in helium, but appears when such a sample is then exposed to hydrogen at 77°K, an estimate of type IV hydrogen can be obtained from the difference between lines I and G. Determining the quantity of type IV hydrogen by this procedure assumes that type II hydrogen has a sufficiently high binding energy so that it will be included in the infrared inactive material irreversibly adsorbed at 295°K. We find values of 34 μmoles g^{-1} for the dry sample and 19 μmoles g^{-1} for the wet sample. If part of the type II hydrogen is removed by our evacuation at room temperature or if the sites responsible for type II hydrogen are modified by exposure to hydrogen at room temperature, our estimate for type IV hydrogen is a lower limit. Since the 2060 cm^{-1} band is removed only after pumping at room temperature while the 2120 cm^{-1} band is removed by pumping at 120°K, it follows that the binding energy of type III is higher than that for type IV hydrogen.

Type V: This form of adsorbed hydrogen is infrared inactive, is not adsorbed at 77°K and must be preadsorbed on the platinum surface before type IV hydrogen can be adsorbed at 77°K. If type II hydrogen is bound tightly enough to resist evacuation at room temperature, the quantity of type V hydrogen can be estimated as the difference in lines G and H of Table 1. This estimate is a lower limit and therefore we conclude that the quantity of type V hydrogen is equal to or greater than 6 μmoles g^{-1} on the dry surface and 66 μmoles g^{-1} on the wet surface.

TABLE 2

DISTRIBUTION OF TYPES OF HYDROGEN ADSORPTION

		% of total H_2 bound at 77°K 100 Torr (lines E + G Table 1)		% of irreversibly bound H_2 at 77° K (line J Table 1)	
Type	Characterization	Aged dry	Wet	Dry	Wet
I	Reversibly bound at 77°K, includes physical adsorption, infrared inactive mostly on support; line F	43	18	—	—
II	Irreversibly bound at 77°K on surface not previously exposed to H_2, infrared inactive; line H	34	7	60	8
III	Activated adsorption, 2060 cm^{-1} band in infrared, reversibly bound at room temperature, binding energy higher than that for type IV; line I − line J or line D − line E	6	24	11	30
IV	2120 cm^{-1} band in infrared, adsorbed at 77°K on sample containing type V, otherwise not adsorbed at 77°K, reversibly bound at room temperature, binding energy a few hundred calories; line I − line G or line D − line F	≤14	≤11	≤25	≤14
V	Adsorbed at 295°K but not at 77°K, necessary for adsorption of type IV, infrared inactive; line G − line H	≥3	≥39	≥4	≥48

Table 2 summarizes the above information. The distribution among types is only approximate, particularly for types II, IV, and V, because it is possible that adsorption of infrared inactive species at room temperature changes the nature of the surface so that a different amount of type II is present after reexposure to hydrogen at 77°K. Uncertainty of the amount of type II adsorbed at room temperature precludes an accurate estimate of the relative amounts of types V and IV, although their sum can be determined, if it is assumed that the quantity of type II is constant at 77°K.

The conclusions drawn here are in remarkable agreement with those obtained by Tsuchiya *et al.* (*1*) by temperature programmed desorption. They find only one kind of hydrogen remaining after exposure to H_2 at 77°K and evacuation. Hence, our type II corresponds to their γ. The fact that γ hydrogen starts to be desorbed slightly above room temperature on platinum black makes it reasonable that some type II hydrogen is lost during room temperature evacuation. Their α can be associated with our type IV in that it is removed at 173°K and is not formed unless the sample is exposed to hydrogen at a temperature higher than 100°K. Their β peak has desorption properties analogous to our type III, although it seems to be desorbed at a slightly lower temperature than for our samples. Finally, their δ hydrogen is analogous to our type V. That the relative amounts of γ and δ vary with temperature of adsorption emphasizes that the division we have made between types II and V is very approximate. Finally, our type I corresponds to their physically adsorbed hydrogen. Since our work was on alumina-supported samples and theirs on platinum black, the agreement is indeed gratifying.

These results, coupled with the infrared studies in the preceding paper (*10*), are in agreement with the observations of Eley *et al.* (*7*) that the infrared active bands are enhanced after reaction of hydrogen with oxygen on a platinum surface. Our results indicate, however, that this phenomena is caused by the water formed in the reaction and not by incomplete reduction as proposed by Eley *et al.* or by a change in surface area as proposed by Darensbourg and Eischens (*8*). We believe, however, that the data of Eley and co-workers are suspect because of carbonyl impurity.

Many structural possibilities exist for the various kinds of hydrogen adsorption on supported platinum. See, for example, the reasonable proposals in Ref. (*1*). Without more definitive experiments, we choose not to speculate.

Hydrogen adsorption and titration of preadsorbed oxygen have been used to estimate the fraction of surface platinum exposed. Considerable controversy concerning the validity and proper application of this technique has developed (*2–6*). Our results suggest that hydrogen adsorption may indeed give a reasonable indication of platinum surface area despite the plethora of types of adsorbed hydrogen. We note that despite wide variation in the distribution of kinds of hydrogen adsorption, the total amount of chemisorption irreversible at 77°K is the same for the wet and dry aged samples (line J in Table 1). The total quantity of hydrogen adsorbed at room temperature, as measured by extrapolation to zero pressure, is also close for the wet and dry samples, but is 15 to 20% lower than the total irreversible chemisorption at 77°K. Our data agree with the conclusion of Wilson and Hall (*5*) that the stoichiometry of the H_2–O_2 titration is not simple. The most accurate single characterization of the surface is probably a determination of total chemisorption at 77°K, although a complete determination of all forms of bound hydrogen is highly desirable. A glance at the columns containing the ratios of adsorbed hydrogen on one surface to that on another as shown in the last two columns of Table 1 quickly indicates whether the two surfaces merely differ in exposed platinum area or have different adsorption properties.

Giordano and Moretti (*9*) have used a flow method to study the effect of water on hydrogen adsorption on supported platinum. They observed a decrease in adsorption at room temperature on wet samples. This apparent disagreement with our data (line A, Table 1) can be explained by noting that their technique measures only irreversibly bound hydrogen, which we also find to be less on a wet surface (line G, Table 1). Since several forms of chemisorbed hydrogen are reversibly adsorbed at room temperature, this flow technique is not reliable for a determination of total chemisorption.

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