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Hydrogen Chemisorption Studies on Supported Platinum Using the Flow Technique

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The chemisorption of H_2 on $Pt/\gamma Al_2O_3$ was studied using the flow technique to investigate the effect of the operating variables and catalyst pretreatment on the chemisorption measurements. The results indicate that the hydrogen uptake is independent of the sample volume and of the amount of catalyst used. Proper degassing of the surface with ultrahigh pure Argon is required to obtain reproducible results. When the catalyst was exposed to oxygen at 500°C, the hydrogen uptake depended on the extent of the catalyst reduction.

INTRODUCTION

The selective chemisorption of gases is one of the most extensively used methods to determine metal dispersion in supported catalysts. This method requires that a chemisorbed monolayer of the gas be formed and that a simple relationship exist between surface atoms and adsorbed molecules. Although the technique is simple in principle, there are several variables involved in determining the two factors listed above. In many instances, the catalyst pretreatment is adopted without further investigation, leading to reproducible but erroneous results. Prompted by seemingly inconsistent results obtained in our laboratory and by a recent paper on the subject (*1*) we carried out a systematic search for the conditions required to obtain results which are reproducible and independent of the surface treatment prior to the chemisorption experiments.

A point which has been the subject of much discussion is whether the hydrogen adsorption stoichiometry is Pt–H or Pt–H_2. Our results indicate that the hydrogen uptake depends critically on the catalyst pretreatment, suggesting that the discrepancy found concerning H_2 adsorption stoichiometry might be due to differences in catalyst pretreatment, which varies substantially from one work to another.

A literature review reveals that the major variables determining the amount of H_2 adsorbed in chemisorption experiments are (a) mode of operation (b) chemisorption temperature, and (c) surface preparation. These factors are briefly analyzed hereafter.

The hydrogen uptake is measured using two different techniques or modes of operation: the static or volumetric technique and the dynamic or flow technique. A common result reported using the static technique (*2–4*) is an instantaneous adsorption which comprises 80–90% of the total hydrogen adsorbed followed by a slow uptake. Gruber (*3*) attributed the slow adsorption process to adsorption on the alumina support. When the total H_2 adsorbed is corrected

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by the adsorption on the support, then the adsorption isotherm is almost a horizontal line. The monolayer coverage of the metal is obtained by extrapolating the corrected data to zero pressure. In the flow mode of operation or dynamic technique, a known volume of H_2 is injected into a carrier gas stream flowing through the catalyst (*5–9*). The hydrogen uptake measured using the flow technique corresponds only to the rapid adsorption observed in the static measurement. Direct comparison between the two methods has been reported by Mears and Hansford (*9*) and indirectly by Freel (*7*).

Another important variable determining the H_2 uptake is the adsorption temperature. The effect of temperature on H_2 adsorption on Pt/SiO_2 was investigated by Poltorak and Boronin (*10*). These authors measured the H_2 uptake in the temperature range −196 to 200°C and found that the H/Pt ratio decreased steadily with temperature from about 1.5 at −196°C to 0.5 at 200°C. Surprisingly, the H/Pt ratio was about 1 at room temperature. Poltorak and Boronin explained their results on Pt/SiO_2 in terms of two types of adsorption processes: a nonactivated adsorption occurring at −196°C and an additional slow adsorption which becomes more and more significant at higher temperatures. When the total uptake was corrected by subtracting the slow-adsorption component, the corrected H/Pt ratio was always less than 1.

An additional factor introduced in the determination of H_2 chemisorption is the use of H_2 titration of oxygen preadsorbed in the catalyst at room temperature. Aston *et al.* (*11*) used this technique to measure surface area of bulk Pt, and Gruber (*3*) applied it at high temperature with the resulting partial oxidation of the metal. Benson and Boudart (*12*) applied the hydrogen titration technique at room temperature on Pt/Al_2O_3 and obtained results similar to those obtained by direct chemisorption measurements. According to these authors, the method provides more sensitivity and makes the measurements independent of surface preparation. Mears and Hansford (*9*) using flow and static techniques found that H_2 chemisorbs to form Pt–H_2 species rather than Pt–H as reported by Boudart. Wilson and Hall (*13*) reinvestigated the problem using a catalyst subjected to different thermal treatments; Hall used H_2 chemisorption, O_2 chemisorption, and electron microscopy to estimate the metal areas. These authors found that, as the Pt surface area decreased, the H_2 uptake fell, while the O_2 uptake remained relatively constant. Areas estimated from electron micrograph particle size distribution showed that H_2 chemisorption properly reflected the changes in metal areas; O_2 chemisorption did not. Hence titration of an oxygen-covered surface with H_2 cannot be used to discriminate between average surface compositions of Pt–H and Pt–H_2. Freel (*14*) using the flow technique and electron microscopy also reported conflicting results on the chemisorption stoichiometry and reported that the H/Pt ratio was a function of catalyst pretreatment.

Recently Prasad and Menon (*1*) reported that, using the H_2 titration flow technique, the results depended on the pulse volume and the mass of catalyst used. These findings prompted part of this investigation which in turn revealed that hydrogen uptake depends on the catalyst surface preparation, which may explain many of the discrepancies found in previous works.

EXPERIMENTAL

(*a*) *Apparatus*

The experiments were carried out in two continuous-flow systems similar to the one described by Freel (*7*). The flow diagrams for both systems are the same but the units differ in the extra capabilities added to them. Unit I is equipped with a temperature programmer for flash desorption experiments, whereas Unit II has a gc sampling system downstream from the catalyst bed to sample the gas-phase composition. A flow diagram of the apparatus is shown in Fig. 1. The catalyst is placed in a quartz tube inside an electric heater. The catalyst temperature is measured by a thermocouple contained in a well inserted into the catalyst bed. The catalyst temperature is kept constant using a proportional temperature controller. A T. C. cell is used to detect the hydrogen pulses downstream from the catalyst bed. The T. C. cell is operated at 100 mA and maintained at room temperature (25°C). Argon, used as a carrier gas, flows from the manifold to a six-port gc sample valve and then to the reactor and detector. Another stream of argon is fed into the reference side of the T. C. cell. A mixture of 19.6% H_2 on argon is circulated through the sample loop of the sampling valve. Pulses of the H_2–argon mixture are injected into the carrier gas stream and adsorbed in the catalyst. When the surface is saturated by hydrogen, the excess hydrogen not adsorbed by the catalyst is measured by the T. C. cell. The detector response was calibrated prior to the experiments against different sample loops to determine the sample valve dead volume. Knowing exactly the pulse volume and the number of pulses adsorbed, one can calculate the amount of hydrogen adsorbed. A central manifold allows passage of oxygen, hydrogen, or argon through the catalyst bed.

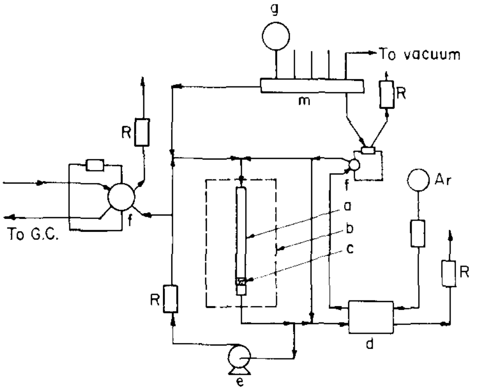

FIG. 1. Schematic diagram of the chemisorption reactor system. (a) Reactor, (b) electrical heater with temperature control, (c) catalyst bed, (d) T. C. cell, (e) recirculation bellows pump, (f) gc six-port sample valve, (g) vacuum gage, (m) manifold.

(b) *Materials*

b. 1. Catalysts. Two types of catalyst were used. Catalyst A was prepared by impregnating γ-alumina (Harshaw, BET area: 192 m^2/g) with chloroplatinic acid. The alumina powder (<200 mesh) was contacted with the solution containing 1% Pt/g of catalyst. The slurry was continuously stirred at 80°C until all the water evaporated. The catalyst was then dried in air overnight at 110°C. A known amount of catalyst was then introduced into the reactor where all measurements were carried out. A highly dispersed catalyst can be obtained by further drying the unreduced catalyst in flowing argon for 3 hr at 110°C. Then the reaction temperature is raised to 500°C in argon flow. Once the reduction temperature is reached the argon flow is replaced by hydrogen. If a highly dispersed catalyst is desired, it is important not to expose the catalyst to oxygen at high temperature prior to the reduction step. All fresh catalysts used were subjected to a 12-hr reduction. The effect of reduction time after exposing the catalyst to oxygen is reported later in this work.

b. 2. Gases. The purity of the gases is a critical variable during flow chemisorption experiments. Impurities present in the part per million level can substantially alter the results. Preliminary runs not reported here demonstrated that traces of oxygen present in the carrier gas gave inconsistent results. Thus all gases used were of the highest purity commercially available. Ultrahigh-purity argon (Linde) and hydrogen (Linde) were further purified by passage through a zeolite and an oxygen trap (oxygen Ap All tech.). Ultrahigh-purity oxygen (Linde) was used without further purification.

TABLE 1

Results Obtained Using Unit I and the Commercial Catalyst[a]

Pretreatment	H_2 pulse size (μl)	Catalyst weight (g)	Oxygen uptake (μl/g of cat.)	Hydrogen uptake (μl/g of cat.)
H_2, 500°C, 1 hr; degassing and cooling in Ar, 1 hr	64.5	3.075	7.3	13.0
			8.2	13.1
			9.0	13.6
			8.9	13.7
	67.7		9.4	13.6
	96.2		9.1	14.0
	117.1		9.4	14.0
O_2, 500°C, 30 min; H_2, 500°C, 30 min; degassing and cooling in Ar, 1 hr	64.5	3.075	20.5	30.9
	67.7		20.9	31.9
	96.2		20.6	30.0
	117.1		20.0	30.2
	64.5	1.745	20.6	31.8
	67.7		20.4	31.6
	96.2		21.0	31.0
	117.1		20.5	31.4

[a] These experiments were carried out in Unit I; the catalyst used was a 0.1% Pt/γ-Al_2O_3 Girdler T-309. The size of the O_2 pulses was equal to 60 μl.

(c) *Experimental Procedure*

Hydrogen titration experiments were carried out in Unit I using the commercial catalyst. The details of catalyst pretreatment are discussed in the next section. In the hydrogen titration experiments, after the catalyst has been pretreated and cooled at room temperature, pulses of oxygen were injected into the carrier gas stream until saturation was obtained. Then the preadsorbed oxygen was titrated by pulses of hydrogen until no more hydrogen was adsorbed. The variables investigated during the titration experiments were: loop size, catalysts pretreatment, and catalyst weight.

Hydrogen chemisorption experiments were conducted in Unit II using the catalyst prepared in our lab (Catalyst A). The main objective of these experiments was to investigate the effect of surface preparation in the adsorption measurements. After the catalyst was pretreated and cooled down to room temperature, pulses of the hydrogen argon mixture were injected into the carrier gas stream until saturation was obtained. The pretreatment procedure varied with the type of variable investigated.

RESULTS

The results obtained with Unit I, using the commercial catalyst, are shown in Table 1. The pretreatment originally used consisted of the following steps: (a) heating the catalyst to 500°C in H_2; (b) reducing with flowing H_2 (20 cm^3/min) at 500°C for 1 hr; (c) cooling the reactor to room temperature and flushing the system with argon (~1 hr). The results shown in Table 1 indicate that oxygen and hydrogen consumption increases and that the H_2/O_2 ratio is about 1.5. The hydrogen sample volume was varied between 67.7 and 117 μl with no significant change in the amount of hydrogen or oxygen adsorption. Thus, according to these results, the sample volume has no effect on the results.

A second pretreatment procedure was used in another set of experiments. In this case, the reactor was heated up to 500°C in flowing oxygen and kept under this condition for 30 min. Then the system was flushed with argon for 10 min and reduced with H_2 at 500°C for 30 min. The reactor was then cooled to room temperature and flushed with Ar before the oxygen chemisorption experiments. The results shown in Table 1 show an increase in both oxygen and hydrogen uptake. The ratio of the amount of H_2/O_2 was the same as with the previous pretreatment, but the amount of oxygen and hydrogen adsorbed is about twice as much as before. Experiments using sample loops of different volumes were also repeated under this new pretreatment, and again we found no effect of the sample volume on the amount of oxygen or hydrogen adsorbed per gram of catalyst. In another set of experiments, the amount of catalyst was reduced to about one-half the amount used in the previous experiments. The second catalyst pretreatment was used in these runs, and, as shown in Table 1, it was found that neither gas sample size nor amount of catalyst has any effect on the volume chemisorbed per unit weight of catalyst, contrary to the results found by Prasad and Menon (*1*).

The results obtained in Unit I indicate that, for a given catalyst pretreatment, one can obtain reproducible results independent of gas sample volume and amount of catalyst. However, a difference in the amounts of oxygen and hydrogen adsorbed was obtained when oxygen was introduced at high temperature. The use of oxygen prior to reduction is a usual pretreatment for catalyst regeneration, consequently, a study was conducted on the effect of the surface preparation prior to adsorption. In the set of experiments described hereafter, hydrogen chemisorption at room temperature, rather than hydrogen titration, was used. These experiments were conducted in unit II; the two variables investigated were degassing and reduction time.

The catalyst used in the experiments described hereafter is the 1% $Pt/\gamma\text{-}Al_2O_3$ catalyst prepared in our laboratory (catalyst A). After drying, the catalyst was reduced for 12 hr in flowing H_2 at 500°C. Prior to the adsorption experiment, the catalyst surface was cleaned from the H_2 previously used during reduction by degassing the catalyst in an inert gas. The gas used during the degassing period must be of ultrahigh purity since parts per million of impurities adsorbed from a flowing stream can significantly modify the adsorption results. Ultrahigh pure argon was passed at 500°C through the catalyst for periods of 1, 3, or 12 hr; at the end of the degassing period, the reactor was cooled down to room temperature. Pulses of the H_2–argon mixtures were injected until saturation was obtained. When the chemisorption runs were completed, the catalyst was heated up again to 500°C for degassing. The results of these experiments are shown in Fig. 2 in terms of H_2 uptake per gram of catalyst versus degassing time; the numbers in Fig. 2 indicate the sequence of runs. The results show a small increase in hydrogen uptake when the degassing time increases from 1 to 3 hr and constant uptake when the degassing time is 7 to 12 hr. An overall conclusion from these results is that extremely good reproducibility can be obtained in flow experiments when using properly purified gases and proper cleaning of the surface from hydrogen previously used in reduction or adsorption. The results shown in Fig. 2 were obtained using a highly dispersed catalyst, the effect of degassing is much more significant when using a catalyst with low dispersion, because in such cases the total amount adsorbed could be close to the difference observed between runs 5 and 6.

To study the effect of the surface state on the chemisorption measurements, prior to each experiment, the catalyst was exposed to oxygen at 500°C for 0.5 hr. After the oxidation period, oxygen was flushed from the system with argon for 15 min, and hydrogen was then introduced in the reactor to reduce the catalyst. The reduction period was varied from 0.5 to 12 hr, whereas the degassing time was kept constant at 12 hr to insure removal of H_2.

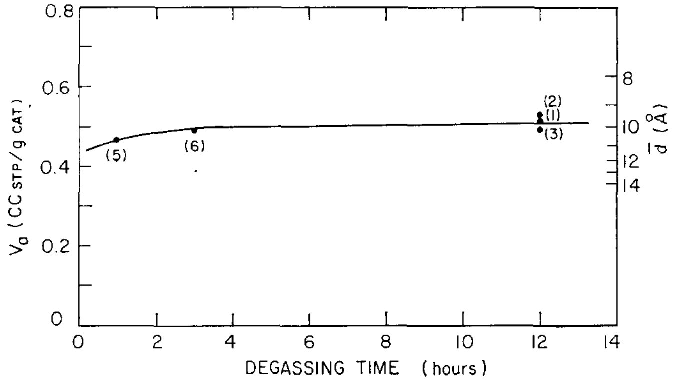

FIG. 2. Hydrogen uptake (cubic centimeters STP per gram) versus degassing time. Catalyst: 1% Pt/γ-Al_2O_3.

The results of these runs are presented in Fig. 3 in terms of H_2 uptake versus reduction time. Comparison of runs 6 (Fig. 2) and 8 (Fig. 3) indicate that exposure to oxygen at 500°C followed by a short reduction period increases hydrogen uptake. As the reduction period increases, the hydrogen uptake decreases, and, after 6 hr of reduction, it reaches a constant and very reproducible value (runs 10–12). Higher uptakes can again be obtained if, after exposure to O_2, only 0.5-hr reduction is used, even though the catalyst has been subjected several times to the O_2–H_2 cycles, as shown by run 13. However, if no reduction is carried out after exposure to O_2, then the uptake decreases again as shown by run 14.

Values of the average crystallite size, shown in the left ordinate of Figs. 2 and 3, were calculated from the corresponding hydrogen uptake assuming a Pt–H stoichiometry. The results in terms of crystallite size suggest that larger crystallites are obtained using longer reduction periods after oxygen exposure at high temperature. The change in crystallite size is more significant when using catalyst with low dispersion, such as the one used in the experiments shown in Table 1. In view of these results, additional experiments were carried out with the commercial catalyst using a 12-hr reduction after exposure to oxygen at 500°C for 20 min. The H_2 uptake obtained after this pretreatment was 11.7 μl/g, which is similar to the results obtained prior to exposure of the catalyst to oxygen (Table 1).

DISCUSSION

The results reported in this work indicate that hydrogen titration and chemisorption, measured using the pulse flow technique, are insensitive to the size of the sample volume and the amount of catalyst used. There are no apparent reasons why the H_2 uptake would depend on such variables, as proven by our experiments.

We found however that, in flow experiments, the state of the catalyst surface prior to the chemisorption experiments is important in obtaining results that reflect a steady value of the metal crystallite size. The effect of degassing time indicates that the surface must be cleaned of the residual hydrogen used during reduction or previously adsorbed. This effect is specially significant when working with catalysts with low dispersion or large crystallites.

Catalyst reduction plays a significant role when the catalyst has been exposed to O_2 at high temperature, a common procedure in catalyst preparation or regeneration. It appears that oxygen preadsorbed at high temperature can substantially modify the Pt surface. Gruber (*3*) found that "oxygen adsorbed a 350°C on a Pt catalyst seem able to penetrate the Pt

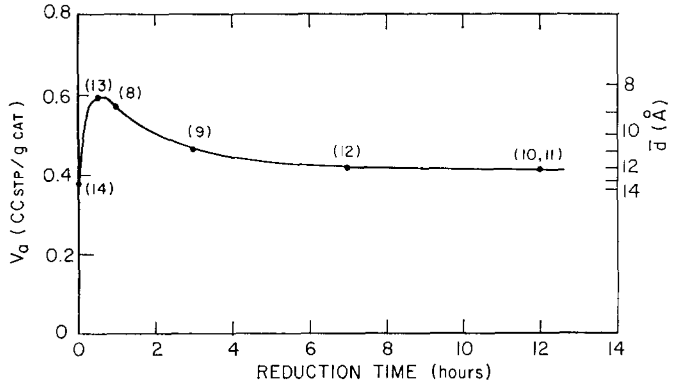

FIG. 3. Hydrogen uptake (cubic centimeters STP per gram) versus reduction time. Catalyst: 1% Pt/γ-Al_2O_3.

lattice to some extent forming surface films which are more than one layer thick." Blakely and Somorjai (*16*) recently reported that, in LEED studies carried out using Pt single crystals, the surface is restructured in an oxidizing environment, and it changes structure again in the presence of a reducing atmosphere. Stephanopoulos *et al.* (*15*) have recently presented evidence of change in surface morphology of small single-crystal spheres of Pt following their use as a catalyst in NH_3, C_3H_8, and CO oxidation reactions. By using scanning electron microscopy, this author observed substantial changes in surface morphology depending on the reaction environment. In our studies, exposure of the catalyst surface to oxygen and subsequent reduction in H_2 can affect both the surface composition and possibly the crystallite size. Fiedorow and Wanke (*17*) reported significant increases in dispersion when the catalyst was exposed to O_2 at 500–550°C and subsequently reduced in H_2 for 1 hr. Our results followed the trend found by the aforementioned works (*15–17*), that is, the surface composition, morphology, or crystallite size can be modified by the pretreatment or environment used prior to adsorption. Proper reduction and cleaning of the surface can lead to conditions wherein the H_2 uptake measured by the flow technique is very reproducible. Under the conditions of our experiments, such conditions were the use of ultrahigh pure gases, more than 3 hr of degassing, and more than 6 hr of reduction.

The H/O ratio of 1.5 obtained in the titration experiments does not agree with stoichiometries previously discussed. However, during the titration experiments (Table 1), the catalyst was not properly pretreated, thus we do not feel that the results shown in Table 1 represent the right stoichiometry. Rather than to use titration, we have selected the direct chemisorption of H_2 as a technique to measure metal areas. The extra sensitivity that characterizes the titration experiments can be easily obtained in the chemisorption experiments by using pulses made of a mixture of H_2 and the carrier gas.

H_2 chemisorption experiments carried out in a flow apparatus show that the H_2 uptake per unit weight of catalyst is independent of the pulse volume and amount of catalyst. It was found that the H_2 uptake depended on the extent of degassing, and, in the case when the catalyst was exposed to oxygen at 500°C, the H_2 uptake depended on the extent of reduction. When proper reduction of the surface is used, the hydrogen uptake gives constant and reproducible results.

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