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Hydrogen Chemisorption Effects in SiO_2 and Al_2O_3-Supported Pt Catalysts of Widely Different Dispersions

INTRODUCTION

There are many reports on the effect of the interaction of H_2 with supported Pt at high temperatures (673–973 K) (for a review see (*1*)). Decreases in chemisorption ability and specific catalytic activity are generally observed (*1*), effects that can be reversed by oxidation treatments.

The largest effects have been reported for TiO_2-supported Pt (*1*). Although a partial electron transfer between the support and the metal was originally proposed to explain the decreases, it is now generally believed that a migration of a Ti suboxide onto the metal surface is the main reason for the observed behavior. For Pt supported on not-so-easy reducible oxides (SiO_2 or Al_2O_3) different explanations of the effect have been advanced (*1*).

Besides Pt other SiO_2 or Al_2O_3-supported Group VIII metals have shown similar behavior (see (*2*) and references cited therein). Based on the recovery of the chemisorption ability by evacuation at temperatures equal to or higher than the reduction temperature, observed in (*2*), the authors discarded explanations like: (i) structural or morphological changes, (ii) alloy formation between the supported metal and Si or Al, and (iii) coverage of the metal by the support or by impurities. The possibility that H_2 spilled over the support at high temperature not removed by evacuation migrates back to the metal preventing further chemisorption was also discarded (*2*). The explanation favored was that the effect was the consequence of self-inhibition by strongly chemisorbed hydrogen on the metals.

Although there is now evidence that this phenomenon is confined to the metal, there are still some open questions like: (i) is this a surface or a bulk phenomenon? (ii) where in the surface (or in the bulk) is the hydrogen located? and (iii) does the support have any influence on it?

In an attempt to answer these questions we conducted a study on the ability for chemisorption and the specific activity for hydrocarbon reactions of SiO_2 and Al_2O_3-supported Pt of widely different dispersions, after low- and high-temperature treatment in H_2. Hydrogen adsorption and methylcyclopentane and neohexane reactions were chosen for that purpose.

EXPERIMENTAL

Table 1 shows the properties of the catalysts (obtained from Professor J. B. Butt) used in this study. Other properties and preparation procedures are reported elsewhere (*3*) (Al_2O_3-supported catalysts are identified as 96.7-Al_2O_3-PtNN and 4.2-Al_2O_3-PtNN in Ref. (*3b*)).

Hydrogen chemisorption measurements. Hydrogen adsorption measurements were carried out in a conventional Pyrex volumetric adsorption apparatus. Adsorption isotherms at room temperature were measured by admitting a known quantity of gas to the adsorption cell and waiting 1 h before reading the equilibrium pressure for the first point. The time allowed the equilibration for subsequent points was 30 min. The range of pressure was 0–250 Torr (1 Torr = 133 N m^{-2}) measured with an absolute pressure gange provided by MKS Instruments Inc. In determining the total H_2 uptake the isotherms were extrapolated to zero pressure. The samples used weighted between

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TABLE 1

Catalysts Properties

Catalyst	Support	Pt loading (w/w%)	$(H/Pt)_{max}$
$Pt-Al_2O_3$-HD	Al_2O_3	0.293	1.19
$Pt-Al_2O_3$-LD	Al_2O_3	0.212	0.096
$Pt-SiO_2$-HD	SiO_2	0.825	1.06
$Pt-SiO_2$-LD	SiO_2	1.910	0.046

0.6 and 7 g depending on metal loading and percentage exposed. The diameter of the catalyst tubes was 8 mm with the exception of the $Pt-Al_2O_3$-LD in which a 25-mm tube was used.

Prior to the study of the adsorption behavior each catalyst was treated in the adsorption system as follows: (a) oxidized in flowing air at 473 K for 2 h, (b) purged in He at that temperature for 10 min, (c) cooled to room temperature in He, (d) reduced in flowing H_2 at 723 K for 2 h, (e) evacuated at 773 K for 3 h, and (f) cooled to room temperature under dynamic vacuum. Following this evacuation and between the subsequents H_2 treatment–evacuation–adsorption measurements cycles the catalyst was kept in He in order to avoid contamination by air. Each H_2 treatment lasted 1 h after which the sample was evacuated for 3 h. The procedure was as follows: with the sample in flowing H_2 the temperature was raised to the desired value (473 or 723 K) and then maintained at that level for 1 h. The evacuation temperature was reached under flowing H_2 when it was lower than the H_2 treatment temperature otherwise the adsorption cell was sealed and the temperature raised to the evacuation temperature under vacuum.

Catalytic activity measurements. The methylcyclopentane (MCP) and neohexane (NH) reactions were performed in a microcatalytic pulse reactor. Purified H_2 was used as carrier gas and the MCP and NH were introduced by injecting in the H_2 stream pulses of H_2 saturated at 298 K (MCP) or at 261 K (NH). The portion of the system between the injection point and the chromatograph was maintained at about 323 K by a heating tape. The amounts of hydrocarbon injected in each pulse were 0.37 μmol (MCP) and 0.30 μmol (NH). The mass of the catalysts were adjusted in order to maintain low conversion levels (between 0.06 and 0.68 g (MCP) and 0.26 and 1.2 g (NH)). The catalyst tube diameter was 6 or 8 mm depending on the mass of the catalyst. The separation of the reaction products was achieved by a DC 200 1.8-m column operated at 303 K. The carrier gas flow was controlled at a rate of 30 $cm^3 \cdot m^{-1}$.

Prior to the study of the catalytic behavior each catalyst was reduced for 1 h in H_2 at 723 K in the case of MCP reaction or at 773 K in the other case, after which, H_2 was replaced by He and the temperature was raised 50 K. The catalyst was maintained in flowing He for an additional 2 h at the final temperature and then cooled to 298 K in the same gas. The subsequent catalytic activity studies were performed as follows: the catalyst was reexposed to H_2 (hydrogen treatment) for 1 h at the reaction temperature (~523 K (MCP), ~563 K (NH)) and then the catalytic activity was determined. Following this, the temperature was raised to 723 K (MCP) or 773 K (NH), kept at that level for 1 h and then lowered to the reaction temperature after which the activity was determined again. During the whole procedure the catalyst was kept in flowing H_2.

Gases and reagents. The H_2 used was AGA Special Grade (99.995%) further purified by passage through a H_2 purifier (Matheson Model 8365). Other gases, He (Matheson quality, 99.9999%), and air (AGA Special Grade 99.997%) were used as received. The methylcyclopentane (purity > 99%) and the neohexane (purity > 99%) were provided by Fluka AG and Alfa Products, respectively.

RESULTS AND DISCUSSION

The results of the chemisorption measurements expressed as H/Pt are shown in Table 2.

TABLE 2

Chemisorption Measurements

Treatment	T_{ht}[a] (K)	T_{evac} (K)	Pt/Al_2O_3		Pt/SiO_2	
			HD	LD	HD	LD
A	473	723	1.19	0.096	1.06	0.046
B	473	573	1.07	0.08	0.99	0.044
C	723	573	0.80	0.065	0.72	0.036
D	—	723	1.13	0.096	0.95	0.041
Percentage decrease in chemisorption ((B − C)/B × 100)			25	19	27	18

[a] Temperature of hydrogen treatment.

The comparison of the results after treatments B and C shows in all cases a decrease in the hydrogen uptake following reduction at the higher temperature. As previously observed (*2*) the phenomenon in reversed by evacuation at high temperature.

Tables 3 and 4 show the results of the catalytic activity for MCP and NH reactions, respectively.

Due to the adsorption of the reactant on the support (and slow desorption from it) following hydrogen treatment at high temperature, it was impossible to carry out the neohexane reaction on Pt/Al_2O_3 under our experimental conditions.

The specific activities of the catalysts after H_2 treatment at the lower temperature, based on percentages exposed of 1 and 0.096 for Pt/Al_2O_3 and 1 and 0.046 for Pt/SiO_2, agree with those reported in the literature for the MCP (*4*) and NH (*5*) reactions.

No deactivation between consecutives pulses at the same reaction temperature was found in the measurements, with the exception of neohexane reaction on the poorly dispersed Pt/SiO_2 catalyst, in which a decrease in activity was observed. The results presented in Table 4 for this case, corrected for the loss in activity observed in three previous injections at the same reaction temperature correspond to consecutive pulses, one before the H_2 treatment at high temperature and the other after it.

As can be seen in Table 3 no significant changes in the specific activities for the MCP reaction are observed despite of the different temperatures used in the hydrogen treatment. The products were 2-methylpentane (2-MP), 3-methylpentane (3-MP), and *n*-hexane. On small Pt particles, the MCP hydrogenolysis occurred nonselectively (statistical ring opening) whereas on large Pt particles 2-MP and 3-MP were formed

TABLE 3

Catalytic Activity for the MCP Reaction

	Pt/SiO_2				Pt/Al_2O_3			
	LD	LD	HD	HD	LD	LD	HD	HD
T_{ht}[a] (K)	533	723	513	723	523	723	513	723
T_{react} (K)	533	533	513	513	523	523	513	513
TON[b] (s^{-1})	0.123	0.123	0.089	0.082	0.048	0.059	0.147	0.096

[a] Temperature of hydrogen treatment.

[b] Based on percentages exposed of 1 and 0.096 for Pt/Al_2O_3 and 1 and 0.046 for Pt/SiO_2.

TABLE 4

Catalytic Activity of Pt/SiO_2 for the NH Reaction

	LD	LD	HD	HD
T_{ht}[a] (K)	593	773	573	773
T_{react} (K)	593	593	573	573
TON (s^{-1})	2.3×10^{-3}	4.0×10^{-5}	8.9×10^{-3}	3.0×10^{-3}

[a] Temperature of hydrogen treatment.

almost selectively. These product distributions (similar to those reported in the literature for Pt catalysts of different particle size (*6*)) were not altered by the different pretreatments.

On the bases that strong hydrogen chemisorption is responsible for the observed effects the lack of change in the activity and selectivity of the catalysts for the MCP reaction regardless of the temperature of the H_2 treatment could indicate either that the strongly held hydrogen participates in the reaction or, more likely, that the reaction takes place in a portion of the surface different from the one on which the strong hydrogen chemisorption occurs.

For the NH reaction on the other hand, lower specific activities were obtained after the high-temperature treatments in H_2 (see Table 4). Among the products we identified: methane, ethane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane. No attempt to identify all the products was made. With regard to selectivity, less lighter hydrocarbons were produced after the high-temperature treatment in H_2.

The results obtained in the present work give further support (although they do not prove) to the existence of strong hydrogen chemisorption. The fact that the effect is reversed by evacuation and it is observed in (i) catalysts with very different particle size with probably different morphology and (ii) catalysts with different support with different kinds and amount of impurities, indicates that alloy formation, morphological changes, and impurity segregation are not likely to occur. Regardless of the true explanation the results obtained indicate: (i) on Pt we are in the presence of a surface phenomenon since it is shown by both highly and poorly dispersed catalysts, (ii) the support in this case does not have any influence on the phenomenon. If the phenomenon is due to strongly chemisorbed hydrogen, it might be located on low coordination sites preferentially. This is suggested by the smaller decrease in the hydrogen chemisorption as well as by the larger effect on the catalytic activity for the NH reaction observed in the poorly dispersed catalysts. Low coordination sites, present in smaller proportion in larger cristallites than in small ones, have been proposed to be the active sites for hydrogenolysis reactions on Pt (*7*).

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