

Influence of Water on H₂-Chemisorption over Supported Metal Catalysts

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Hydrogen chemisorption measurements on Pt impregnated alumina have been carried out by a flow method (slug technique). Competitive chemisorption of water points out to the existence of two kinds of surface sites: hydrogen chemisorbed on type I sites is scavenged by water, while hydrogen held by type II sites is not.

The dispersion of supported platinum catalysts has been extensively studied by both physical and surface chemistry methods (1-10). Among the latter, hydrogen chemisorption (1-3, 5, 7, 10) and hydrogen-oxygen titration (3, 7, 8, 10) appear to offer the best approaches to the problem. There is however a considerable disagreement regarding the stoichiometry of these reactions: for instance in hydrogen-chemisorption experiments, values of either 1 or 2 have been reported for hydrogen: platinum ratio. Correspondently, hydrogen-oxygen uptake ratio of 3 or 4 (3, 7, 8, 10) would be expected for hydrogen titration. It has been suggested (10) that the observed discrepancies probably result from differences in the outgassing procedure used to obtain a "clean" surface. While the results reported in the present study do emphasize the importance of this viewpoint, they also provide evidence that water, hence the degree of hydroxylation of the surface, is an important factor in the system. As shown below, an understanding of the effects bound to variable degrees of surface hydroxylation might help to find an answer to this debated question.

In the present paper, we report some preliminary results obtained in H₂-chemisorption experiments wherein the influence of back addition of water to the catalyst has been studied. Notably, no such investigation has been reported so far, although

the importance of a controlled state of the surface has been repeatedly claimed.

The platinum-alumina catalyst used in the present study was prepared by an impregnation procedure. The support, an alumina-gel Alcoa F-110, sized from 42 to 65 mesh, was impregnated with a solution of 0.09 M chloroplatinic acid. Platinum content, as determined by atomic adsorption, was 0.57%. Prior to chemisorption experiments the catalyst underwent either one of the following pretreatments:

Type A: 16-hr drying at 110°C;

Type B: after drying as for type A, the sample was outgassed 2.5 hr at 140°C under a flow of purified nitrogen (3.0 liters/min), in a fluidized bed; hydrogen (4.5 liters/min) was then started through the sample and temperature was raised to 500°C. Reduction at this temperature was carried out for 2.5 hr after which the sample was cooled to room temperature, in a flow of nitrogen. Surface area of type B was 160 ± 5 m²/g.

The adsorption flow method first suggested by Gruber (4) was used in this study. The experimental procedure during each chemisorption cycle was as following: a sample of catalyst (1 g) placed in a U-tube is outgassed 1 hr at 110°C in a flow of nitrogen (10 ml/min); then the temperature is raised to a value T_R (temperature of reduction) at which H₂ is started. Reduction is carried out for different lengths of

time (from 2 to 8 hr) after which nitrogen is readmitted (10 ml/min) at T_N (temperature of elution). Following a 16–20-hr outgassing, temperature is stabilized at a preselected value T_C (temperature of chemisorption): at this point a known amount of H₂ (0.94 ml) is injected, as a slug, into the nitrogen stream and the effluent analyzed by a thermal conductivity cell. The volume of the slug, always in excess of the chemisorptive capacity of the sample, enables saturation to be reached with only one slug: subsequent slugs were used, for calibration.

The sequence of steps during each chemisorption cycle is illustrated in Table 1. As many as 6–10 cycles were run in each experiment, either in the absence or in the presence of water: in the latter, slugs of water were injected oddly or evenly according to the sequence outlined in Table 1. Experiments were carried out under various operated conditions, with T_R , T_N , and T_C made to vary within very broad limits.

While a full exploitation of all this information is in progress and will be reported shortly, a few exemplary results at

$T_R = T_N = 470^\circ\text{C}$ and $T_C = 300^\circ\text{C}$ (Table 2 and Fig. 1) will be illustrated in the present report. In Fig. 1, upper curve gives the values of H₂ chemisorption in the absence of water. The net H₂-chemisorption following back addition of water is given by the lower lines. (The abscissa represents the total time of elution with N₂, as described in Table 1. If correction is made for the duration of the chemisorption steps, b + c steps, no significant deviations in the shape of the figures are introduced.) With reference to results given in Fig. 1 it becomes apparent that, for H₂-chemisorption, in the absence of water, the ratio H/Pt tends to a value of 2, at a time close to zero. As time of operation progresses, chemisorption of H, hence the H/Pt ratio, decreases progressively tending to an asymptotic value as time tends to infinite. (Apparently the very first slugs deviate from this picture. The reasoning behind this deviation is very complex and we report it, in greater detail, in a later paper.) Water added back strongly affects the H₂-chemisorption, the value of the H₂-uptake being

TABLE 1

TYPICAL SEQUENCE OF STEPS IN THE EXPERIMENTAL PROCEDURE FOR H₂-CHEMISORPTION RUNS

Indicated sequence refers to runs with "water added back." For other conditions—no water added—disregard steps b.^a

Progressive no. of hr	No. of the cycle	Steps in the cycle	Description
2–8	Prerun	Prerun	Reduction " <i>in situ</i> " at T_R , for different lengths of time, as indicated
18–28	1	1a	Elution with purified N ₂ , at T_N , for 16–20 hr
		1b	After cooling down to the temperature of chemisorption T_C , a slug of water (amount as indicated) is injected
		1c	Chemisorption with H ₂ is measured at T_C , after 10 min from the injection of water
34–48	2	2a	Temperature is raised up to a value of T_N , then the same procedure as in 1a follows
		2c	Same as 1c
50–68	3	3a	Same as 1a
		3b	Same as 1b
		3c	Same as 1c
66–88	4	4a	Same as 1a
		4c	Same as 1c

^a Type B catalyst was prerduced while type A had not been treated.

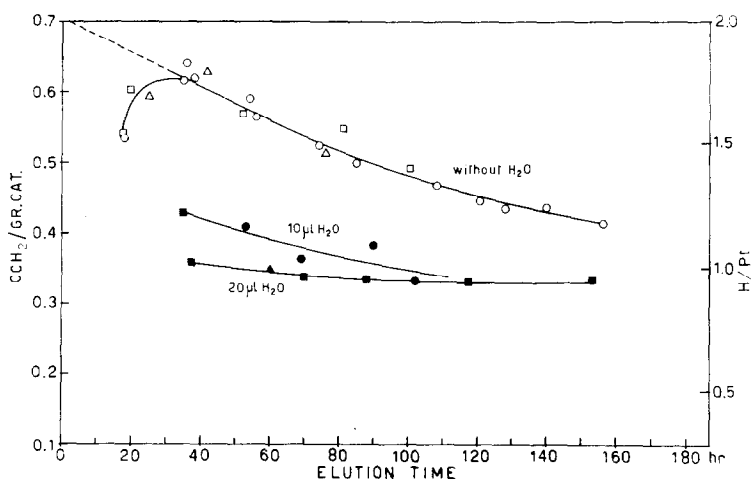


FIG. 1. Typical behavior of a Pt-Al₂O₃-type B sample, in the chemisorption of H₂ (with or without water added back), for conditions: $T_R = T_N = 470^\circ\text{C}$ and $T_C = 300^\circ\text{C}$; Catalyst wt = 1 g; volume of the H₂ slug = 0.94 ml; water added back = 10–20 μl .

Reduction time	No. of runs	Without H ₂ O	With H ₂ O
2 hr in H ₂	3	○	●
2 hr in H ₂ /N ₂	2	□	■
8 hr in H ₂ /N ₂	1	△	▲

now almost halved with respect to the initial value: correspondingly the H/Pt ratio approximates unity, a situation which is always met whenever saturation of sur-

face with water is insured (20 μl of water has a slightly larger effect than 10 μl).

Considering the effects induced by water added back to the system, two different

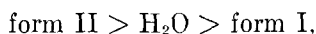
TABLE 2
COMPARISON OF RESULTS OBTAINED IN H₂-CHEMISORPTION RUNS ON TYPE A AND B CATALYSTS
AT $T_N = 470^\circ\text{C}$ AND $T_C = 300^\circ\text{C}$

Catalyst type	No. of the cycle	Water (μl)	cm ³ of H ₂ (STP)/g of cat.	H/Pt	Specific surface area (m ² of Pt/g of Pt) ^a
A. Reduced <i>in situ</i> for 2 hr at 500°C	1	No	0.261	0.740	102.0
	2	No	0.331	0.940	129.5
	3	No	0.324	0.920	126.0
	4	No	0.320	0.910	125.5
	5	No	0.311	0.885	122.0
B. Reduced <i>in situ</i> for 2 hr at 470°C	1	No	0.543	1.540	212.0
	2	10	0.429	1.220	
	3	No	0.570	1.620	223.0
	4	20	0.340	0.965	
	5	No	0.498	1.410	195.0
	6	10	0.351	0.990	
	7	No	0.445	1.260	174.0
	8	20	0.333	0.945	
	9	No	0.412	1.170	161.0

^a These values have been calculated according to Spenadel and Boudart (1), except that a H: Pt ratio of 2 has been assumed.

forms of hydrogen seem to be present on supported Pt-catalysts (at least on type B catalysts): the fraction of sites scavenged by water holds the least strongly bound form of H₂ (form I), while the fraction of sites not affected by water binds H₂ more strongly (form II).

The ordered sequence of the adsorption strengths found in these experiments,



is exactly the same which emerges from the literature. Two types of hydrogen adsorption have been in fact postulated previously (11-17) to explain the results of other experimental techniques: thus Pliskin and Eischens (11), working on IR spectra of hydrogen on a Pt-silica catalyst, found the presence of two bands which were assigned to the strongly and weakly bound forms of hydrogen, both adsorbed as atoms. For alumina-supported platinum, Kubokawa *et al.* (12) found heats of adsorption of 21-23 and 9-10 kcal/mole, respectively, for the two types of H₂ adsorption. The stoichiometric ratio of H/Pt equal to 2 and the arguments advocated by Mears and Hansford (10) also suggest two forms of hydrogen differently held. In agreement with the above scheme are the results of Mignolet (13), Sachtler and Dorgelo (14), Suhrmann *et al.* (15), Eley *et al.* (16) and the theoretical calculation by Toya (17). To pinpoint the position occupied by water, direct calorimetric measurements would be highly desirable; unfortunately this possibility is ruled out, due to the very high heat of adsorption of the support. The only information reported so far is by Chon *et al.* (18) who gave a value of 11 kcal/mole for the heat of adsorption of water, on platinum black.

Another important finding emerging from the results of this study is that the least strongly held form of H₂ (form I) is more sensitive to time than form II (compare upper and lower curves of Fig. 1). Notably, the rate of decreasing of form I with elution time is of the same order of magnitude as reported by Herrmann *et al.* (19) for the sintering of Pt-Al₂O₃ catalysts at 564°C in N₂, by Gruber (4) and Hughes *et al.*

(6) at 500°C in H₂. On the contrary, H₂-chemisorption following back addition of water, remains very much constant with time of operation, the rate of decrease of chemisorption capacity being now much slower than in form I.

Results obtained on a type A sample (Table 2) emphasize how conflicting results can be borne out from differences in the mode of preparation of the sample. On type A catalyst, which, we recall, is characterized by not being prerduced (see text), the total uptake of H₂ is close to unity and decreases with time less sharply than on type B samples.

This observation makes it clear again that variations in the preparative steps, might lead to striking differences in the surface situation, for instance with or without possibility of accommodating different kinds of sites, hence different forms of H₂. To distinguish among them and to establish more precise rules for testing the degree of dispersion of supported metals, competitive chemisorption studies are strongly suggested. Useful reassignments are to be expected also on related aspects, i.e., sintering and catalytic activity. An account of the work along these directions, will be published shortly.

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