

Studies of the Hydrogen Held by Solids

XVIII. Hydrogen and Oxygen Chemisorption on Alumina- and Zeolite-Supported Platinum

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The chemisorption of H₂ and of O₂ on Pt particles, supported on alumina, was studied. Measurements made following sintering at successively higher temperatures showed that the H₂ chemisorption values fell, while those for O₂ remained relatively constant or sometimes increased as the Pt surface area decreased. Areas estimated from electron micrograph particle size distributions showed that H₂ chemisorption properly reflected the changes in metal surface area; O₂ chemisorption did not. Hence, titration of an oxygen covered surface with H₂ cannot be used to discriminate between average surface compositions of Pt-H and PtH₂. The particle size distributions from the micrographs were consistent with the 1:1 = H/Pt(surface) stoichiometry, however, even at high dispersions where H/Pt(total) was near unity. The variable stoichiometry of the oxygen chemisorption also complicates the titration method of determining Pt surface areas, although the error introduced probably cannot exceed 16.7%. Three cases where H/Pt(total) > 1 have been reported were reinvestigated and two were shown to be of dubious reliability. The third, the Pt-zeolite system, was found to be more complicated than supposed and not necessarily an example of two H atoms held by each exposed Pt.

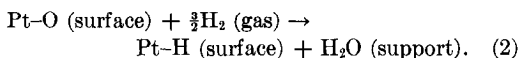
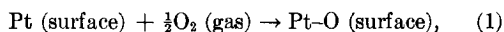
INTRODUCTION

Many workers have used the selective chemisorption of gases such as H₂, O₂, and CO to estimate the surface areas of supported metal particles. Platinum, in particular, has been intensively studied (1-10). By assuming a stoichiometry for the reaction between a surface metal atom and the chemisorbing gas, it is possible to calculate the ratio of surface to total metal atoms. If, in addition, the metal particles are assumed to have a certain geometry, the particle size can be calculated. The assumptions involved in such calculations have been discussed by Spenadel and Boudart (3), Adler and Keavney (4), Adams *et al.* (6), and Hughes *et al.* (8). This technique allows particles to be detected, which have an average size below that measurable by X-ray diffraction.

The literature is in general agreement

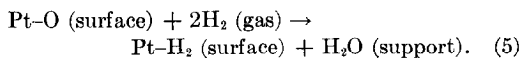
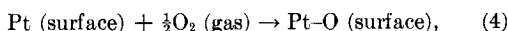
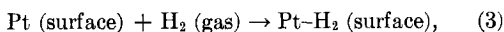
that platinum on supports such as alumina (3-5, 7, 8), silica-alumina (8, 11), and silica gel (2, 6, 9, 10) is extremely well dispersed in freshly prepared catalysts which have not been reduced at temperatures above 500°C. This conclusion has been inferred from observed H, O, or CO to total Pt atom ratios close to unity. In each case, it has been assumed that one surface metal atom chemisorbs only one atom of hydrogen, or one molecule of carbon monoxide. In some instances this assumption has been supported by measurements of chemisorption on platinum blacks of known surface area; e.g., Spenadel and Boudart (3) found that the area of their sample, calculated from hydrogen chemisorption, agreed with its BET area to within a few percent. Others have been less successful; e.g., Adler and Keavney (4) reported that with a foil, the H/Pt (surface) ratio was only 0.55.

Benson and Boudart (12) pointed out that the sensitivity of the direct chemisorption method could be improved by a factor of three by titrating chemisorbed oxygen with H_2 and by 50% by using CO instead of H_2 . The stoichiometry assumed (7, 12) was:



The water formed was taken up by the hydrophilic support, making it a simple matter to measure the hydrogen uptake. This stoichiometry was supported by their observed ratio of 3.2 for hydrogen titration/oxygen chemisorption.

Recently, Mears and Hansford (13) re-examined the stoichiometry of these reactions and questioned the postulates of Benson and Boudart (12). Their results indicated instead (for conditions of 25° and H_2 pressure of 10 Torr or greater):



In agreement with this stoichiometry, ratios of about 2:1:4 were reported for hydrogen chemisorption (HC):oxygen chemisorption (OC):hydrogen titration (HT), respectively, instead of 1:1:3 inferred by Benson and Boudart (12). It was suggested that the discrepancy between their results and those of Benson and Boudart stemmed from incomplete removal of chemisorbed hydrogen during the relatively short evacuation time used by the latter authors but evidence was not presented. Implicit in their proposed stoichiometry was the assumption that one oxygen atom was chemisorbed per surface Pt atom. We hoped to be able to shed further light on the true nature of these reactions by extending the earlier work of Hall and Lutinski (14).

The chemistry suggested by Mears and Hansford would lead to $H/Pt(\text{total})$ ratios greater than unity for Pt particles less than about 17 Å in diameter. We are aware of three cases (4, 15, 16) where $H/Pt > 1$ have been reported. Adler and Keavney

(4) found $H/Pt = 1.5$ at 200° for a catalyst containing 0.58% Pt mounted on γ -alumina. Their pretreatment procedure was, however, open to criticism. After calcination in air at 593°, their sample was reduced in 10 Torr of H_2 at 500° for only 20 sec. This short contact time may have been inadequate to completely remove oxygen from the catalyst. Residual oxygen would subsequently have lead to an anomalously large uptake of H_2 . Larson (16) found ratios of 1.1 to 1.4 for catalysts containing 1% or less Pt supported on Alon C. We have repeated, but not confirmed, this work using his catalysts. Rabo *et al.* (15) measured the H_2 uptake of a 0.5% Pt on calcium-Y-zeolite. After calcination in air at 500° and evacuation for 1 hr at the same temperature, the sample took up an amount of hydrogen equivalent to $H/Pt(\text{total}) = 4.23$. Subsequent hydrogen chemisorption at 100–250° on the reduced sample after evacuation at 500° for 1 hr yielded $H/Pt(\text{total}) \approx 2$. These results were interpreted (15) to indicate that each Pt atom was associated with two H atoms, two additional atoms having been required to reduce Pt^{2+} to Pt^0 . These workers maintained that by introducing the metal by ion exchange on to a zeolite support, the metal remained atomically dispersed on reduction. We have reinvestigated this system and found it more complicated than described above.

Benesi and co-workers (17) examined a Pt on silica catalyst, prepared by ion exchange. As measured by electron microscopy, 70% or more of the Pt was present in particles having diameters between 5 and 30 Å (av = 15 Å). H_2 chemisorption measurements on the same samples gave $H/Pt(\text{total}) = 1 \pm 0.2$.

Moss and co-workers (18), working with similar Pt-silica catalysts, combined H_2 and CO chemisorption measurements with X-ray diffraction and electron microscopy to show that 1.02 H atoms were chemisorbed on each surface Pt atom in both highly disperse crystallites (av size 15 Å), and in less disperse cases (av size 42–142 Å). There is, therefore, good evidence in the literature that ratios close to unity obtain for Pt-

silica catalysts. An object of the present work was to resolve the question: Does Pt on alumina behave differently than Pt on silica in the chemisorption of H_2 ?

EXPERIMENTAL METHODS

Catalysts

(1) **A-0.75.** The preparation of this catalyst was described by Hall and Lutinski (14). It contained 0.75% Pt supported on high purity alumina. The Pt was introduced by shaking 60 g of alumina (30–60 mesh) for 96 hr with 600 ml of deionized water, containing the required amount of hexachloroplatinic acid. The catalyst was dried in an oven at 105° overnight and finally calcined in a stream of high purity nitrogen at 600° for 4 hr. Three samples of this preparation were used. Sample A-0.75-i (4.309 g) had originally been used by Hall and Lutinski (14). It was given a complete pretreatment cycle as follows: after evacuation at room temperature for 1 hr, the sample in its original tube was heated to 250° at $\sim 2^\circ/\text{min}$; evacuation was continued for 1 hr at 250°, after which the temperature was increased to 550° at $\sim 2^\circ/\text{min}$. Oxygen (500 Torr) was then circulated over the catalyst at 550° for 2 hr, followed by evacuation; finally, hydrogen was circulated for 2 hr at 550° while the water formed was removed by a trap cooled to -196° . Samples A-0.75-ii (6.236 g) and A-0.75-iii (6.416 g initially) were pretreated in a different manner; in particular, the oxidation step was omitted. Evacuation was commenced at room temperature and continued (15–30 min) while the samples were heated to 150–200°. H_2 was then flowed over the catalyst as the temperature was raised at about $2^\circ/\text{min}$ to 300° where the reduction was continued for 16 to 18 hr. Finally, the temperature was raised to 500°, where it was held for 15–30 min before the catalyst was given final evacuation.

(2) **A-2.85.** This catalyst contained 2.85% Pt. It was prepared in the same way as A-0.75 from similar materials, except that the calcination was omitted. The pretreatment was the same as that described above for A-0.75-ii and -iii.

(3) **AC-0.2.** Catalyst AC-0.2 contained 0.2% Pt supported on alumina (Alon C). It was prepared by Gulf Research & Development Co., using the usual techniques of impregnation with hexachloroplatinic acid and calcination in air (at 532° for 16 hr). The pretreatment procedure was identical with that described above for A-0.75-ii and -iii. The weight of the sample was 5.179 g.

(4) **AC-0.8.** This catalyst was prepared and pretreated in the same way as AC-0.2 above, but it contained 0.8% Pt. The sample weighed 4.513 g.

(5) **Z-0.5.** Platinum equivalent to 0.5% was contained in this catalyst which was supplied by Dr. P. E. Pickert of the Union Carbide Co., and corresponded closely to one used in his work (19). The platinum had been introduced into the zeolite support ($\sim 45\%$ La^{3+} , $\sim 45\%$ NH_4^+ exchanged) by ion exchange. As supplied, the catalyst had been calcined in air at 550°. Four samples of this material were used and all were pretreated as follows: after evacuation at room temperature for 1 to 1.5 hr, they were heated to 150° at $\sim 2^\circ/\text{min}$ where evacuation was continued 1 hr. The temperature was then raised to 550° at $\sim 2^\circ/\text{min}$ where evacuation continued for 18 hr.

Gases

H_2 (Baker Prepurified Grade) and D_2 (General Dynamics), used in isotherm determinations or for circulation experiments, were diffused through individual heated Pd thimbles. When a flow of H_2 was required, as in the reduction of some catalysts, further purification of cylinder hydrogen (Baker Prepurified) was effected by passage through $MgClO_4$ and an activated charcoal trap thermostated at -196° . O_2 (Linde) and CO (Matheson CP Grade) were dried by passage through a trap thermostated at -78° . He (Air Reduction) was purified by passage through $MgClO_4$ and an activated charcoal trap thermostated at -196° .

Equipment

The apparatus consisted of a conventional high vacuum system similar to that described by Cheselske *et al.* (20). It included an all glass circulation system and

a BET volumetric system. A modified CEC 21-611 mass spectrometer was connected to the circulation loop through a glass capillary leak. This enabled H_2 - D_2 exchange reactions to be monitored continually.

Adsorption Measurements

Two procedures were employed to determine the amount of adsorption which occurred on the metal portion of the catalyst. The method primarily used was to determine the intercept of the isotherm obtained by static adsorption in a BET system. (Adsorption on the support is eliminated by the extrapolation to zero pressure.) Except where noted, the reduced catalysts were evacuated for 1 hr at 500° prior to H_2 or O_2 chemisorption and the isotherms were measured at room temperature with the sample thermostated in a water bath. After O_2 chemisorption, the samples were evacuated for 1 hr at 25° and then titrated with H_2 . Equilibration of gases with most samples was complete within 10–15 min. The dead space determinations were made with He. The second method employed D_2 in the isotope dilution method to determine the amount of hydrogen previously chemisorbed on the Pt (14).

Particle Size Determinations

Electron microscopy was done with a Philips EM 300 microscope, using the biological stage which permitted resolution to about 5 Å. Samples were prepared by mulling the catalyst in a 4% (w/w) solution of collodion in amyl acetate. A film containing the particles was obtained by spreading a drop of the suspension on water. The film was supported on standard 200-mesh copper grids and coated with a layer of carbon about 200 Å thick. The micrographs were obtained using a magnification at the photographic plate of $215,000\times$. Photographic enlargement to $10^6\times$ was used to provide a suitable image for particle size counting, which was done with a Zeiss TGZ-3 particle size analyzer. Specimen contamination in the microscope was minimized by metal blades, cooled by liquid nitrogen, which were placed adjacent to the sample.

X-Ray diffraction patterns were obtained using a Picker diffractometer utilizing $Cu-K_\alpha$ radiation, a nickel filter and a gas proportional counter detector. The average platinum crystallite size was determined from the width of the (311) reflection, when it was resolved. At best, for alumina supports, this is only a qualitative tool.

TABLE 1
THE EFFECT OF EVACUATION TIME UPON THE AMOUNT OF HYDROGEN CHEMISORBED ON 0.75% Pt ON ALUMINA CATALYST^a

Sample	Evacuation		Hydrogen chemisorbed			
	Time (hr)	Temp ($^\circ C$)	Isotherm intercept method		Deuterium exchange method	
			[ml (NTP)]	H/Pt(total)	[ml (NTP)]	H/Pt(total)
A-0.75-i	1.0	550	0.93	0.51	1.11 ^b	0.60
	1.0	550	0.93	0.51	—	—
	4.3	550	—	—	1.03 ^b	0.55
	16.0	550	0.93	0.51	1.15 ^b	0.60
A-0.75-ii	1.0	490	2.35	0.88	2.37 ^c	0.89
	1.0	500	2.56	0.96	—	—
	15.0	463	2.56	0.96	—	—

^a Each entry represents a different run.

^b Hydrogen chemisorbed at $-196^\circ C$ and sample evacuated 1 hr at $-196^\circ C$ prior to exchange.

^c Hydrogen chemisorbed at $-196^\circ C$ and sample evacuated 1 hr at $25^\circ C$ prior to exchange.

TABLE 2
 THE DEPENDENCE OF THE RATIO OF HYDROGEN CHEMISORPTION: OXYGEN CHEMISORPTION: HYDROGEN TITRATION UPON PRETREATMENT
 TEMPERATURE OF CATALYSIS CONTAINING 0.75% Pt ON ALUMINA

Sample		Reduction		Evacuation		Isotherm intercepts [ml (NTP)/g]						Ratio		Ratio		Surface area (m ² /g of Pt)	Av particle size (Å)		
Sample	wt (g)	Temp (°C)	Time (hr)	Temp (°C)	Time (hr)	HC	OC	HT	HC	OC	HT	HC	OC	HT	H/Pt ^a	O/Pt ^a	Surface area (m ² /g of Pt)	Av particle size (Å)	
Sintering procedure before hydrogen chemisorption																			
A-0.75-i	4.309	550	16	550	1	0.216	0.132	0.480	1.64	1.00	3.63	0.50	1.00	3.63	0.50	0.31	137	17	
		700	15	700	1	0.100	0.100	0.320	1.00	1.00	3.20	0.23	1.00	3.20	0.23	0.23	63	37	
A-0.75-ii	6.236	316	19	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
		500	0.2	500	1	0.417	0.192	0.824	2.17	1.00	4.28	0.97	1.00	4.28	0.97	0.45	267	9	
		500 ^c	0.3	463	1	0.411	0.237	0.901	1.70	1.00	3.80	0.95	1.00	3.80	0.95	0.55	262	9	
		545	16.5	545	1	0.257	—	0.712	—	—	—	0.54	—	—	0.54	—	149	16	
		545	8	540	15	0.289	0.225	0.747	1.29	1.00	3.33	0.67	1.00	3.33	0.67	0.52	185	13	
		—	—	545	1	0.289	—	—	—	—	—	0.67	—	—	0.67	—	185	13	
		587	15.5	587	1	0.282	0.183	0.683	1.54	1.00	3.74	0.66	1.00	3.74	0.66	0.42	182	13	
		636	16	636	1	0.249	0.199	0.633 ^d	1.25	1.00	3.19	0.58	1.00	3.19	0.58	0.46	160	15	
		636	2	636	1	0.244	0.212	0.611	1.15	1.00	2.89	0.57	1.00	2.89	0.57	0.49	157	15	
		695	14.5	695	1	0.231	0.242	0.630	0.95	1.00	2.60	0.54	1.00	2.60	0.54	0.56	149	16	
		697	2.5	697	17	0.197	0.231	0.564	0.85	1.00	2.44	0.45	1.00	2.44	0.45	0.54	124	19	
		622 ^e	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
		528	16	528	1	0.069	0.069	0.156	1.00	1.00	2.26	0.16	1.00	2.26	0.16	0.16	44	53	

A-0.75-iii	6.416	500	0.5	500	1	0.343	0.176	0.708	1.95	1.00	4.02	0.80	0.41	221	11
		500	1.2	500	1.2	0.340	0.171	0.695	1.98	1.00	4.05	0.79	0.40	218	11
	5.969	545	15.5	545	1	0.275	0.194	0.643	1.41	1.00	3.31	0.64	0.45	176	13
	5.568	583	15.5	583	1	0.250	0.208	0.596	1.20	1.00	2.86	0.58	0.48	160	15
	5.158	625	16.5	625	1	0.229	0.233	0.553	0.98	1.00	2.38	0.53	0.54	146	16
	4.429	690	16	690	1	0.226	0.257	0.461	0.88	1.00	1.79	0.52	0.60	143	16
		690 ^f	16	508	1	0.158	—	—	—	—	—	0.37	—	102	23
		690 ^g	16	508	1	0.160	0.156	0.431	1.03	1.00	2.77	0.37	0.36	102	23

^a Total platinum atoms.

^b Calculated from H₂ chemisorption data.

^c Catalyst treated a total of 0.75 hr in hydrogen and 3-hr evacuation at 500°C prior to this series.

^d Based on a single point isotherm.

^e Sintered in 1 atm air for 2 hr.

^f Sample treated 16 hr at 508°C in flowing H₂ to remove water formed in preceding titration.

^g Two CO chemisorption isotherms were run prior to this series; the CO was removed after each by a 30-min treatment in circulating H₂ at 505°C followed by the usual 1-hr evacuation at ~500°C.

RESULTS

The Effect of Evacuation Time upon the Amount of Hydrogen Chemisorbed

Comparative results using the hydrogen isotherm and the deuterium exchange techniques are shown in Table 1 for samples A-0.75-i and A-0.75-ii. The former method gives the measured chemisorptions and the latter, the residual hydrogen left after the evacuation. Evidently, a monolayer of chemisorbed hydrogen is retained at room temperature, but only a short time is required at 500° to clean the surface. Additional support for this conclusion was obtained from the fact that no H₂ or HD appeared when catalyst A-0.75-i was treated with D₂ at 25° after evacuation at 550° for 1 hr or more. Extending the evacuation time from 1 to 16 hr did not alter the results as would have occurred had the Pt been reoxidized by H₂O evolved slowly from the support.

The Effect of Calcination upon the Isotherm Intercepts

The isotherm intercept values for H₂ chemisorption (HC), O₂ chemisorption (OC) and H₂ titration (HT) and the ratios, relative to O₂ chemisorption, are given in Table 2. During preparation, catalyst A-0.75 was calcined in high purity N₂ for 4 hr at 600°. The H/Pt(total) values approached unity (e.g., A-0.75-ii) after reducing in H₂ at 500°, suggesting that the N₂ calcination did not cause sintering of the Pt. Sample A-0.75-i gave H/Pt = 0.91 after the pretreatment described by Hall and Lutinski (14), which included a period of 2 hr at 550° in flowing O₂. After a second similar pretreatment cycle, this value had fallen to 0.50. The drastic sintering caused by O₂ at higher temperatures is clearly demonstrated by the results presented as the last entry of Table 2 for A-0.75-ii. When heated in H₂ to 697°, the H/Pt ratio decreased from ~1 to ~0.5. Subsequent treatment in air at 1 atm and 622° for 2 hr, followed by reduction, resulted in a decrease in H/Pt from 0.5 to 0.16. Except for this last step, the O₂ chemisorption values did not reflect the growth of the Pt crystal-

lites suggested by the H₂ chemisorption data.

The Effect of Sintering in Hydrogen

Tables 2 and 3 present the results of experiments where samples of catalysts A-0.75 and A-2.85, respectively, were heated in H₂ at progressively higher temperatures. The usual procedure was to circulate hydrogen over the catalyst, at a particular temperature, overnight. Any water produced was removed by a trap cooled to -196°. In this way, the alumina was dehydroxylated at each temperature, prior to the evacuation step, thus minimizing the likelihood of reoxidation of the Pt surface during the evacuation step. The presence of H₂ in the gas phase ensured a fully reduced Pt surface. In these experiments, the samples were evacuated (prior to H₂ and O₂ chemisorption) at the same temperatures used for sintering. Note that the ratios changed from the stoichiometry of Mears and Hansford (13) to that of Benson and Boudart (12) as the Pt was sintered at successively higher temperatures.

As the sintering temperature was raised, the hydrogen chemisorption (HC) fell, reflecting a decrease in Pt surface area; concomitantly, the oxygen chemisorption (OC) remained fairly constant and sometimes increased, suggesting that the Pt crystals were not growing at all. Following the experiments listed in Table 3, electron micrographs were made and the Pt particle size distributions were determined for each of the catalyst samples. These distributions are shown in Fig. 1, and the surface areas calculated therefrom are given in parentheses in Table 3. In making these calculations cubic geometry was assumed and the area of five faces was counted. This corresponded to similar calculations made in the literature (3, 8, 10). The vertical broken line of Fig. 1 was drawn at 11.5 Å so that 56% of the area is to the left for the sample which was reduced at 475°. As the pretreatment temperature was raised, the distribution shifted to the right so that after reducing at 680°, most of the Pt area was provided by particles having dimensions larger than 11.5 Å. These data show

TABLE 3
 THE DEPENDENCE OF THE RATIO OF HYDROGEN CHEMISORPTION: OXYGEN CHEMISORPTION: HYDROGEN TITRATION UPON PRE-TREATMENT
 TEMPERATURE OF CATALYST CONTAINING 2.83% Pt ON ALUMINA

Sintering procedure before hydrogen chemisorption		Evacuation		Isotherm intercepts [ml (NTP)/g]						Ratio		Pt ^a		
Sample wt (g)	Reduction Temp (°C)	Time (hr)	Temp (°C)	Time (hr)	HC	OC	HT	HC	OC	HT	Ratio		Surface area (m ² /g of Pt)	Av particle size (Å)
											H/Pt	O/Pt		
5.443	300	15	—	—	1.268	0.658	2.793	1.93	1.00	4.24	0.78	0.40	215(190) ^d	11
	475	0.5	475	1	1.053	0.744	2.741	1.42	1.00	3.68	0.65	0.46	179(183)	13
4.597	540	12.5	540	1	0.842	0.861	2.523	0.98	1.00	2.93	0.52	0.53	143(161)	16
4.122	613	15	613	1	0.641	0.774	1.972	0.83	1.00	2.55	0.40	0.49	110	21
3.540	680	16.3	680	1	0.723	0.610	2.028	1.18	1.00	3.32	0.46	0.38	127	18
	464 ^b	15.5	662	1	0.723	0.658 ^c	2.068	1.10	1.00	3.14	0.46	0.41	127(137)	18

^a Calculated from H₂ chemisorption data.

^b Sample originally sintered at 680°C.

^c Sample cooled from 662°C in 100 torr helium.

^d This column was calculated from electron micrographs, see text.

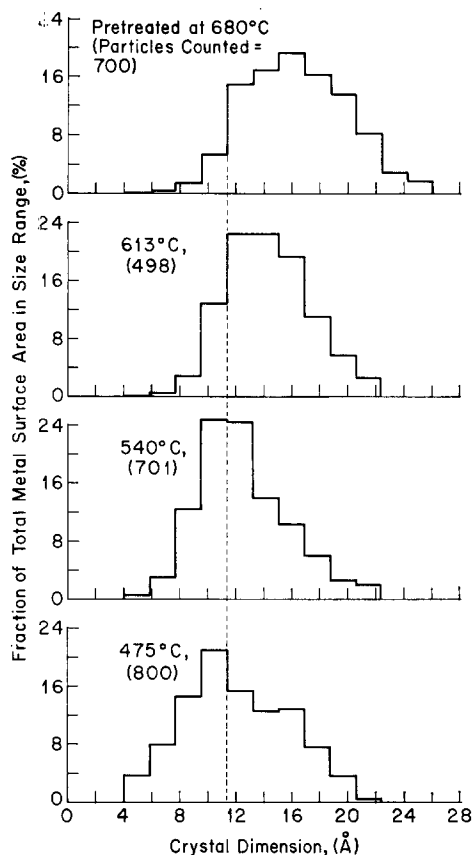


FIG. 1. Particle size distributions for Pt supported on alumina catalysts of Table 3.

that H_2 chemisorption, not O_2 chemisorption, properly reflects changing crystal dimensions. The number of particles counted in deriving the distributions are given in parentheses on Fig. 1. In all cases the statistics were adequate.

X-Ray diffraction patterns were attempted with the samples listed in Tables 2 and 3, after completing the adsorption measurements. However, Pt diffraction lines were observed with only one sample, viz., a portion of A-0.75-ii after calcination in air at 622° and re-reduction at 528° . Hence, this one sample ($H/Pt = 0.16$) contains larger crystals and has a lower Pt area than any of the others.

Chemisorptions on Platinum-Alon C Catalysts

A sample of AC-0.2 (5.179 g) gave intercept values of $OC:HC:HT$ of 1:1.21:3.47.

The hydrogen chemisorption on the metal corresponded to $H/Pt(\text{total}) = 0.62$.

Isotherms obtained over AC-0.8 (4.513 g) are shown in Figs. 2 and 3; these data are typical of results given in the literature (3, 7). The intercept of the room temperature hydrogen isotherm was 1.88 ml (NTP), corresponding to $H/Pt(\text{total}) = 0.91$. At the end of this isotherm, the temperature was raised to 250° and the isotherm was redetermined with the same gas. Spenadel and Boudart (3) showed that adsorption on the support is negligible at this temperature and that the Pt surface is saturated with chemisorbed hydrogen at pressures above about 240 Torr. Larson (16) used these conditions in his experiments. The uptake at 240 Torr was 1.76 ml (NTP) or $H/Pt = 0.85$, in fair agreement with the intercept at 25° . O_2 chemisorption and H_2 titration isotherms gave intercepts of 1.28 and 4.74 ml (NTP), respectively. The ratios $HC:OC:HT$ were, therefore, 1.47:1:3.70. After the titration, the water formed was removed to the -195° trap by

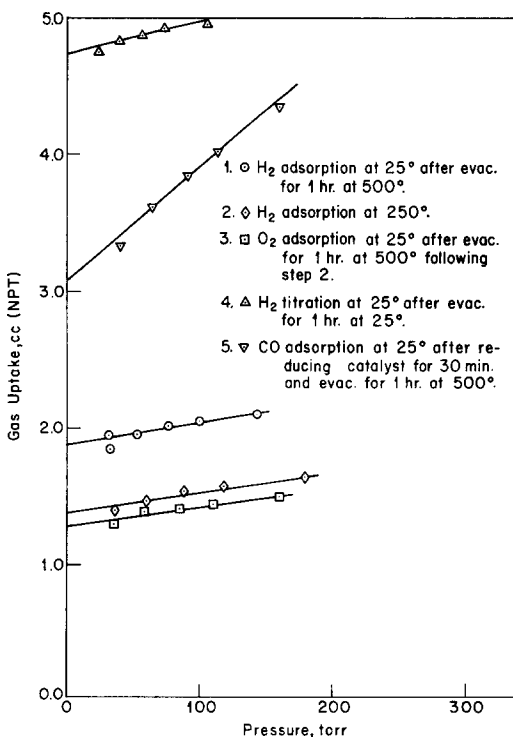


FIG. 2. Adsorption isotherms for catalyst AC-0.8.

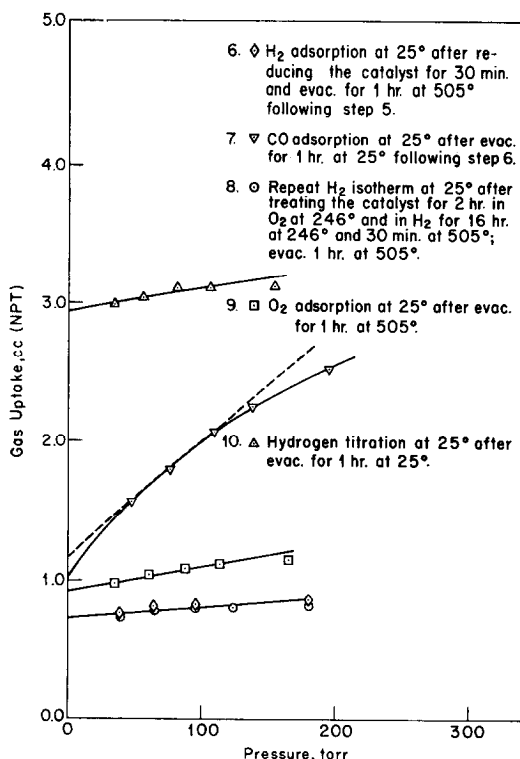


FIG. 3. Adsorption isotherms for catalyst AC-0.8. circulating hydrogen for 0.5 hr at 500°. Following evacuation for 1 hr at this temperature, a CO isotherm was determined at room temperature. The intercept was 3.08 ml (NTP), a little less than twice that for the H_2 chemisorption. (Also, compare $CO/Pt = 0.71$ with $H/Pt = 0.86$.) This is typical and indicates about 22% bridge-bonding (8, 10, 21).

H_2 was circulated over the catalyst for 0.5 hr at 505° to remove chemisorbed CO and the H_2 chemisorption was redetermined at 25°. The intercept of the isotherm (Fig.

3) was 0.72 ml (NTP). Either the CO was not completely removed by this procedure or else the chemisorption of CO, or treatment of the catalyst with H_2 at 500°, caused a sintering of the Pt. This was reflected in the lower CO chemisorption which was then determined (Step 7); the intercept was 1.15 ml (NTP). Next oxygen was circulated over the sample for 2 hr at 246°, before it was treated with H_2 for 16 hr at 246° and 0.5 hr at 500°. Subsequent H_2 chemisorption yielded an isotherm identical with the one obtained before the CO isotherm (Step 8). The relationship between the CO and H_2 chemisorption data for these experiments is shown in Table 4.

O_2 chemisorption and H_2 titration isotherms (Steps 9 and 10) gave intercepts of 0.92 and 2.94 ml (NTP), respectively. The intercept ratios for HC:OC:HT were, therefore, 0.78:1:3.20. The H_2 chemisorption intercept (data not shown) was increased to 0.85 ml (NTP) after the sample was treated in O_2 while the temperature was raised from 25 to 450° at $\sim 2^\circ/\text{min}$ before reducing with H_2 . Larson's finding (16) of $H/Pt(\text{total}) \geq 1.0$ was not confirmed.

Platinum-Zeolite Catalysts (Z-0.5)

(1) **The initial reduction of calcined samples.** After evacuating the catalyst samples (~ 5 g) at $\sim 550^\circ$, the uptake of H_2 was followed at 300° over a period of ~ 20 hr, although there was no observable change after 0.5 to 1 hr. Of four samples investigated, three yielded $H/Pt = 3.7$ to 3.8 in fair agreement with Rabo *et al.* (15); one gave a value of 3.2. (These data were

TABLE 4
COMPARISON OF HYDROGEN AND CARBON MONOXIDE CHEMISORPTION

Isotherm no.	H_2 chemisorbed		CO chemisorbed		H_2/CO	Bridged (%)
	[ml (NTP)]	H/total Pt	[ml (NTP)]	CO/total Pt		
1	1.88	0.86	—	—	—	—
5	—	—	3.08	0.71	0.61	22
6	0.72	0.33	—	—	—	—
7	—	—	1.16	0.26	0.62	24
8	0.72	0.33	—	—	—	—

calculated assuming the hydroxyl groups, or H_2O formed concomitantly with the reduction of the Pt^{2+} remained attached to the zeolite. This was substantiated by re-circulating the H_2 over the catalyst and through a trap thermostated at -195° following one of the adsorption experiments. No H_2O was recovered. The data also were not corrected for adsorption of H_2 on the support, the extent of which was not known.)

(2) **Hydrogen chemisorption on reduced samples.** These results were not as straightforward as those for Pt on alumina. The hydrogen chemisorption more than tripled on raising the temperature from 25° to 300° , indicating that equilibrium was not achieved at the lower temperature. Consider the data listed in Table 5 for Z-0.5-iii, where the results taken from Figs. 4 and 5 are summarized. After evacuating the raw catalyst for 16 hr at $\sim 550^\circ$, the initial H_2 consumption in the static reduction at 300° corresponded to $\text{H}/\text{Pt} = 3.7$. After 20 hr, the sample was evacuated as the temperature was raised to $\sim 500^\circ$, where H_2O

was eliminated, suggesting that the Pt surface may have been partially reoxidized. In contrast with the Pt on alumina results, however, the uptake of H_2 at 25° (Curve 1 of Fig. 4) was only 0.20 ml (NTP), corresponding to $\text{H}/\text{Pt} = 0.14$ (Table 5). Curve 1 was not reversible; on lowering the pressure, the desorption curve (No. 2) showed hysteresis and indicated an intercept of 0.42 ($\text{H}/\text{Pt} = 0.30$). When Rabo's conditions (15) were established (300° and 248 Torr), the adsorption increased, rather than decreased (Curve 3). On cooling to room temperature, however, the intercept (Curve 4) agreed well with the 300° value; the H/Pt ratios were 1.07 and 1.09, respectively. At this point, the tube was opened and a small aliquot of the catalyst was removed for electron micrographs. These revealed a relatively narrow particle size distribution having a maximum near 25 Å.

The catalyst was re-reduced for 0.5 hr at 300° , plus 19 hr at 500° , and a similar series of experiments was carried out (Fig. 5). The behavior was now more typical of

TABLE 5
HYDROGEN CHEMISORPTION ON A Pt-Y-ZEOLITE

Sample	Pretreatment		Evacuation		Hydrogen uptake			
	Temp ($^\circ\text{C}$)	Gas (hr)	Temp ($^\circ\text{C}$)	Time (hr)	H/Pt (total)	Temp ($^\circ\text{C}$)	Pressure (mm)	
Z-0.5-iii			550	16	3.7	300	638	
		First step	508	1 ^a	0.14 0.30 1.07 1.09	25	0	
						25	0	
						300	248	
						25	0	
		500	H_2 (19) ^b	500	1	0.34	25	0
					0.34	300 ^c	266	
Z-0.5-ii ^e			550	18	3.8	300	638	
		First step	504	1	0.98	250	264	
					0.98	25	0	
		507	H_2 (0.2)	507	1	0.30	25	0
		250	H_2 (1)	—	—	0.45 ^d	250	283

^a 1.1 ml (NTP) of water removed from 4.901 g of dry catalyst.

^b 6.3 ml (NTP) of water removed from 4.305 g of dry catalyst.

^c Intercept ratio, $\text{HC}:\text{OC}:\text{HT} = 1.1:1:3.7$.

^d Intercept ratio, $\text{HC}:\text{OC}:\text{HT} = 1:1:3.3$.

^e Dry wt = 4.841 g.

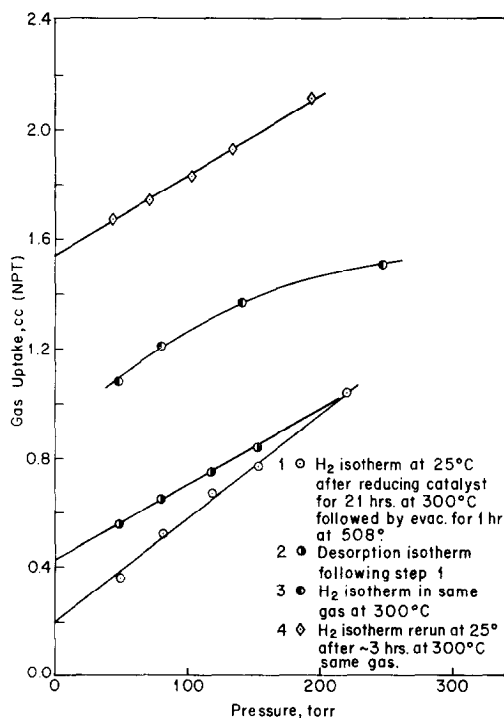


FIG. 4. Adsorption isotherms using single inlet of H_2 for Pt-zeolite catalyst reduced at 300°C.

Pt on alumina. No additional uptake occurred when the temperature was raised from 25 to 300°; instead, the amount adsorbed at 266 Torr at 300° about equaled the intercept of the 25° isotherm and corresponded to $H/Pt = 0.34$. Subsequent O_2 chemisorption and H_2 titration isotherms (Fig. 4) yielded: $HC:OC:HT = 1.12:1:3.67$.

These results were complimented with those from a related experiment (Z-0.5-ii of Table 5). The initial H_2 consumption in the static reduction corresponded to $H/Pt = 3.8$. After evacuation of the catalyst as the temperature was raised to ~500°, the H_2 chemisorption at 250° and 264 Torr corresponded to $H/Pt = 0.98$. Even a short treatment with H_2 at 500° was sufficient, however, to markedly sinter the Pt, as shown by the last two entries of Table 5. An electron micrograph taken at the end of the experiment ($H/Pt = 0.45$) showed a wide distribution of Pt particle sizes ranging from 20 to 90 Å. Evidently, Pt crystals grow much more readily when

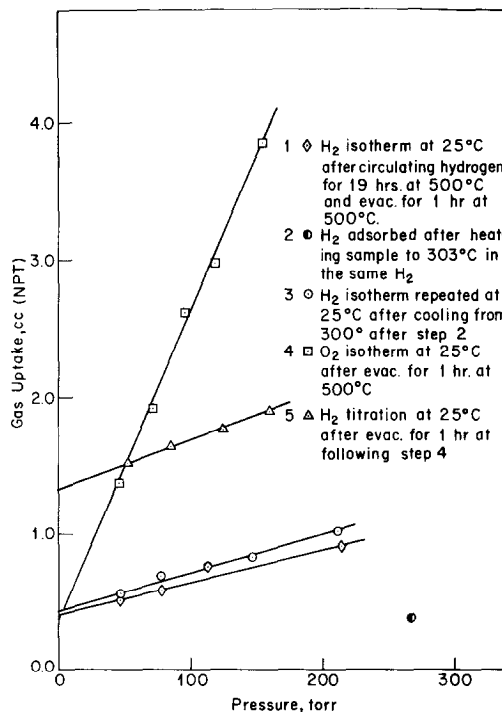


FIG. 5. Adsorption isotherms for Pt-zeolite catalyst reduced at 500°C.

supported on zeolite than when mounted on alumina. In disagreement with Rabo *et al.* (15), H/Pt values significantly greater than unity were not observed, when chemisorptions were measured on reduced catalysts.

DISCUSSION

The present work has shown that it is possible to vary the ratios of H_2 chemisorption: O_2 chemisorption: H_2 titration from 2:1:4 to 1:1:3 by heat treatment of the catalyst in a way which is likely to produce sintering of the metal. The conflicting results reported by Mears and Hansford (13) and Benson and Boudart (12) have thereby been both confirmed and reconciled. The cause for this change in stoichiometry is evident from the data listed in Tables 2 and 3. The H_2 chemisorption decreased as the metal was sintered more and more severely while the O_2 chemisorption remained more or less constant; in some cases it actually increased. Hence, the two measurements are in disagreement

concerning whether or not the metal surface area decreased (the metal crystallite size increased) as the catalyst was sintered to higher and higher temperatures.

Evidently, the stoichiometry of one or the other of the two reactions, gas with metal, was affected by heat treatment. If the metal surface area remained nearly constant, as suggested by the O_2 chemisorption data, the number of H atoms held per surface Pt fell as the catalyst was sintered. If, on the other hand, the metal surface area fell with heat treatment as suggested by the H_2 chemisorption data, the number of O atoms held per surface Pt must have increased. To decide which of these alternatives was more nearly correct required that the Pt surface area (or particle size) be estimated independently using aliquots of the same catalysts used in several sintering steps. A qualitative answer was provided by the X-ray measurements. Mostly, the samples were amorphous to X-rays, but in one or two cases lines appeared indicating a substantial fraction of particles having diameters larger than 50 Å units. In these cases, the catalysts had been extensively sintered. Hence, heat treatment did cause growth in crystal size.

Catalyst A-0.75 was unsuitable for study with the electron microscope because of its low Pt content. Work with catalyst A-2.85, however, revealed that the metal surface areas calculated from the particle size distributions from electron micrographs agreed within experimental error with those obtained by H_2 chemisorption when it was assumed that each surface Pt atom chemisorbed one H atom. Moreover, the effects of sintering and pretreatment determined by the H_2 chemisorption data were reflected at least semiquantitatively by the particle size distributions determined from the micrographs. Hence, it must have been the O_2 chemisorption which changed in stoichiometry as the catalyst was sintered.

It follows from the above results that the titration technique cannot be reliably used to determine Pt surface areas. Benson and Boudart (12) introduced this method to improve the accuracy in the determination of small Pt surface areas by

taking advantage of the 3-fold magnification. An even larger magnification is potentially available by the method of Hall and Lutinski (14). By exchanging the chemisorbed hydrogen with D_2 , a tenfold magnification should be easy to obtain. The good agreement between the two methods shown in Table 1 suggests that this provides an attractive alternative.

The particle sizes corresponding to different ratios of surface to total Pt atoms were calculated for two different crystal geometries (3, 27) and the results are listed in Table 6. Also given are the corresponding H/Pt ratios expected for the two proposed stoichiometries (12, 13). These calculations form the basis for another test which can be made to distinguish between the two stoichiometries. The catalysts for which the particle size distributions are given in Fig. 1 had H/Pt ratios varying between 0.78 and 0.46. Accordingly, the average crystallite size for these two extremes should be about 11 to 12 Å and 17 to 23 Å, respectively, if each surface Pt holds a single H; or between 21 to 30 Å and 34 to 53 Å, respectively, if each surface Pt holds two H. The values corresponding to the 1:1 stoichiometry are consistent with the data of Fig. 1; values corresponding to the 2:1 stoichiometry are not.

To satisfy the HC:OC:HT ratios which they observed, Benson and Boudart (12) assumed that each surface Pt atom could hold either one H or one O atom [Eqs. (1) and (2)]. To explain their different ratios, Mears and Hansford (13) retained the assumption that each surface Pt atom could hold one O atom, but assumed that two H atoms could be held on the same site. An alternative not considered was the possibility that the stoichiometry for H_2 chemisorption remained 1:1, i.e., Pt-H, but that the stoichiometry for O_2 chemisorption became Pt_2O for their catalyst samples, which incidently yielded H/Pt(total) values approaching unity. This assumption would have led equally well to the observed ratios, HC:OC:HT = 2:1:4. On this basis, as the Pt crystallites grow from a very small size where H/Pt(total) \approx 1 to larger well-developed crystals having H/Pt < 0.5, the

TABLE 6
 DISTINCTION OF HYDROGEN CHEMISORPTION STOICHIOMETRY BY ELECTRON MICROSCOPY

Proposed H/surface Pt	H/Pt(total) observed	Surface Pt/total Pt	Particle size (Å) model	
			Cubooctahedral ^a	Cubic ^b
1 (B & B) ^c	1	1	7.5	8.5
2 (M & H) ^d	2	1	7.5	8.5
2 (M & H)	1	0.5	22.5	16.9
1 (B & B)	0.8	0.8	11.5	10.6
2 (M & H)	0.8	0.4	30.0	21.1
1 (B & B)	0.5	0.5	22.5	17.0
2 (M & H)	0.5	0.25	52.5	33.7

^a Based on model presented by Bond, Ref. (27).

^b Based on cubic model of Spenadel and Boudart, Ref. (3).

^c B & B refers to Benson and Boudart, Ref. (12).

^d M & H refers to Mears and Hansford, Ref. (13).

stoichiometry changes from an overall surface composition Pt₂O to Pt-O; the latter was assumed by Benson and Boudart (12), leading to their ratios of 1:1:3. Qualitatively, this can be understood as follows: the valence requirements of H and of O are not the same. With small crystals O/Pt ratios should be about half the corresponding H/Pt. With larger crystals, where electrons can be furnished from the bulk, ratios more nearly equal may be achieved. Other factors may also be involved. Tucker (28) found using LEED that oxygen was chemisorbed on (111) planes with the stoichiometry Pt₂O and on (100) planes with the stoichiometry Pt-O. A change in the ratios of exposed crystal faces may well be a factor with supported Pt catalysts. The proportion of low index faces may increase as the crystals grow and become more nearly perfect.

Only Mears and Hansford (13) measured both H₂ and O₂ chemisorption at room temperature on the same sample. Their results, confirmed by our work, showed that highly dispersed samples (H/Pt ≈ 1) chemisorbed only about half as much O₂ as H₂. Brennan *et al.* (22) estimated that O₂ chemisorption on Pt films at room temperature amounted to about 0.63 atoms per surface Pt. Other data in the literature are contradictory in that some workers report that a monolayer is achieved (12, 23) while

others claim that it is not (1, 22, 24-26). It cannot be concluded, therefore, that each surface Pt will hold one O atom under all circumstances.

An examination of the experimental procedures used by Benson and Boudart (12) and by Mears and Hansford (13) showed two major differences. The pretreatment used by Benson and Boudart consisted of a 4-hr calcination in air at 593° followed by reduction at 500° for 12 hr. The catalyst was then outgassed for 1 hr at this temperature to obtain a "clean" Pt surface. Mears and Hansford apparently omitted the calcination step; they treated the catalyst in flowing H₂ while the temperature was raised from 150 to 500° over a period of 2 to 3 hr and continued the reduction for an additional 2 hr before outgassing overnight at the same temperature. The present work (Table 1) has demonstrated that the H₂ chemisorption was not affected by the length of the outgassing period at 500°. Our data also suggest that the high temperature calcination in air used by Benson and Boudart was particularly effective in increasing the Pt particle size following reduction, and, therefore, in effecting the stoichiometry which they reported. Dorling and Moss (9) showed recently that the particle size of Pt crystallites supported on silica increased with the calcination temperature, in air, between 120 and 800°. A

similar effect was reported by Mills *et al.* (5) for Pt on alumina calcined in air for various amounts of time at 450°.

Reports of H/Pt(total) greater than unity are rare, whereas values approaching unity are quite common. Similarly, ratios of CO/Pt \approx 1 are found at high dispersion. Hence, a molecule of chemisorbed CO is approximately equivalent to an atom of chemisorbed H₂. Since Dorling and Moss (10, 18) have shown that both correspond approximately to one surface Pt atom when this metal is supported on silica, it is reasonable to suppose that the situation is the same when alumina is the support. Moreover, were the stoichiometry proposed by Mears and Hansford (13) correct, it is a little surprising that values of H/Pt \geq 1 have not been observed more frequently. If two H were chemisorbed by each surface Pt atom, a spectrum of H/Pt values approaching 2.0 would be expected when the metal crystallite size becomes so small that a large fraction of the metal atoms are exposed to the gas, just as a limiting value of unity follows naturally from the stoichiometry of Benson and Boudart (12). Thus the literature, with the notable exceptions discussed below, generally favors the latter stoichiometry.

The present authors are aware of three cases where H/Pt(total) ratios greater than unity have been claimed. One of these (4) is of doubtful significance because the catalyst may not have been completely reduced before the H₂ chemisorption was measured. The other two cases were reinvestigated. Catalysts AC-0.2 and AC-0.8 were taken from the same batch used by Larson (16). Despite the fact that our samples were reduced in a manner expected to give less sintering than that employed by him, both catalysts gave H/Pt ratios less than unity, i.e., Larson's result could not be reproduced.

The third case involved the reaction of H₂ with Pt²⁺ base exchange cations of zeolites. It was proposed (15) that 2H per Pt were required to reduce the ions to metal atoms. Each metal atom supposedly chemisorbed two more H atoms leading to H/Pt (total) = 4. An experimental value of 4.23

was reported (15). On evacuation and re-adsorption of H₂, an amount of hydrogen equivalent to H/Pt(total) = 2 was observed. It was concluded, therefore, that the Pt remained atomically dispersed following reduction. This picture was used again recently (19) to explain a linear increase in catalytic activity with Pt content of a catalyst similar to the one studied herein.

The objectives of our reinvestigation of the Pt-zeolite were limited. The questions to be answered were: (a) does the Pt remain atomically dispersed following reduction, and (b) must we believe that the data for this system demonstrate the ability of exposed Pt atoms to chemisorb two H atoms under some circumstances? Negative answers to both of these questions were obtained. In the course of this work, however, it was found that the system was more complicated than previously supposed. Hence, although we do not completely understand this system, the results of Rabo and co-workers (15) should not be taken as proof that each surface Pt can chemisorb more than one H atom.

Following Rabo *et al.* (15), the hydrogen consumption was first measured during reduction of the degassed catalyst. Values of 3.7 to 3.8 were obtained (Table 5) in fair agreement with the earlier work. Assuming no reactions with, or adsorption on, the support and that only divalent Pt²⁺ was present initially (no Pt⁴⁺), these data would indicate that each Pt atom was left holding two H atoms. Were this the case, it should be possible to remove the chemisorbed hydrogen and then to remeasure the chemisorption. The 2:1 stoichiometry would then be reflected by H/Pt(total) \approx 2. This was not found; rather, values close to unity were obtained in both cases. These data do not prove the 1:1 stoichiometry, however, because the particle size distribution (mean diameter = 25 Å) obtained for the sample having H/Pt = 1.09 (Table 5) was more nearly consistent with the 2:1 stoichiometry (Table 6). However, the electron micrographs demonstrated that Pt atoms do not remain atomically dispersed; they crystallize. Pt crystals appear to grow under

much milder conditions when supported on the zeolite lattice than they do when supported on alumina. These findings confirm those recently published by Lewis (29).

The values of the hydrogen uptake listed in Table 5 have not been corrected for the contribution due to the support and may therefore be too high. At the time these measurements were made it was supposed that, as with alumina, this contribution would be negligible at 300°. Lewis (29) found, however, that a Pt-free Na-X-zeolite absorbed up to 40% as much H₂ as the Pt-zeolite at 300°. However, Rabo *et al.* (15) reported a negligible blank for a Ca-Y-zeolite under these conditions.

The H₂ chemisorption on the Pt-zeolite was slow (29), about doubling between 2 to 3 hr and 24 hr; there was no further increase in 88 hr. X-Ray adsorption edge measurements indicated, however, that this additional chemisorption did not take place on the Pt surface. Surprisingly, Lewis reported that adsorption on the support was negligible at 100°, although the H₂ uptake remained very slow. A similar slow time-dependent chemisorption was noted at 25° in the present work (Fig. 4). Such time-dependent processes do not occur with Pt supported on silica or alumina with "clean" systems and they deserve further study. Eley *et al.* (30) showed recently that the H₂ chemisorption on such catalysts is modified both in strength, kind, and perhaps in amount by the presence of chemisorbed oxygen and/or water, and this may be a factor here. The point is that if the zeolite support plays an important role, some of the H/Pt ratios listed in Table 5 may be fictitious and too high by a significant amount. Consider first the raw data of Lewis (29) in conjunction with those of Table 5. (His determinations were made by a flash desorption technique with condensable gases removed by a liquid nitrogen trap; H₂ was exposed to the raw catalyst so H/Pt = 2 has been added to values calculated from his data to include H₂ required for the reduction of Pt²⁺ to Pt⁰.) At 300° in 3 hr, the total uptake amounted to H/Pt = 2.9. Corrected for adsorption on the Na-zeolite the value was 2.5, suggesting

a true H/Pt of about 0.5. To this point, the adsorption edge responded to the adsorption. On standing for 23 hr at 300°, however, the total uptake increased to H/Pt = 4.0, but there was no change in the adsorption edge indicating that the additional adsorption was not on the Pt crystal surface. These data are in good agreement with the results from the first steps of the experiments of Table 5. They show that the high H/Pt ratios cannot be used to demonstrate that more than one H atom is bonded to Pt. Subsequent steps did not produce H/Pt ratios significantly greater than unity, even when uncorrected for adsorption on the support.

Electron micrographs taken in the present work, in agreement with Lewis (29), showed mostly Pt particles too large to be accommodated within the zeolite lattice. Hence, this Pt apparently crystallized outside the zeolite crystals where there is no reason to suppose it should behave differently than when supported on silica or alumina. Such Pt adsorbs hydrogen with approximately the 1:1 stoichiometry. However, Lewis found that about 60% of the Pt of his catalyst was soluble in HF. This he attributed to much smaller crystals, although it may have been due to incompletely reduced or reoxidized platinum (31-33). Therefore, some of the puzzle remains to be unraveled.

CONCLUSIONS

The present work has shown that it is possible to vary the ratios for H₂ chemisorption:O₂ chemisorption:H₂ titration from 2:1:4 to 1:1:3 by heat treatment of the catalyst in a way likely to produce sintering. The conflicting results reported by Benson and Boudart (12) and Mears and Hansford (13) are thereby reconciled. We believe that our results are consistent with a model requiring Pt to take up only one hydrogen atom during chemisorption or titration. H₂ chemisorption reflects changes accompanying sintering, but O₂ chemisorption appears unreliable as a measure of the available Pt area. In consequence, the titration method is also unreliable. The reports in the literature of H/Pt ratios greater than

one, for H₂ chemisorption on reduced catalysts, seem to be dubious, particularly in the case of Pt-zeolite samples. We, therefore, can find no justification for the proposal of Mears and Hansford (13) that each surface platinum atom chemisorbs two hydrogen atoms.

Previous reports by Rabo and co-workers (15) that Pt atoms supported on Ca-zeolite each adsorb two hydrogen atoms appear to have been misinterpreted due to the complicating feature of a support effect.

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