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Chemisorption on Molecular Sieve Supported Platinum

I. Hydrogen, Oxygen and the Hydrogen–Oxygen Titration

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Chemisorption of hydrogen, oxygen and the titration reaction on molecular sieve supported platinum was investigated using a gas chroatmographic technique in order to measure the specific surface of platinum. Comparative measurements were carried out on Spence-alumina-supported platinum. Chemisorption of both hydrogen and oxygen on both the supports is negligible at room temperature; water formed during the room temperature reaction of hydrogen with oxygen on platinum is scavenged by both the supports and desorption of H_2 from the sintered supported platinum is completed within 3 hr for both types of sample. Platinum surface is saturated from an oxygen pulse for a molecular sieve 5A supported platinum but not for alumina supported platinum, as demonstrated by a higher consumption of hydrogen for titration of oxygen adsorbed on the sample from an oxygen stream. Chemisorption of oxygen at temperatures of 300°C and higher proved to exceed the amount corresponding to a theoretical monolayer on alumina supported platinum (as reported by other workers). This was not found for molecular sieve 5A supported platinum.

Distribution curves of platinum crystallite size in molecular sieve 5A supported platinum were measured by electron microscopy for both reduced and nonreduced material. From the electron microscope results the mean diameter of platinum crystallites in a reduced sample of 46 Å was calculated. Based on this value the specific surface of platinum in this 0.3% Pt containing material was found to be 0.150 or 0.180 m^2/g depending on the supposed geometry of the crystallites. The respective corresponding ratios Pt_{surf}/Pt_{tot} of 0.18 and 0.22 were calculated. The good agreement of these ratios with the H/Pt_{tot} and O/Pt_{tot} found by room temperature chemisorption on this sample, namely 0.16–0.18 and 0.15–0.20, respectively, indicates that H/Pt_{surf} and O/Pt_{surf} equal unity.

INTRODUCTION

Although methods of investigation of the metal surface of supported platinum catalysts have been extensively investigated over the last two decades, many problems still remain. It is generally agreed that specific chemisorption, or titration of one chemisorbed gas with another, offers the most convenient measurement, but different workers favor different adsorbates and report a range of stoichiometries. At least part of this discrepancy may be due to the necessity and the difficulty of producing a clean surface on which adsorption can proceed. Attention has been directed in the present work to establishing conditions for metal surface cleaning, and to characterizing a system with molecular sieve 5A support by a variety of techniques (hydrogen and oxygen chemisorption, H_2–O_2 titration, electron microscopy). Comparison with alumina supported platinum is presented. Chemisorption of carbon monoxide is treated in Part II (*1*).

The principle of surface area measurement by gas adsorption can be schemat-

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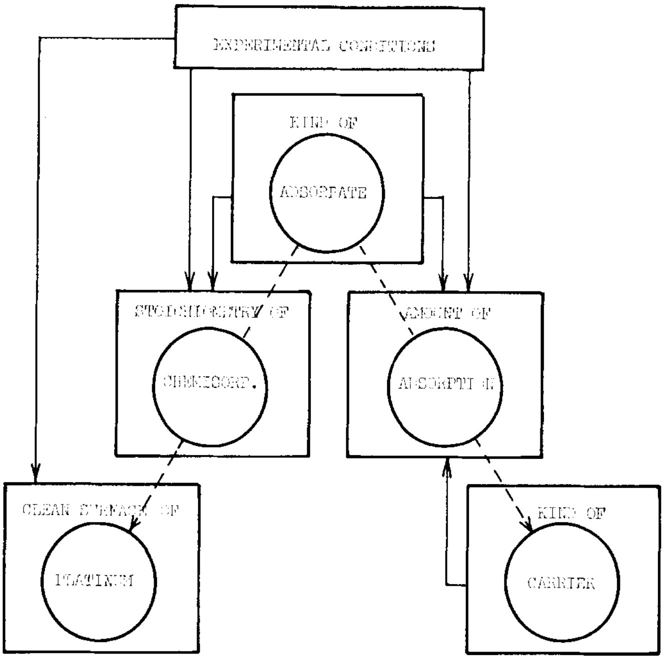

FIG. 1. Scheme of the presented investigations on measurement of specific surface of platinum in bicomponent catalysts.

ically represented as in Fig. 1, where the processes and interactions are illustrated by circles and broken lines. The effect of different factors on the processes are shown by solid lines.

The first essential in any chemisorption experiment is to attain a metal surface uncontaminated by preadsorbed gas or any other impurity. This is usually effected by a reduction and hydrogen–desorption sequence and methods used by different workers are summarized in Table 1.

EXPERIMENTAL METHODS

Materials

Carriers used included (i) Union Carbide molecular sieve 5A $\frac{1}{16}$ in. pellets, (ii) activated alumina Type A, Peter Spence and (iii) Union Carbide molecular sieve 5A treated with NH_4Cl solution in a way analogous to the preparation of molecular sieve supported platinum (see below). The carriers for blind measurements were crushed and sieved to 28–48 mesh.

A platinum–molecular sieve 5A catalyst was prepared by an exchange procedure (*22*) using a solution of platinum ammine chloride complex $[Pt(NH_3)_6Cl]$. The product was drained, repeatedly washed with distilled water, heated for 4 hr in air at 300°C and then for 2 hr at 425°C. The pellets were crushed and sieved to 28–48 mesh. The platinum content was 0.30 wt% (catalyst designation 5A-0.30). On Spence alumina, platinum was supported using the same procedure. The platinum content in this catalyst (SpAl-0.48) was 0.48 wt%.

Equipment and Procedures

Pulse chemisorption measurements were carried out in a flow system, fitted with a high sensitivity Varian aerograph 90P thermoconductivity detector. A bypass of the carrier gas to the detector allowed the pretreatment and oxygen flow treatment procedures *in situ*. The gas line could be operated at pressures of up to 2 atm. and was made from nonreactive materials.

TABLE 1

Desorption Conditions after Reduction of Catalyst

Ref. No	Catalyst	Reduction conditions			Desorption conditions		
		Time (hr)	Temp (°C)		Time (hr)	Temp (°C)	
(*2*)	Pt/Al_2O_3	2	500	Flowing H_2	16	500	Evac.
(*14*)	Pt/Al_2O_3	12	150–500	Flowing H_2	1	500	Evac.
(*9*)	Pt/SiO_2-Al_2O_3 Pt/Al_2O_3	3	450	500 ml H_2/min	?	450	Evac.
(*11*)	Pt/silica gel	1	485	1 mm Hg H_2	3	480	Evac.
(*7*)	Pt/Al_2O_3	2	150–500	100 ml H_2/min	16	500	Evac.
	Pt/SiO_2	2	500				
(*3*)[a]	Pt/Al_2O_3	2	500	Flowing H_2	3	500	Blowing with He or Ar
(*3*)[b]	Pt/Al_2O_3	2	500	Flowing H_2	16	500	Evac.
(*13*)	Pt/Al_2O_3	1	200–300	Flowing H_2	16	500	Evac.
(*4*)	Pt/Al_2O_3	2	500	Flowing H_2	16	470	Elution with purified N_2
(*20*)	Pt/zeolite CaY	24	300	Flowing H_2	1	500	Degassed
(*10*)	Pt/silica	2	210	Flowing H_2			Degassing not mentioned
(*21*)	Pt/alumina	16	500	Flowing H_2 then exposed to atmosphere at room temp	16	500	Flow of carrier gas 35 ml/min
		2	500	50 ml H_2/min	16	500	
(*19*)	Pt/silica	2	400				Not mentioned
(*12*)	Pt/Al_2O_3	2	Heated from 25 to 450				
		0.5	450				
		0.5	Heated from 450 to 550	200 ml H_2/min	2	550	Evac.
		1	550				

[a] Gas chrom. apparatus.
[b] Static apparatus.

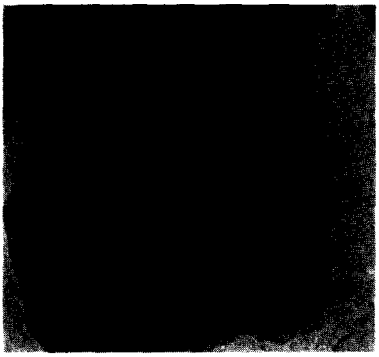

FIG. 2. Electron micrograph of reduced 5A-0.3 (magnification 240 000×).

Electron microscopic investigations were carried out by means of a Siemens Elmiscop I 207 instrument. A carrier, an unreduced and a reduced form of 5A-0.3 were investigated. The samples were finely ground to smaller than 400 mesh, shaken with water and the smallest particles (which did not sink to the bottom) were placed on an organic film. The electron micrographs were taken at an electron microscope magnification of 80 000 times, and a part of an electron micrograph of the reduced sample is shown in Fig. 2

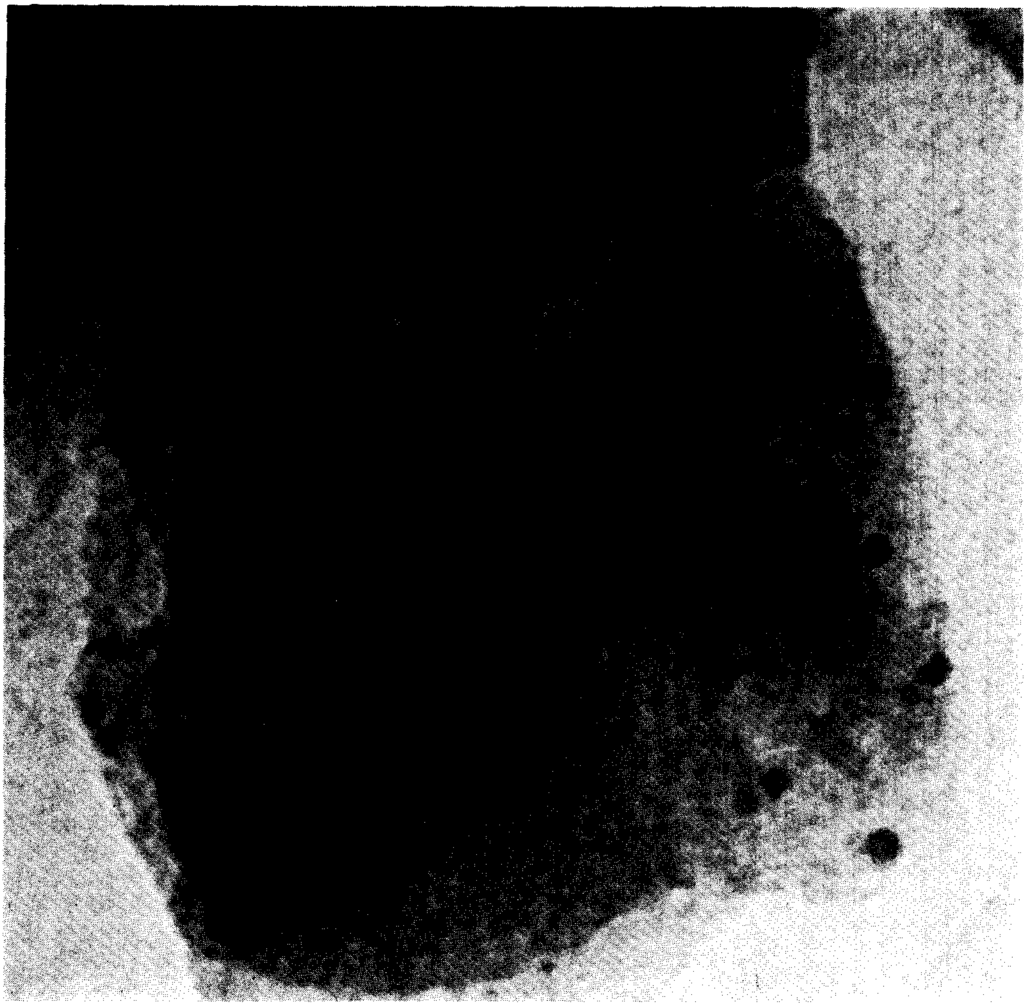

FIG. 3. Electron micrograph of reduced 5A-0.3 (magnification 640 000×).

(240 000 times magnification). The spots of platinum crystallites on pictures are distinct, but a distribution curve of their size is only obtained with difficulty. Further photographic enlargements (e.g., see Fig. 3) did not improve the accuracy of the crystallite size estimation, but did enable the smallest (visible) particles to be measured. At a total magnification of 640 000 times it was possible to distinguish crystallites of 11 Å in diameter and larger.

Flynn and co-workers (*23*) have demonstrated how defocus can influence the accuracy of particle size determination, and how the photographic treatment of an electron micrograph can influence the information obtained. The different thickness of the investigated particles of catalysts causes some new platinum particles to appear on the picture while others disappear as the developing time is varied. This is illustrated in Fig. 4. Thorough studies of every electron micrograph allowed statistically representative results to be obtained from the pictures, providing that an optimal contrast between platinum crystallites and a carrier was maintained.

RESULTS AND DISCUSSION

Clean Surface of Platinum

Hydrogen left on the surface of the catalyst after reduction must be quanti-

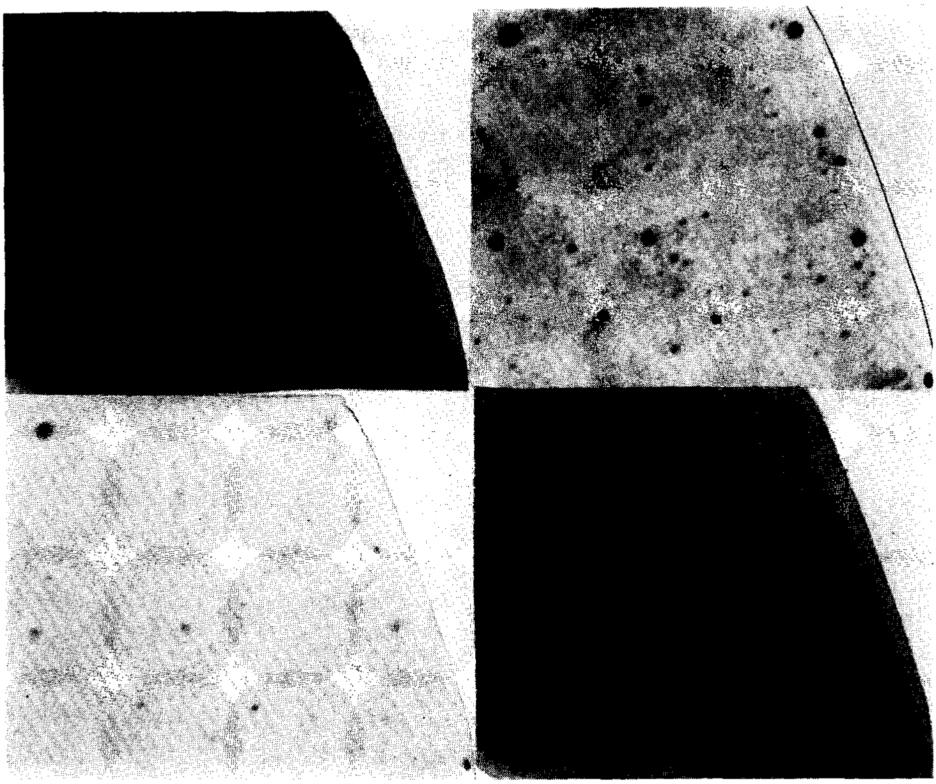

FIG. 4. Different photographic exposures of electron micrograph of a reduced 5A-0.3 (magnification 240 000×).

tatively removed when (i) the specific surface of platinum has to be estimated by chemisorption of either oxygen or hydrogen; (ii) the stoichiometry of chemisorption either of hydrogen, oxygen or of the titration reaction is investigated. To establish a suitable pretreatment procedure, the rate of desorption of residual hydrogen at 485°C was investigated for both degassing *in vacuo* and flushing with an inert gas. It was found that desorption of residual hydrogen by purge gas from SpAl-0.48 as well as 5A-0.30 is completed within the first 3 hr.

Temperature-change thermodesorption experiments of hydrogen adsorbed at 25°C on the 5A-0.3 material revealed the existence of at least two differently strong forms of hydrogen–platinum bond with a desorption temperature $T_{des} = 150°C$ for the less stable one. The main contribution to the desorption of hydrogen started at 250°C and reached a maximum at ca. 450°C. Tsuchiya and co-workers (*24*) have reported the existence of four different forms of H_2-adsorption on platinum (the two weakest with $T_{max} < 0°C$). They have found that with an increasing experimental temperature of adsorption the desorption temperature of hydrogen also increases as well as the percentage of the most strongly adsorbed form. Thus, it can be expected that hydrogen chemisorbed on platinum at room temperature would desorb more easily at 485°C than hydrogen which remained bonded on platinum after its reduction at this high temperature.

As a result, the pretreatment procedure for the samples on which investigation of estimation of platinum surface have been

TABLE 2

Adsorption on 0.30% Pt on Linde 5A at Room Temperature

Section:	1			2		3			4		
Amount of dry cat. (g)	Adsorption from O_2-pulse			Titration of O_2-pulse with H_2-pulse		Titration of O_2-flow with H_2-pulse			Adsorption from H_2-pulse		
	Heated at 485°C total (hr)	Consumed (μl)	O/Pt_{tot}	Consumed (μl)	H/O	Heated at 485°C total (hr)	Consumed H_2 (μl)	Theor.: H/Pt_{tot}	Heated at 485°C total (hr)	Consumed (μl)	H/Pt_{tot}
1.92	22	57.3	0.173	149.0	2.6	47	163.0	0.168[a]			
	28	57.0	0.172	153.0	2.69			0.126[b]			
1.72	29	64.0	0.204	212.0	3.31	30	236.0	0.267[a]	29.5	46.5	0.158
	33.7	44.2	0.150	172.0	3.89			0.20[b]	33.0	53.5	0.181
1.725	22.5	—[c]		158.0		73	157.0	0.177[a]	20	30.0	0.101
	41.0	61.1	0.206	158.0	2.58			0.132[b]	20.7	37.0	0.125
									22.2	47.0	0.159
1.765	50	64.0	0.211	226.0	3.53						

[a] $\frac{1}{3}$ of the H/Pt_{tot} in accordance with Benson and Boudart's (*14*) stoichiometry.

[b] $\frac{1}{4}$ of the H/Pt_{tot} in accordance with Mears and Hansford's (*7*) stoichiometry.

[c] The O_2-pulse has been sent through but its registration was disturbed. It was, however, possible to measure the consumption of H_2 necessary for the titration of the O_2 chemisorbed on this sample.

carried out was standarized:

Procedure	Duration (hr)
1. Evacuation at room temperature	0.05
2. Temperature increased to 150°C while evacuating	1.0
3. Evacuation at 150°C	0.5
4. Temperature increased to 485°C while evacuating	1.0
5. Evacuating at 485°C	2.0
6. Flushing with 3 ml H_2/min at 485°C	0.2
7. Flushing with 20 ml H_2/min at 485°C overnight	9–16
8. Flushing with 35 ml Ar/min at 485°C	3
9. Cooling to room temperature in a stream of an inert gas.	

This procedure was repeated after each adsorption.

Chemisorption on Carriers

The experimental measurements have shown that: (i) Chemisorption of both hydrogen and oxygen on molecular sieve 5A is negligible at room temperature. (ii) The same has been found for the room temperature chemisorption on alumina. (iii) None of the room temperature chemisorption types of hydrogen on alumina reported by Amenomiya (*15*) appeared when the pulse technique was used. (iv) Chemisorption of oxygen at 485°C amounts to 5.5 μl/g on alumina and 31 μl/g on NH_4Cl-treated molecular sieve 5A.

Water Formed in the Titration Reaction

Water formed in the titration reaction between hydrogen and oxygen was found to be quantitatively scavenged by the molecular sieve support at low temperatures. In the first experiment the H_2–O_2 titration was carried out on 5A-0.3 at room temperature, sending first the oxygen pulse and thereafter the hydrogen pulse through the sample. The amount of the gases in the pulses was in excess of that necessary to saturate the sample. No trace of water could be determined by gas chromatographic analysis. In a second experiment, a cooled U-tube trap (−78.5°C) was placed between the reactor containing the 5A-0.3 sample and the detector. The sample was flushed with oxygen for 1 hr at room temperature, washed with a flow of carrier gas and then the chemisorbed oxygen was titrated with a pulse of hydrogen at room temperature. After removing the cooling bath, no peak which could correspond to water formed during the reaction was registered on the chromatogram. This was confirmed by repeated experiments. When, however, the sample was heated to 485°C after the reaction was accomplished, the removal of the cooling trap did result in the appearance of a water peak.

Chemisorption at Room Temperature

The amount of oxygen adsorbed from a pulse by the 5A-0.3 and SpAl-0.48 materials was measured. Thereafter, a pulse of hydrogen was sent through the sample on which oxygen was chemisorbed and the amount of hydrogen consumed in the H_2–O_2 reaction on platinum was measured. The results are given in Sect. 1 and 2 of Tables 2 and 3. Also reported are the periods for which the samples were heated at 485°C before every individual measurement. In the last column of these sections the calculated stoichiometric ratios for the respective measurements are reported. On the 5A-0.3 samples, the H/Pt_{tot} and the O/Pt_{tot} values amounted to 0.1–0.18 and 0.11–0.20, respectively. Saturation of the samples by oxygen was established in the following test. The samples on which oxygen had been chemisorbed from pulses were pretreated again, flushed with a flow of 40 ml O_2/min for 1 hr at room temperature, and washed with a flow of argon for 1 hr at room temperature. A pulse of hydrogen was then sent through the sample. The consumption of hydrogen necessary for both reaction with the irreversibly sorbed oxygen and successive chemisorption of

TABLE 3

Adsorption on 0.48% Pt on Spence Alumina at Room Temperature

Section:	1			2		3			4
Amount of dry cat. (g)	Adsorption from O_2-pulse			Titration of O_2-pulse with H_2-pulse		Titration of O_2-flow with H_2-pulse[2]			Ads. from O_2-flow/ ads. from O_2-pulse
	Heated at 485°C total (hr)	Consumed (μl)	O/Pt_{tot}	Consumed (μl)	H/O	Heated at 485°C total (hr)	Consumed H_2 (μl)	Theor: H/Pt_{tot}	
1.705	13	36.8	0.078	128.5	3.5	16	322	0.228 0.342	2.50
1.972	75.5	42.7	0.078	125.5	2.93	87	388	0.238 0.356	3.09
1.978	164.5	34.0	0.063	77	2.26	176	222	0.135 0.202	
	252	39.8	0.073	153.5	3.86				
						233.5	232	0.142 0.212	2.32
						261	349	0.163 0.32	
						270	268	0.163 0.245	

hydrogen on platinum was measured. The results obtained are presented in the Sect. 3 of Tables 2 and 3. Measurements on 5A-0.3 showed that the consumption of hydrogen necessary for titration is about the same when oxygen is chemisorbed from pulses or from the stream. Using SpAl-0.48, however, much more hydrogen was consumed for titration after the sample was flushed with an oxygen flow. The ratio of these two H_2-consumptions is presented in Sect. 4 of Table 3. Further studies on this problem revealed that oxygen is adsorbed in successively smaller amounts from successively injected pulses. For example, from a second pulse, 8.5 μl oxygen was retained by a re-pretreated sample of 1.987 g of SpAl-0.48 (Table 3). The H_2-titration values obtained on 5A-0.3 samples were in the range 2.6–2.9 but the explanation of Wilson and Hall (*13*), given for the case of Pt-on-alumina, that this value varies from 4 to 3 by a heat treatment of the catalyst in a way likely to produce sintering could not explain the variation in this case. Measurements car-

TABLE 4

Hydrogen–Oxygen Titration at Higher Temperatures

Catalyst and wt of cat. (g)	Temp (°C)	Theor H_2 (μl)	Consumption from pulses								
			O_2		H_2 (μl)	O_2		H_2 (μl)	O_2		H_2 (μl)
			(μl)	O/Pt_{tot} (corr.)		(μl)	O/Pt_{tot} (corr.)		(μl)	O/Pt_{tot} (corr.)	
0.3% Pt/5A											
1.735	485	300	219	0.55	340	178	0.41	330	115	0.38	
1.78	300	307	233	0.58	550						
0.48% Pt/ Al_2O											
1.729	485	476	1250	2.6	1320	750	1.55	1120	600	1.24	1170
1.972	485	543	1270	2.32	1370						
1.972	300	543	846	1.54	1210						

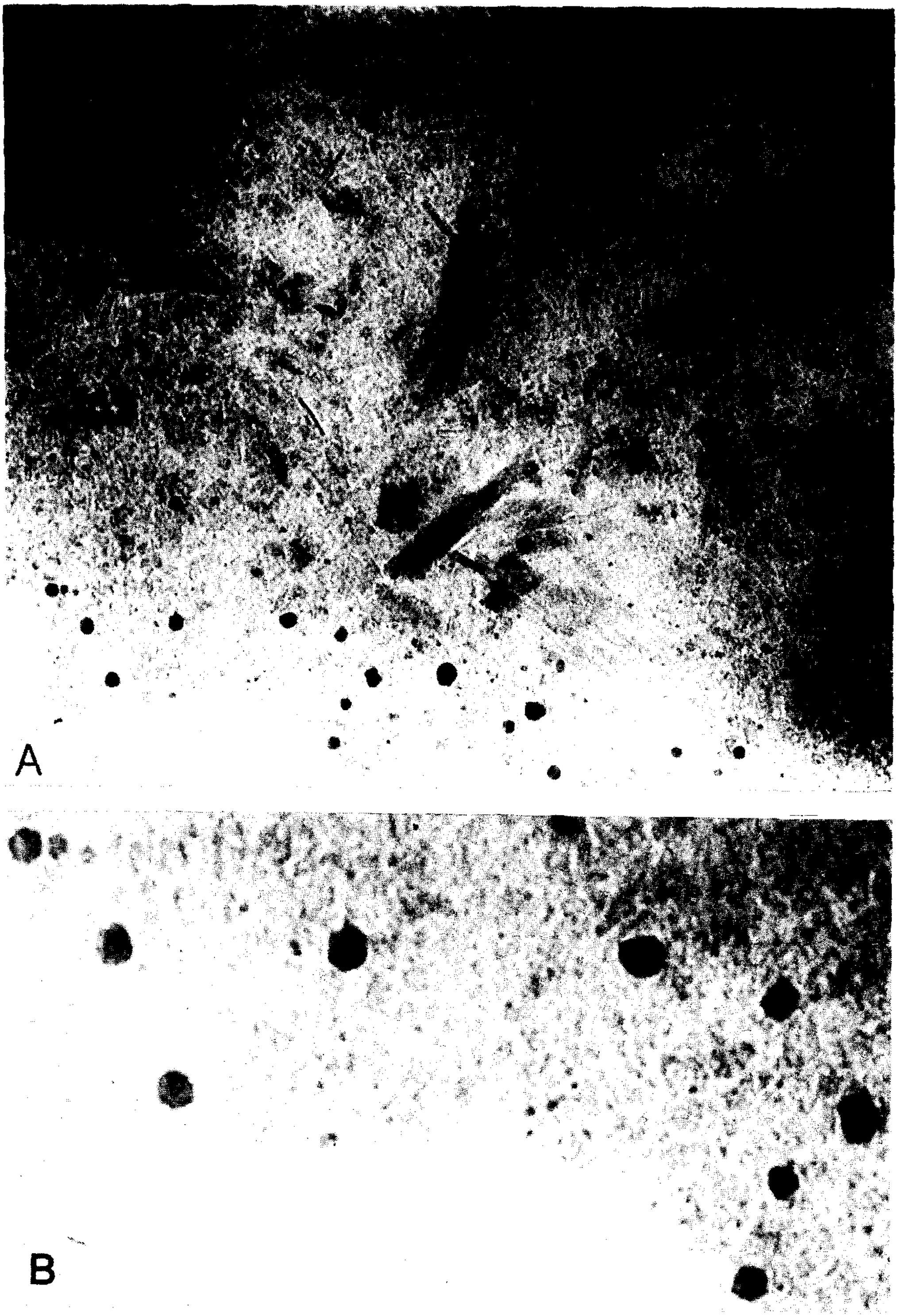

FIG. 5. A part of the electron micrograph of unreduced sample 5A-0.3. (A) Magnification 240 000×; *(B) part of A at magnification 640 000×.*

ried out on alumina supported platinum SpAl-0.48 resulted in $O/Pt_{tot} = 0.063$–0.078 (Table 3). These very low values point, to very big platinum crystallites being formed during the pretreatment process. The H/O ratio resulting from the

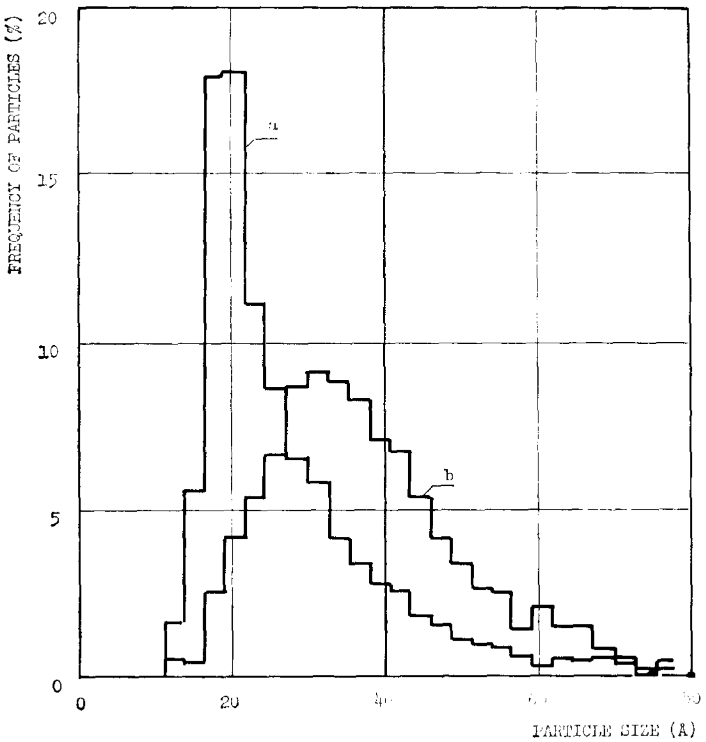

FIG. 6. Size-distribution of platinum crystallites in (a) unreduced and (b) reduced samples of 0.3% Pt on molecular sieve 5A.

titration experiments was in the range 2.3–3.9.

Chemisorption experiments carried out on Pt-zeolite material by Wilson and Hall (*13*) show good agreement with the present results. Wilson and Hall (*13*) have used a vacuum volumetric apparatus and measured adsorption isotherms on a material containing 0.5% Pt. At 25°C they obtained $H/Pt_{tot} = 0.14$. Chemisorption and titration with H_2 yielded H_2-chemis.:O_2-chemis.:H_2-titr. = 1.12:1.0:3.67.

In the last columns of Sect. 3 of Tables 2 and 3 are presented the theoretical ratios H/Pt_{tot} calculated on the basis of Benson and Boudart's (*14*) stoichiometry (the upper value) and Mears and Hansford's (*7*) stoichiometry (the lower value).

Chemisorption at Higher Temperatures

In Table 4 are presented results of H_2–O_2 titration measurements carried out at higher temperatures. Before every measurement, the samples were carefully reduced by pulses of H_2 at 485°C to reduce sintering. In the third column of Table 4 theoretical amounts of diatomic gas consumed are given assuming that 1 gas atom is chemisorbed on 1 platinum atom of a sample in which platinum is atomically dispersed. In the fourth column values of consumption of O_2 by SpAl-0.48 and 5A-0.3 are presented. The O/Pt_{tot} ratios given in the fifth column are values corrected for consumption of oxygen on the carrier. As the extent of the oxygen chemisorption on the two types of carriers was measured only at 485°C, an approximation that the same amount of oxygen would be consumed by the carriers at 300°C was made.

The high values of O/Pt_{tot} obtained for the Pt-on-alumina system are in good agreement with the findings published by

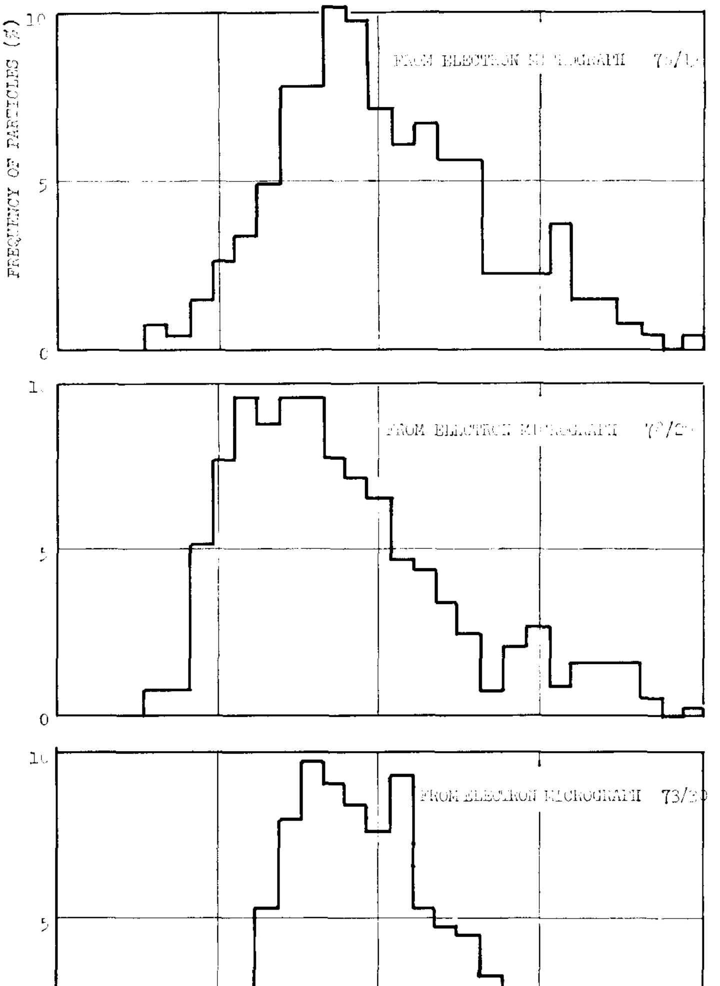

FIG. 7. Distribution curves of platinum particle size on a reduced sample 5A-0.3.

other workers (*3*, *12*, *27*). This phenomenon has not been found for chemisorption of oxygen at temperatures of 300°C and above for molecular sieve 5A supported platinum. For this system the O/Pt_{tot} ratio is lower than 1.

In the sixth column of Table 4 the amounts of H_2 consumed in the O_2-titration reaction are given. The consumption of H_2 by the alumina-supported platinum was only slightly higher than the consumption of oxygen by this material indicating that, at higher temperatures, a part of the retained oxygen penetrated the crystal lattice of platinum and therefore did not form water quantitatively with the hydrogen from the pulse. On the other hand, however, the difference in the consumption of hydrogen by this material at 300 and 485°C points to the possibility of some of the interstitially bonded oxygen still reacting to water, the extent of this reaction being higher at higher temperatures at which also more oxygen is consumed.

Before any desorption of H_2 at 485°C could occur, a new chemisorption cycle was started by injecting a pulse of oxygen. The results of such successive cycles are presented in Table 5, columns 7–12. It can be seen that, after saturation with the adsorbates in the first cycle, a lower consumption in further cycles was registered.

The newly published information on the effect of catalyst amount and the effect of pulse volume (*25*) takes up new aspects of the technique applied. It would be of interest in the future to investigate these phenomena along with the phenomenon of hydrogen spillover (*26*) on these and similar materials to complete the information obtained in the present and similar studies.

Size of Platinum Crystallites by Electron Microscopy

Unreduced material. The size of 2834 platinum crystallites registered on the electron micrograph (Fig. 5), was measured. The Pt crystallite distribution curve obtained is presented in Fig. 6.

Reduced material. The size of platinum crystallites was measured on electron micrographs of three different samples with an error of ±3.3%. The electron micrographs of the reduced catalyst contained 265, 365, and 376 crystallites. The respective distribution curves given in Fig. 7 show a good similarity, indicating that reliable information can be obtained from an electron micrograph containing about 300 crystallites. The net distribution curve, summarizing some 1005 Pt crystallites, is given in Fig. 6. In a similar study (*13*), a zeolite catalyst containing 0.5% of platinum was reported to posses a wide distribution of platinum crystallite size, of average 20–90 Å in diameter. Such a distribution is also representative of the distribution curve obtained in the present work on the reduced sample. The two distribution curves given in Fig. 6 differ widely: while most platinum crystallites (more than one third) in the unreduced sample are of about 18 Å in diameter, the pretreatment procedure causes an agglom-

TABLE 5

Comparison of the Results of Chemisorption with Electron Microscopic Investigations for 5A-0.3

Form of platinum on the support[a]	Cryst. size (Å)	Calcd surface of platinum (m^2/g sample)	Calc Pt_{surf}/Pt_{tot}	
Atomic dispersion (theoretical)	No cryst.	0.83	1	
Cube, 5 accessible faces	46	0.15	0.18	
Sphere (equal to half-sphere)	46	0.18	0.22	
		Measured values[b] (chemisorption)	H/Pt_{tot}	O/Pt_{tot}
		On all samples	0.11–0.20	0.12–0.23
		On this sample	0.16–0.18	0.15–0.2

[a] Results based on electron micrographs.

[b] Results based on chemisorption.

eration resulting in the diameter of platinum crystallites increasing to ca. 30 Å. On a percentage basis the distribution curves directly depict how the large number of small crystallites sinter in the pretreatment process to smaller number of large crystallites.

Based on the electron microscope investigations, the value of the mean surface diameter for the reduced sample was calculated to the 46 Å. From this value, calculation of the specific surface of platinum in the reduced sample has been made assuming the crystallites (a) to be cubes with five accessible faces and (b) to be spheres. The results are given in Table 5a. The ratio of surface platinum atoms to total number of platinum atoms was obtained as Pt_{surf}/Pt_{tot} = specific surface of platinum/specific surface of platinum at atomic dispersion. Comparison of the values of Pt_{surf}/Pt_{tot} obtained from electron microscopic investigations (Table 5a) with the results of the measurements of chemisorption of hydrogen and oxygen on the same sample (Table 5b), gives support for the stoichiometry of $H/Pt_{surf} = 1$ and $O/Pt_{surf} = 1$. The reduction procedure and the different period of treatment at 485°C for the different samples, resulting in a different degree of agglomeration of the platinum particles, is the probable reason for the wide spread of the chemisorption results as shown in the next to last line of Table 5.

The internal cavities of the cubooctahedral unit in the Linde 5A molecular sieve are 11 Å in diameter. Thus the platinum crystallites are of a size to fit in the largest cavities (Fig. 6). A pore distribution measurement of a reduced material 5A-0.3 has shown that no pores are of sizes larger than 25 Å. Thus, by the cation exchange procedure used in the present work, it is mainly the outer cations of the molecular sieve structure that have been exchanged by platinum. The large crystallites are present on the outer surface and in the cracks of the carrier structure.

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