

Studies of the Hydrogen Held by Solids. XIX. H₂ and O₂ Chemisorption on Silica-Supported Platinum

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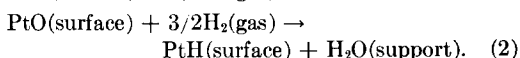
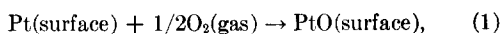
Hydrogen chemisorption, oxygen chemisorption and the titration of chemisorbed oxygen with H₂ were studied on two platinum supported on silica catalysts, viz., a preparation in which the Pt was reacted (base exchanged) onto the surface and one made by impregnation. The Pt particle size determinations were made from electron micrographs and from X-ray line broadening experiments following the chemisorption measurements on samples sintered in H₂ to various temperatures. With one notable exception, these data were in fair agreement with those calculated from the H₂-chemisorption data with the assumption that H/Pt (surface) = 1. With the impregnated catalysts, the ratios of H₂-chemisorption:O₂-chemisorption:H₂-titration changed from about 1.6:1:3.8 to about 1:1:3 as the particle size increased, reflecting a change in the stoichiometry of the chemisorptions. With the exchanged preparations, the ratios remained nearly constant on sintering to 770°, but the H/Pt (total) ratio decreased. Independent measurements of particle size showed that the crystals had not grown correspondingly in this case, thus suggesting that part of the Pt had become inaccessible to the gas.

INTRODUCTION

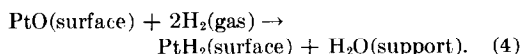
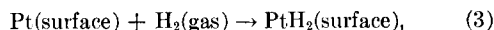
The selective chemisorption of gases such as H₂, O₂, and CO has been used for many years to estimate the surface areas of supported transition metals such as Pt, particularly when dispersed upon high area alumina (1-9), silica-alumina (6, 10) and silica gel (11-17). Recently, the question of the appropriate stoichiometry required to convert the chemisorption values into metal surface areas has stimulated renewed interest in this field (8, 9, 13-16, 18-20). In our previous work (18), this question was discussed in detail with reference to alumina as a support; the present paper deals with silica supports.

In 1965, Benson and Boudart (8) proposed the use of titration of chemisorbed oxygen with hydrogen, as a means of increasing the sensitivity of the direct hydrogen chemisorption measurements by a factor of three, this being particularly desirable when the platinum level was less than 1%. Their alumina-supported plati-

num catalyst appeared to conform to Eqs. (1) and (2):



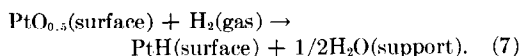
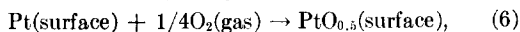
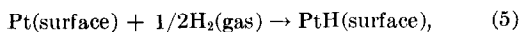
Mears and Hansford (9) repeated and extended this work to include silica-supported platinum. Their results, however, appeared to conform to the stoichiometries represented by Eqs. (1), (3), and (4).



Thus, the observed ratios of the intercepts of the linear isotherms obtained at 25°C were in the ratio H₂-chemisorption:O₂-chemisorption:H₂-titration = 2:1:4 as compared with the corresponding values of 1:1:3 inferred from the work of Benson and Boudart (8).

Recently, we (18) reported that the O₂-chemisorption did not properly reflect

changes in surface area of highly dispersed samples of Pt on alumina during sintering, and that for preparations where H/Pt (total) ≈ 1 , the following stoichiometry was appropriate:



This again led to the ratios of uptakes of 2:1:4. As the dispersion was decreased to H/Pt(total) < 0.6 by sintering in hydrogen, the ratios shifted until they corresponded to those observed by Benson and Boudart. The stoichiometry of Eq. (5) was shown to apply in both cases by the agreement between the platinum particle sizes calculated from the H/Pt (total) values by the method of Spenadel and Boudart (1) and those obtained by direct examination of the catalysts by electron microscopy. For catalysts having H/Pt (total) = 0.8 to 1.0, Eq. (5) predicts particle sizes of 8.5–10.6 Å [based on the cubic model (1)], whereas Eq. (3) requires particles of 16.9–21.1 Å. The values predicted by the cubooctahedron model are 7.5–11.5 and 22.5–30.0 Å, respectively (19, 20).

Similar confirmation has been reported by Benesi and co-workers (12, 13) and by Dorling, Burlace, and Moss (16) for silica-supported platinum. Moss and co-workers (14–16) have also applied a method of independent particle size determination to determine the stoichiometry of CO-chemisorption on Pt. However, neither group investigated the O₂-chemisorption or titration reactions represented by Eq. (1) and (2) or (4), respectively. The present work supplies this information. A dividend was the finding that the results were dependent upon the method of preparation of the catalyst.

Despite the accumulating evidence that metal surface areas and crystallite sizes can be estimated correctly by assuming that one H atom is chemisorbed *irreversibly* on each surface Pt atom, a number of perplexing problems remain. Similarly, although recent papers (21–24) have con-

tributed much to our understanding of these systems, they have raised new questions. Barbaux *et al.* (21) have confirmed the postulated *irreversible* chemisorption of one H per surface Pt below room temperature, but their data also suggested that a second H is adsorbed *reversibly* in 200 Torr of H₂. This view conforms to the findings of Pliskin and Eischens (25) who found two ir bands for the Pt–H vibrations, one of which was pressure dependent. Hausen and Gruber (22) studied the chemisorption at various temperatures by a chromatographic method and argued that the pressure-dependent part of their isotherms could not correspond to spill-over onto the support. When static adsorption measurements are made and extrapolated to zero pressure, as in our work, it has been supposed that the contribution of physical adsorption on the support is eliminated. Apparently, the contribution from the chemisorption of a second H per surface Pt is also removed. This is in agreement with the view that the Pt area can be measured from these data by assuming H/Pt (surface) = 1.

Hausen and Gruber (22) studied the adsorption between 60° and 510°, and observed that the reversible portion increased as the temperature was raised. Moreover, the amounts adsorbed at constant pressure decreased substantially with increasing temperature. The data thus indicated that an increasing part of the first H attached to Pt becomes reversibly adsorbed as the temperature is raised. If more than an atom monolayer can be adsorbed under one set of conditions and less than a monolayer under others, it may not be possible to define a set of conditions which will correspond exactly to a given stoichiometry under all circumstances. Thus, it is entirely fortuitous that the absolute magnitude of the adsorption at 120 Torr and 250° is about equal to the extrapolated intercept of the isotherm at room temperature, the one being used by the Russian workers (23) and the other herein. Moreover, probably neither is an exact measure of the atom monolayer. The present work confirms our earlier contention (18), however, that a good estimate of Pt-surface area can

usually be obtained by these methods if it is assumed that H/Pt (surface) is unity.

EXPERIMENTAL

Catalysts prepared by two different methods were used in this work. Those designated *ES* were made by the ion exchange technique described by Benesi (13), while those designated *IS* were made from a conventional impregnation using hexachloroplatinic acid. Numerals following the *IS* or *ES* designation indicate different samples taken from the same parent preparations. Physical properties of the catalysts are given in Table 1.

ES Catalyst

Preparation duplicated as nearly as possible that of Benesi *et al.* (13). The method involved reaction of the terminal hydroxyl groups of the silica with $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$. On reduction with H_2 , the resulting catalysts contained highly dispersed Pt (13). The ion-exchanged silica gel was filtered and oven dried overnight at 125°, and the dry catalyst contained 3.6% Pt. The same type of silica gel was employed as well as similar techniques. Moss and co-workers (16) used the preparation technique of Poltorak and Boronin (17), but similar catalysts probably resulted.

IS Catalyst

Preparation involved impregnation of 23 g silica gel (oven dried at 125°) to in-

ipient wetness with 30 cm³ of H_2PtCl_6 solution having the concentration required to give a 3% Pt catalyst. The catalyst was then oven dried at 125° overnight.

Pretreatment of Catalysts

Aliquots of the oven-dried catalyst were sealed into quartz reactor tubes and handled by conventional high-vacuum techniques. After evacuation for 0.5 hr at room temperature, a flow of purified H_2 (~100 ml/min) was passed while the temperature was raised to 100° at ~4°/min. The sample was held at 100° in flowing H_2 for 0.5 hr before the temperature was again raised to 250° where it was held for 0.5 hr. The temperature was then raised to the final value listed in Table 2 at ~3°/min, where it was held for 0.5–1 hr. The total reduction time was 4–6 hr. Except where noted, the samples were evacuated (10^{-5} – 10^{-6} Torr) for 1 hr at 500°.

Gases

Hydrogen (Baker-prepurified grade) used in isotherm determinations was diffused through a heated Pd thimble. When a flow of H_2 was required, further purification of cylinder hydrogen (Airco Electrolytic Grade, 99.95% purity) was effected by passage through MgClO_4 , and an activated charcoal trap thermostated at -196°. Helium (Airco, 99.995% purity) was similarly treated. Oxygen (Linde U.S.P., 99.5%

TABLE I
SURFACE AREAS AND PORE SIZE DATA FOR EXCHANGED AND IMPREGNATED CATALYSTS

Sample	Pretreatment in H_2		Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (Å)
	Temp. (°C)	Time (hr)			
Support	125 ^a	16	262	1.02	97
Support	530	1	267	1.03	99
Pt- <i>ES</i>	125 ^a	16	234	0.95	113
Pt- <i>ES-i</i>	500	0.5	246	0.96	107
Pt- <i>ES-ii</i>	460	0.5	246	0.97	96
Pt- <i>ES-iii</i>	556	0.5	246	0.95	97
Pt- <i>ES-iv</i>	770	1	234	0.97	97
Pt- <i>IS</i>	125 ^a	16	260	0.98	91
Pt- <i>IS-i</i>	500	0.5	261	0.97	91

^a Oven dried only.

TABLE 2
HYDROGEN CHEMISORPTION, OXYGEN CHEMISORPTION AND HYDROGEN TITRATION AS A FUNCTION OF PLATINUM PARTICLE SIZE

Catalyst	Pretreatment		Isotherm Intercepts (cm ³ (STP)/g)				Ratios of intercepts			Ratio	
	Red. temp. (°C)	Weight (g)				HT (calc) ^e				H/Pt (total)	O/Pt (total)
			HC	OC	HT		HC	OC	HT		
Pt-ES-ii ^a	460	2.568	1.994	1.168	4.494	4.330	1.71	1	3.85	0.97	0.56
Pt-ES-i	500	2.838	1.677	1.092	4.010	3.861	1.54	1	3.67	0.81	0.53
Pt-ES-iii	556	2.461	1.820	1.105 ^d	4.242	4.030	1.65	1	3.84	0.88	0.53
Pt-ES-iii	556	2.461	—	1.105 ^d	—	—	—	—	—	—	—
Pt-ES-iv	770	2.538	0.587	0.347	1.300	1.281	1.69	1	3.75	0.28	0.17
Pt-IS- <i>i</i> ^b	500	2.493	0.842	0.554	2.018	1.950	1.52	1	3.64	0.52	0.35
Pt-IS-ii	490	2.510	0.809	0.498	1.968	1.805	1.62	1	3.95	0.50	0.31
Pt-IS-ii	600	0.510	0.450	0.482	1.470	1.414	0.93	1	3.05	0.28	0.30
Pt-IS-ii	^c	0.716	0.022	—	—	—	—	—	—	0.003	—

^a Pt-ES = 3.6% Pt "ion exchanged" according to the method of Ref. (13).

^b Pt-IS = 2.8% Pt prepared by impregnation with H₂PtCl₆.

^c Portion of sample reduced at 600°C was calcined in air for 4 hr at 800°C and re-reduced for 4 hr at 470°. This treatment followed that of Ref. (14); it was used to provide a severely sintered sample with 100% of Pt visible to X-ray.

^d Sample evacuated 18 hr at 511°C.

^e HT (calc) = 2OC + HC.

minimum purity) was dried by passage through a trap thermostated at -78°.

Adsorption Measurements

The apparatus consisted of a conventional BET system. The chemisorptions were determined from the zero pressure intercepts of the isotherms, thus eliminating any reversible adsorption, particularly that on the support. The H₂- or O₂-chemisorption measurements were made at room temperature (23°) in this order, following evacuation at 500°. After the O₂-chemisorption, the sample was again evacuated for 1 hr (at room temperature), and an H₂ isotherm determined in which the remaining oxygen was titrated with the H₂. Equilibration of gases with most samples was complete within 10-15 min. The free spaces were determined with He.

Surface Area and Pore-Volume Determination

The total surface area was measured after the hydrogen, oxygen, and titration isotherms, using the BET method. Pore-

volume distributions were determined by the method of Ballou and Doolen (26).

Particle Size Determinations

Electron micrographs were made with a Philips EM-300 instrument, using a biological stage which permitted resolution to about 5 Å. Particle size distributions were determined using a Zeiss TGZ-3 analyzer. Procedures and specimen preparation were the same as outlined earlier (18) for alumina-supported platinum. It was found, however, that the silica support was much more susceptible to sintering in the beam, than alumina. Consequently, exposure times and electron beam energy were minimized. X-Ray diffraction patterns were obtained utilizing CuK radiation with a Picker diffractometer fitted with a nickel filter and a gas proportional counter detector. The average platinum crystallite size, *d*, was determined from the width of the (111) reflection, following Moss (15). This method should approximate the size of a particle containing the average number of Pt atoms.

RESULTS AND DISCUSSION

"Ion-Exchanged" (ES) Catalyst

The 23° isotherms were all linear and typical of those in the literature (9, 12, 18). Their intercepts at $p = 0$ are listed in Table 2 along with the ratios of hydrogen chemisorption (HC), oxygen chemisorption (OC) and hydrogen titration (HT). The isotherm ratios HC:OC:HT were approximately constant at 1.6:1:3.8 for samples treated in hydrogen at 460, 500, 556, and 770°. These ratios approximate the 2.09:1:4.04 reported by Mears and Hansford (9) for 0.93% Pt on silica gel reduced at 500°. If Eq. (5) is applicable, the stoichiometry of the O₂-chemisorption is evidently approximated by Eq. (6).

The high dispersion indicated by the H/Pt (total) values of 0.8–1.0 for samples reduced at 460, 500, and 556° were comparable with those reported by Benesi *et al.* (13) and by Poltorak and Boronin (17). It may be inferred from the arguments developed in our previous publication (18) that the constancy of the HC:OC:HT ratios, even after treatment at 770° in H₂, is indicative of nearly constant average platinum particle size. This was confirmed by independent measurement. X-Ray and electron micrograph techniques showed that the average size of the metal particles

did not increase very much on heating to 770° (Table 3). The diffractometer tracings were similar to those reported by Benesi (13) for his ion exchanged catalyst; they were indicative of Pt particles of approximately 10–15 Å. The particle size distributions shown in Fig. 1 support the X-ray results. However, the absolute hydrogen chemisorption of the sample reduced at 770° [H/Pt (total) = 0.28] indicated an average crystallite size of about 30 Å. Therefore, some of the Pt must have become unavailable for H₂-chemisorption during the treatment at 770°. This was the only case in which we have found the particle size calculated from chemisorption of H₂ [assuming Eq. (5)] much larger than that determined by physical measurements, and this may be related to the breakdown of the silica support. Benesi (13) speculated, from results of sintering experiments with both exchanged and impregnated catalysts, that the loss of Pt area occurred by occlusion of the Pt during the 20% collapse of the silica structure near 800°, rather than by actual growth of the metal crystallites. As shown in Table 1, however, the silica structure did not undergo gross changes on heating. Hence, the encapsulation must be superficial. The formation of a metal surface silicate, resulting in a "silica skin" was proposed by Schuit and

TABLE 3
SUMMARY OF CRYSTALLITE SIZE AND AREA MEASUREMENTS^a

Catalyst	Red. temp. (°C)	H/Pt (Total)	Crystallite size (Å)			Metal Area (m ² /g)	
			H(ads)	X-Ray	Micrograph ^b	H(ads)	Micrograph ^c
Pt-ES-ii	460	0.97	9	<10	—	267.	—
Pt-ES-i	500	0.81	10	<10	14	223.	159
Pt-ES-iii	556	0.88	10	10	—	242.	—
Pt-ES-iv	770	0.28	30	15	16	77.	150
Pt-IS-i	500	0.52	16	27 ^e	21	144.	106
Pt-IS-ii	490	0.50	17	—	—	138.	—
Pt-IS-ii	600	0.28	30	32 ^f	26	77.	88
Pt-IS-ii	600 ^d	0.003	326	336	—	0.8	—

^a Footnotes to Table 2 apply here.

^b Cubic particles assumed; half the surface area stems from crystals this size or smaller.

^c Areas integrated over distributions shown in Fig. 1. Area of five exposed faces counted.

^d After calcining in air at 800°; see footnote (c), Table 2.

^e 40% of Pt was detected assuming 100% for last entry.

^f 27% of Pt was detected assuming 100% for last entry.

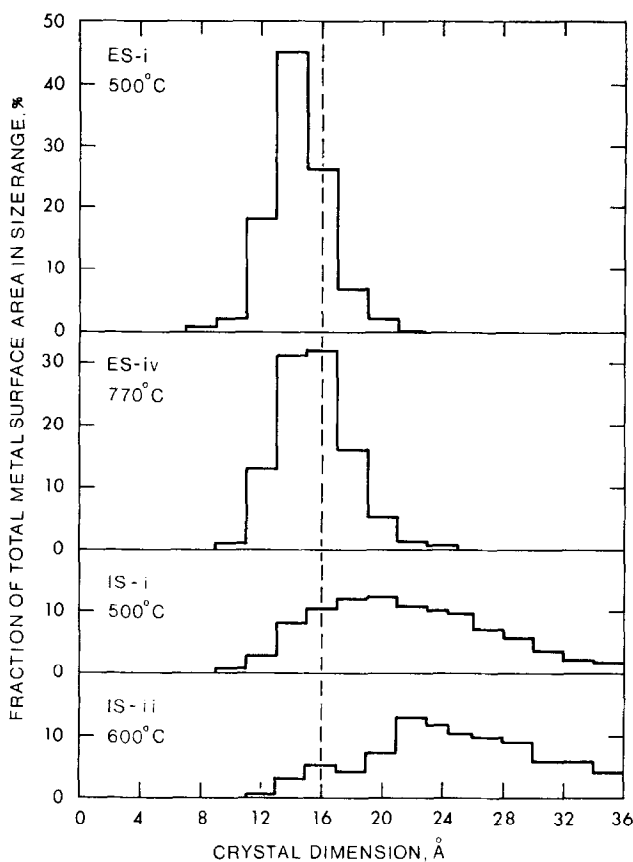


FIG. 1. Particle size distribution for platinum supported on silica catalysts.

van Reijen (27) to explain the inaccessibility to chemisorbing gas of a portion of the metal in a Ni-silica catalyst.

The particle size distributions for the *ES* series were relatively narrow (Fig. 1). Under these circumstances, fairly good agreement between metal areas determined by H_2 -chemisorption and those determined by integrating over the particle size distribution might be expected. Reference to Table 3 shows, however, that agreement was much poorer for these catalysts than for either the impregnated samples or the alumina-supported catalysts studied earlier. We have already explained why the chemisorption area for the catalyst pretreated at 770° is low. The opposite result for the catalyst pretreated at 500° suggests that a portion of the Pt atoms are dispersed in clusters of sizes below the resolving power

of the microscope, but we have no convincing evidence that this is so.

Impregnated (IS) Catalysts

The isotherm-intercept ratios obtained using the impregnated samples *IS-i* and *IS-ii* reduced at 500° and 490° , respectively, were in reasonable agreement with those obtained with the ion-exchanged catalysts *ES-i*, *ES-ii*, and *ES-iii* (Table 2). The dispersion of Pt in these catalysts was, however, considerably poorer than that observed with the *ES* series. Values of H/Pt (total) ~ 0.5 rather than ~ 0.9 were obtained, and the independent measurements indicated much larger average crystallite sizes. This is much more apparent from the distributions shown in Fig. 1 than from the averages given in Table 3. These data

confirm the results of Benesi (13) and of Moss (16).

The response of this catalyst to heat treatment in H_2 was similar to that previously reported by us for alumina-supported platinum catalysts (18) prepared by impregnation of H_2PtCl_6 . Thus, in contrast with the ion-exchanged silica catalysts, the HC:OC:HT ratio shifted to 0.93:1:3.05 when the reduction temperature of the *IS-ii* sample was increased to 600°, and the Pt particle size calculated from the X-ray line broadening data was in reasonably good agreement with the sizes calculated from hydrogen chemisorption, assuming H/Pt (surface) = 1.

With neither series of catalysts did the ratios approach closely the 2:1:4 values found for alumina-supported Pt (9, 18). With a single exception, neither did they approach the 1:1:3 ratios of Benson and Boudart (18). Rather, except for the last entry of Table 2, they approximated those in the transition region (18) where it may be supposed a bimodal distribution exists of particles obeying Eqs. (1) and (6), respectively. Qualitative support for this view is found in the data for the *IS*-series. Both the H/Pt and O/Pt ratios and the absolute values of the specific chemisorptions of Pt-*IS-i* (500°) and Pt-*IS-ii* (490°) were in fair agreement. Moreover, when the reduction temperature was raised to 600°, the O_2 -chemisorption (or O/Pt) did not change significantly, but the H_2 -chemisorption (or H/Pt) fell to half its initial value. It should be easy, therefore, to determine whether the change in the HC:OC:HT ratios reflects a change in the stoichiometry of the H_2 - or the O_2 -chemisorption by assessing which properly measures the corresponding change in Pt surface area. Reference to Fig. 1 shows qualitatively that the Pt crystal size underwent substantial growth during the sintering to 600°C. We infer from this that the H_2 -chemisorption is properly measuring the Pt surface area (77 vs 88 m^2/g) and, in variance with the work of Charcosset *et al.* (28), that it is the O_2 -chemisorption which is changing in stoichiometry. Unfortunately, this conclusion was not veri-

fied by the quantitative calculations of Table 3. Percentage-wise, the decrease in metal surface area derived from the micrographs was not nearly as large as that expected from the H_2 -chemisorption. The discrepancy can be traced directly to the low value (106 m^2/g) derived from the micrograph for Pt-*IS-i*.

Another interesting feature of the data was the ratios (1.6:1:4) found for Pt-*IS-ii* pretreated at 490°, for which H/Pt (total) was 0.50. With alumina as the support, the ratios generally approximated 1:1:3 when the average particle size was so large that only half of the Pt atoms were exposed. An exception was found in our work [first entry of Table 2 of Ref. (18); 1.6:1:3.6 for H/Pt (total) = 0.50], and one was reported by Mears and Hansford [Catalyst J, Table 2 of Ref. (9); 2:1:4 for H/Pt (total) of 0.51]. These anomalies suggest that factors other than crystallite size may be involved in controlling the stoichiometry of chemisorption. These may include differences in the type of particle size distribution or the distribution of crystal faces exposed; these in turn may reflect the influence of the support, the sequence of pretreatment steps and the method of preparation.

At the time of our previous writing (18), we were aware of three instances where H/Pt (total) ratios greater than unity had been reported. These were reinvestigated and it was concluded that none could be taken as convincing evidence that a surface Pt atom chemisorbs more than one H atom under the conditions used in the experiments. More recent data (23, 24, 30) have reopened this question. It is always easy to suppose that a ratio in excess of unity stems either from formation of H_2O by reaction of H_2 with sources of oxygen in the system or from spill over onto the support. Such effects would be magnified at the lowest Pt loadings. This was precisely what was found by the Russian workers (23), who reported ratios approaching two as the loading approached zero. They suggested, however, that isolated Pt atoms became predominant at low Pt levels and that each such atom chemisorbed two H atoms. This

interpretation may be correct; it has likewise been offered to explain high initial uptakes with zeolites containing Pt^{2+} base-exchange cations (18, 29, 30). Nevertheless, these high uptakes invariably occur when the adsorption temperature is in the range 200–300°, and are frequently found to be rate controlled (18, 30), suggesting a reaction with the support. Consequently, it is our opinion that such results should be viewed with suspicion until they have been checked and verified by other techniques.

CONCLUSIONS

The work of Benesi *et al.* (12, 13) has been confirmed for a similar catalyst. It was shown that the platinum particle sizes calculated by the method of Spenadel and Boudart (1) are substantiated by X-ray line broadening or electron microscopy data, thus demonstrating the stoichiometry of Eq. (5). The same conclusion was reached by Dorling, Burlace, and Moss (16) for ion-exchanged platinum-silica catalysts prepared by the method of Poltorak and Boronin (17) and for impregnated platinum-silica catalysts. Their approach involved the combination of X-ray diffraction and electron microscopy in such a way that the number of surface Pt atoms in the catalyst could be calculated. This value was then combined with the observed hydrogen chemisorption (obtained at 1 Torr) to yield H/Pt (surface) values close to unity for catalysts in which the Pt dispersion varied widely. The stoichiometry of Eq. (5) for platinum supported on silica seems, therefore, to be well established.

It was also demonstrated, as with alumina-supported platinum, that the titration method is complicated by variable stoichiometry, expressed by Eqs. (1)–(6). Apparently care should also be exercised when interpreting hydrogen chemisorption data on samples of platinum-silica prepared by ion exchange and treated at high temperature.

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REFERENCES

1. SPENADEL, L., AND BOUDART, M., *J. Phys. Chem.* **64**, 204 (1960).
2. ADLER, S. F., AND KEAVNEY, J. J., *J. Phys. Chem.* **64**, 208 (1960).
3. MILLS, G. A., WELLER, S., AND CORNELIUS, E. B., *Acies Congr. Int. Catal.*, **2nd**, 1960 **2**, 2221 (1961).
4. HERRMANN, R. A., ADLER, S. F., GOLDSTEIN, M. S., AND DEBAUN, R. M., *J. Phys. Chem.* **65**, 2189 (1961).
5. GRUBER, H. L., *J. Phys. Chem.* **66**, 48 (1962).
6. HUGHES, T. R., HOUSTON, R. J., AND SIEG, R. P., *Ind. Eng. Chem. Process Des. Develop.* **1**, 96 (1962).
7. HALL, W. K., AND LUTINSKI, F. E., *J. Catal.* **2**, 518 (1963).
8. BENSON, J. F., AND BOUDART, M., *J. Catal.* **4**, 704 (1965).
9. MEARS, D. E., AND HANSFORD, R. C., *J. Catal.* **9**, 125 (1967).
10. ROCA, F. F., DEMOURGUES, L., AND TRAMBOUZE, Y., *J. Gas Chromatogr.* **6**, 161 (1968).
11. BOBESKOV, G. K., AND KARNAUKHOV, A. P., *Zh. Fiz. Khim.* **26**, 1814 (1952).
12. ADAMS, C. R., BENESI, H. A., CURTIS, R. M., AND MEISENHEIMER, R. G., *J. Catal.* **1**, 336 (1962).
13. BENESI, H. A., CURTIS, R. M., AND STUDER, H. P., *J. Catal.* **10**, 328 (1968).
14. DORLING, T. A., AND MOSS, R. L., *J. Catal.* **5**, 111 (1966).
15. DORLING, T. A., AND MOSS, R. L., *J. Catal.* **7**, 378 (1967).
16. DORLING, T. A., BURLACE, C. J., AND MOSS, R. L., *J. Catal.* **12**, 207 (1968).
17. POLTORAK, O. M., AND BORONIN, V. S., *Russ. J. Phys. Chem.* **39**, 1476, 2491 (1965); *ibid.* **40**, 2671 (1966).
18. WILSON, G. R., AND HALL, W. K., *J. Catal.* **17**, 190 (1970).
19. VAN HARDEVELD, R., AND VAN MONTFOORT, A., *Surface Sci.* **4**, 396 (1966).
20. BOND, G. C., *Int. Congr. Catal. 4th Moscow*, Prepr. 67 (1968).
21. BARBAUX, Y., ROGER, B., BEAUFILS, J. P., AND GERMAIN, J. E., *J. Chim. Phys. Physicochim. Biol.* **67**, 1035 (1970).
22. HAUSEN, A., AND GRUBER, H. L., *J. Catal.* **20**, 97 (1971).
23. ZAIMAN, N. M., DZIS'KO, V. A., KARNAUKHOV,

- A. P., KRASILENKO, N. P., KOROLEVA, N. G., AND VISHNYAKOVA, G. P., *Kinet. Katal.* **9**, 863 (1968); *ibid.* **10**, 652 (1969); BUYANOVA, N. E., IBRAGIMOVA, N. B., AND KARNAUKHOV, A. P., *ibid.* **10**, 397 (1969).
24. GIORDANO, N., AND MORETTI, E., *J. Catal.* **18**, 228 (1970).
25. PLISKIN, W. A., AND EISCHENS, R. P., *Z. Phys. Chem.* (Frankfurt am Main) **24**, 11 (1960).
26. BALLOU, E. V., AND DOOLEN, O. K., *Anal. Chem.* **32**, 532 (1960).
27. SCHUIT, G. C. A., AND VAN REIJEN, L. L., *Advan. Catal.* **10**, 242 (1958).
28. CHARCOSSET, H., BARTHOMEUF, D., NICOLOVA, R., REVILLON, A., TOURNAYAN, L., AND TRAMBOUZE, Y., *Bull. Soc. Chim. Fr.* **1967**, 4555.
29. RABO, J. A., SCHOMAKER, V., AND PICKERT, P. E., *Proc. Int. Congr. Catal. 3rd. (Amsterdam) 1964* **2**, 1264 (1965).
30. WELLER, S. W., AND MONTAGNA, A. A., *J. Catal.* **20**, 394 (1971).