JOURNAL OF CATALYSIS 4, 704–710 (1965)

Hydrogen–Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas

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Received March 23, 1965; revised April 12, 1965

The reaction of hydrogen at room temperature with oxygen adsorbed on supported and unsupported platinum catalysts has been used to measure the surface area of the metal. The new method has distinct advantages over that of carbon monoxide adsorption, but the two methods are in essential agreement.

INTRODUCTION

The dispersion of platinum on different supports has been studied repeatedly (*1–12*). Because of the extremely high dispersion found in the case of platinum supported on alumina, the usual physical techniques are not satisfactory, at least for freshly prepared commercial catalysts containing small amounts of metal. However, the selective chemisorption of gases, principally hydrogen and carbon monoxide, provides a measure of the exposed metal surface area. There is general agreement concerning some particularly important points revealed in these studies.

First, for freshly prepared platinum-alumina catalysts with platinum contents in the range of those used industrially and which have not been subjected to severe heat treatment, it appears that a large fraction of the total platinum is available for chemisorption. This does not imply complete dispersion of the metal, since the methods of measurement are not necessarily capable of discriminating between separated individual atoms and continuous monolayer "islands" on the surface of the support. However, in regard to this point, several workers (*2, 7, 12*) have inferred that the platinum is not truly atomically dispersed; for example, as pointed out by Spenadel and Boudart (*2*), it would be difficult to account for the rapid uptake of one hydrogen atom per platinum atom in the sample if a considerable portion of the platinum exists as discrete atoms capable of adsorbing only one hydrogen atom each.

Second, after use under industrial conditions or after excessive heating in various atmospheres or in vacuum, the extent of gas adsorption decreases. This decrease in accessible platinum surface area is accompanied by the appearance in X-ray investigations of platinum diffraction patterns which are not observable with fresh catalysts (*6*). In the limit of rather severe crystal growth, satisfactory agreement is obtained between mean metal particle sizes as calculated from gas adsorption and from X-ray diffraction line-broadening (*2, 9*). Thus it appears that the loss of platinum surface area is due primarily to the growth of platinum crystallites on the surface of the support at the expense of the more finely divided metal.

Although there is qualitative agreement between the data of gas adsorption and the dispersion of platinum in fresh and sintered platinum-alumina catalysts, quantitative agreement in the case of catalysts with low platinum content and of sintered catalysts

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with low surface area is subject to interpretation. The inadequacy of adsorption measurements in such cases lies in the relatively large correction due to adsorption on the support itself. There is therefore a need for a more sensitive method for determining the dispersion in such catalysts in order that smaller surface areas of platinum may be determined with precision and in order that more subtle changes in the dispersion of the platinum may be followed.

In an independent study of the reaction of hydrogen at room temperature with oxidized platinum-alumina catalysts (*13*), it became apparent that a technique based on this reaction might provide a simple and accurate method for the determination of the metal surface area of these catalysts. A careful study, reported here, confirmed these expectations. In retrospect, the success of the technique seems evident in view of the volumetric measurements of Gruber (*7*), who performed the hydrogen–oxygen reaction on platinum-alumina at high temperature, and the work of Aston *et al.* (*14*), who followed calorimetrically a titration of oxygen adsorbed on platinum black by means of hydrogen. These workers interpreted their results in terms of the following reaction:

$$\mathrm{PtO(surface)} + 3/2\ \mathrm{H_2(g)} \rightarrow \mathrm{PtH(surface)} + \mathrm{H_2O(g)} \quad (1)$$

We reasoned that in the case of platinum-alumina the alumina should scavenge the water formed in the reaction and that one should therefore be able to measure the loss of three hydrogen atoms from the gas phase for every surface platinum atom with a consequent increase of sensitivity of measurement of threefold over hydrogen chemisorption and of at least 50% over carbon monoxide chemisorption. Furthermore, the adsorption of hydrogen on the oxidized alumina should contribute a very small amount to the total uptake of hydrogen, and consequently the blank should be small. Finally, since the method relies on the room temperature reaction of oxygen adsorbed on the platinum, the careful preparation of the platinum surface necessary in the hydrogen and carbon monoxide chemisorption methods could be avoided, and the method should be simple and convenient.

EXPERIMENTAL

The apparatus was a conventional gas volumetric system in the modification of Krieger (*15*), with the exception that adsorption bulbs with thermocouple wells and a capillary exhaust line and stopcock were used for those catalysts which were reduced *in situ* before measurement. The gas burette of six bulbs with a total volume of 300 ml was jacketed with water. Auxiliary equipment consisted of a mercury diffusion pump backed by a mechanical pump and isolated from the adsorption apparatus by a liquid nitrogen trap. The adsorbents were protected from mercury vapor by means of a small trap filled with gold powder and were held in place by a minimum amount of Pyrex glass wool which had been boiled in concentrated nitric acid to remove oils.

The adsorbents used in the investigation were from three sources. Platinum black from Engelhard Industries, Inc., stated to be 100% pure, was used as received. A series of platinum-alumina catalysts supplied by California Research Corporation were prepared by impregnation of η alumina from Davison Chemical Company with four different concentrations of aqueous chloroplatinic acid; the catalysts contained 0.10%, 0.35%, 1.0%, and 3.5% platinum by weight and were supplied and used in the form of coarse granules. These catalysts, along with a sample of the η alumina, had been dried at 120°C for 4 hr, calcined in air at 450°C for 3 hr, reduced in hydrogen at 2 liters/hr for 1 hr at 260°C and then for 4 hr at 510°C and then exposed to the air. Eta alumina and three catalysts containing 0.05%, 0.30%, and 1.96% platinum by weight were obtained from Esso Research and Engineering Company. The η alumina was prepared from β alumina trihydrate obtained from Davison Chemical Company by calcining in air for 4 hr at 595°C. The nitrogen BET specific surface area of the resulting η alumina was 200 m^2/g. The η alumina powder was impregnated with aqueous chloroplatinic acid solutions of the proper strength to give the desired platinum concentrations and then calcined in air at 593°C for 4 hr. The catalysts were obtained in the form of unreduced pellets which were ground in a clean mortar and then sieved. Samples which had passed a 100-mesh screen were used in the work reported here. All of the catalysts were weighed before and after use, but the weight of the used, dry catalyst was the basis of the calculations.

Carbon monoxide adsorption data were taken on the η alumina and the supported catalysts after a 2-hr reduction in hydrogen at 500°C. These measurements were made in the laboratories of the California Research Corporation by the procedure described by Hughes, Houston, and Sieg (*8*).

Electrolytic hydrogen from The Matheson Company was purified by passage through a Milton Roy Company palladium thimble purifier. Extra-dry oxygen from The Matheson Company was dried further by passage through a Dry Ice-acetone trap. Matheson helium was used for dead space determinations after passage through a liquid nitrogen trap; the dead space was always determined at the end of an experiment to minimize contamination of the surfaces with traces of oils.

Samples of 5 to 20 g of the Esso catalysts were outgassed *in situ* for 30 min at room temperature and 3 hr at 150°C; hydrogen at 75 ml/min was then started through the samples and the temperature raised to 500°C. Reduction was carried out for 12 hr at this temperature, following which the samples were outgassed at 500°C for 1 hr and cooled to room temperature while pumping. Oxygen was admitted to the samples at room temperature and roughly 1 atm and allowed to contact the samples for 1 hr. After pumping out the oxygen for 1 hr, the hydrogen uptake was measured over a pressure range at room temperature. In all the experiments performed on these highly reduced catalysts the isotherms were linear, and after correction for the small adsorption on the support they were quite flat. Individual points were reproducible with a precision of about ±0.2 μmole/g after the small slow uptake of hydrogen had occurred. Equilibrium was rapidly established; a waiting time of about 45 min was required for the first point, after which 5 or 10 min was more than sufficient.

Samples of 5 to 12 g of the California Research catalysts were outgassed *in situ* for 1 hr at room temperature and for 1 hr at 125°C before the hydrogen uptake was measured at room temperature. Since these catalysts were undoubtedly only partially reduced, a standardized procedure was adopted to determine the uptake: The hydrogen pressure was set at about 500 Torr and the net uptake, corrected by a previously determined isotherm on the η alumina alone, was determined at the end of 1 hr. It was observed that these catalysts exhibited a protracted uptake of hydrogen which became more pronounced as the platinum content increased, but the drift amounted to less than 5% of the uptake after 1 hr.

The treatments of the platinum black varied with the particular experiment and are described in detail in the next section.

RESULTS AND DISCUSSION

Platinum Black

Because of disagreement in the literature on the degree of oxidation of platinum when exposed to oxygen or air (*4, 7, 14, 16*), we measured the uptake of oxygen on a 6-g sample of platinum black of known surface area. After evacuation at room temperature for 30 min and at 125°C for 30 min, the surface of the platinum was cleaned by treatment with excess hydrogen at room temperature for 12 hr and then at 125°C for 30 min. After outgassing, the oxygen uptake of the clean, sintered surface was measured at room temperature. The isotherm was completely flat over a pressure range of 100 to 650 Torr and showed negligible drift after 1 hr. The uptake was 296 μatoms O/g. Following this the sample was outgassed and the BET nitrogen (16.3 Å^2) surface area was found to be 13.4 m^2/g. Using 8.4 Å^2/site (an average of the site densities of the 100, 110, and 111 planes) the surface site density is thus 266 μmoles of sites/g. The O/Pt ratio is therefore 1.1.

The small discrepancy from unity is probably due to uncertainty as to what crystal planes are exposed. Thus, using the 100-plane site density of 7.7 Å^2/site gives an O/Pt ratio of unity. Also, a small amount of sintering may occur during the oxidation (*16*), which would make the BET surface area low. We conclude, in agreement with Aston *et al.* (*14*), that the platinum surface is completely oxidized to PtO under the conditions used in this study. This conclusion is supported by Weidenbach and Fürst, whose paper (*17*), brought to our attention during the preparation of this paper, reports a flow method based on the hydrogen-oxygen reaction on clay-supported platinum; their assumed stoichiometry of the reaction seems, however, to be in error.

The stoichiometry of the titration proposed by Gruber (*7*) and Aston (*14*) and shown in Eq. (1) was verified in another experiment in which 17 g of platinum black, interspersed with 4 g of η-alumina pellets for which the hydrogen and oxygen uptakes were known (see Fig. 1), were subjected to alternate treatment with hydrogen and oxygen. After cleaning the surface with hydrogen as described above, the platinum took up 95 μmoles O_2/g; after outgassing, this oxidized surface reacted with 245 μmoles H_2/g and was badly sintered in the process. After removal of the hydrogen left on the surface by outgassing, the clean, sintered surface took up 40 μmoles H_2/g. Assuming that 40 μmoles H_2/g were present on the surface at the end of the first treatment with hydrogen, 205 μmoles H_2/g thus reacted with 95 μmoles O_2/g. We therefore conclude that in the titration two hydrogen atoms react with each surface oxygen atom (and hence for each surface platinum atom), and a hydrogen atom is left on each surface platinum atom.

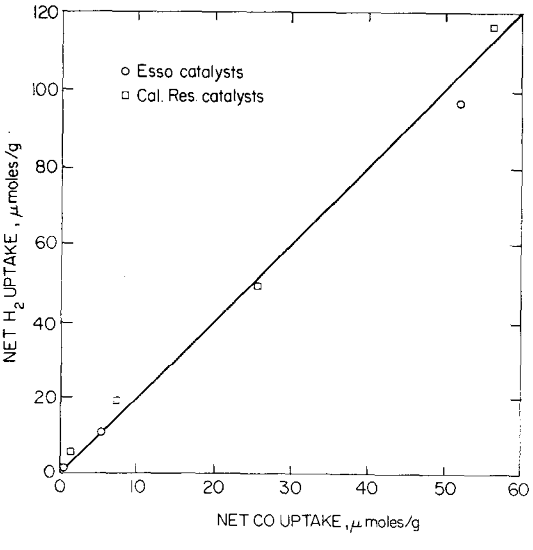

FIG. 1. Room temperature uptakes of hydrogen and oxygen.

Supported Catalysts

With supported catalysts, which will resist sintering during the titration, there should therefore be three hydrogen atoms taken up for each oxidized surface platinum atom if platinum-alumina behaves like platinum black. Although direct measurement of the oxygen uptake on supported catalysts is difficult because of the large oxygen blank on the support, we checked the stoichiometry of the reaction on the Esso 1.96% Pt catalyst. Reduced and outgassed in the usual way, this catalyst took up, after correction for adsorption on the support, 30 μmoles O_2/g and in turn 97 μmoles H_2/g; the ratio H_2/O_2 is 3.2, in good agreement with the ideas presented in the introduction to this paper and with the results of Gruber (*7*), who measured a ratio of 2.9 under different conditions. Because of this result, we believe that the conclusions reached in the experiments on platinum black are applicable to alumina-supported platinum.

The results obtained over a range of pressure at room temperature on the two supports and on the Esso catalysts are presented in Fig. 1. Since the hydrogen isotherms on the Esso catalysts are closely parallel to those for the Esso η alumina, it is apparent that one does not really need to know the adsorption of hydrogen on the support; it is sufficient to measure the uptake over a range of pressures and extrapolate to zero pressure to get the blank-free net uptake. *The method described here therefore can be used for catalysts for which the platinum-free support is not*

TABLE 1

Summary of Hydrogen and Carbon Monoxide Data[a]

Catalyst	(1) Total H_2 uptake	(2) Net H_2 uptake	(3) Total CO uptake	(4) Net CO uptake	(5) Net H_2/ net CO ratio
Esso η alumina	—	0.0	3.3	—	—
Esso 0.05% Pt	—	1.6	4.1	0.8	2.0
Esso 0.30% Pt	—	10.2	8.7	5.4	1.9
Esso 1.96% Pt	—	97.0	57.0	53.7	1.8
Cal. Res. η alumina	—	0.0	3.8	—	—
Cal. Res. 0.10% Pt	6.1 (460 Torr)	5.4	5.2	1.4	3.8
Cal. Res. 0.35% Pt	20.5 (600 Torr)	19.5	10.7	6.9	2.8
Cal. Res. 1.0% Pt	49.8 (500 Torr)	49.0	29.3	25.5	1.9
Cal. Res. 3.5% Pt	118 (650 Torr)	117	59.7	55.9	2.1

[a] All uptakes are in μmoles/g.

available. Adsorption of both hydrogen and oxygen on the two supports clearly obeys Henry's Law. It should be noted that the oxygen blank on the Esso support is about five times that of hydrogen; probably alumina adsorption sites which are produced during the high-temperature reduction and outgassing are covered by oxygen during the oxidation of the platinum and thus do not adsorb hydrogen at room temperature.

In Fig. 1 the squared points for the 0.30% Pt catalyst were obtained by outgassing the titrated catalyst for 20 min and repeating the oxidation and titration steps. The reproducibility is very good and suggested that one could perform the titration directly on a reduced (or even on a partially reduced) catalyst which had been exposed to air. To test this idea, this short and convenient procedure was followed with the California Research catalysts.

From Fig. 1 the net hydrogen uptakes for the Esso catalysts given in column 2 of Table 1 were obtained by extrapolation to zero pressure. Column 1 gives the total uptake and the gas pressure at the end of 1 hr at room temperature for the California Research catalysts; these values were corrected for adsorption on the support with the aid of the alumina blank in Fig. 1, and the net uptake values given in column 2 were thus obtained. Table 1 also lists the total and net CO uptake for the various catalysts, measured in the laboratories of the California Research Corporation.

By means of Fig. 1 one may estimate the blank corrections for the hydrogen method at any pressure for the Esso catalysts. In Table 2 are the total uptakes and the blank corrections at an arbitrarily chosen pressure of 200 Torr for the hydrogen data and the corresponding blank corrections for the CO data, obtained from columns 3 and 4 of Table 1. The considerable improvement over CO adsorption is evident. At low platinum content the very large blank for CO adsorption makes this method very difficult to use as a careful measure of the platinum surface area. In the case of the hydrogen titration, one can work on catalysts of much lower platinum content, and even in the case of the 0.05% Pt catalyst, one obtains a net adsorption (1.6 μmoles/g) which is twice the blank correction at 200 Torr. Measuring the hydrogen uptakes at low pressure, where the adsorption on the support would be negligible, should allow one to extend the method to very low concentrations of platinum.

TABLE 2

Comparison of H_2 and CO Blank Corrections

Catalyst	Total H_2 uptake at 200 Torr (μmole/g)	Blank correction (% of total uptake) for	
		H_2	CO
Esso η alumina	0.7	—	—
Esso 0.05% Pt	2.3	30	80
Esso 0.30% Pt	11.1	6.3	38
Esso 1.96% Pt	97.9	0.7	5.9

The values of the ratios of net hydrogen to net carbon monoxide uptake given in column 5 of Table 1 are very interesting. In the limit of relatively large concentrations of platinum, this ratio is quite constant at about 2, and this suggests that the two methods parallel each other. At low concentrations of platinum the blank correction for CO on the support becomes prohibitively high, and an error in measurement of this blank would affect the ratio of H_2/CO strongly. Since the hydrogen blank on the Esso support is higher than on the California Research support (Fig. 1), whereas the CO blanks are in the reverse order (Table 1), it is likely that the CO uptakes for the 0.10% Pt and 0.35% Pt catalysts have been overcorrected in the determination of the net CO adsorption. In view of the obvious problems associated with the CO measurements at low platinum concentrations, it is a credit to the method that it is still able to give reasonable values for the net adsorption.

Since three hydrogen atoms react for each surface platinum atom, one would of course expect the ratio of net H_2 to net CO to be 1.5, that is, three hydrogen atoms for each CO, if one CO is adsorbed for each surface platinum atom. However, Gruber (7) has shown that for high platinum dispersions less than one CO is adsorbed for each surface platinum. His data indicate that for the catalysts studied by us a value of about 0.75 CO/surface platinum is reasonable; this value is also suggested by the H_2/CO ratios reported in Table 1. In any event the hydrogen titration method does not seem to have the ambiguity of the CO adsorption method.

The data in columns 2 and 4 of Table 1 have been plotted in Fig. 2, a correlation of the hydrogen and carbon monoxide data. Over a seventy-fold change in platinum concentration the two methods compare favorably. It is in fact gratifying that the correlation holds for both the highly reduced Esso catalysts and the partially reduced California Research catalysts.

It must be noted that the data in Table 1

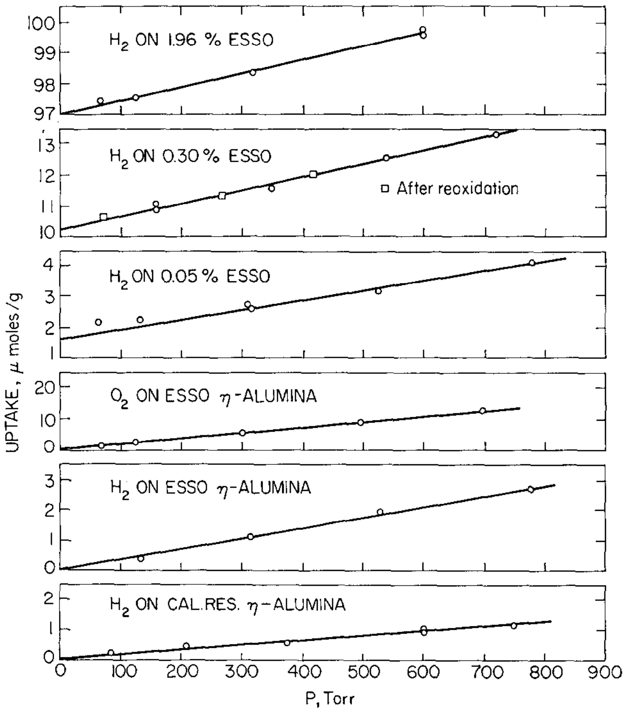

FIG. 2. Correlation of hydrogen and carbon monoxide data.

can be translated into platinum surface areas. This translation, which rests on assumptions that have been discussed elsewhere (*2*), was not carried out here since it adds nothing to the demonstration of the feasibility of Aston's titration technique in the case of supported catalysts.

CONCLUSIONS

The measurement of the platinum surface area on supported catalysts can conveniently be carried out volumetrically by the room-temperature titration of oxygen adsorbed on the metal with gaseous hydrogen. While this had already been demonstrated calorimetrically by Aston and coworkers (*14*) for bulk platinum and more recently by Gruber (*7*) and Weidenbach and Fürst (*17*) on supported catalysts under different conditions from those used here, our work shows that the volumetric titration can be performed with platinum supported on alumina, which absorbs the water formed. Since three hydrogen atoms are consumed for each accessible platinum atom, there is a threefold increase in sensitivity over direct hydrogen chemisorption and more than a 50% increase over carbon monoxide chemisorption. Because the sample is deliberately exposed to oxygen, there is no need to exclude oxygen from the sample, and the sample need not be completely reduced prior to measurement. *Because of the small blank on the alumina support, the present method offers a distinct advantage* over conventional adsorption techniques with hydrogen and carbon monoxide on prereduced samples. The advantages appear decisive in the case of samples containing small amounts of platinum. Although the carbon monoxide adsorption and the hydrogen titration methods are in essential agreement, the titration method is subject to less interpretation.

ACKNOWLEDGMENTS

We are greatly indebted to Drs. Hughes, Houston, and Sieg, at California Research Corporation, for their splendid collaboration which gave a decisive impetus to this investigation. Partial financial support by the National Science Foundation (GP-2305) is gratefully acknowledged. Our thanks are also due Esso Research and Engineering Company for a gift of the experimental catalysts used in this work. One of us (J.E.B.) gratefully acknowledges a National Science Foundation Science Faculty Fellowship, during the tenure of which this work was done.

REFERENCES

1. BORESKOV, G. K., AND KARNAUKHOV, A. P., *Zh. Fiz. Khim.* **26,** 1814 (1952).

2. SPENADEL, L., AND BOUDART, M., *J. Phys. Chem.* **64,** 204 (1960).

3. ADLER, S. F., AND KEAVNEY, J. J., *J. Phys. Chem.* **64,** 208 (1960).

4. MILLS, G. A., WELLER, S., AND CORNELIUS, E. B., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2,** 2221 (Editions Technip, Paris, 1961).

5. SOMORJAI, G. A., "Small-Angle X-ray Study of Metallized Catalysts," dissertation, Univ. of California, Berkeley, 1960.

6. ADLER, S. F., HERMANN, R. A., GOLDSTEIN, M. S., AND DEBAUN, R. M., *J. Phys. Chem.* **65,** 2189 (1961).

7. GRUBER, H. L., *J. Phys. Chem.* **66,** 48 (1962).

8. HUGHES, T. R., HOUSTON, R. J., AND SIEG, R. P., *Ind. Eng. Chem. Process Design Develop.* **1,** 96 (1962).

9. ADAMS, C. R., BENESI, H. A., CURTIS, R. M., AND MEISENHEIMER, R. G., *J. Catalysis* **1,** 336 (1962).

10. DEBYE, P., AND CHU, B., *J. Phys. Chem.* **66,** 1021 (1962).

11. CHU, B., *J. Phys. Chem.* **67,** 1916 (1963).

12. HALL, W. K., AND LUTINSKI, F. E., *J. Catalysis* **2,** 518 (1963).

13. KOHN, H. W., AND BOUDART, M., *Science* **145,** 149 (1964).

14. CHON, H., FISHER, R. A., TOMESZKO, E., AND ASTON, J. G., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **1,** 217 (Editions Technip, Paris, 1961).

15. KRIEGER, K. A., *Ind. Eng. Chem.* (*Anal. Ed.*) **16,** 398 (1944).

16. BRENNAN, D., HAYWARD, D. O., AND TRAPNELL, B. M. W., *Proc. Roy. Soc.* (*London*) **A256,** 81 (1960).

17. WEIDENBACH, G., AND FÜRST, H., *Chem. Tech.* (*Berlin*) **15,** 589 (1963).