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On the Slow Uptake of Hydrogen by Platinized Carbon

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The net slow uptake of hydrogen by platinized carbon is decreased drastically or suppressed altogether when the carbon contaminant on the platinum surface is burned off prior to the adsorption measurements. Contamination of the metal by carbon seems to provide bridges permitting surface diffusion of hydrogen atoms from platinum to the carbon support. A convenient manostat is described for use in adsorption and kinetic studies at constant pressure.

INTRODUCTION

A number of recent studies in chemisorption and catalysis have stressed the importance of a phenomenon called spillover (*1*) which has been particularly well demonstrated in the case of hydrogen. The phenomenon consists in the dissociative adsorption of hydrogen on a metal, say platinum, with subsequent surface diffusion of adsorbed hydrogen atoms across the interface between platinum and some other material e.g., carbon (*2*), tungsten trioxide (*3*), silicagel or alumina (*4*). The material invaded by the adsorbed atomic hydrogen coming from the metal is in each instance incapable of adsorbing sizable amounts of molecular hydrogen directly under the conditions of the experiment.

A case studied in considerable detail is that of platinum supported on Spheron-6 (Pt/C). A kinetic study of hydrogen adsorption on Pt/C led Robell *et al.* (*2*) to propose a model shown on Fig. 1a. Although the phenomenon of spillover was clearly established in this investigation, a quantitative fit of the kinetic curves by diffusion equations based on the proposed model could be achieved only at the price of an unverified assumption. What had to be assumed for a Pt/C sample with 0.2 wt % Pt was that the number of sources of surface hydrogen atoms was $3.2 \cdot 10^{17}\ g^{-1}$, whereas the number of platinum particles calculated from their average size determined by X-ray line broadenig was only $2.8 \cdot 10^{14}\ g^{-1}$. As no way could be found to resolve this difficulty and still provide a quantitative fit of the kinetic data, it was postulated that the diffusional sources of hydrogen atoms on the equilibrated carbon zones shown on Fig. 1a consisted of very small platinum particles, too small to be detected by X-rays.

More recently, the Pt/C samples used in this study of spillover were used as catalysts in the isomerization and hydrogenolysis of neopentane (*5*). It was found that, as a result of their pretreatment, these catalysts had a platinum surface contaminated with carbon. When these Pt/C samples were treated cautiously in oxygen, the subsequent catalytic activity for the reactions of neopentane was found to increase one hundredfold without any change in selectivity (*6*). It was concluded that contamination of the platinum surface by carbon was removed by the treatment in oxygen. These observations made it very desirable to reinvestigate hydrogen adsorption on Pt/C samples and to reexamine the quantitative conclusions of Robell *et al.* In particular, it was felt necessary to study hy-

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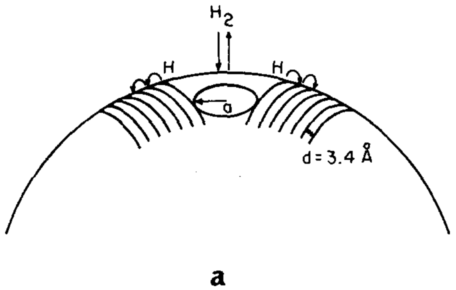

FIG. 1a. Spillover of adsorbed atomic hydrogen from a very small particle of platinum, across an equilibrated zone of radius a, consisting of a basal graphitic plane, into edge sites of the carbon lattice.

drogen chemisorption on Pt/C samples both before and after oxygen clean-up of the platinum surface. This paper presents the results of such a study.

EXPERIMENTAL

A sample containing 1 wt % Pt on Spheron-6 was prepared as described earlier (*2*). Hydrogen was diffused through a commercial palladium purifier. Oxygen (99.5%, Liquid Carbonics) was passed through a liquid nitrogen cold trap. Samples were contained in a quartz adsorption cell used in the earlier study (*2*).

The gas volumetric system has been described (*7*) and was adapted to a constant pressure system similar to that of Robell *et al.* (*2*). A photo-electric cell and light source were used in lieu of tungsten probes to detect changes of pressure, which produced fluctuations in the mercury manometer. The cell and source were enclosed in black cardboard cylinders and placed on a sliding frame about the manometer. This sensing device eliminated glass-to-metal seals and easily allowed selection of the desired pressure. Aberration was reduced by shining the light through a small pinhole in the end of the cylinder. This provided very sensitive control (±0.2 torr). The control system is pictured in Fig. 2.

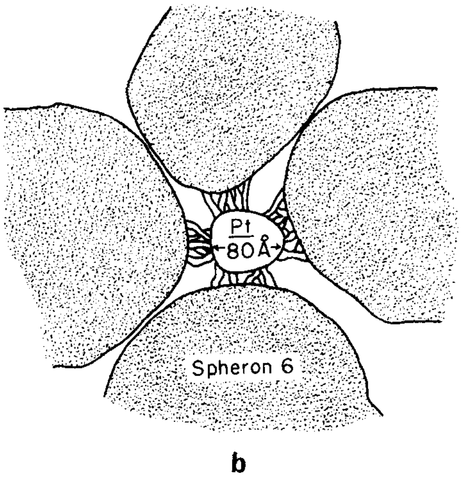

FIG. 1b. Spillover of adsorbed atomic hydrogen from a platinum surface contaminated with carbon in the form of small particles and bridges to neighboring Spheron-6 particles.

Light striking the cell as the mercury level dropped actuated a relay which opened a Hoke solenoid valve. This allowed compressed air to pass through a Hoke needle valve into a two-liter surge tank and thence into the mercury reservoir of the pressure-control burette. A vacuum release was connected to the surge tank. The movement of the mercury in the control burette was governed by adjustment of the micrometer needle valve, the compressed air pressure, and the orifice size of the glass tube extending into the mercury reservoir. A circuit diagram of the relay incorporating the photoelectric cell is shown in Fig. 3.

The pretreatment employed in the earlier work (*2*, *8*), designated pretreatment A, consisted of reduction of the sample at 500°C for 5 hr in flowing hydrogen, evacuation at 500°C and continued evacuation at 900°C for 16 hr.

Another pretreatment used in this study (pretreatment B) consisted of reduction as in pretreatment A, evacuation, exposure to 160 Torr oxygen at 350°C for 15 min, evacuation at 350°C, heating from 350 to 900°C in flowing hydrogen, continued heating in hydrogen at 900°C for 16 hr (run 2) or 3 hr (run 3), then 3 hr evacuation at 900°C.

A third mode of pretreatment (C) consisted in reduction as in pretreatment A, exposure to oxygen as in pretreatment B, evacuation, exposure to hydrogen for 30 min, followed by a 16 hr evacuation at 350°C.

All measurements of hydrogen uptake were conducted at 350°C and 600 torr. The

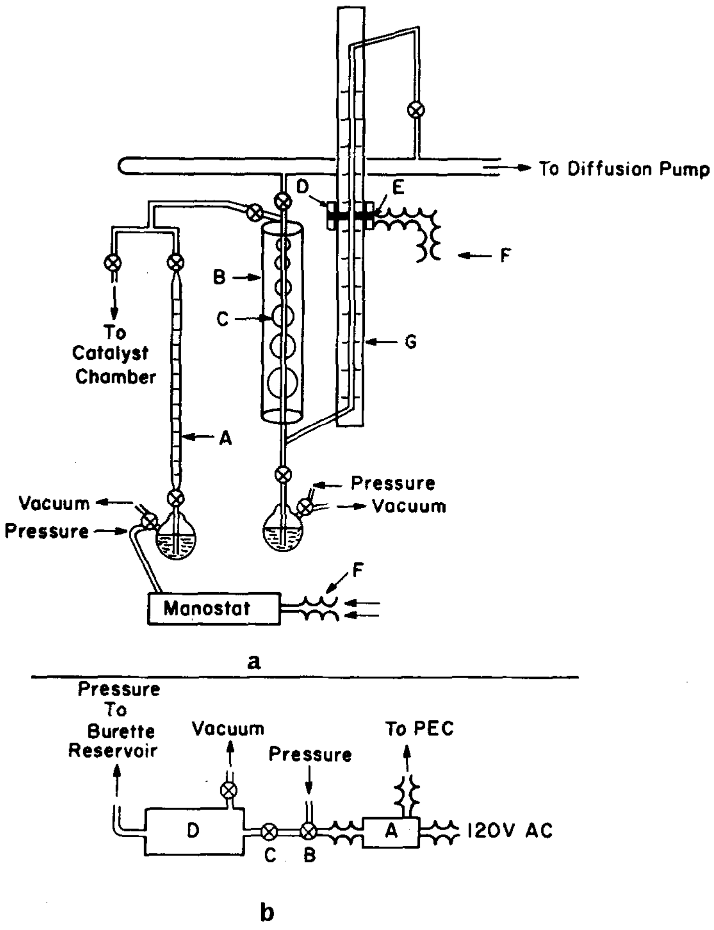

FIG. 2a. Gas Adsorption Apparatus: Constant Pressure Device A. Graduated burette, B. Water jacket, C. Gas burettes, D. Light source, E. Photoelectric cell (PEC), F. Electrical leads from PEC to manostat, G. Manometer.

FIG. 2b. Manostat components: A. Relay, B. Solenoid switch, C. Hoke micrometer valve, D. Surge tank.

net uptake was determined as in Ref. (*2*) by subtracting from the measured value the corresponding value obtained separately in the earlier work on unplatinized Spheron 6.

To determine the surface-weighted mean particle size of platinum, $\bar{l}_s$, a hydrogen titration technique was used as described earlier (*7*). To obtain the volume-weighted average dimension of the metal particles, l_v, measurements of X-ray line broadening were obtained with a General Electric XRD-5 unit. To study the distribution of particle size and compare the average particle size obtained from the distribution to $\bar{l}_s$ and $\bar{l}_v$, electron micrographs were taken with a Philips electron microscope. All these measurements of platinum particle size were performed on a sample of Pt/C from the same origin as that used in the present work.

RESULTS

Net hydrogen uptakes are shown in Fig. 4. The data of Ref. (*2*) and our present data (run 1) obtained on a similar sample after the same kind of pretreatment can be seen to be in satisfactory agreement. The agreement is even better than indicated on Fig. 4 if it is kept in mind that uptakes of hydrogen by a given Pt/C sample have been found to decrease somewhat with re-

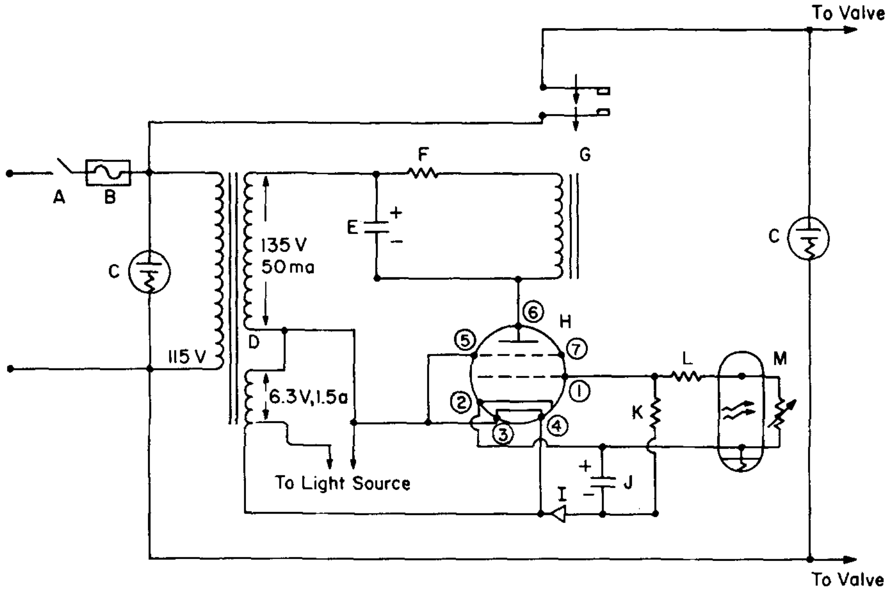

Fig. 3. Circuit Diagram for Manostat
A: On-off switch, 115V line
B: Fuse, 8a–32V
C: Pilot lights
D: Transformer triad, 115V/135V, 50 mA/6.3V, 1.5A
E: Capacitor, 4/8 μfd, 200V working (6408)
F: Resistor, 10KΩ (RN 80 B)
G: Solenoid switch
H: Vacuum tube (2D21)
I: Transistor (INH 61)
J: Capacitor, 100 μfd (GS 13 A)
K: Resistor, 1 Megohm
L: Resistor, 100KΩ (RN 70 B)
M: Photoelectric cell (PEC), 10V working

peated use of that sample, the change amounting to about 0.1 cc (*8*).

Following pretreatment B, uptakes were greatly diminished as shown in runs 2 and 3. But following pretreatment C, net uptakes became negligible within experimental error (run 4).

The dispersion of the metal was found to be 12%. This corresponds to an average particle size of 83 Å for a sample which yielded a particle size equal to 80 Å from X-ray line-broadening and a distribution of particle sizes from electron micrographs as shown on Fig. 5. From this distribution, values of $\bar{l}_s = 70$ Å and $\bar{l}_v = 78$ Å can be calculated, in good agreement between each other and with the titration and X-ray results, respectively.

Discussion

With the good agreement between four different values of average size of platinum catalysts, all in the vicinity of 80 Å, it is now clear that the distribution of sizes is quite narrow and that there are very few particles less than 20 Å in diameter. Consequently, the assumption made in the earlier work concerning the existence of a very large number ($3.2 \cdot 10^{17}$ g^{-1}) of very small crystals of platinum, is untenable. Rather, the number of platinum particles per g must be about 10^{15}.

How then can we explain the results of the preceding work, fully confirmed in this investigation (run 1). We must account for a net amount of approximately 75 μmole of

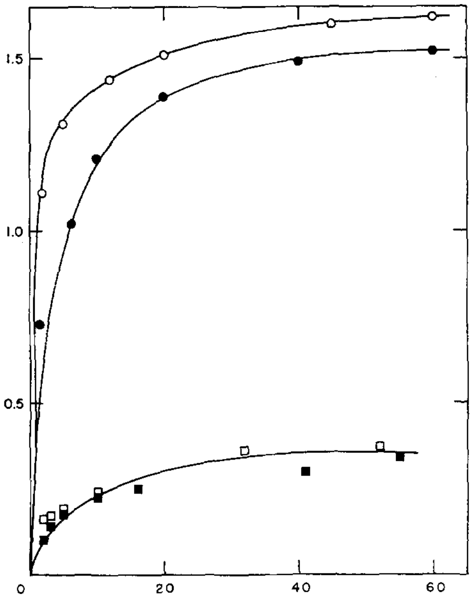

FIG. 4. Net hydrogen uptake (350°C, 600 Torr) in NTP cc/g as a function of time in min:
○ from (*2*), Fig. 5
● Run 1, pretreatment A
☐ Run 2, pretreatment B
■ Run 3, pretreatment B

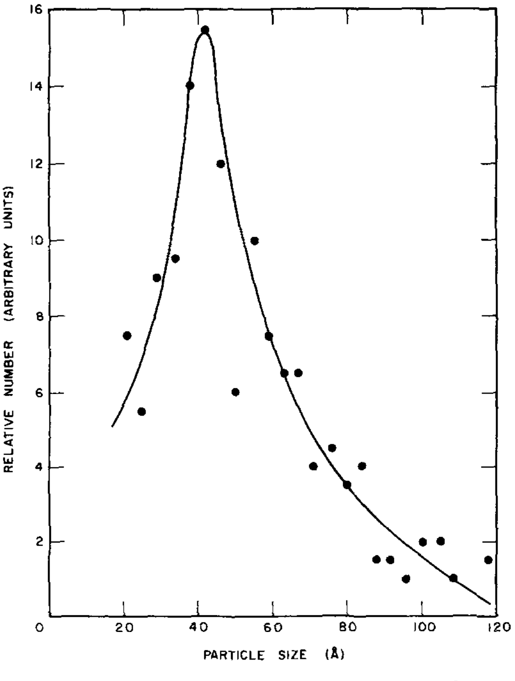

FIG. 5. Particle size distribution (radius, Å) for Pt/C sample from electron micrographs.

hydrogen taken up after 1 hr on a 1 g sample, the platinum part of which could adsorb only about 1 μmole at the temperature and pressure of the run; the carbon part of which has already been subtracted from the stated amount and is very small in any event in the absence of platinum.

The explanation by surface diffusion of adsorbed hydrogen atoms from platinum to carbon as proposed in the previous work must remain valid but the model shown in Fig. 1a must be modified so as to eliminate the need for the large number of small platinum crystallites.

A simple modification is suggested by the present knowledge that samples pretreated as in the previous work (pretreatment A, run 1) are heavily contaminated with carbon.

How can this contamination occur? It is known that a carbon surface, after exposure to oxygen, contains a large quantity of oxygenated groups that are evolved, largely as carbon monoxide, upon evacuation at higher temperatures, especially between 600 and 800°C (*9*). It is likely then that, in vacuo, CO can disproportionate, with platinum acting as a catalyst, to carbon and CO_2 in this temperature range. Contamination by carbon could then be decreased by heating up the sample through the dangerous temperature range not *in vacuo* but in hydrogen, with reduction of CO to CH_4 catalyzed by platinum in the critical range instead of disproportionation.

Runs 2 and 3 show the result of such a procedure. A Pt/C sample, after treatment in oxygen to remove any carbon contamination, was brought up to 900°C *in flowing hydrogen.* If somehow contamination is linked to slow uptake of hydrogen, then these runs show that contamination has been cut down considerably by pretreatment B. Thus, in this case, *more* contamination means *more* adsorption and not less as normally expected.

If hydrogen uptakes and contamination are linked, it then follows that pretreatment B, although diminishing the amount of contamination, has not succeeded in eliminating it altogether. Pretreatment C was used in the hope of removing carbon completely. This attempt was indeed successful when hydrogen uptake is measured on a sample that is evacuated at temperatures not higher than 350°C following reduction and oxygen treatment, the results of run 4 are obtained. No net hydrogen uptake can be detected. It may be objected that the lack of measurable uptake of hydrogen is due to the inadequate cleaning of the carbon surface by evacuation at too low temperatures. If this were so, the results of run 4 would simply reinforce the views that the large uptakes recorded in run 1 are due to hydrogen spilling over from platinum to a properly cleaned carbon surface.

The model shown on Fig. 1b attempts to explain all observations reported here and in the previous work. It shows how a sample of Pt/C after pretreatment A would be contaminated by carbon. This carbon would cover part of the platinum surface and provide bridges to transport hydrogen atoms across from the platinum surface to the neighboring particles of Spheron 6. The number of these bridges serving as diffusion sources as in the older model of Fig. 1a can be quite large and the objection to the interpretation based on Fig 1a is thereby removed. In fact, all details of the interpretation proposed earlier and the attempt to calculate a diffusion coefficient for hydrogen on carbon may still hold with the new model although the carbon contamination now indicates that the system under investigation is unfortunately much more complex than believed earlier.

In particular, as bridges are prevented from forming (runs 2 and 3), the slow uptake by hydrogen decreases considerably in spite of the fact that the ultimate conditions of evacuation at 900°C are the same as those leading to the large uptake values of run 1. It must also be stressed that hydrogen uptakes such as those of run 1 are far too large to be explained away by adsorption on the bridges alone.

CONCLUSION

Spillover is an interesting phenomenon that can lead to new and interesting catalytic effects (*1*). In the case of Pt/C, it is now appreciated that contamination of the surface by carbon plays a decisive role in providing bridges for hydrogen atoms to be transported away from platinum to the carbon support itself. The necessity for such bridges may be a general requirement for spillover to be important. The role of water in the Pt/WO_3 system may be, in part, to provide such bridges (*3*).

ACKNOWLEDGMENTS

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REFERENCES

1. Boudart, M., Vannice, M. A., and Benson, J. E., *Z. Physik. Chem. N. F.* **64,** 171 (1969).
2. Robell, A. J., Ballou, E. V., and Boudart, M., *J. Phys. Chem.* **68,** 2748 (1964).
3. Benson, J. E., Kohn, H. W., and Boudart, M., *J. Catal.* **5,** 307 (1966).
4. Sinfelt, J. H., and Lucchesi, P. J., *J. Amer. Chem. Soc.* **85,** 3365 (1965).
5. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11,** 35 (1968).
6. Aldag, A. W., Ph.D. Dissertation, Stanford University, Stanford, California 1968.
7. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 704 (1965).
8. Robell, A. J., Ph.D. Dissertation, University of California, Berkeley, California (1964).
9. Anderson, R. B., and Emmett, P. H., *J. Phys. Chem.* **56,** 753 (1952).