

chem. Ber. Bunsenges. Physik. Chem. **60**, 838 (1956).

8. ELEY, D. D., AND INOKUCHI, H., *Z. Elektrochem. Ber. Bunsenges. Physik. Chem.* **63**, 29 (1959).

9. KONDOW, T., MORI, Y., AND INOKUCHI, H. Private communication.

H. INOKUCHI
N. WAKAYAMA
T. HIROOKA

*The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo, Japan*

Received June 26, 1967

Thermal Titration of Platinum Black and the Initial Heat of Adsorption for Hydrogen

Chon *et al.* (1) reported a method for preparing a platinum black surface by thermal titration of the adsorbed oxygen monolayer with gaseous hydrogen. In that paper and others (2, 3, 4), there are reported different values for the initial heat of adsorption for hydrogen and there are disagreements on the shape of the heat of adsorption curve at low coverage. In this note, data are reported which show that thermal titration does indeed provide a clean and reproducible surface and that the initial heat of adsorption of hydrogen on platinum black at 280°K is 17.5 ± 0.2 kcal/mole H_2 .

These data were obtained using a calorimeter similar to that used by Greyson and Aston (5) except that the adiabatic shields and the heat exchanger were automatically controlled. The automatic shield controls allowed convenient observation of temperature changes of the sample for 8–10 hr and longer until temperature equilibrium was established. The system for handling and measuring the amount of gas introduced into the calorimeter was similar to that previously described (6). The volumetric and manometric equipment were calibrated.

Both hydrogen and oxygen gases used contained less than 10 ppm of impurities. These gases in addition were transferred to the glass supply bulbs from the high-pressure steel cylinder sources through liquid nitrogen cold traps. In the case of hydrogen the cold trap contained activated charcoal.

The platinum black, obtained from Engelhard Industries, Newark, N.J., was cleaned by initially outgassing at 470°K to a final pressure $<10^{-5}$ mm Hg, then titrating with hydrogen at 280°K. The water formed was removed from the sample by desorbing into a liquid helium cold trap and weighed. As the hydrogen added approached the amount of oxygen in the monolayer (calculated from BET surface area and crystallographic site density), the volume of the hydrogen increments was reduced and the water formed was removed after prolonged pumping by the cold trap. From the material balance, the excess hydrogen was removed as water by back-titrating with gaseous oxygen.

A small amount of helium ($<10^{-2}$ mm Hg) was introduced into the calorimeter to facilitate heat conduction within the sample and to minimize sintering from localized high temperatures. After cleaning the platinum black by the above process, two series of measurements were made with the surface of the platinum partially covered with known amounts of oxygen. In the first series, the oxygen coverage, θ_{PtO} , was 0.160 and in the second series θ_{PtO} was 0.050 (designated \blacktriangle and \blacksquare , respectively, in Fig. 1). Figure 1 should be interpreted as follows: the curve to the left side of center ordinate, $\theta = 0$ represents the reaction $H_2 + Pt-O_{(ads)} \rightarrow Pt(H_2O)_{ads}$ while the curve on the right side of center ordinate represents $H_2 + 2Pt \rightarrow 2Pt-H_{ads}$. In each series of measurements, the hydro-

gen equivalent to the adsorbed oxygen was first added in small increments and the apparent heat of adsorption measured for each increment. The heat of adsorption of hydrogen was then determined at various increments of hydrogen up to $\theta = 0.2$. In each case, all of the water corresponding to the known amounts of oxygen and hydrogen used was recovered.

no sharp decrease in the plot at low hydrogen coverages on the nickel film. A value for the heat of adsorption close to the above value may be obtained by an extrapolation to zero coverage of the relatively flat portion (θ values between about 0.2 and 0.6) of the heat curve given in an earlier publication (1) on calorimetric heat of adsorption experiments. The experi-

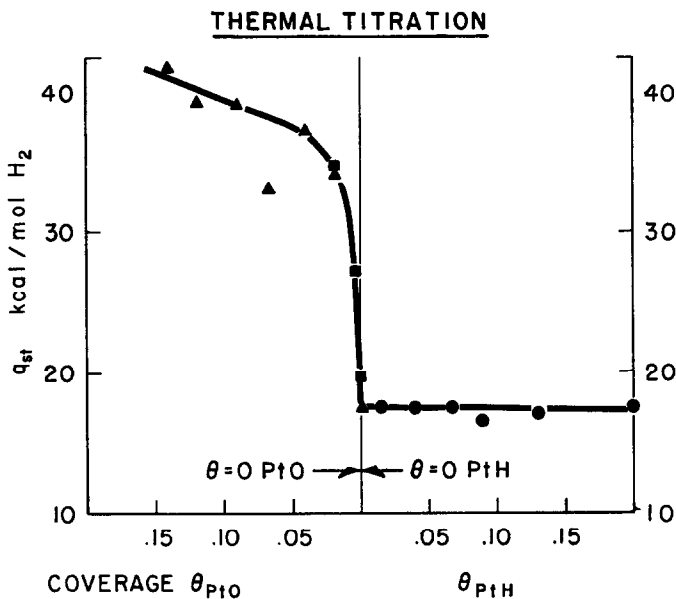


FIG. 1. Partial molar heats of adsorption at 280°K of hydrogen on platinum black partially covered with oxygen and on platinum black freed of oxygen and water:

$$q_{st} = 22\,414 (C_{cal} + C_{ag} + C_{fg}) \frac{\Delta T}{\Delta V} + V_{cal} \frac{\Delta P}{\Delta V}$$

in which; T is temperature; p , pressure; ΔV , volume of gas adsorbed in cc STP; C_{cal} , heat capacity of the calorimeter plus adsorbent; C_{ag} , heat capacity of adsorbed gas; C_{fg} , heat capacity of free gas in calorimeter free space V_{cal} . θ is the amount of gaseous species (oxygen or hydrogen) adsorbed relative to the amount required to form a monolayer based on BET surface area.

The heat of adsorption for hydrogen on the clean surface is shown in the figure to be 17.5 ± 0.2 kcal/mole H_2 (73.2 ± 0.8 kJ/mole H_2). There is no sharp decrease in the heats of adsorption with increasing coverage which is usually the case with reported heat of adsorption data for a number of gases on various metals (1, 7). The adsorption of hydrogen on nickel film has been reported (8) and these results show similar behavior of the heat of adsorption versus coverage to our data, i.e.,

ments herein reported support the validity of this type of extrapolation and show that on a clean surface the values of the heat of adsorption at low coverage have no sharp decrease.

REFERENCES

1. CHON, H., FISHER, R. A., AND ASTON, J. G., *J. Am. Chem. Soc.* **82**, 1055 (1960).
2. TAYLOR, G. B., KISTIAKOWSKY, G. B., AND PERRY, J. H., *J. Phys. Chem.* **34**, 799 (1930).

3. MAXTED, E. B., AND HASSID, N. J., *J. Chem. Soc.* p. 3313 (1931).
4. KWAN, T., *J. Res. Inst. Catalysis (Hokkaido)* **1**, 81 (1949).
5. GREYSON, J., AND ASTON, J. G., *J. Phys. Chem.* **61**, 610 (1957).
6. ASTON, J. G., TOMESKO, E. S. J., AND FISHER, R. A., *J. Am. Chem. Soc.* **86**, 2097 (1964).
7. BOND, G. C., "Catalysis by Metals," p. 57. Academic Press, London, 1962.
8. BROCKER, F. J., AND WEDLER, G., *Discussions Faraday Soc.* **41**, 87 (1966).

EDWARD S. J. TOMESKO*
GEORGE T. FURUKAWA

National Bureau of Standards
Washington, D. C.
Received May 23, 1967

* Now with ARCO Chemical Company, Division of Atlantic Richfield Company, 500 S. Ridgeway Avenue, Glenolden, Pennsylvania 19036, to whom inquiries should be sent. NBS-NRC Research Associate 1962-1964.

The Retention of Hydrogen by Supported Metal Catalysts

There are many reports extant of the use of flow systems and microcatalytic reactors for the study of the hydrogenation of unsaturated hydrocarbons (1, 2, 3). In most of these studies helium has been used as the carrier gas, and the normal procedure has been to reduce the catalyst in hydrogen at an elevated temperature ($\geq 200^\circ\text{C}$), followed by treatment in a stream of helium at the reduction temperature. The object of the latter is presumably to remove adsorbed hydrogen from the catalyst surface (2).

Using alumina-supported palladium, rhodium, and platinum catalysts and a microcatalytic reactor technique, we have investigated the extent to which hydrogen is retained in a reactive form after treatment of the catalyst in helium: this has formed part of a program of investigation of the adsorption, retention, and self-hydrogenation of hydrocarbons on supported metal catalysts. The procedure which we adopted was (i) reduction of the catalyst in a stream of hydrogen at 200°C for 1 hr, (ii) flowing helium over the catalyst at 200°C for a minimum of 1 hr (longer times did not make any significant difference to the subsequent behavior), and finally (iii) cooling the catalyst in a stream of helium to the required temperature. Following this treatment, 0.5 ml (NTP) volumes of ethylene or higher olefins were

injected into the helium gas stream immediately above the catalyst and the eluant from the reactor was monitored by gas chromatography. Two types of behavior were observed: (i) a fraction of the olefin was irreversibly adsorbed on the catalyst and (ii) the eluant gas contained saturated hydrocarbon. With both rhodium and palladium catalysts, the only hydrocarbon eluted following the first injection of ethylene was ethane. Several injections were necessary before ethylene was the sole product. With platinum, the ethane yield from the first injection was substantially less than with either rhodium or palladium.

To investigate further the mode of ethane production, i.e., whether by self-hydrogenation of ethylene—a common phenomenon on metal catalysts (4)—or by reaction with surface hydrogen not removed in the helium pretreatment, experiments were carried out with tritiated hydrogen. The catalysts were reduced as described previously and were then treated with helium at 200°C for various times as shown in Table 1. Two milliliters of tritiated hydrogen (total activity $20 \mu\text{c} = 1.6 \times 10^7$ disintegrations) was injected into the helium stream. The activity of the reactor eluant was monitored using a flow proportional counter (5). The time taken for the activity of the eluant to fall to the background