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On the Preparation of Platinum Black with a Clean Surface. Preliminary Heats of Adsorption of Hydrogen

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Ordinary platinum black is covered with a complete monolayer of oxygen. The technique of thermal titration has been used to prepare a sample of platinum black with a clean surface. Preliminary heats of adsorption of hydrogen on this sample as a function of coverage are reported at a temperature of 0°.

Introduction

The technique of using evaporated films provided a convenient way of obtaining clean metallic surfaces. However, even in the case of evaporated films freedom from contamination is by no means certain. Evaporated films, because of their relatively small surface areas, are very susceptible to serious contamination. Since a large surface area is convenient in chemisorption studies, a method of producing a clean and reproducible surface for a powder sample is highly desirable.

The catalytic recombination of hydrogen and oxygen takes place rapidly and completely on platinum at room temperature and the water formed is easily removed.[1,2] Therefore, this could readily be used as a means of removing either hydrogen or oxygen from a platinum black sample. By using this catalytic recombination of hydrogen and oxygen at room temperature, it is unnecessary to treat the sample to outgassing at high temperatures. High temperature treatment of a high area sample is not desirable since sintering occurs.

The heat due to the recombination of hydrogen with chemisorbed oxygen or of oxygen with chemisorbed hydrogen is much higher than the heat of chemisorption of either hydrogen or oxygen on platinum. Thus a rather sharp fall in the heats after completion of the hydrogen and oxygen recombination on the platinum surface is to be expected. From a simple outgassing of the sample at high temperature or by reduction with an excess of hydrogen and subsequent outgassing, the degree of contamination remaining on the surface is uncertain. On the other hand, because hydrogen adsorbed on platinum is mobile, it is possible to obtain a well defined, clean, reproducible platinum surface by means of a thermally indicated titration of the contaminating hydrogen or oxygen, using oxygen or hydrogen respectively for the titration.

Experimental

Apparatus.—Measurement of the heats of adsorption was made using an adiabatic calorimeter. The sample of platinum black was packed uniformly in the platinum calorimeter vessel between equally spaced platinum discs to provide good heat conduction. Details of its construction and of the platinum calorimeter vessel are given elsewhere.[3] A conventional high vacuum pumping and gas filling system was used in connection with the calorimeter. Attached to this system is a trap constructed from German silver tubing. This trap when immersed in a dewar of liquid helium condenses the gas desorbed from the calorimeter vessel. A small glass vial in conjunction with this helium trap serves as a means for collecting and weighing the desorbed water.

Temperatures were measured using a strain free platinum resistance thermometer constructed and calibrated in this Laboratory. Pressures were measured using a wide bore mercury manometer and a Gaertner cathometer accurate to 0.02 mm. of Hg. A calibrated gas pipet attached to the manometer system was used to measure volumes.

Materials.—The platinum black sample was obtained from Baker and Company, Newark, New Jersey. A nitrogen surface area for this sample was obtained using the conventional BET method. The nitrogen monolayer of the 163.4 gram sample was 1.090 l. STP. This corresponds to an area of 29.2 m.^{2}/g. using 16.3 Å.^{2} as the area of a nitrogen molecule. The hydrogen monolayer volume was calculated from the nitrogen monolayer volume to be 1.097 l. STP. This calculation assumed that each surface platinum atom chemisorbs one hydrogen atom and that the area per platinum atom is 8.09 Å.^{2} This area was obtained by averaging the areas of the platinum atoms present in the 100, 110 and 111 crystallographic planes of platinum. The average particle size of the platinum black aggregates is, according to the data supplied by Baker and Company, 100 Å. on a side.

The hydrogen was prepared by electrolysis in this Laboratory. Before entering the calorimeter vessel, the hydrogen was passed through a trap packed with activated charcoal and cooled to liquid nitrogen temperatures. A mass spectrographic analysis showed it to be 99.99% pure. Oxygen was obtained through thermal decomposition of reagent potassium permanganate and then by passage through activated silica gel and potassium hydroxide. It was further purified by condensation in a trap immersed in liquid nitrogen. The liquefied oxygen then was allowed to evaporate into a storage bulb connected to the gas pipet system.

Cleaning the Surface.—The platinum black sample, which had been exposed to the air, was subjected to outgassing for a week at about 70° until the residual pressure was less than 1×10^{-6} mm. of Hg. Small increments of hydrogen were then added to the sample and the differential heats of adsorption determined. The differential heats fell from an initial value of 54 kcal./mole H_2 to 44 kcal./mole H_2 at 0.1 of the hydrogen monolayer volume. From this point the heats remained nearly constant until almost 2 l. STP of hydrogen had been added. Here another sharp fall in the differential heats took place.

Equilibrium time was relatively short (on the order of 30 minutes) for about the initial 10% of the titration. For the remainder of the titration, a fast uptake of each increment of hydrogen was observed followed by a slow process. The time take for this slow process became progressively longer as more hydrogen was added. After 2.20 l. STP of hydrogen had been added, the equilibrium time progressively *decreased*.

About 60% of the excess hydrogen added and most of the water formed from the titration was recovered by heating the calorimeter vessel to about 60–80°. This hydrogen and the water were condensed in the trap by immersing it in liquid helium. The amount of hydrogen desorbed was measured by replacing the liquid helium with liquid nitrogen and allowing the hydrogen to evaporate into the gas pipet where it was measured manometrically. After first pumping away the hydrogen, the water was transferred from the trap to the glass vial by removing the liquid nitrogen and immersing the vial in liquid nitrogen. After transfer, the vial was weighed and the amount of water determined.

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(1) D. L. Chapman and P. W. Reynolds, *Proc. Roy. Soc.* (*London*), **156A**, 284 (1936).

(2) H. Reischauer, *Z. physik. Chem.* (*Leipzig*), **B26**, 399 (1934).

(3) J. Greyson and J. G. Aston, *J. Phys. Chem.*, **61**, 610 (1957).

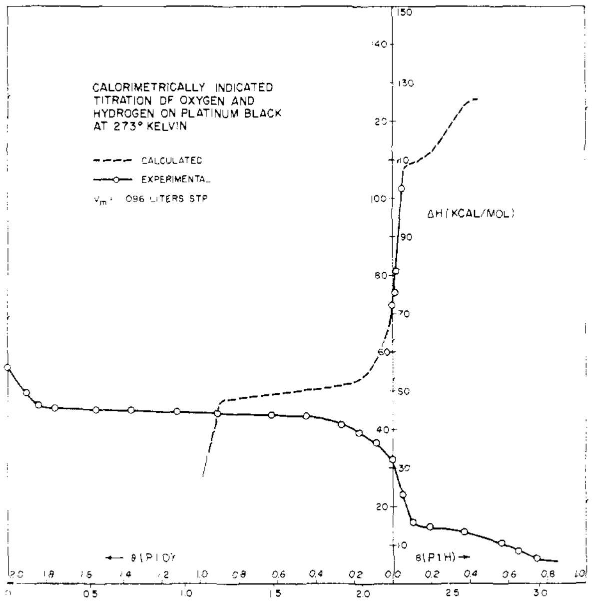

Fig. 1.—Thermally indicated titration for platinum black. The upper curve shows the effect of adding oxygen in excess to the platinum surface containing preadsorbed hydrogen. It is on the basis of one mole of O_2. The lower curve represents the titration of adsorbed oxygen with hydrogen, with the subsequent addition of excess hydrogen. The amount of hydrogen in moles necessary to remove adsorbed oxygen, compared to a monolayer of hydrogen, is indicated by θ (PtO). θ(PtH) indicates the relative amount of hydrogen adsorbed on the platinum surface. Thus, the scale is twice that of the upper curve. The amount of nitrogen necessary to form a monolayer is given by V_m as determined from a BET experiment.

To remove the remaining hydrogen, oxygen then was added. The differential heats dropped sharply from 103 kcal./mole O_2 to 75 kcal./mole O_2 after passing the neutral point corresponding to 2.20 l. STP of hydrogen added. The small excess of oxygen then was back titrated with hydrogen. The water formed was recovered using the procedure described above. Total recovery of water amounted to 96% of the total amount formed from the titrations.

Discussion

The results prove that the platinum black sample was covered with a complete monolayer of oxygen, that is, assuming that one oxygen atom occupies one platinum site, with 1.097 l. STP of oxygen. Of the 3.100 l. STP of hydrogen added, 2.194 l. STP formed water by catalytic recombination with the chemisorbed oxygen. The remaining 0.900 l. STP of hydrogen was chemisorbed on the platinum black surface thus filling 82% of the surface.

The equations (a) to (f) summarize the chemical reactions involved

$$H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -58 \text{ kcal./mole } H_2 \qquad (a)$$

$$H_2O(g) \longrightarrow H_2O(\text{ads.}) \quad \Delta H = -11 \text{ kcal./mole } H_2O \qquad (b)$$

$$PtO + H_2(g) \longrightarrow Pt + H_2O(\text{ads.}) \qquad (c)$$

$$2PtH + {}^1/_2O_2(g) \longrightarrow 2Pt + H_2O(\text{ads.}) \qquad (d)$$

$$H_2(g) + 2Pt \longrightarrow 2PtH \quad \Delta H = -17 \text{ kcal./mole } H_2 \qquad (e)$$

$${}^1/_2O_2(g) + Pt \longrightarrow PtO \quad \Delta H = -60 \text{ kcal./mole } O_2 \qquad (f)$$

The heat evolved due to the recombination of hydrogen with the chemisorbed oxygen, reaction c, was calculated to be 39 kcal./mole H_2 using reactions (a) + (b) − (f). This is in agreement with our measured value of 42 kcal./mole H_2. The heat of chemisorption of hydrogen on platinum black has been found to be 16–18 kcal./mole H_2 by several investigators.[4-6] This is the value for the heat we observed after passing the point where 2.20 l. STP hydrogen had been added in the titration with hydrogen. The back titration of the excess hydrogen with oxygen, reaction d, can be described by the reaction obtained from combining reactions (a) + (b) − (e). This gives a value of 104 kcal./mole O_2 which is in good agreement with our measured value of 103 kcal./mole O_2. For the heat of chemisorption of oxygen on platinum, Maxted's value of 60 kcal./mole O_2 was used.[7] This is used in reaction d for the purpose of calculation. No measurements of the heat of adsorption of water on platinum black have been carried out. Therefore, we tentatively used a value of 11 kcal./mole for this heat which was based on our two measured heats of desorption of water during the water recovery process.

In Fig. 1 is shown a complete thermal titration curve for platinum black. The dotted portion of the oxygen curve is obtained from calculations using the above equations and our measured values of the heats for reaction e and c. The initial high value for the reaction of hydrogen with the chemisorbed oxygen may be attributed to the combination of less tightly bound oxygen with hydrogen. Oxygen with a lower heat of chemisorption will react first giving higher heats according to the reaction given by (a) + (b) − (f).

Indirect evidence of the mobility of hydrogen on nickel even at 90° K. was provided by Beeck.[8] According to Takaishi,[9] the potential barrier for the migration of hydrogen on platinum was calculated to be between 0.011 to 0.014 ev. This suggests that hydrogen would be mobile at room temperature. The initial fall of the differential heats during the titration indicates the mobility of the oxygen film on platinum.

Otherwise, since the adsorption pressure of oxygen is too small to allow evaporation, removal or addition of oxygen would start to take place from the top of the calorimeter. Thus each platinum grain exposed to oxygen or hydrogen would be completely covered with oxygen or all the oxygen completely removed before the grains below were affected. This argument also proves that hydrogen is mobile on the platinum surface. Otherwise, a completely flat titration curve (with a differential heat equal to a proper average value of that for reaction with oxygen and for adsorption) would be obtained.

Preliminary heat capacities of a monolayer of oxygen on platinum black are those of a two dimensional classical monoatomic, and/or a diatomic

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(4) G. B. Maxted and N. J. Hassid, *J. Chem. Soc.*, 3313 (1931).

(5) Takao Kwan, *J. Research Inst. Catalysis, Hokkaido Univ.*, **1**, 81 (1949).

(6) Maidanovski and B. Bruns, *Acta Physicochim., U.R.S.S.*, **9**, 927 (1938).

(7) G. B. Maxted and N. J. Hassid, *Trans. Faraday Soc.*, **29**, 698 (1933).

(8) O. Beeck, *Advances in Catalysis*, **2**, 151 (1950).

(9) T. Takaishi and A. Kobayashi, *J. Chem. Phys.*, **26**, 1542 (1957).

gas, each with a potential barrier, and not those corresponding to bending and stretching of bonds. This can only be true if the oxygen layer is mobile.

Differential heats of adsorption usually fall with increasing surface coverage. Attempts have been made to correlate this variation of the differential heats of adsorption with physical properties of the surface. However, due to lack of sufficient experimental data on the same system, this problem still remains unsolved. The presence of oxygen as a surface contaminant will cause a large heat effect for the initial adsorption of hydrogen on some metals. Upon this effect will be superimposed the effect due to the intrinsic surface heterogeneity. Incomplete elimination of hydrogen after a reduction of a sample will also produce high initial heats for an adsorption of oxygen on a metal. Thus the extremely high initial heats of chemisorption of hydrogen and oxygen on metal systems which have been reported may be attributed in part to the presence of incompletely removed hydrogen and oxygen.

Also, the different properties of powders and films may be attributed to incomplete elimination of the surface contamination of the powder. Using nickel, Roberts observed that a thoroughly reduced powder surface showed adsorption characteristic almost identical with those associated with nickel films.[10]

(10) M. W. Roberts, *Chemisorption*, 172 (1957).

It is of great importance to obtain a well defined, reproducible, clean surface in studies of surface phenomena. Our method serves as a means for preparing such a surface for platinum black samples in the study of the hydrogen, oxygen, platinum system. This method for preparing a surface through a thermally indicated titration with hydrogen and oxygen may be extended to other metal powders. In the study of the chemisorption of different gases, other reactions may be used for a thermal titration provided that the reaction takes place on the metal being investigated and at least one of the reactants is mobile on the surface of this metal at the temperature being used. The products of the reaction also should be easily removable. The use of a thermally indicated titration also provides an excellent method for determining surface areas of samples. The surface monolayer volume of 1.10 l. STP for hydrogen obtained from our hydrogen titration, while removing oxygen, agrees well with the value of 1.10 l. STP hydrogen calculated from the BET nitrogen determination.

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The Absorption of Oxygen by Nickel Dimethylglyoximate in Strong Alkaline Solutions[1]

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Nickel dimethylglyoximate dissolved in strong alkaline solutions appears to absorb oxygen in a reversible manner. Deoxygenation of the solutions may be accomplished by heating, by bubbling an inert gas through the solution or by reducing the pressure above the solution. Spectral measurements of deoxygenated solutions proved them to be identical to a solution prepared in the absence of oxygen. The oxygenated solutions are diamagnetic. Careful neutralization of the basic solutions yielded a weakly paramagnetic red complex believed to contain some of the nickel (III) complex with the formula $Ni(DH)_2OH$ (DH^- is the dimethylglyoximate anion). This is the first report of an oxygen-carrying nickel chelate. Palladium dimethylglyoximate does not show this behavior.

Introduction

Although there have been numerous studies on the oxidation of nickel dimethylglyoximate in alkaline solutions, there is little agreement to be found in the literature. Various nickel(IV) species have been postulated having nickel to dimethylglyoxime ratios of 1:2, 1:3 and/or 1:4.[3] Likewise there are reports of Ni(III) species with the nickel to ligand ratios of 1:1, 1:2, 1:3 and/or 1:4.[4] From a survey of this literature on the alkaline oxidation of $Ni(DH)_2$,[5] it is obvious that the products formed depend upon these several variables: the *p*H, the oxidant, the presence of excess DH_2 and whether ammonia or alkali hydroxide is used to obtain the basic conditions.

When oxygen was bubbled through a strongly alkaline solution of $Ni(DH)_2$, the orange-red color deepened considerably. Further investigation of the effect of oxygen on these alkaline solutions proved that the oxygen was being absorbed in a reversible manner, the soluble nickel chelate apparently acting in the capacity of a reversible oxygen carrier. Slow neutralization of the alkaline solution yielded a red compound believed to be a mixture of $Ni(DH)_2$ and the trivalent nickel com-

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(1) This article is based upon part of a dissertation submitted in partial fulfillment of the requirements for the M.S. degree at the Louisiana State University, 1959.

(2) Celanese Corporation Fellow in Chemistry, 1958–1959.

(3) F. Feigl, *Ber.*, **57B**, 759 (1924); M. Hooreman, *Anal. Chim. Acta*, **3**, 635 (1949); A. Okac and M. Simek, *Chem. Listy*, **52**, 1903 (1958); K. Yamasaki and C. Matsumoto, *Nippon Kagaku Zesshi.*, **77**, 1111 (1956).

(4) E. Booth and J. D. H. Strickland, THIS JOURNAL, **75**, 3017 (1953); K. B. Yatsimirsku and F. M. Grafova, *Zhur. Obshchei Khim.*, **22**, 1726 (1952); L. S. Nedezhiua and P. M. Kovalenko, *ibid.*, **24**, 1734 (1954); V. M. Peshkova and N. V. Mel'chakova, *Metody Analyza Redkikhi Tsvet. Metal. Sbornik*, 53 (1956).

(5) In this article DH_2 is used to designate the dimethylglyoxime molecule, DH^- to represent the univalent ion with one hydrogen ion removed, and $D^=$ to represent the bivalent ion with two hydrogen ions removed.