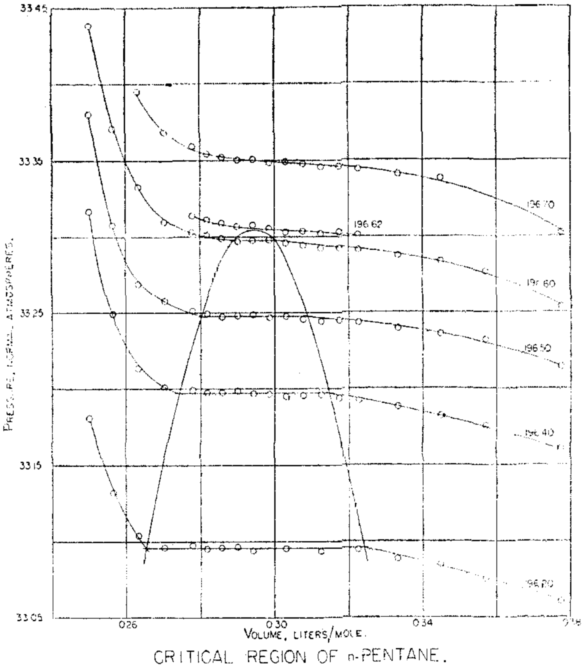

Fig. 1.—Isotherms of normal pentane in the critical region. The radius of each circle is 0.002 atm.

by the API Project 6 at the National Bureau of Standards. The impurities were stated to be 0.15 ± 0.07 mole per cent. We are very grateful to Dr. Rossini for furnishing the sample. No further purification was carried out by us except repeated freezing, distillation, and pumping in the loading system to remove air.

The purity of the pentane especially as regards contamination by permanent gases is indicated by the results given in Table I. The vapor pressure of the sample was determined at 100° while the vapor volume was varied from 95 to 0.26 ml. The increase in pressure, 0.009 atm., indicated a satisfactory purity.

The measured vapor pressures are presented in Table II together with the deviations from the equation

$$\log_{10} p(\text{atm.}) = 3.752453 - \frac{1225.960}{T} + 8.06841 \times 10^{-4}\, T \quad (T = t°\text{C.} + 273.16) \quad (1)$$

There are also included the results of Rose-Innes and Young and of Sage and Lacey. The agreement with the measurements of Sage and Lacey is excellent.

The observations on the compressibility of pentane in the critical region are given in Table III and these results are plotted in Fig. 1. From the plot we find the critical constants listed in Table IV. The agreement with the earlier work of Rose-Innes and Young is fairly satisfactory.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 12, 1951

[CONTRIBUTION FROM THE BASIC COTTON RESEARCH LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Preparation of a Platinum Oxide Catalyst of Reproducible Activity[1]

BY VERNON L. FRAMPTON, JOSEPH D. EDWARDS, JR., AND HENRY R. HENZE

A procedure is described for the preparation of a platinum oxide catalyst of reproducible activity, which depends upon the essentially instantaneous heating of platinic chloride to 520° in the presence of sodium nitrate. A volumetric hydrogenation apparatus is also described.

Adams and Vorhees,[2] and later Adams and Shriner,[3] observed that a platinum oxide prepared by fusing a mixture of sodium nitrate and chloroplatinic acid at 540° was far more active, and more consistent in its activity, as a catalyst for the hydrogenation of carbon–carbon double bonds, carbonyl compounds, etc., than the platinum black catalysts prepared by previously known procedures. We found, however, in a study of the hydrogenation of gossypol, a considerable degree of variability in the activities of the catalyst preparations prepared by the procedure described by Adams, *et al.* For example, the hydrogenation of gossypol was substantially complete (with the production of a crystalline product melting at 258–260°)[4] in about 45 minutes with the most active preparations we obtained, but with other preparations obtained under conditions as nearly comparable as we could make them, from 48 to 72 hours were required for the hydrogenation, and with still other preparations, no hydrogenation was obtained. In each instance the catalyst was active, since test compounds were readily hydrogenated, and spontaneous combustion occurred when the hydrogen-saturated suspension of the catalyst was filtered in air.[5]

Preparation of the Catalyst.—The following procedure for the preparation of an extremely active platinum oxide catalyst of essentially reproducible activity evolved during the course of our efforts to hydrogenate gossypol.

Add 10 ml. of a 10% solution of chloroplatinic acid to 9 g. of sodium nitrate in a 50-ml. beaker, and evaporate to dryness over an open flame, stirring all the while with a glass

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[1] Taken in part from a thesis presented by Joseph D. Edwards, Jr., to the graduate faculty of the University of Texas in partial fulfillment of the requirements for the Ph.D. degree, June, 1950. This research was supported by funds appropriated by the Cotton Research Committee of Texas.

[2] R. Adams and V. Vorhees, THIS JOURNAL, **44**, 1683 (1922).

[3] R. Adams and R. L. Shriner, *ibid.*, **45**, 2171 (1923).

[4] Unpublished data from the studies on the hydrogenation of gossypol carried out in the Basic Cotton Research Laboratory, Oct., 1948–Jan., 1949.

[5] According to the Adams procedure, the mixture of chloroplatinic acid in sodium nitrate is first heated gently until all of the water is driven off, and then it is heated more strongly until a temperature of 540° is reached, and until almost all of the oxides of nitrogen have been expelled from the melt. We find that, although one may sense if a given preparation will be active, or only moderately so, he may not produce at will an extremely active catalyst by following the procedure. This experience relating to the variability in the activity of these platinum oxide catalysts is not unique to this Laboratory.

rod. Care must be taken not to fuse the sodium nitrate during the heating process, but the mixture must be reduced to a dry powder. One hundred grams of sodium nitrate are heated to 520° in a 400-ml. beaker, the temperature being determined with a thermocouple sealed in a glass tube. The dry salt is then added in its entirety to the molten sodium nitrate, and the source of heat is removed from under the magma. The platinum is quantitatively precipitated as an olive brown oxide immediately upon the addition of the dry salt mixture and the oxide settles to the bottom of the beaker. The 400-ml. beaker will not break upon solidification of the sodium nitrate if the contents of the beaker are stirred with a glass rod in a manner such that the material is deposited on the sides of the beaker as the mass cools. After the magma has cooled, the sodium nitrate is dissolved in about 2 l. of water, and the brown oxide is recovered by filtering the suspension through a retentive filter paper in a buchner funnel. The oxide will not be peptized during the subsequent washing with water if the precaution is taken of never permitting it to dry until the desired quantity of distilled water has passed over it. The oxide is then collected and dried over calcium chloride in a vacuum desiccator under reduced pressure. It is essential that the catalyst be thoroughly dry if one wishes to obtain the maximum activity.

Ten batches of catalyst, prepared consecutively by the method outlined above, were used in securing the data recorded. The apparatus diagrammed in Fig. 1 was used in these determinations. After two minutes the moles of hydrogen absorbed per mole of maleic with the ten preparations were 0.17, 0.17, 0.14, 0.17, 0.17, 0.16, 0.16, 0.16, 0.17 and 0.19. The corresponding data after four minutes were 0.39, 0.37, 0.31, 0.35, 0.37, 0.35, 0.31, 0.33, 0.36, 0.39; after eight minutes they were 0.85, 0.72, 0.65, 0.71, 0.74, 0.71, 0.62, 0.70, 0.72, 0.84; after 12 minutes they were 0.92, 0.92, 0.85, 0.91, 0.90, 0.89, 0.84, 0.90, 0.89, 0.94.

It is not possible to make a direct comparison of the data included above with those recorded for maleic acid by Adams, *et al.*, since the conditions for the hydrogenations in the two laboratories were not identical. We find, however, that the catalysts prepared in the manner directed, when used in the hydrogenation of gossypol, are as active as the most active catalysts we ever obtained following the Adams procedure, and the consistency observed in the hydrogenation of gossypol corresponds to that observed with maleic acid.

We do not know if the composition of the catalysts prepared by the two methods is identical. The brown oxide obtained with our procedure forms a fine suspension in ethyl alcohol, and other organic solvents, but on becoming saturated with hydrogen, it turns black and settles to the bottom of the flask as a heavy sediment. The brown oxide is insoluble in *aqua regia*, but the black hydrogen-saturated oxide is soluble. No suggestion is offered to account for this physical (or possibly chemical) transformation, since one may not rely completely upon chemical analysis in the establishment of the identity of colloid precipitates obtained in the manner described.

Black oxides of platinum were obtained in instances where the dry salt was added portionwise to the magma when the temperature of the molten mass was not carefully controlled. These black oxides were very active catalysts, but they were in no way comparable with the brown oxides obtained when the dry salt mixture was added all at once to the magma. When the temperature of the magma was not permitted to fluctuate more than 1° or 2° during the portionwise addition, brown oxides were obtained that were comparable in their activities with those recorded above.

Volumetric Hydrogenation Apparatus.—Chamber A in Fig. 1 was a 200-ml. boiling flask equipped with a ground socket orifice large enough to receive the magnetic bar of a magnetic stirrer. Chamber B was constructed from a 100-ml. boiling flask, and chamber E was a 100-ml. gas buret. This all-glass apparatus was mounted in a thermally insulated cabinet, and a constant temperature (±0.1°) was maintained in the cabinet by a suitable thermostatic arrangement. A uniform temperature throughout the cabinet was assured by the rapid circulation of the air by a fan running at 5,000 revolutions per minute. The necessary observations were made through a glass window, and most of the manipulations were carried out without opening the cabinet.

Use is made of stopcock D in the apparatus when it is desired to make additions to the system after the hydrogenation has been initiated. In such cases stopcock D and C are closed, and the addition is made through the ground glass orifice at the top of chamber B. The system is then evacuated and filled with hydrogen, as in the initial preparation of the apparatus for the hydrogenation, *vide infra*. Stopcocks D and C are then opened after thermal equilibrium is established, and the hydrogenation is continued.

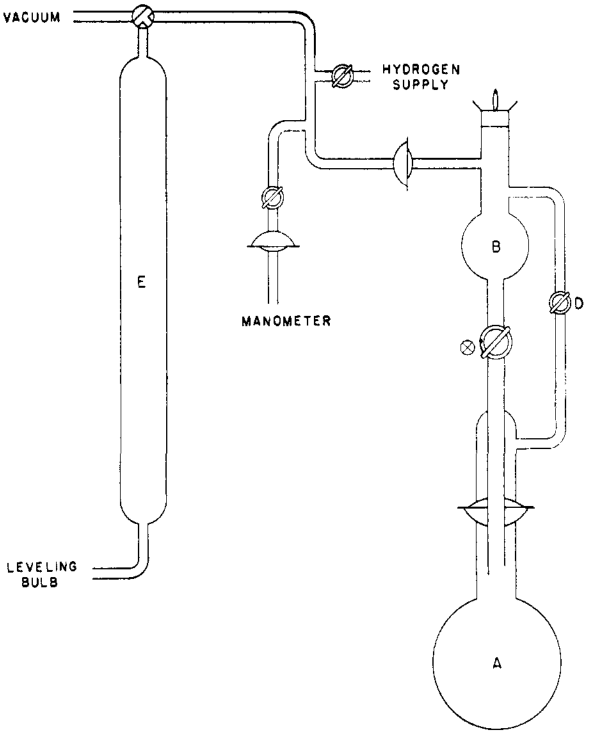

Fig. 1.

The manometer may be placed in communication with the apparatus in instances where there is a prospect that the barometric pressure will change during the course of a hydrogenation, and where one wishes to make comparisons without repeated calculations. The manometer may also be used when it is desired to carry out hydrogenations at pressures that differ slightly from atmospheric pressure.

Determination of the Hydrogen Absorbed.—In the several determinations recorded, 15 ml. of ethyl alcohol, 0.1000 g. of catalyst and the magnetic bar (for stirring) were placed in chamber A. Three hundred milligrams of maleic acid in 35 ml. of ethyl alcohol was placed in chamber B. With stopcock C closed, and D open, the system was repeatedly evacuated and refilled with hydrogen, and finally filled with hydrogen. After thermal equilibrium was established, stirring of the platinum oxide suspension was initiated, and the stirring was continued so long as the oxide took up hydrogen. The quantity of hydrogen absorbed by the catalyst was calculated from the change in volume in the gas buret and from the calculated partial pressure of the hydrogen in the apparatus. After the catalyst was saturated with hydrogen, the volume of gas in the buret was adjusted to approximately 100-ml. Stopcock C was then opened after thermal equilibrium was again established, and the contents from B were permitted to flow into A. The quantity of hydrogen absorbed by the substrate was calculated in the manner indicated above.

Discussion

No correlation was observed between the quantity of hydrogen absorbed by the catalyst, prior to the addition of the substrate, and the speed of hydrogenation of either gossypol or maleic acid.

The catalytic properties of the catalysts produced by fusing a mixture of chloroplatinic acid and sodium nitrate are probably related to the nature of the surface produced, and this in turn is a function of the history of the preparation. It is suggested that the mode of heating is critical, and the variability commonly observed with catalysts prepared by the older procedure may be accounted for by variations in the heating process.

The temperature of 520° is not critical, since catalysts prepared at 500° and at 540° were almost as active as those prepared at 520°. Decreased activities are obtained with temperatures in excess of 540°.

Whereas specific data are given for maleic acid, a corresponding degree of reproducibility was obtained with gossypol, and pertinent data relating to the hydrogenation of this toxic pigment will be reported elsewhere.

Reagents Used.—The ethyl alcohol was distilled from an alkaline suspension of colloidal silver oxide. The maleic acid, C.P. grade, was removed from the manufacturers container and recrystallized three times from diethyl ether. The hydrogen was a commercial grade of electrolytic hydrogen. The chloroplatinic acid was C.P. grade, and it was taken directly from the manufacturers container. The sodium nitrate was reagent grade.

Acknowledgment.—The authors wish to express their appreciation to John Douglas McCoy and to Edward Dew for their technical assistance in connection with this study.

AUSTIN 12, TEXAS RECEIVED DECEMBER 29, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Carbonyl Nickel Films as Hydrogenation Catalysts

BY LOUIS L. BAKER, JR.,[1] AND RICHARD B. BERNSTEIN

Thin nickel films produced by the thermal decomposition of nickel carbonyl on Pyrex glass have been found to be active hydrogenation catalysts. Films of nominal thickness of 0.1 μ were satisfactory catalysts for the reaction of hydrogen with propylene. Small quantities of carbonyl nickel catalysts were readily prepared using a static decomposition method. A continuous flow method was found suitable for obtaining large amounts of catalyst. Several series of experiments were carried out with catalysts formed on Pyrex wool at 150°, employing about 90 mg. of nickel, as well as thin films (*ca.* 4 mg.) deposited directly on the walls of a Pyrex vessel. For equimolar mixtures of hydrogen and propylene at 37 and 80°, the rate of the reaction could be expressed accurately by the equation: $-dp/dt = kp^2/(1 + Kp)^2$, where p is the partial pressure of either reactant. This suggests that the operative mechanism is competitive adsorption of both reactants with no interference from product. It was not found possible to produce surfaces of reproducible catalytic activity. The films were quite susceptible to poisoning.

Introduction

Although nickel carbonyl has been used as a catalyst for various reactions,[2] the catalytic behavior of pure nickel produced from the thermal decomposition of nickel carbonyl does not appear to have been investigated. This report is concerned with the direct use of carbonyl nickel films as catalysts for kinetic investigations. A brief study of the hydrogenation of propylene was undertaken to ascertain the suitability of such catalysts for controlled kinetic experiments. Previous investigations have employed evaporated nickel films,[3a] nickel filaments activated by oxidation and reduction,[3b] bulk nickel from the decomposition of nickel carbonate with subsequent reduction,[4] and Raney nickel.[5] Except for the evaporation technique, these methods lead to uncertainty in the initial condition of the surface, particularly with regard to dissolved and adsorbed hydrogen. It is thought that the preparation of a pure nickel film from nickel carbonyl combines many desirable features of the evaporation technique with relative simplicity of procedure. It is certain that the surface may be obtained initially free of hydrogen, which may be of value in studies involving isotopes of hydrogen. The total surface area and crystalline state should depend upon the decomposition temperature, the initial pressure of nickel carbonyl, the area of the hot wall at which decomposition occurs, and the out-gassing conditions. These may possibly be controlled more easily than the many variables involved in some of the other preparatory methods.

Experimental

Materials.—Nickel carbonyl (International Nickel Co.) prepared by the Mond process and subsequently distilled, is stated to contain <0.004% Fe, other metals and sulfur absent. The liquid was out-gassed at −78° directly before use.

Propylene (Phillips "Pure" Grade) was purified by bulb-to-bulb distillation. Mass spectrometric analysis showed 1.3% propane, with no other impurity.

Electrolytic tank hydrogen was purified by diffusion through a heated palladium tube.

Apparatus.—The experiments were carried out in a Pyrex high vacuum system, consisting of a conventional gas purification and storage arrangement, a gas mixing and Toepler transfer system for introduction of hydrogen and propylene into the reaction chamber, and several different nickel carbonyl decomposition vessels. A capillary mercury manometer was used to follow the hydrogenation reactions. In order to minimize the introduction of mercury vapor by diffusion, the cell was never connected with the manometer while under vacuum. Reactant gases were passed through a packed tin trap before admitting to the cell.

Two methods of catalyst preparation were employed. For large amounts, a known quantity of nickel carbonyl was allowed to flow through a heated tube packed with Pyrex wool; for small deposits, a static method was used whereby a known quantity of the gas was decomposed on the heated walls of a Pyrex vessel. After deposition of the film, the catalyst chamber was out-gassed at temperatures above 300°, and in certain cases allowed to cool in the presence of hydrogen (*ca.* 2 cm.). The details of a typical experiment of each type are presented below.

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(1) Taken from M.S. thesis of L. Baker, Illinois Institute of Technology, 1951.

(2) For example, see: G. DuPont, P. Piganiol and J. Vialle, *Bull. soc. chim. France*, 529 (1948).

(3) (a) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1940); (b) O. Toyama, *Rev. Phys. Chem. Japan*, **14**, 86 (1940).

(4) E. S. Corner and R. N. Pease, *Ind. Eng. Chem., Anal. Ed.*, **17**, 564 (1945).

(5) R. Paul, *Bull. soc. chim.*, **7**, 296 (1940).