been determined by the capillary rise method.

2. From the minima in this curve the dimensions of the sodium palmitate molecule were calculated to be 23×10^{-8} cm. $\times 6.2 \times 10^{-8}$ cm. $\times 3.7 \times 10^{-8}$ cm.

3. The smallest cross section area and the length of the molecule do not differ greatly from similar quantities measured by the Langmuir film method.

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[CONTRIBUTION FROM THE ESSO LABORATORIES, STANDARD OIL DEVELOPMENT COMPANY]

Preparation of Platinum Oxide Catalyst from Spent Material

BY E. L. BALDESCHWIELER AND L. A. MIKESKA

It has been the experience of this and other laboratories that a platinum hydrogenation catalyst prepared according to the method of Voorhees and Adams[1] generally exhibits low activity when any of the H_2PtCl_6 used has been recovered by the usual methods from spent catalyst. It is believed that this low activity is probably due to the presence of small amounts of impurities (catalytic poisons) introduced during the hydrogenation procedure.

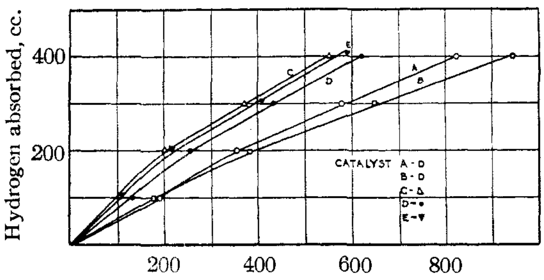

Fig. 1.—Hydrogenation of heptadecyl-*n*-butylphenylethylene.

Various recovery methods have therefore been studied in order to determine the best procedure for the preparation of an active catalyst from spent material. As a result of this work, a method is recommended which has given very satisfactory results and should be of interest to other laboratories engaged in similar work.

Experimental

The following impurities are generally found in the spent catalyst: (1) organic compounds left after hydrogenation and the filter papers used in separating the catalyst from the hydrogenated compounds; (2) inorganic constituents such as (a) copper and some of the other metals of the platinum group present as impurities in the original H_2PtCl_6 from scrap metal and small amounts of (b) iron, aluminum, calcium and magnesium introduced by ashing the filter paper.

A number of catalysts were prepared (according to the method of Voorhees and Adams) from H_2PtCl_6 obtained from spent material treated as follows.

(A) The spent catalyst was carefully separated by scraping from filter papers and the H_2PtCl_6 solution prepared according to the recovery method described in "Organic Syntheses."[2] This material therefore contained impurities listed in 1 and 2a, but very little of those listed in 2b.

(B) The material including the filter paper was ignited in a muffle furnace and the resulting ash treated as in A. The H_2PtCl_6 thus prepared contained only the inorganic impurities discussed under 2.

(C) The ignited material was purified by the procedure described by Wichers[3] except that only one ammonium chloride precipitation was carried out instead of three and that carbon monoxide was used as the reducing agent after ignition of the $(NH_4)_2PtCl_6$ precipitate. The method is briefly described below.

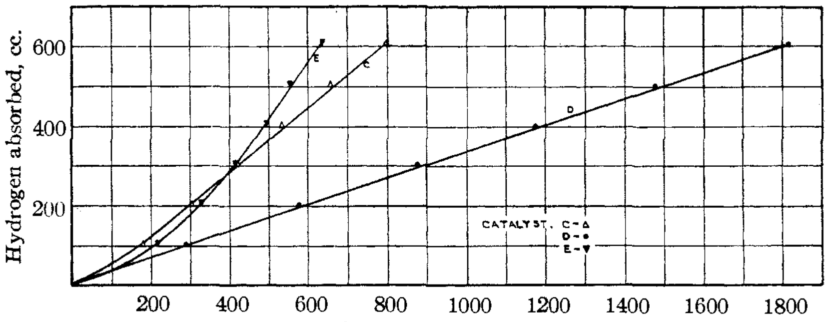

Fig. 2.—Hydrogenation of maleic acid.

Dissolve the ignited material in aqua regia. filter off any insoluble and evaporate the filtrate three times to

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[1] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

[2] "Organic Syntheses," John Wiley & Sons, Inc., New York, 1932, Coll. Vol. 1, p. 457.

[3] Wichers, THIS JOURNAL, **43**, 1268 (1921).

dryness with excess hydrochloric acid. Take up the residue with dilute hydrochloric acid, filter if necessary and precipitate with excess solid ammonium chloride. Add 95% alcohol (about one-third of the volume of the solution), let stand one hour and filter. Dry at 100°, detach the precipitate from the filter and ignite carefully in an unglazed porcelain crucible or an alundum thimble. Reduce to metallic platinum by placing the covered crucible into a large porcelain crucible, filling the space between the crucibles with charcoal (pea size) and heating to dull redness for one hour. Dissolve the weighed platinum in aqua regia and prepare a 10% H_2PtCl_6 solution by evaporating the aqua regia solution three times to dryness with hydrochloric acid, taking up with the calculated amount of dilute hydrochloric acid to give the required concentration.

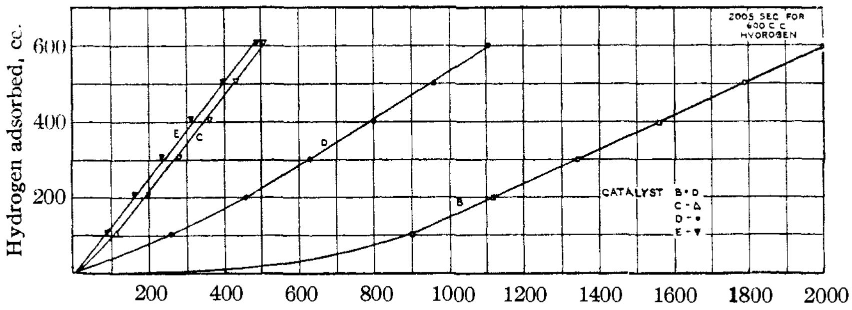

Fig. 3.—Hydrogenation of benzaldehyde.

The H_2PtCl_6 solution thus prepared was practically free from all impurities with the possible exception of some of the other platinum metals, in particular a little iridium, which is difficult to separate completely from platinum.

(D) The material C was further purified by two additional ammonium chloride precipitations and ignitions, as recommended by Wichers. This method gives practically pure H_2PtCl_6.

(E) The H_2PtCl_6 was prepared from sheet platinum purchased from Eimer and Amend, New York.

The above catalysts were tested under identical conditions by hydrogenating various types of compounds, the velocity of the reaction being a criterion for the quality of the catalyst. The results are shown graphically in Figs. 1, 2, 3 and 4, which give the hydrogenation velocities of, respectively, heptadecyl-N-butylphenylethylene, maleic acid, benzaldehyde, and nitrobenzene with the various catalysts. From the shape of the curves it is evident that the time of absorption of the first 100 cc. of hydrogen should be taken as the induction period of the reaction. Catalyst A was found to be completely inactive except for the first compound, while B showed an absorption of 90 cc. of hydrogen after 1800 seconds, with benzaldehyde, and only 70 cc. of hydrogen with nitrobenzene. These experiments are therefore not graphically represented.

The results show that catalysts A and B are decidedly unsuitable for hydrogenation purposes. Catalyst C compares very favorably with the standard E, while the product D, although fair, is inferior to both C and E. The lower activity of D is probably due to overpurification of the material, resulting in the removal of some of the other platinum metals which seem to be promoters.

The authors wish to express their appreciation to Mr. M. D. Morgan and Mr. E. Lieber of these Laboratories for their help in preparing and testing the catalysts.

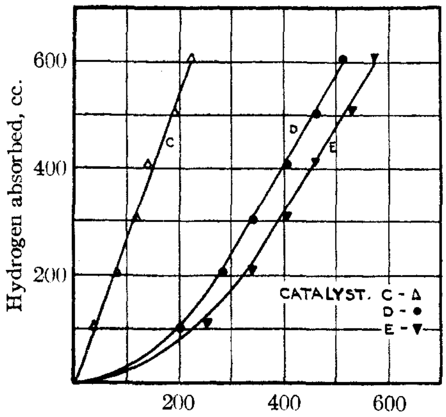

Fig. 4.—Hydrogenation of nitrobenzene.

Summary

It is shown that a suitable platinum hydrogenation catalyst can be prepared from spent material by a modification of Wichers' purification method.

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