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Some Observations on the Handling of Adams' Platinum-Oxide Hydrogenation Catalyst¹

LYMAN R. CASWELL² AND ROBERT D. SCHUETZ³

Abstract. Two problems are present in the measurement of the exact quantities of catalyst used in hydrogenations with platinum oxide. The first arises from the fact that platinum oxide is highly adsorbent and rapidly gains weight due to adsorption of atmospheric components when it is exposed to air. A procedure is described for making an approximate correction for this weight gain. The second problem is the identity of the actual catalytic material. The observations indicate that this is platinum metal, and it is shown that the platinum content varies with the batch of catalyst.

Exact studies of the kinetics of catalytic hydrogenation provide a multiplicity of problems encountered in few other organic reactions. Two of these problems involve the questions: Exactly how much catalyst is being used? What chemical substance is the actual catalyst?

These questions became pertinent to a series of studies (Caswell, 1956) of the hydrogenation kinetics with Adams' platinum-oxide catalyst. Smith and his co-workers (1945) had shown that the rate of catalytic hydrogenation on platinum oxide was directly proportional to the weight of platinum oxide used. It was found in the present study that the weights of samples of platinum oxide in the neighborhood of 0.2 g could not be reproducibly determined to more than two significant figures, because of weight gains when the samples were exposed to air.

In the case of platinum oxide it has long been assumed that the actual catalyst was platinum metal resulting from the reduction of the oxide at the start of the hydrogenation process, but at the time of this work, no conclusive experimental evidence had been presented in support of this view. This possibility raised the question, for careful quantitative hydrogenation studies, of just what fraction of the drop in hydrogen pressure was due to reduction of the catalyst.

EXPERIMENTAL

Materials. Adam's platinum-oxide catalyst was obtained from the American Platinum Works. Two different batches, "A" and "B", were examined.

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Baker's "Analyzed" glacial acetic acid was used without further purification. All samples were taken from the same bottle.

Hydrogen obtained from the Ohio Chemical and Surgical Co. was used without purification.

Apparatus. The hydrogenation apparatus used in these studies was a Parr Model 3911 low-pressure apparatus, modified so that pressure measurements could be made manometrically. The reaction chamber was a 250-ml wide-mouth pressure bottle constructed by the H. T. Martin Co. of Evanston, Illinois, and encased in a heating element. The details of the construction and calibration of these have been described elsewhere (Schuetz, Caswell, and Sternberg, 1959).

All weighings were made with the same analytical balance, using the same set of weights.

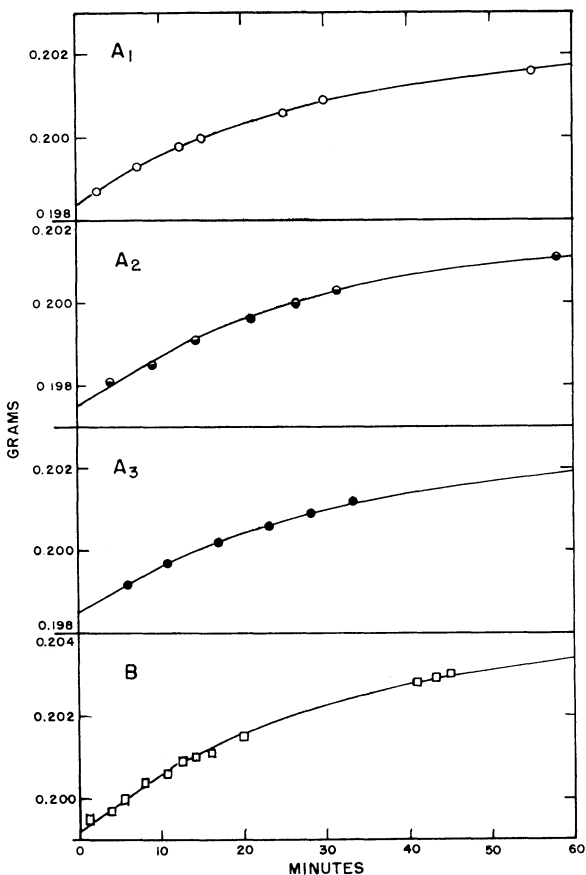


Figure 1. Gain of weight by platinum oxide on exposure to air.

Catalyst-Weighing Technique. Samples of platinum oxide weighing approximately 0.20 g were measured into tared weighing bottles and stored in an evacuated desiccator over solid KOH for 24 hours before exact weighings were attempted. To determine the weight gain by three samples of batch "A" and one sample of batch "B" on exposure to air, these samples were weighed at intervals during a period of one hour, and the total weights of each sample were plotted against the time in minutes (Figure 1). A rectilinear expression of these data was obtained by plotting the rate of weight change between successive weighings, in milligrams per minute per gram of material, against the total weight change, in milligrams, from the time of opening the desiccator (Figure 2).

The equation for the rectilinear plots is:

$$\frac{d\Delta w}{dt} \cdot \frac{1}{W} = -a\Delta w + b \quad (1)$$

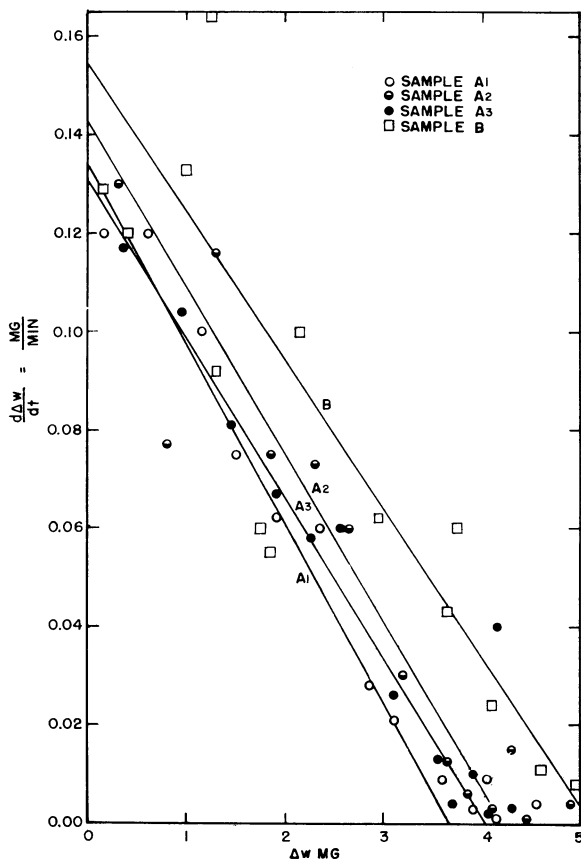


Figure 2. Differential plot of weight gain by platinum oxide on exposure to air. Published by UNI ScholarWorks, 1961

in which Δw is the total weight change in milligrams, W is the approximate weight of the sample in grams, t is time in minutes, and a and b are constants. Graphical evaluation of a and b gives the values reported in Table 1.

Table 1. Constants for Correction of Catalyst Weights.

Sample	a	b
A1	0.18	0.67
A2	0.17	0.76
A3	0.16	0.66
Average	0.17	0.70
B	0.15	0.77

The actual measurement of the masses of the catalyst samples was then accomplished in the following manner. After removal from the desiccator, each uncovered weighing bottle and its contents was weighed four times with intervals of 1.5 minutes between weighings. The values obtained in this manner for $d\Delta w/dt$ were averaged and substituted, with the constants a and b for the appropriate batch of catalyst, into equation (1) to calculate the weight correction Δw . This weight correction was subtracted from the average of the four measured weights and the result was used as the best approximation of the weight of the sample.

Analysis of Platinum-Oxide Catalyst. Three samples of catalyst from batch "A", and two from batch "B", were suspended in glacial acetic acid in the hydrogenation apparatus and reduced under usual hydrogenation conditions. The reduced catalyst samples were isolated by filtering with a tared, sintered-glass filter, and were then washed on the filter with 95% alcohol and dried at 125°C for 12 hours. The material recovered from the batch "A" samples averaged 79.45% of the original catalyst weight, and the material from the batch "B" samples averaged 78.52%. The calculated platinum content of platinum (IV) oxide monohydrate, $\text{PtO}_2 \cdot \text{H}_2\text{O}$, is 79.60%.

Attempted Measurement of The Reduction Rate of Platinum Oxide.

An attempt was made to determine the hydrogen uptake and to evaluate the rate at which platinum oxide was reduced at three temperatures. The results are plotted in Figure 3 in accordance with the first-order rate law:

$$\log \frac{n_0}{n} = \frac{kt}{2.303} \quad (2)$$

in which n_0 is the number of moles of hydrogen initially in the apparatus, n is the number of moles at t minutes, and k is the rate constant.

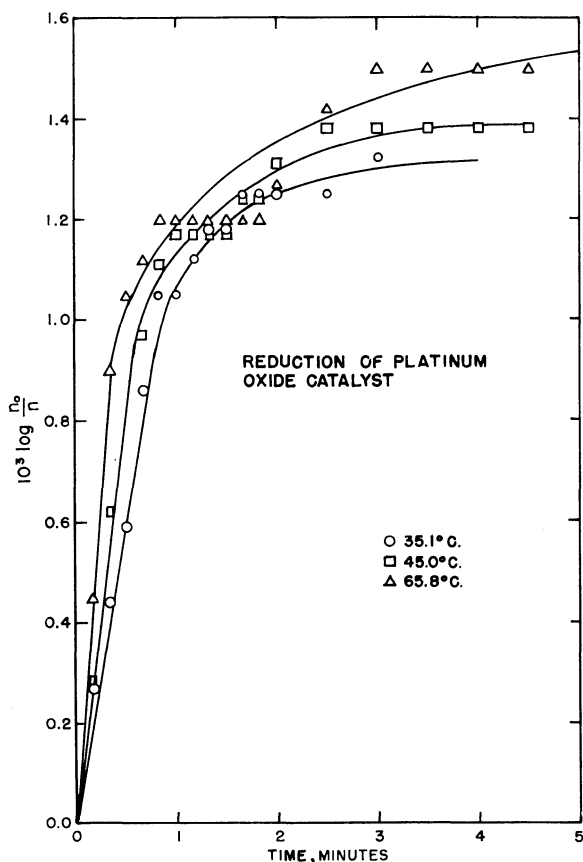


Figure 3. First order plot for reduction of platinum oxide.

DISCUSSION

The low degree of reproducibility of measurements of the kinetics of catalytic hydrogenation is well-known to those who have studied this subject. The results herein described suggest two more factors to be considered in such comparisons.

The weights of platinum which have been measured in previous studies undoubtedly included weights of adsorbed materials. The amounts of these adsorbates will vary from one batch of catalyst to another for samples of equivalent size, and will also vary with the length of time during which the catalyst is exposed to air.

It appears that platinum is the actual catalyst and that the platinum content of platinum oxide varies with the catalyst batch, though all batches of catalyst presumably have been

prepared in an identical manner. The rate of hydrogen uptake by platinum oxide found in these measurements was so rapid that it was uncertain whether the actual rate of reduction was being measured, or the rate of diffusion of hydrogen to the catalyst, or possibly even the rate at which the measuring device responded to a very fast pressure change. The reduction of platinum oxide has recently been found by Yao and Emmett (1961) to be much faster in glacial acetic acid than in a wide variety of other media, and measurements made by these authors for other media show that very little hydrogenation of the substrate occurs until at least part of the platinum oxide has been reduced. The supposition that metallic platinum is the effective catalyst is thereby strongly supported.

These findings show the customary reference to platinum oxide as a catalyst to be a dubious one. The terms *catalyst precursor* or *procatalyst* are proposed as preferable designations.

It is tempting to assume, after the amount of actual catalyst has been determined, that the kinetics of catalytic hydrogenations determined with catalyst samples from different batches can be compared. Unfortunately this is not the case. For example, the activation energy for the catalytic hydrogenation of *o*-xylene on samples from batch "A" was 4300 cal/mole, but 5300 cal/mole on samples from batch "B". With *m*-xylene, "A" gave 4900 cal/mole, and "B" gave 6400 cal/mole. All of these values were determined from rate constants determined for one gram of platinum metal.

An explanation for these differences seems to involve two factors. First, the catalytically active surface area of the catalyst must vary from one batch to another in a manner not dependent upon the platinum content. Second, the ability of the catalytic surface to accommodate different substrates must similarly vary with factors as yet unknown. The experiments for quantitatively evaluating these possibilities and identifying the factors involved are as yet to be devised.

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