On the Retardation of Catalysis. The Catalytic Reaction between Acetylene and Hydrogen

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Introduction

Generally speaking, when acetylene and hydrogen react on a hydrogenating catalyst, there occur three kinds of reaction simultaneously, that is, hydrogenation of acetylene to ethylene and, further, to ethane, and hydrogenation-polymerization of acetylene.

In the case of palladium-alumina (1 : 100) catalyst, as shown in the preceding paper,(1) the hydrogenation of acetylene proceeds in two distinct steps at room temperature. The first step consists of the reduction and polymerization of acetylene and the second step the reduction of ethylene to ethane. The second

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(1) K. Tamaru, *Bull. Chem. Soc., Japan*, **23**. 64 (1950).

reaction starts when all acetylene has been consumed, accompanying a sudden increase in the rate of hydrogenation. This phenomenon shows that acetylene is so strongly adsorbed on the surface of the catalyst that ethylene is not to be reduced till all acetylene has been used up. Consequently, it was found that the final products of the hydrogenation can be wholly made to ethylene or ethane by taking the proper composition of the reactants at the beginning.

As polymers, the polymerization products of acetylene, retard the hydrogenation reaction, the rates of hydrogenation should be corrected for this retardation in the kinetical treatment. In this study, experiments were carried out on the retardation of both steps of the hydrogenation by polymers as well as by some salts. And some considerations were given for the property of the "active region" on the catalyst surface.

Experimental

Hydrogenation of acetylene on the palladium-alumina (1:100) catalyst was investigated by the static method. The preparation of the catalyst and the experimental procedure were the same as those in the preceding paper.⁽¹⁾

The initial hydrogenation velocity of the first step was strictly proportional to the amount of the catalyst, but as the reaction proceeded the polymers that deposited on the surface of the catalyst retarded the reaction with degrees varying according to the amount of the catalyst and thus no proportionality was seen between the amount of the catalyst and the reaction rate. From the same reason the second step of the reaction had also no proportionality between them.

Thus, being able to calculate the amount of the deposited polymers from the gas analysis and the pressure decrease as shown in the previous paper,⁽¹⁾ the relation between the hydrogenation rate of ethylene (k_2) and the amount of the polymers were obtained by varying the amount of the catalyst or the composition of the reactant. This is shown in Fig. 1, where the amount of the deposited polymers were represented by the volume of acetylene in abscissa. The retardation curve of the first step (k_1) was obtained in the following ways. In the first method, k_1 was obtained from the reaction velocity at the last moment of the step, that is just before all acetylene had been used up, and the dependence of k_1 upon the amount of the deposited polymers was found. In the second method, the catalyst was used repeatedly and the progressive retardation caused by the accumulation of the polymers was observed in both steps. The results are shown in Fig. 2, where k_1 in the ordinate was obtained from the initial velocity of the first step and k_2 in the abscissa was the velocity constant of the following second step calculated without any correction for the retardation of the polymers. Combining this with k_2 curve in Fig. 1, the dependence of k_1 upon the amount of the deposited polymers could also be obtained. Both results coincide with each other as shown in Fig. 1, where the results by the first method is represented by the white circles and the other by the black circles. The value of k_2 at no retardation was obtained from the reaction between ethylene and hydrogen.

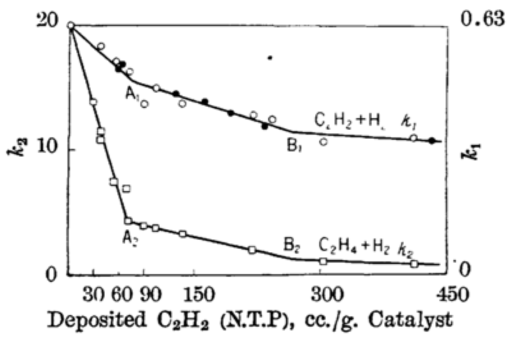

Fig. 1.—Retardation by deposited polymers at 30°C. (Catalyst: Pd-Alumina (1:100)).

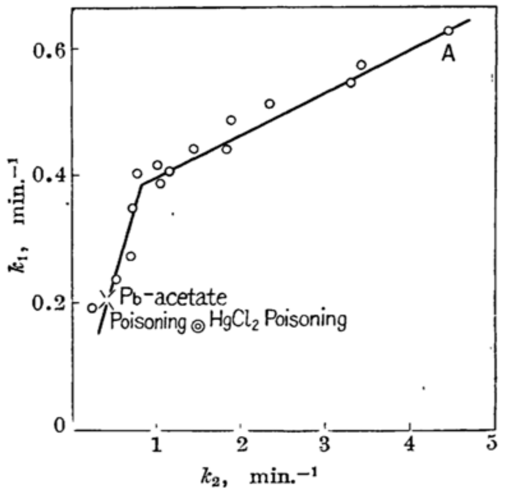

Fig. 2.—Progressive retardation by polymers and poisoning by salts.

It is shown in Fig. 1 that the retardation curves of k_1 and k_2, as it were, consist of three linear parts up to 450 cc. of acetylene deposited per gram catalyst and the two reflection points are designated by A_1, B_1 and A_2, B_2, respectively.

The hydrogenation rates were affected by washing the catalyst with solutions of some salts. The results of the poisonings by lead acetate and mercuric chloride solutions of which concentrations were 1.0% and 0.003%, respectively, were shown in Fig. 2, where the experimental conditions were the same as those used in the experiments of the progressive retardation mentioned above.

Consideration

Without correcting the retardation of the polymers the hydrogenation rate of acetylene was roughly expressed by the following equation as shown in the preceding paper,

$$-\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{k_1P_{H_2}}{1+bP_{C_2H_2}} \qquad (1)$$

where P denotes the pressure of the gas in mm.-Hg, t, time in minute, b and k_1 the constants. This equation was analogous to that given by Cremer and co-workers.⁽²⁾

But when we correct the retardation referring to Fig. 1, it was found that the net hydrogenation velocity of acetylene is to be expressed by the following empirical formula,

$$-\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{k_1P_{H_2}}{1+b\sqrt{P_{C_2H_2}}} \qquad (2)$$

instead of Eq. (1). The value of k_1 at 30°, as calculated from Eq. (2), is shown in Table 1, the mean value of which is 0.63, while b is 0.0774. It is seen that the hydrogenation velocity is independent on the pressure of ethylene. k_1 is also obtained to be 0.63 from Fig. 3, in which the hydrogenation velocity of acetylene and the pressure of hydrogen at the moment just before all acetylene has been used up are plotted.

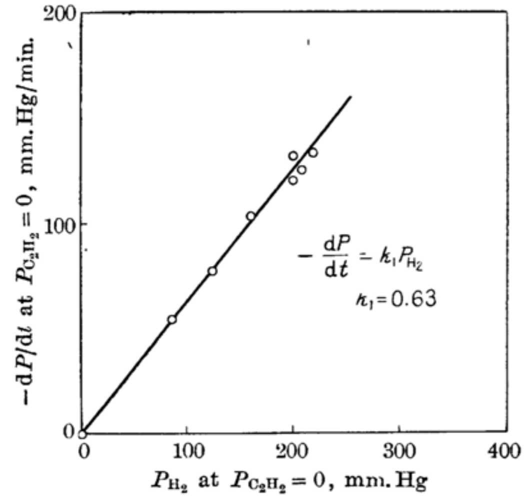

Fig. 3.—A relation between the reaction velocity and hydrogen pressure at the last moment of the acetylene hydrogenation.

All the deposited polymers are not necessarily to be considered to cover the surface of palladium, as they are also possibly adsorbed by the carrier. Consequently, the reflections of k_1 and k_2 curves in Fig. 1 may be attributed to the sudden change in the deposition of the polymers on the palladium surface, for example, when they saturate the palladium surface. It may also be attributed to another reason, for instance, to the discontinuous change in the fraction of the "active regions" on the catalyst surface by the preferential deposition of the polymers.

Table 1

Velocity Constant of the Hydrogenation of Acetylene at 30°C.

C_2H_2, mm.Hg	H_2, mm.Hg	Acetylene Content, %	k_1, min.$^{-1}$
78	404	16.2	0.60
66	193	25.4	0.67
120	350	25.5	0.63
182	332	35.4	0.64
70	124	36.3	0.68
104	189	35.6	0.61
187	288	39.4	0.59
235	250	48.5	0.65
263	207	55.9	0.69
270	167	61.8	0.68

But when we plot k_1 against the corresponding k_2 of equal retardation calculated from the velocity of the first step at the last moment of the step and the velocity constant of the following step, a reflection is observed at A, while not at B as shown in Fig. 4, where

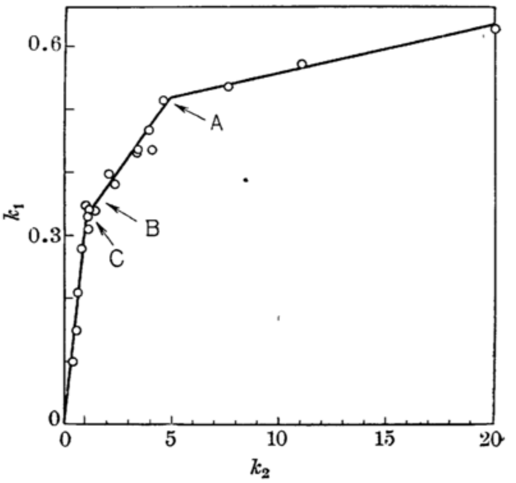

Fig. 4.—k_1-k_2 relation at equal retardation.

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(2) E. Cremer, C. A. Knorr and H. Plieniger, *Z. Elektrochem.*, **47**, 737 (1941).

A corresponds to A_1 and A_2, and B to B_1 and B_2 in Fig. 1. Thus we shall see that the reflection at A_1 or A_2 in Fig. 1 is not caused by the discontinuous change in the deposition of the polymers on the surface of the palladium, but the discontinuous change in the fraction of the "active regions" on the catalyst surface itself. It is not the case, however, at B_1 or B_2, as it shows no reflection in Fig. 4.

According to the statistical mechanical treatment on the heterogeneous reaction by J. Horiuti,(3) the rate of the elementary reaction which proceeds in G equivalent seats of critical complex is given by the following equation,

$$\overrightarrow{k} = \kappa \frac{kT}{h} G q \Theta_0 a_1$$

where Θ_0 is the probability that the critical complex is absent and a_1 is the activity of the initial complex of the elementary reaction and q is approximately equal to $e^{-\varepsilon/kT}$, where ε is the activation energy of the reaction.

In the present case κ, kT/h, G, a_1, in the equation are assumed to be constant in each step, so that

$$\overrightarrow{k} = C e^{-\varepsilon/kT} \Theta_0 .$$

Now if we assume that the value of ε is constant and the rate-determining step of the reaction does not change throughout the retardation, the reaction rates are only dependent on Θ_0 and thus k_1 and k_2 are to be parallel.

In Fig. 4 three linear parts are observed and this may be associated with the three kinds of seat of critical complex or of "active region" on the catalyst surface. Accordingly, it seems to be possible to express from Fig. 4 that the ethane formation proceeds on the two kinds of the "active regions", while the hydrogenation of acetylene to ethylene on three kinds of them and that the first "active region" catalyzes the major part of the former, while only one fifth of the latter, and the third one about half of the latter and almost none of the former.

It is to be noted, however, that the preceding consideration is derived by the kinetical treatment of the reaction and, accordingly, is not necessarily associated with any physical meaning such as, for example, plane or edge of the catalyst.

The assumptions which are made for the preceding consideration may not all be available, especially when Θ_0 approaches to zero, but it is likely to be considered to suggest that the two reactions of ethylene and ethane formation proceed on the various "active regions" with different ratios.

E. F. G. Herington(4) suggested that acetylene and ethylene are adsorbed on the various planes of nickel or cobalt with different ratios and that acetylene should be held on the long spacing of 3.50 Å., whereas ethylene on the short spacing of 2.47 Å. In the present experiment it is shown that the "active region," on which acetylene is not adsorbed, whereas ethylene hydrogenation can occur, is not present, as the inhibition of the ethane formation by acetylene is pronounced.

When the catalyst was washed by the solution of lead acetate or mercuric chloride, both rates of the hydrogenation were retarded as shown in Fig. 2. It was found that the former solution retards the ethane formation much more than the ethylene formation. T. Yamanaka(5) recently reported that palladium-kieselguhr catalyst treated by the lead acetate solution was good to apply to ethylene formation from acetylene by the flow method and this fact coincides with the result of the present experiment by the static method. As to the poisoning of mercuric chloride, k_1 and k_2 were approximately equally retarded. The results by the two salts suggest that the inorganic salts do not analogously poison the catalyst.

Summary

1) The retardation of hydrogenation of acetylene on the palladium-alumina (1 : 100) catalyst by the deposited polymers and some inorganic salts were investigated.

2) By correcting the retardation of the polymers, which deposited on the surface of the catalyst during the reaction, it was found that the net hydrogenation rate of acetylene was expressed by the following equation,

$$-\frac{dP}{dt} = \frac{k_1 P_{H_2}}{1 + b\sqrt{P_{C_2H_2}}} .$$

3) It was suggested that both catalytic hydrogenations of acetylene and ethylene proceeded on a few "active regions" of the catalyst with different ratios, and taking some assumptions, the rôle of the various "active regions" on the two hydrogenations was considered.

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(3) J. Horiuti, *Bull. Chem. Soc. Japan*, **15**, 210 (1938).

(4) E. F. G. Herington, *Trans. Farad. Soc.*, **37**, 361 (1941).

(5) T. Yamanaka, *J. Phys. Chem. Res. Inst., Tokyo*, **25**, 329, 481 (1949).

4) It was shown that lead acetate solution poisoned the ethylene hydrogenation much more than the acetylene hydrogenation and this fact coincides with the result of the flow method.

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