Selective Catalysis. The Catalytic Reaction between Acetylene and Hydrogen

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(Received December 28, 1949)

Many investigations have already been made on the hydrogenation of acetylene.(1)–(12) Most of them, however, deal with the products of hydrogenation by the flow method, no attention being paid on the kinetics of reaction. Generally speaking, when acetylene and hydrogen react on a hydrogenation catalyst, there occur three kinds of reactions simultaneously, that is

1) $C_2H_2+H_2=C_2H_4$
2) $C_2H_4+H_2=C_2H_6$
3) $nC_2H_2+mH_2=C_{2n}H_{2(n+m)}$

These reactions are considered as proceeding at various rates according to the reaction conditions and the state of the catalyst. The reason for the remarkable change of the reaction velocities is not well clarified yet. Some interesting results were obtained by Kwan(11) and Farkas(8) on nickel and platinum catalysts repectively. The plausible explanations, however, on the selective action of the catalysts have not been obtained. In the present report some results of the experiments are described on the kinetics of the reactions between acetylene and hydrogen using palladium alumina as catalyst.

Experimental Procedure

The acetylene gas was generated from calcium carbide and water, and purified by the usual method.* Hydrogen was obtained by the electrolysis of water. Palladium alumina catalyst (1 : 100) was prepared by Sano's method(13) from palladium chloride solution. The alumina used was the sample made for the purpose of chromatography by Nippon Aluminium Co.

The experiments were undertaken by the usual static method, the volume of the reaction vessel being about 120 cc. The reacting gas was taken out by a Toepler pump and analysed. The analysis of acetylene and ethylene was carried out according to the method of Treadwell(14) modified by Fujio.(15) Acetylene, ethylene and heavy

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* Refer Vanino's "Präparativen Chemie"

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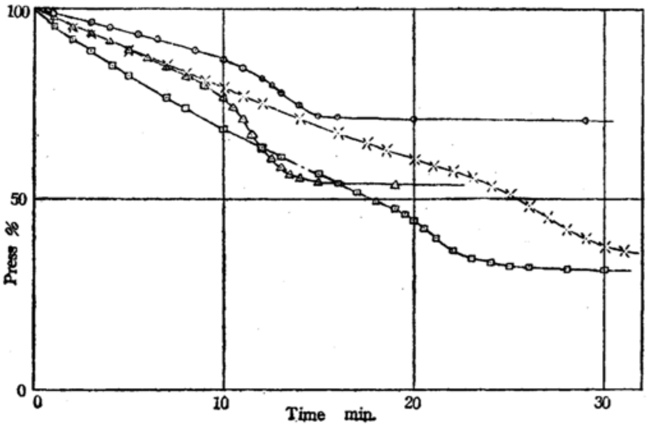
hydrocarbons were determined by absorption with the solution of mercuric cyanide, mercuric nitrate and fuming sulfuric acid respectively. After the removal of the above gases, hydrogen and saturated hydrocarbons were estimated by the explosion method using oxygen gas.

Experimental Results

The results of experiments at 30° are shown in Fig. 1, the abscissa of which being pressure and the ordinate time. In the course of reaction it was observed that the rate of hydrogenation increased rapidly at a certain stage. An example of the change of composition with time is shown in Fig. 2. In this figure the solid line shows the total gas pressure, and the dotted lines show the partial pressures of the component gases. It can be seen, from Fig. 2, that the hydrogenation of acetylene proceeds in two distinct stages. At first all acetylene is hydrogenated or polymerized, and after that ethylene is hydrogenated to ethane. The start of the second stage is indicated by a sudden increase in the rate of hydrogenation. The sudden drop of the gas pressure corresponds to the moment when all acetylene has been used up.



	C_2H_2	H_2 mm.Hg	
Fig. 1 —⊙—	78	404	(0.044g catalyst)
—▲—	120	350	(0.082g 〃)
—×—	200	258	(0.147g 〃)
—◆—	235	250	(0.261g 〃)

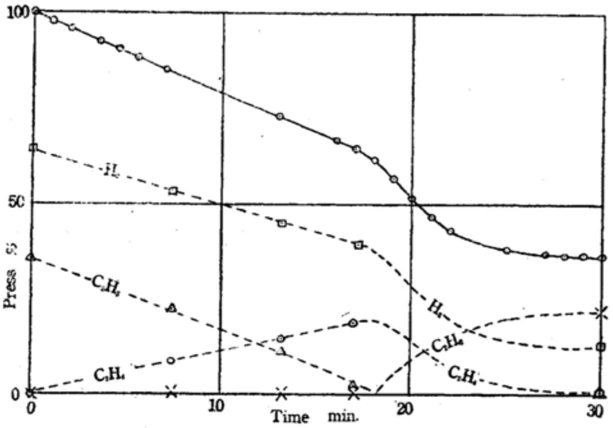


Fig. 2.—C_2H_2 $182_{mm.Hg}$+H_2 $332_{mm.Hg}$, Pd-Alumina catalyst 0.105 g. at 30°.

The initial velocity of hydrogenation is proportional to the amount of the catalyst used. The dependence of the reaction products on the initial composition is shown in Fig. 3, the ordinate of which shows the final pressure relative to the initial one, and the abscissa the initial content of acetylene. The initial pressures of gas range from 450 to 500 mm. Hg. The solid line shows the dependence of the total gas pressure of the reaction product on the initial composition, and the dotted lines the final content of hydrogen, ethylene, ethane or acetylene. The broken line indicates the ratio of final non-polymerized acetylene to the initial one, taking in the ordinate the ratio in percentage of acetylene. The chain line expresses the values of the velocity constant calculated from each experiment. The way of calculation of the velocity constant will be given later. Fig. 3 shows that if the initial content of acetylene is approximately 41% or 51%, the reaction products are wholly ethane or ethylene respectively, and that the polymerized portion of, acetylene increases with the initial content of acetylene.

The hydrogenation of ethylene which occurred in the last half of the reaction, is faster than the formation of ethylene at 30°, but as the reaction temperature is raised, the difference in the rates of the two reactions grows smaller till the former in turn becomes slower than the latter. An example of the experiment at 74° is shown in Fig. 4. It is to be noticed that at higher temperature the formation of ethane proceeds appreciably while acetylene is being hydrogenated.

From these results the energy of activation for the hydrogenation of acetylene is calculated to be 12 kilocalories. This figure is somewhat higher than the energy of activation for the hydrogenation of ethylene, which has been determined to be 9 kilocalories in the same catalyst and at the same temperature range.

Discussion

The feature of the hydrogenation of acetylene on palladium alumina catalyst at room temperature is that the hydrogenation takes place in two distinct steps. At the first step the acetylene is converted into the ethylene and the

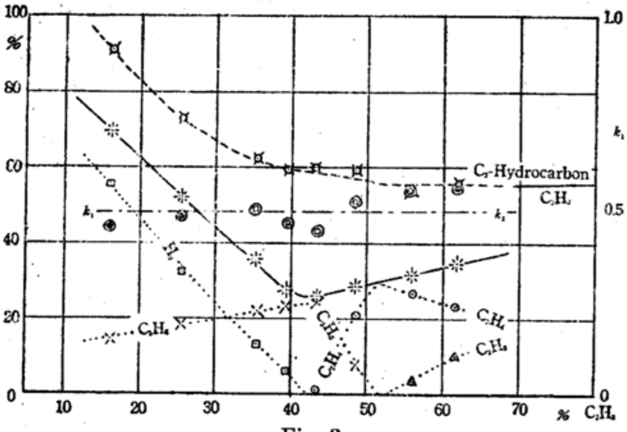


Fig. 3.

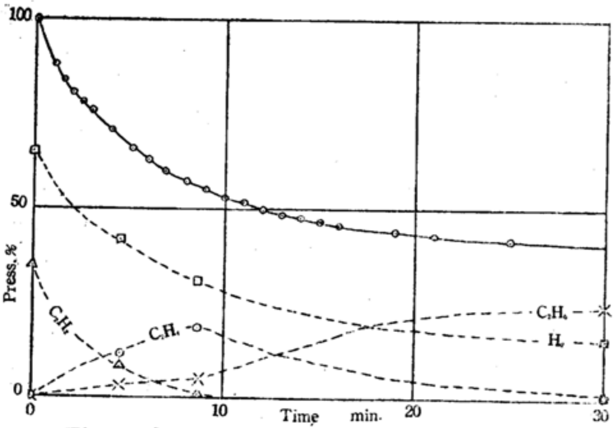


Fig 4.—C_2H_2 182 mm.Hg + H_2 331 mm.Hg Pd-Alumina 0.025 g.

polymers, and at the second step the ethylene is hydrogenated to ethane. The second reaction proceeds after all acetylene has been used up.

The author considers that the selective hydrogenation may be due to the difference of the adsorbability of acetylene and ethylene on the catalyst, and not to the difference of the velocity of the hydrogenation reaction. The dependence of the rate of hydrogenation on the pressure of acetylene and hydrogen can readily be explained by the strong adsorption of acetylene on the catalyst. The velocity of the first stage of hydrogenation of acetylene may be expressed by the following equation, which is analogous to the one given by Cremer,(9)

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

where P denotes the pressure of gas, t the time and, b and k_1 the constants. The velocity constant k_1 calculated from the initial velocities by using the value $b=0.0031$ is given in Fig. 3, the pressure being expressed in mm. Hg and the time in minutes. However, as the polymers produced in the first stage cover the surface of the catalyst, some corrections must be applied for the retarding action in the calculation. The second stage of the reaction, the hydrogenation of ethylene, can be treated approximately as a first-order reaction.

At high reaction temperature, the first stage becomes faster than the second one, the activation energy of the former being greater than that of the latter. In this case the ethane formation is observed during the first stage. This suggests the fact that the adsorption of acetylene decreases at the raised temperature and the ethane formation can, consequently, proceed on the uncovered surface of the catalyst.

Considered from the results of the present experiments, it will be expected that the yield of ethylene by the flow method can be increased with the decrease of acetylene content in the initial reactant, by controlling the various reaction conditions, and that the reaction product can be wholly ethylene or ethane by making properly the initial composition.

Summary

1) The catalytic hydrogenation of acetylene was investigated by Pd-Alumina under various conditions.

2) The hydrogenation of acetylene proceeds in two distinct steps. The first step consists of the reduction and polymerization of acetylene, and the second step the reduction of ethylene to ethane. The second reaction starts after all of the acetylene is reduced to ethylene, and is indicated by a sudden increase in the rate of hydrogenation.

3) The results indicate that acetylene is strongly adsorbed on the surface of the catalyst and the inhibition of the hydrogenation by acetylene is pronounced.

4) It was found that the final products of the hydrogenation can be made wholly into ethylene or ethane and that the highest yield of ethylene is obtained possibly, when acetylene content is small, by avoiding the polymerization of acetylene.

The author expresses his sincere thanks to Prof. J. Sameshima and Dr. H. Akamatu for their kind guidance and encouragement throughout this work.

The expense for the exeriments has been defrayed from the Scientific Research Expenditure of the Department of Education.

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