Dispersity of Catalyst and Catalytic Activity. Catalytic Hydrogenation of Acetylene on the Pd-Kieselguhr Catalyst

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Introduction

In general by the term "carrier" is meant an inert material which acts as a support for the catalyst.(1) A carrier may be used because it provides a larger contact surface and, at the same time, a more equal distribution of the catalyst. By preventing recrystallization, or baking together, it preserves a fine dispersion of the catalyst and hinders aggregation which otherwise would occur. A carrier may influence indirectly the activity of a catalyst by protecting it from poisons. Thus, many functions of a carrier are thought to vary with individual cases. But among these functions the case that a carrier may influence the properties of the catalyst proper is of interest.

Adadurow(2) suggested that a carrier is not at all an indifferent support for a catalyst, but that it produces a deforming action upon the atoms or molecules of the catalyst, changing their catalytic properties.

K. Yoshikawa(3) found that when acetylene is hydrogenated on a Pd-kieselguhr catalyst by the flow method, the yield of ethylene was much affected by the dispersity of palladium on the carrier, and that the catalyst with 500 ~ 1500 parts of kieselguhr being added to one part of palladium was well employed to get ethylene from acetylene. This markedly selective action of the catalysts produced by varying the dispersity of the catalytic agent on an inert substance, can not be explained from the standpoint of the problem of the surface area of the catalyst.

To explain this fact, Yoshikawa assumed the co-activation of neighbouring active centers on the catalyst surface by the heat of the reaction. He thought that the heat produced by the reaction on one active center activates the neighbouring hitherto inactive center, and the newly activated center excites in the same manner the next center as well as the original active point by further reaction and thus the proportion of stimulated active points increases and the reaction is correspondingly accelerated. If the dispersity of the catalytic agent is sufficiently large, the distance between the neighbouring active points may be long enough to disable the efficient co-activation, so that the catalytic centers can not display their full activities. There may be cases where the hydrogenation of acetylene to ethylene is possible but the hydrogenation to ethane is impossible.

Recently T. Yamanaka(4) and T. Takeshima,(5) having investigated the reaction on the Pd-kieselguhr catalyst by the flow method, discussed the mechanism the reaction on the basis of the modified coactivation theory.

The present author(6) previously investigated

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(1) S. Bergman, J. C. Morrell and G. Egloff, "Catalysis" P. 426, New York (1940).

(2) Adadurow, *Zhur. Fiz. Khim.*, **3**, 489, 496 (1932); **6**, 206 (1935); *Zhur. Khim. Prom.*, **6**, 805 (1928).

(3) K. Yoshikawa, *Bull. Chem. Soc., Japan.*, **7**, 201 (1932).

(4) T. Yamanaka, *Sci. Rep. Sci. Res. Inst., Tokyo*, **25**, 329, 481 (1949).

(5) T. Takeshima, *ibid.*, **24**, 199, 303 (1948).

(6) K. Tamaru, this Bulletin, **23**, 28 (1950).

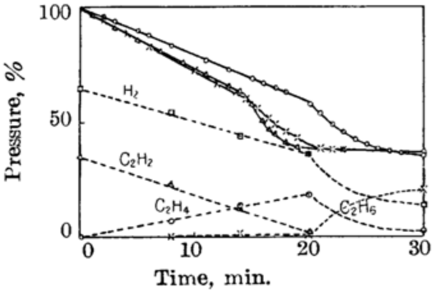
the hydrogenation of acetylene on Pd-alumina catalyst by the static method and found that the hydrogenation of acetylene proceeds in two distinct steps at room temperature. The first step consists of the reduction and polymerization of acetylene and the second step the reduction of ethylene to ethane. The second reaction starts after all acetylene is used up, accompanying a sudden increase in the rate of hydrogenation, and this fact was explained by the strong adsorption of acetylene on the surface of the catalyst proper.

In this study experiments were carried out on the Pd-kieselguhr catalyst of various dispersities and the rôle of the carrier or the problem of the dispersity of the catalyst was considered.

Experimental

As in the previous experiments,⁽⁶⁾,⁽⁷⁾ Pd-kieselguhr catalyst was prepared from palladium chloride solution, into which kieselguhr⁽⁸⁾ was added, by reduction to metal with formaldehyde. The dispersity of palladium on the kieselguhr was determined by the ratio of palladium to the carrier.

The experiments were carried out by the static method and their procedure was the same as that in the preceding papers.



—×—×—: Pd-Kieselguhr (1 : 750) Catalyst (0.600 g.) C_2H_2, 156 mm.Hg; H_2, 295 mm.Hg.

—⊙—⊙—: Pd-Kieselguhr (1 : 250) Catalyst (0.192 g.) C_2H_2, 155 mm.Hg; H_2, 288 mm.Hg.

—△—△—: Pd-Kieselguhr (1 : 100) Catalyst (0.098 g.) C_2H_2, 148 mm.Hg; H_2, 285 mm.Hg.

Fig. 1.—The experiments were carried out at 30° and the composition change of the reactant in the second experiment is shown by the broken lines.

The results of the experiments with the catalysts of various dispersities at 30° are shown in Fig. 1. The second step of the hydrogenation is retarded by the polymers deposited on the catalyst surface as discussed in the preceding paper⁽⁷⁾ and, consequently, the velocity of the ethylene hydrogenation was obtained separately from the reaction between ethylene and hydrogen, the results of which are shown in Fig. 2, where the velocity constants are taken to the ordinate and the ratio of palladium to kieselguhr to the abscissa.

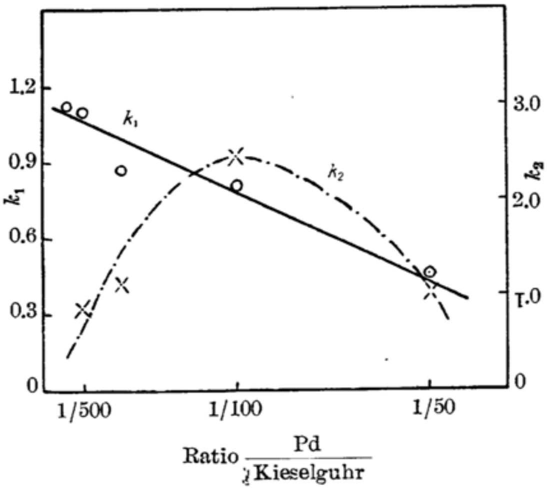


Fig. 2.—The relation between the catalytic activity (velocity constant) and the dispersity of catalyst in the two hydrogenation reactions (k_1 is the velocity constant in acetylene hydrogenation and k_2 in ethylene hydrogenation.)

It is shown in Fig. 2 that the second step of the hydrogenation or ethylene hydrogenation to ethane becomes slower relative to the hydrogenation rate of acetylene when the dispersity gets larger. This tendency is also observed in Fig. 1, in which no correction was made for the retardation of polymers.

As the reaction temperature was raised, the second step became slower as compared to the first step, because the activation energy of the former was smaller than that of the latter, and the catalyst becoming less, the amount of the polymers deposited on the unit area of the catlyst surface was increased, thus retarding the former more extensively than the latter as shown in the preceding paper.⁽⁷⁾

The results of the experiments at various temperatures by Pd-kieselguhr (1 : 750) catalyst are shown in Fig. 3, along with the change of the composition of the reacting gas. It is seen that the second step becomes slower than the first step at the transition of the first and the second steps in the experiment at 74.0°.

The reaction rates of the two steps at various temperatures were expressed by the Arrhenius' equation, respectively, and the activation energy of the reaction was 10 and 8 kcal. in the first and the second steps, respectively.

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(7) K. Tamaru, *ibid.* **23**, 180 (1950)

(8) For this sample commercial kieselguhr was purified by boiling with hydrochloric acid.

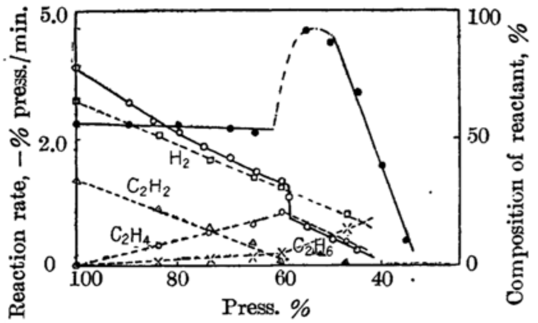

Fig. 3.—Reaction rates in the course of the hydrogenation of acetylene by Pd-Kieselguhr (1 : 750) catalyst at 30° and 74°. (The former is shown by the curve —●—●—, and the latter by the curve —○—○—, and the composition change of the reactant in the latter case is given by the broken lines.)

Consideration

It had been found,⁽³⁾ as mentioned previously, that acetylene is selectively hydrogenated by Pd-kieselguhr catalyst of larger dispersities by the flow method. This fact was explained by the assumption of co-activation of the neighbouring active centers on the catalyst surface, and it was assumed in this case that the active centers, not displaying their full activities, proceed the hydrogenation of acetylene to ethylene, but not of ethylene to ethane.

But present experiments showed all the catalysts of various dispersities to catalyze the hydrogenation of ethylene as well as acetylene and that in two distinct steps quite similarly with the Pd-alumina catalyst.

We see in Fig. 2 that the hydrogenation rate of the first step increases when the dispersity grows larger and that the ratio of k_1 to k_2 differs according to the dispersity of the catalyst.

If the carrier provides only a larger effective surface of the catalyst proper, the ratio should not differ by the dispersity, though the velocity constants of k_1 and k_2 may increase with the dispersity. This fact suggests that the dispersity contributes to the property, as well as to the area, of the catalyst surface.

In the preceding paper⁽⁷⁾ it was suggested that the hydrogenations of acetylene and ethylene proceed on the various "active regions" with different ratios. Hence, the difference of dispersity is considered to have connection with the appearance of various "active regions" with different ratios, as the ratio of the two hydrogenation rates are differed by the dispersity.

For the practical purpose to obtain ethylene from acetylene by the flow method it was suggested in Fig. 1 and Fig. 2 that the catalysts of larger dispersities are good to apply, as the rate of ethane formation is slow relative to that of ethylene formation. This is supported by the above-mentioned results of Yoshikawa by the flow method.

The reaction rate of the second step became slower than that of the first step at the transition of the two steps as shown in Fig. 3. This inversion temperature was not characteristic to the catalyst proper itself, but was dependent on the dispersity of the catalyst.

The fact that the hydrogenations of acetylene and ethylene proceeded independently, obeying the Arrhenius' equation, and that the two reaction rates at the transition of the two steps inverted each other show that the adsorption of hydrogen on the catalyst surface or the supply of the reacting hydrogen is not rate-determining in the hydrogenation of ethylene, provided that the state of the reacting hydrogen is the same in both hydrogenations.

Summary

1) Hydrogenation of acetylene on the Pd-kieselguhr catalyst of various dispersities was investigated.

2) It was shown that the hydrogenation of acetylene proceeded not only to ethylene, but also to ethane by all the catalysts of various dispersities, and that in two distinct steps quite similarly with the Pd-alumina (1:100) catalyst.

3) The ratio of the hydrogenation rate of acetylene to that of ethylene was affected by the dispersity, suggesting the appearance of the various "active regions" of the catalyst surface to be connected with the dispersity. It was large for the catalyst of larger dispersities and this fact explains the results previously obtained by the flow method.

4) Some considerations were given to the rate-determining step in the hydrogenation of ethylene.

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