On the Action of Carriers in the Catalytic Hydrogenation of Acetylene by Palladium Catalyst

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Introduction

The author previously investigated⑴ the hydrogenation of acetylene on Pd-alumina (1:100) catalyst by the static method. It was 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 hydrogenation of ethylene to ethane. The second step started after all acetylene was used up, accompanying a sudden increase in the rate of hydrogenation, and this phenomenon was explained by the strong adsorption of acetylene on the surface of the catalyst. Poisoning or retarding both steps of the hydrogenation simultaneously, it was suggested⑵ from the kinetical treatment of the reaction that the hydrogenation of acetylene occurs on the various "active regions" with different proportions from that of ethylene.

Palladium catalysts which was deposited on kieselguhr with various dispersities proceeded the hydrogenations of the two hydrocarbons with different relative rates. Hence, this fact was considered to suggest⑶ the difference of the dispersity of the catalyst to have connection with the appearance of the various "active regions" of the catalyst surface with different ratios.

In this study experiments were carried out on the palladium catalyst deposited on the various carriers and the rôle of the carrier, along with the mechanism of the hydrogenation of acetylene, was considered.

Experimental

Palladium was deposited on the various carriers by the similar method with that of the previous experiments, that is, suspending the carriers in the palladium chloride solution, potassium hydroxide solution and formaldehyde were added to deposit the palladium on the carriers. Silica gel, french chalk, carbon black, active charcoal, quartz sand, Japanese acid clay, alumina and kieselguhr were used as carriers⑷ and the ratio of palladium to the carrier was 1/100 for each carrier.

The experiments were carried out by the static method and their procedure was the same as the previous experiment⑴. The results of the several experiments at 30.0° are shown in Fig. 1. The

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(1) Kenzi Tamaru, This Bulletin, **23**, 64 (1950).
(2) Kenzi Tamaru, This Bulletin, **23**, 180 (1950).
(3) Kenzi Tamaru, This Bulletin, **23**. 184 (1950).

(4) The used carriers were as follows: Silica gel and Japanese acid clay were prepared by the Takeda Pure Chemicals Ltd. Osaka; French chalk by the Hirasawa Pharmaceutical Laboratory, Tokio; carbon black by the Nihon Kasei Co. Ltd.; active carbon (powder) by E. Merck, Darmstadt, and quartz sand by the Schering-Kahlbaum A. G. Berlin.

The granular active carbon was prepared from the charcoal impregnated by phosphoric acid and each granule was about 0.02 to 0.05 g. in weight.

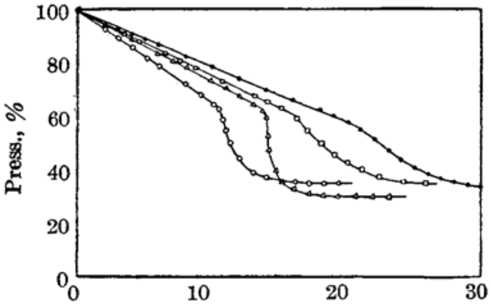

Fig. 1.—Hydrogenation of acetylene by Pd-catalyst on the various carriers at 30°.

	Total press., mm.-Hg	C_2H_2, %
—□——□—: Pd-French chalk (0.210 g.)	439	32.5
—●——●—: Pd-Japanese acid clay (0.165 g.)	474	36.1
—△——△—: Pd-active carbon (Merck) (0.519 g.)	402	33.7
—○——○—: Pd-carbon Black (0.545 g.)	422	35.0

change of the composition of the reactant with time was qualitatively similar with that in the experiments on Pd-alumina or Pd-kieselguhr catalyst in the preceding papers, and the hydrogenation of acetylene first proceeded linearly with time, and when acetylene was used up, the second step, or ethane formation, began with a faster rate.

When the granular active carbon was used as a carrier, the change of the total pressure of the reactant with time was very different from Fig. 1, as shown in Fig. 2 by the full line, and the reaction rate was appreciably different according to the sizes of the granules. The change of the composition of the reactant was given by the broken lines in the figure. In this case no inhibition of the ethane formation by acetylene was observed and both hydrogenations of acetylene and ethylene were simultaneously occurred, showing a typical successive reaction.

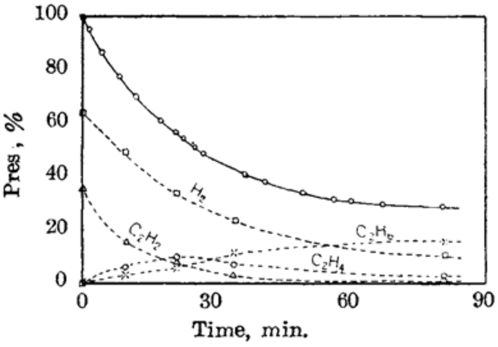

Fig. 2.—Hydrogenation of acetylene by Pd-granular active carbon at 30°: Catalyst, 0.425 g.; total press., 511 mm.-Hg; C_2H_2, 36.0%.

But when the catalyst was powdered in the mortar, the hydrogenation proceeded in a different way from the granular one, as shown in Fig. 3 by the full and the broken lines, that is, a new reflection point appeared, which is indicated by the arrows in the figure. The change of the composition of the reactant was shown by the dotted lines in Fig. 3 in the case of the initial composition of 27.6% acetylene content. The ethane formation was already observed while acetylene was being hydrogenated and the reflection point corresponded to the moment that all acetylene was consumed.

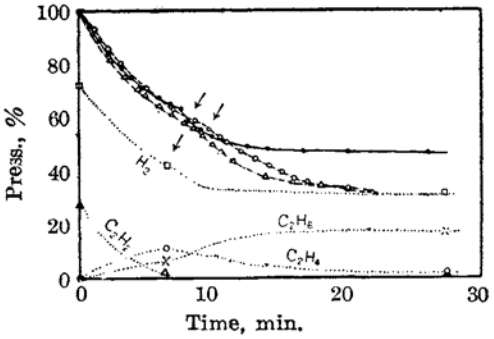

Fig. 3.—Hydrogenation of acetylene by Pd-powdered active carbon and Pd-silica gel at 30°.

	Total press., mm.-Hg	C_2H_2, %
--○----○--: Pd-powdered active carbon (0.248 g.)	495	36.7
—●——●—: Pd-powdered active carbon (0.096 g.)	514	27.6
—·△—·—·△—·: Pd-silica gel (0.620 g.)	405	36.4

The result of the Pd-silica gel catalyst is shown in Fig. 3 by the chain line and this is very similar to that of Pd-powdered active carbon catalyst. It was shown by gas analysis that the reflection point was the point that all acetylene was used up and that ethane formation was to be seen before the point, similarly with the case of Pd-powdered active carbon catalyst.

When quartz sand was used as a carrier the result was appreciably different from the other carriers, and ethane and ethylene formations proceeded simultaneously as shown in Fig. 4. When the initial composition was changed, the reaction proceeded, for example, as shown in Fig. 5 and no self-retardation of acetylene was observed in this case.

The hydrogenation rate of acetylene and ethylene by palladium on the various carriers were shown in Table 1, where the reduction rate of ethylene to ethane was obtained through the hydrogenation of ethylene without retardation of polymers and was given in the table by the reaction constant of the first order reaction.

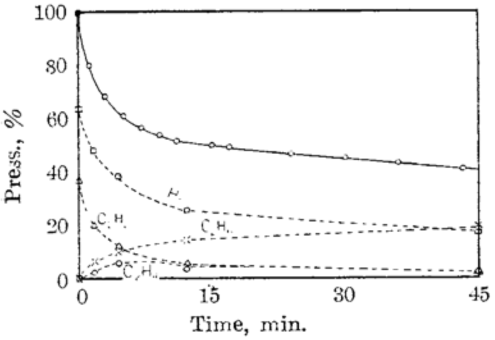

Fig. 4.—Hydrogenation of acetylene by Pd-quartz sand catalyst at 30°: Catalyst, 0.387 g.; total press., 521 mm.-Hg.; C_2H_2, 36.5%.

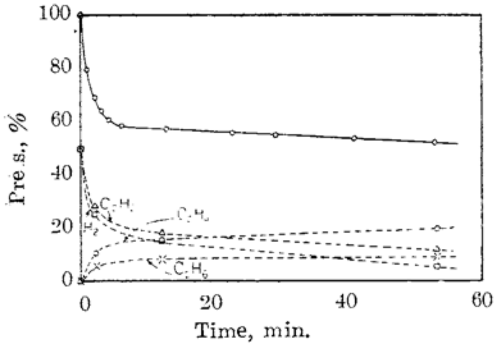

Fig. 5.—Hydrogenation of acetylene by Pd-quartz sand catalyst at 30°: Catalyst, 0.467 g.; total press., 550 mm.-Hg; C_2H_2, 49.8%.

Table 1

The Hydrogenation Rates of Acetylene (V_1) and Ethylene (k_2) by Palladium on the Various Carriers

Carriers	V_1*, %/10 min.	k_2
Alumina	21.0	20.0
Kieselguhr	25.0	24.6
Japanese acid clay	13.3	—
French chalk	11.9	8.0
Carbon black	6.6	6.0
Active carbon (Merck)	5.2	9.0
Powdered active carbon	28.1	—
Silica gel	11.8	—
Quartz sand	59.5	—

* The initial rate of hydrogenation of acetylene per gram catalyst when the total pressure of the reactant was 400 to 500 mm.-Hg and acetylene content approximately 35%.

From the dependence of the hydrogenation rate of acetylene upon temperature, the activation energies of the reaction on the various carriers were obtained as follows: carbon black 10, French chalk 11, quartz sand 11, powdered active carbon 11, kieselguhr 10, alumina 12 kcal. per mole.

Now we come to consider the experimental data mentioned above to study the functions of the carriers for the various cases.

Consideration

We have observed the various types of the reaction curves in the several figures. Now we shall consider how and why these different types of the reaction can occur by the palladium catalyst on the various carriers and study on the functions of carriers for individual cases.

In the preceding paper several functions of a carrier were referred and it was suggested from the kinetical treatment of the reaction that the dispersity of catalyst has connection with the appearance of various "active regions" of the catalyst surface.

As we see in Fig. 1, in the case of such carriers as carbon black, active carbon (Merck), French chalk and Japanese acid clay, the hydrogenation of acetylene proceeded in two distinct steps quite similarly to the case of kieselguhr or alumina and the hydrogenation of ethylene to ethane could not proceed while acetylene was present in the reactant, because of the strong adsorption of acetylene on the palladium surface.

If the carriers provide only a larger effective surface of the catalyst proper, the ratio of the hydrogenation rate of acetylene to that of ethylene is not to be altered by the carriers, though the rate of the hydrogenations may be changed by them. In fact, the ratio of the two hydrogenation rates changed according to the carriers as shown in Table 1. While the activation energies of the hydrogenation of acetylene showed approximately the same value for the carriers, it may be said from the kinetical treatment that the effective area of the various "active regions" of the catalyst will be changed by the kinds of carriers not only their area, but also the proportions of the individual "active regions."

As shown in Fig. 2, the hydrogenation of acetylene proceeded on the Pd-granular active carbon in a different way from such carriers as alumina or kieselguhr, and the hydrogenations of acetylene and ethylene occurred side by side, not proceeding in two distinct steps. Thus it was shown that the granular active carbon is not to be used as a carrier in practice for the selective hydrogenation of acetylene.

But when the catalyst was powdered in the mortar, the reflection point appeared, at which, as the gas analysis showed, all acetylene was consumed, while the ethane formation was already observed before the point. This fact shows that the different type of the curve in Fig. 2 is not to be ascribed to the disappearance of the self-retardation of acetylene, but to the heap of the carrier. Hence, it is to be explained as follows: in the case of the granular carrier the rate of diffusion of the reactant or acetylene into the inner part of the granule is not so fast as the reaction rate at the part, the self-retardation of acetylene, therefore, is not to be seen there, being deficient in the gas, and proceeding the ethane formation, while acetylene is present in the bulk space. When the catalyst was powdered, the proportion of the inner part of the granule practically decreased and the ethane formation in the presence of acetylene could not proceed so much as the granular one, while the reflection point appeared somewhat later than the normal carriers. Hence, the self-retardation of acetylene was also to be observed by the experiments as shown in Fig. 3, and when the acetylene content in the initial composition of the reactant was increased, the reaction rate was appreciably retarded as in the case of such carriers as alumina and others.

In the case of Pd-silica gel catalyst the reaction curve was very similar with that of powdered active carbon, suggesting the similar mechanism of the hydrogenation. It is suggested, consequently, that from these reaction curves we can study the structural property of materials, using them as a carrier of this reaction.

When the quartz sand was used as a carrier, the hydrogenation proceeded in a different way from others. As shown in Fig. 4, the ethane and ethylene formations occurred simultaneously, showing no self-retardation of acetylene. The Pd-quartz sand catalyst was, as it were, a mixture of palladium metal and quartz sand, because of the scanty adsorbability of the carrier and the experiments were not so reproducible as the other carriers, as the distribution of the palladium was not so homogeneous. But it was observed that the initial reaction rate was not so retarded by the increased content of acetylene in the reactant as shown in Fig. 5. The following explanation will possibly be given in this case: scanty adsorbability of the carrier resulted in the much deposited polymers on the surface of the catalyst proper. Hence, the adsorption rate of acetylene was retarded in such an extent that the rate became slower than that of the reaction rate on the catalyst surface. Thus, the effective surface of the catalyst being not covered by acetylene, both hydrogenations of acetylene and ethylene proceeded side by side, showing no self-retardation of acetylene. The considerably fast rate of hydrogenation of acetylene on this catalyst, as given in Table 1, is also considered to support this explanation, as the scanty adsorbability of the carrier should result in the smaller area of the catalyst surface if acetylene covers the catalyst surface as in the other carriers.

Summary

Aceytlene was hydrogenated by palladium deposited on such carriers as carbon black, active carbon (Merck), Japanese acid clay, French chalk, silica gel, granular active carbon, and quartz sand, and the functions of the carriers were considered for individual cases.

The catalysts deposited on the first four carriers catalyzed the hydrogenation in two distinct steps at 30° in the same manner as alumina and kieselguhr, that is, hydrogenation and polymerization of acetylene proceeded in the first step and then ethylene was reduced to ethane in the second step, showing a pronounced self-retardation of acetylene. It was suggested that the kind of carriers has connection with the appearance of various "active regions" with different ratios.

When the granular active carbon was used as a carrier, the hydrogenations of acetylene and ethylene proceeded not in two steps, but simultaneously. This phenomenon was explained by the slow diffusion velocity of acetylene into the inner part of the granule. Powdering the catalyst, the reflection point appeared in the hydrogenation curve and the curve was very similar to that of silica gel, suggesting a similar mechanism of the reaction.

When the quartz sand was used as a carrier, the hydrogenations of the two hydrocarbons occurred at the same time. This is explained by the retardation of the adsorption rate of acetylene by the deposited polymers to such an extent as the adsorption rate becomes to be rate-determining.

It was shown, therefore, that the granular active carbon and quartz sand are not to be used in practice for the selective hydrogenation of acetylene.

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