HOKKAIDO UNIVERSITY

Title	EFFECT OF THE HYDROGEN PRETREATMENT OF PALLADIUM ON ITS CATALYTIC PROPERTIES FOR OLEFIN HYDROGENATION
Author(s)	SATO, Shinri
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 27(2), 89-93
Issue Date	1979-09
Doc URL	https://hdl.handle.net/2115/25062
Type	departmental bulletin paper
File Information	27(2)_P89-93.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 27 No. 2, pp. 89 to 94 (1979)

—**Note**—

EFFECT OF THE HYDROGEN PRETREATMENT OF PALLADIUM ON ITS CATALYTIC PROPERTIES FOR OLEFIN HYDROGENATION

By

Shinri SATO*)

(Received March 26, 1979)

Palladium is a very active catalyst for various reactions, especially for the hydrogenation of unsaturated hydrocarbons. Its catalytic activity for a reaction involving hydrogen, however, sometimes decreases remarkably by repeating the reaction or by pretreatment with hydrogen.[1]

It was found in the present study that pretreatment of Pd with hydrogen reduces its activity for the hydrogenation of ethylene and propene whereas it enhances the activity for the hydrogen exchange between adsorbed olefin and gaseous hydrogen during the reaction of olefin with deuterium. These characteristics of Pd were investigated in connection with conditions of the pretreatment.

The reaction apparatus and the procedure of experiment were the same as used in previous studies.[2,3] Evaporated Pd film and alumina-supported Pd were used as catalysts. The film was prepared at 300°C under a vacuum of 3×10^{-7} mmHg and its geometrical area was ca. 42 cm^2. Alumina-supported Pd (0.5 wt. % Pd, pellet) was obtained from Nippon Engelhard Co. Ltd. After outgassing at 400°C, Pd/Al_2O_3 was reduced by hydrogen at 350°C for three days followed by outgassing at the same temperature. Reaction was commenced by admitting an equimolar mixture of olefin and hydrogen at the total pressure of 40 mmHg. No polymerized products of olefin were detected in the products of reaction.

A freshly evaporated Pd film showed a high activity for the hydrogenation of ethylene and propene but the activity decreased with repetition of the reaction. The decrease in the activity for propene hydrogenation at 20°C is shown in Fig. 1. In this experiment the catalyst was treated with hydrogen (ca. 40 mmHg) at 350°C for 12 hr or more after each run and outgassed at the same temperature until the pressure fell to 5×10^{-7} mmHg (we will refer to this procedure as hydrogen pretreatment). Slight decrease of the activity of Pd/Al_2O_3 was also observed.

*) Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan.

Evaporated films of other transition metals show a similar decrease of the activity for olefin hydrogenation after first and second runs of the reaction. The activity, however, usually becomes constant after a few runs of the reaction, when the film is treated with hydrogen at 200 or 300°C after each run.[2,3] Mann and Lien[4] also found that pumice-supported Pd quickly lost its activity for propene hydrogenation with repetition of the reaction and they ascribed this decrease in the activity to poisoning by mercury vapor. The activity decrease of Pd in the present study, however, is not due to mercury vapor since the catalyst was protected from it by a dry ice trap.

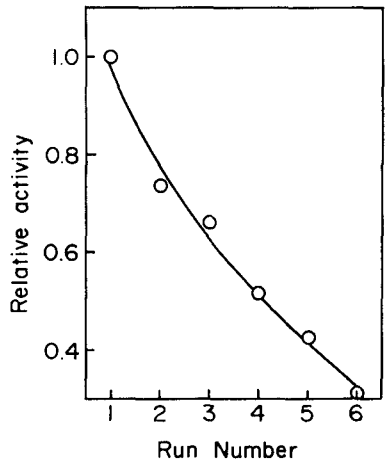

Fig. 1. Change of the activity of evaporated Pd film for the reaction of C_3H_6 with D_2 at 18°C. Before each run (except for Run 1) the film was treated with hydrogen followed by outgassing at 350°C.

The activity decrease of Pd may arise from dissociative adsorption of olefin during the hydrogenation. In order to examine the dissociative adsorption of propene, a mixture of C_3H_6 and C_3D_6 was contacted with Pd film and Pd/Al_2O_3, both of which were used for a few runs of propene hydrogenation. Hydrogen exchange between heavy and light propene on these catalysts took place at 0°C only in the presence of hydrogen, suggesting associative adsorption of propene.

During the deuteration of olefin, H_2 and HD as well as deutero-olefin were produced by the hydrogen exchange between adsorbed olefin and adsorbed hydrogen. It was found that the rates of H_2 and HD formation during the reaction on Pd film increase with repetition of the reaction (Fig. 2) despite the considerable decrease in the hydrogenation rate, while the rate of deutero-olefin formation decreased in proportion to the decrease in the hydrogenation rate. Similar phenomena were observed in the reaction on Pd/Al_2O_3; however, the formation of H_2 and HD was considerably faster than in the case of Pd film even for the first run. On the other hand, the deuterium distribution in propane formed from propene deuteration on Pd film also changed with repetition of the reaction (Fig. 3), *i. e.*, the maximum of deutero-propane shifted from propane-d_0 at the first run to propane-d_1 at the fourth run and the average deuterium number in propane increased from 1.3 to 1.6. The increase of the deuterium number in propane is due to increase in the fraction of deuterium in adsorbed hydrogen with repitition of the reaction, since a broad and nearly random distribution of deutero-propanes indicates a fast hydrogen exchange between adsorbed propene and adsorbed hydrogen. The increase in the deuterium fraction of adsorbed hydrogen may arise

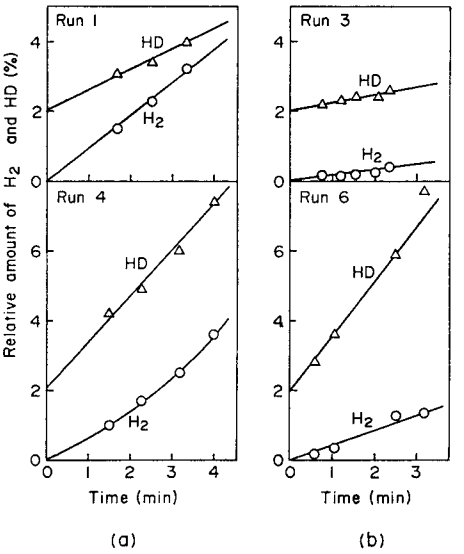

Fig. 2. Time courses of the formation of H_2 and HD during (a) $C_3H_6+D_2$ at 20°C and (b) $C_2H_4+D_2$ at 0°C on evaporated Pd film. Pretreatment of the film is the same in Fig. 1.

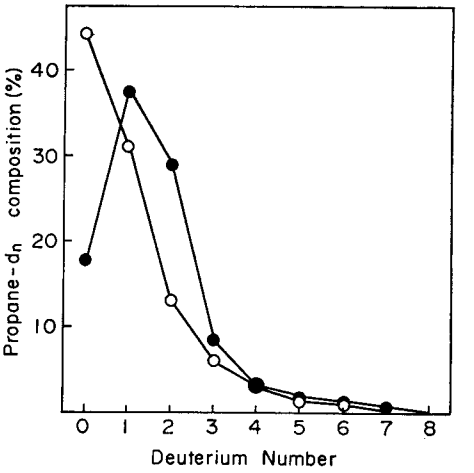

Fig. 3. Deuterium distribution in propane formed from the reaction of C_3H_6 with D_2 at 20°C: ○, Run 1; ●, Run 4. Propane was sampled at ca. 25% conversion of hydrogenation.

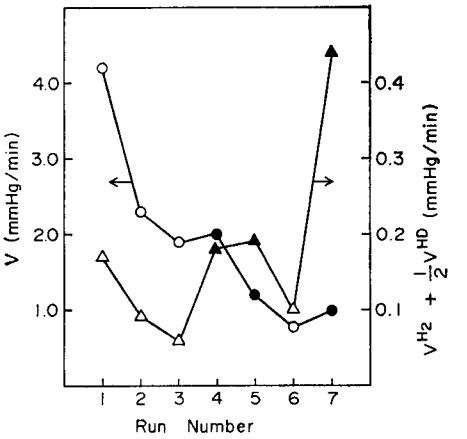

Fig. 4. Change of the activities of Pd film for the hydrogenation of propene (○, ●) and the hydrogen exchange (△, ▲) at 0°C: open symbols, the film was evacuated at 0°C after preceding run; closed symbols, treated with hydrogen and outgassed at 350°C; V, hydrogenation rate; V^{HD} and V^{H_2}, formation rates of HD and H_2.

from acceleration of the exchange between gaseous and adsorbed hydrogen.

To our knowledge such phenomena as mentioned above have never been observed in the deuteration of olefin on other transition metals; the formation rates of all isotopic isomers usually decrease along with decrease in the hydrogenation activity of a metal.[2)]

Figure 4 shows that the acceleration of H_2 and HD formation results from the hydrogen pretreatment of Pd. When Pd film was evacuated at the reaction temperature after the preceding run, the rates of H_2 and HD formation as well as the hydrogenation rate decreased. However, the rates of H_2 and HD formation increased when Pd film was pretreated with

hydrogen at 350°C. The hydrogen pretreatment at temperatures below 100°C did not accelerate H_2 and HD formation.

In order to check for the existence of hydrogen retained by the Pd film after the hydrogen pretreatment, D_2 was used for the pretreatment and then the reaction of C_2H_4 with H_2 was carried out at 0°C. At the initial stage of reaction, a small amount of HD (0.1% of hydrogen) was detected, while deutero-ethylene and deutero-ethane were not detected. The fraction of HD did not increase with the progress of the reaction and deutero-ethylene was still not detected. This result may indicate that the deuterium retained by Pd is rapidly replaced with gaseous hydrogen at the early stage of reaction. The amount of deuterium replaced with hydrogen is estimated to be 0.01 cc (STP) from the amount of HD evolved.

Hydrogen retained by Pd, however, is probably not responsible for the acceleration of H_2 and HD formation, because when the film was outgassed thoroughly at 450°C after the hydrogen pretreatment the acceleration was still observed.

It may be possible that the hydrogen pretreatment of Pd results in a change of the state of adsorbed olefin or the mechanism of hydrogen exchange between hydrogen and adsorbed olefin. In order to examine the adsorption state of propene, the reaction of C_3D_6 with H_2 was carried out on Pd films pretreated in two ways, one was evacuated after the preceding run and another pretreated with hydrogen, and the position of H atoms incorporated into propene during reaction was determined by NMR. Results are shown in Table 1. If propene adsorbs associatively during the reaction, then D atoms in the methylene and methyl groups of C_3D_6 exchange with adsorbed H atoms *via* adsorbed *sec*-propyl, and hence the number of H atoms in the methylene group should be two thirds of that in the methyl group throughout the reaction.[5] All the results in Table 1 do not satisfy this necessary condition for the associative adsorption of propene, indicating that the dissociative adsorption of propene occurred to some extent during the reaction. It is also found from these results that the position of H

TABLE 1 Position of H atoms incorporated into propene during the reaction of C_3D_6 with H_2 on Pd film

Run No.	Pretreatment[a] of catalyst	Temp. (°C)	Conv.[b] (%)	H. N[c]	Position of H atoms (%)		
					CH_2	CH	CH_3
3	evacuation	0	50	0.48	42.9	13.1	43.9
8	hydrogen	0	38	0.36	44.8	15.5	39.6
10	hydrogen	20	52	0.84	42.7	11.8	45.5

a) "evacuation", evacuated at reaction temperature after the preceding runs; "hydrogen", treated with D_2 and outgassed both at 350°C.
b) Conversion of propene to propane.
c) Average number of H atoms in propene.

atoms in propene is not affected much by the hydrogen pretreatment. Therefore, it can be considered that the hydrogen pretreatment has little effect upon the state of adsorbed propene.

The structure of Pd film was determined by X-ray diffraction before and after the hydrogen pretreatment in order to examine its effect on the structure. The film evaporated at 300°C exhibited (111) oriented structure. Its lattice parameter as well as its bulk structure was found to be fairly unchanged after several repetitions of propene hydrogenation and the hydrogen pretreatment. The surface structure, however, could be altered.

Although the structure analysis by X-ray diffraction failed to find a structural change of Pd film by the hydrogen pretreatment, it can be assumed that the phenomena resulting from the hydrogen pretreatment are related to a formation of Pd hydride. Palladium hydride ($\alpha+\beta$ phase) is thermodynamically stable below 30°C at the hydrogen pressure used in the present study.[1] However, Pd hydride would be hardly formed during the hydrogenation of olefin on a freshly evaporated Pd film, because olefin adsorbs so strongly on pure Pd[2,6] that hydrogen adsorption is retarded by adsorbed olefin and adsorbed hydrogen is immediately consumed by the hydrogenation. The hydrogen pretreatment may change this situation; it may lead to cracking of crystallites of the surface layer due to the absorption of hydrogen into Pd,[1] and as a result the surface layer of Pd may easily undergo hydride formation. The hydride thus formed is presumably inactive for the hydrogenation of olefin but active for the hydrogen exchange between hydrogen and adsorbed olefin.

References

1) W. Palczewska, Adv. in Catalysis, **24**, 245 (1975).
2) S. Sato and K. Miyahara, J. Res. Inst. Catalysis, Hokkaido Univ., **23**, 1 (1975).
3) S. Sato, T. Iyama and K. Miyahara, J. Catalysis, to be published.
4) R. S. Mann and T. R. Lien, J. Catalysis, **15**, 1 (1969).
5) S. Sato and K. Miyahara, J. Catalysis, to be published.
6) S. Sato, J. Res. Inst. Catalysis, Hokkaido Univ., **24**, 127 (1976).