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Dispersion State of Platinum on Zeolite and Hydrogenation of Ethylene

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Some metal cations loaded on a zeolite by ion exchange are readily reduced by heating in a hydrogen stream. The reduced metals are highly disperesed in the cavities of the zeolite and show high catalytic activity for hydrogenation of unsaturated compounds. Strel'nikova and Lebedev[1] proposed a hypothesis that the catalytic hydrogenation is carried out on a "mixed ensemble" consisting of a metallic atom and an active center of the carrier. However, this is not in line with the findings that the reduction of cations in the cavities of zeolite gives tiny crystallites with diameters ranging 5—30 Å.[2]

A number of papers[3,4] have reported that catalytic behaviors of supported metal are dependent on the crystallite size or the degree of dispersion. Rabo[5] showed that zeolite catalyst loaded with platinum by ion exchange was less affected by sulfur compounds than similar catalysts prepared by impregnation.

We studied the behavior catalysis of the zeolite catalyst loaded with metals in a given dispersion state. Zeolite(NaY)-supported platinum catalysts were prepared either by ion exchange or impregnation method. After reduction with hydrogen, the platinum subjected to ion exchange was supposed to exist mainly in the cavity. While the impregnation method gave rather large platinum crystallites exclusively on the outer surface of zeolite. The two different catalysts were compared for their activities for the hydrogenation of ethylene.

Experimental

Two types of catalysts, (A) and (B), were prepared from zeolite-NaY with Si/Al ratio of 2.5. (A) was prepared by ion exchange with $Pt(NH_3)_4^{2+}$ aqueous solution, followed by drying at 100—110°C in the air and reduction with hydrogen at 200°C for 3 hr. (B) was prepared by impregnation with ($PtCl_6^{2-}$) aqueous solution, followed by drying and reduction under the same conditions as for (A).

Platinum content was 0.2 or 0.5 wt%. The catalytic activities were tested for hydrogenation of ethylene by use of pulse-technique. In the reactor, 0.1 g of catalyst was placed, and 0.15 m*l* of ethylene gas was injected into a large excess of hydrogen stream continuously flowing down the reactor. The product stream was analyzed by gas chromatography. Hydrogen was supplied from a commercial cylinder after purification over Deoxo catalyst and silica gel. The flow rate was 30 m*l*/min, and the pressure 300 mmHg (gauge).

Results and Discussion

Figure 1 shows that the activity of (A) at reaction temperature 35°C or 45°C rapidly decreases in the first ten injections of ethylene gas with 10 min intervals, and then reaches a constant level.

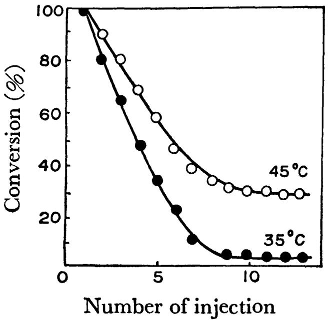

Fig. 1. Change of activity *vs.* number of injection. 0.5 wt% Ion exchanged catalyst (A)

The activity was completely recovered by heating the catalyst at 100°C for 30 min. This seems to be due to an adverse effect of water vapor in the hydrogen stream on the activity of (A). The activity of (B), however, is not affected by water vapor in the hydrogen stream as shown in Fig. 2.

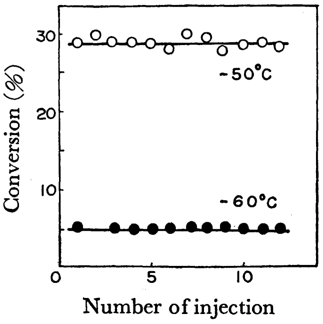

Fig. 2. Change of activity *vs.* number of injection. 0.5 wt% Impregnated catalyst (B)

Over 0.1 g of (A) kept at room temperature, hydrogen stream was introduced at a given flow rate. After 1 hr of hydrogen flow, without ethylene pulse injection, the catalyst lost its activity for ethylene hydrogenation at room temperature, *ca.* 20°C. This experiment suggests that the deactivation of the catalyst (A) is due to some impurity in the hydrogen. The hydrogen was analyzed for water content giving approximately 1—2 mg/*l*. When the hydrogen stream completely dried by refrigeration with liquefied nitrogen was used, (A)

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1) Zh. V. Strel'nikova and V. P. Lebedev, *Intern. Chem. Eng.*, **7**, 199 (1967).

2) C. S. Brooks and G. L. M. Christopher, *J. Catalysis*, **10**, 211 (1968).

3) M. Boudart, A. W. Aldag, L. P. Ptak, and J. E. Benson, *ibid.*, **11**, 35 (1968).

4) G. C. Bond, The IV Intern. Congress on Catalysis No. 67 (1968) (Moscow)

5) J. A. Rabo, V. Schomaker and P. E. Pickert, The III Intern. Congress on Catalysis Sect. 2, No. 4 (1964) (Amsterdam)

was found to give 100% conversion of ethylene to ethane even at the reaction temperature −60°C. In this experiments, a pronounced tailing of gas chromatographic peak of ethane was observed. This could be attributed to the largely prolonged contact time due to strong adsorptive affinity of ethylene on zeolite surface. The catalytic activity never decreased in the presence of completely dried hydrogen.

Observation by electron microscope of (A) revealed that no platinum crystal with diameters larger than 10 Å, the limit of resolution of the electron microscope employed, existed. This means that the reduced platinum presumably exists as atoms and/or as tiny crystallites with diameters less than 10 Å in the cavities of zeolite. Therefore, the decrease in catalytic activity shown in Fig. 1 may be interpreted by the adsorption of water vapor sealing off the cavity mouth of the zeolite to prevent the access of the reactant to platinum site. After the water adsorption equilibrium which depends on temperature is attained, the activity of (A) becomes constant.

On the other hand, electron micrographs of (B) showed that platinum crystallite diameters were 30—100 Å. Platinum crystallites of these dimensions cannot exist in a cavity whose maximum diameter is 13 Å. The adsorption of water vapor on platinum crystallites, if any, might be negligibly small compared with that on zeolite. Consequently, the activity of (B) is constant as shown in Fig. 2.

Table 1. Influence of H_2O in H_2 gas on activation energy

	Catalyst	H_2 Reduction	H_2O/H_2 (mg/l)	Activation Energy (kcal/mol)
1)	0.5 wt%[a]	200°C, 3 hr	2.3	34 (30— 50°C)
2)	0.5 wt%[b]	200°C, 3 hr	2.3	10 (−60——30°C)
3)	0.2 wt%[a]	200°C, 3 hr	1.1	10 (−15— 19°C)
4)	0.2 wt%[b]	200°C, 3 hr	1.1	12 (−15— 18°C)

a) Ion exchanged. b) Impregnated.

After the activity of catalyst attained a constant level by repeated ethylene pulse injection, a logarithmic plot of $(1-x)^{-1}$ (x=conversion of ethylene, mole fraction) against T^{-1} (T=reaction temperature, $°K^{-1}$) was made, giving rise to an Arrhenius straight line. Since an excess of hydrogen was supplied, the hydrogenation rate was assumed to obey the pseudo-first-order kinetics for ethylene. Apparent activation energies from the above plots are shown in Table 1. These results indicate that apparent activation energy over the ion exchanged catalysts (A) is remarkably affected by the water content in a hydrogen stream, but not over the impregnated catalysts. The activation energy for hydrogenation of ethylene previously reported is 8.4 kcal/mol over Pt–SiO_2 catalyst⁶⁾, 9.9 kcal/mol over Pt-Al_2O_3,⁷⁾ and 10 kcal/mol over platinium plate.⁸⁾ These results are in fairly good agreement with those of 2), 3), and 4) in Table 1.

Another catalyst (C) was prepared by ion exchange followed by calcination at 350°C in the air for 3 hr and reduction at 200°C for 3 hr. The slope of the line below 0°C corresponds to an activation energy of 10 kcal/mol. Electron micrographs of (C) show the presence of platinum crystallites with diameters 20—70 Å. This means that platinum was partly aggregated on the surface and possibly exists in part in the cavity. Activity of the catalyst was tested for hydrogenation of ethylene in a hydrogen stream containing 2.3 mg/l of water. A logarithmic plot of $(1-x)^{-1}$ against T^{-1} gave two straight lines with different slopes intersecting at *ca.* 0°C. These results suggest that, below 0°C, ethylene reacts with hydrogen on platinum crystallites outside the cavity. The platinum in the cavity does not seem to be available at this temperature range because adsorbed water is frozen in the cavity to plug it. This is supported by the agreement of activation energy below 0°C for (C) with that for (B). Above 0°C, adsorbed water is released from cavity with the rise in reaction temperature, and the active site in the cavity is allowed to participate in hydrogenation. Thus, the apparent activation energy is larger than that below 0°C by *ca.* 20 kcal/mol, and agrees with that of catalyst (A), In this connection, it might be interesting to note that Dzhigit *et al.*⁹⁾ reported the heat of adsorption of water on Na-Faujasite to be 20—13.5 kcal/mol.

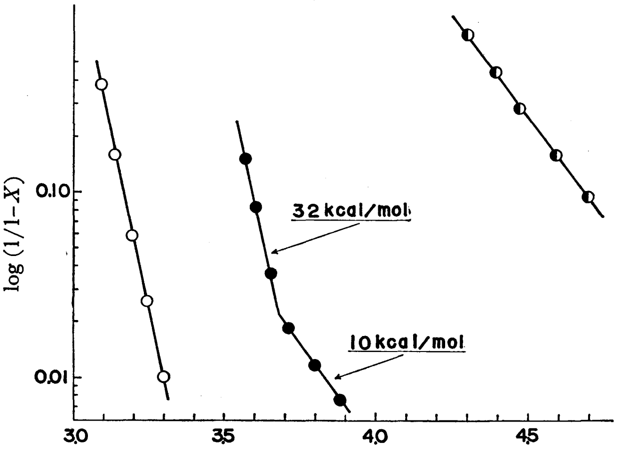

Fig. 3. Plot of $\log(1/1-x)$ vs. $1/T$ ($°K^{-1}$).
Catalyst weight 0.100 g, sample size 6.7×10^{-6} mol, H_2 pressure 303—304 mmHg, H_2 flow rate 33 ml/min, H_2O content 2.3 mg/l.
—○— Catalyst (A) —◐— Catalyst (B)
—●— Catalyst (C)

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8) A. Farkas and L. Farkas, *J. Amer. Chem. Soc.*, **60**, 22 (1938).

9) O M. Dzhigit, A. V. Kiselev, K. N. Mikos, and G. G. Muttik, *Zh. Fiz Khim.*, **38**, (7), 1791 (1964).