Metal Catalysts Supported on Zeolite. II. Dehydrogenation of Cyclohexane and Hydrodemethylation of Toluene over Zeolite-Supported Platinum Catalysts

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Correlations between the amount of hydrogen adsorption and the catalytic activities of the zeolite-supported platinum catalysts were interpreted in terms of the dispersion state of platinum particles. The activities for dehydrogenation of cyclohexane and hydrodemethylation of toluene were directly proprotional to the amount of hydrogen adsorption. The tiny platinum particles with diameters of less than 20 Å, which had little ability to chemisorb hydrogen, showed a poor activity in both reactions.

The correlation between the amount of hydrogen adsorption on metal particles and their catalytic activity for hydrogenation or dehydrogenation has been an interesting subject of catalytic study.[1-4] Our previous work[5] demonstrated that zeolite-supported platinum catalysts with a given dispersion state could be obtained by calcining the ion exchanged zeolite in the air and by subsequently reducing in a hydrogen stream. A pronounced effect was observed of the calcination in the air on the growth of the platinum to form particles. Low temperature calcination was found to give a catalyst which had supposedly tiny platinum particles with diameters below 20 Å that chemisorb very little hydrogen. The optimum size of the particles obtained by calcination at 300°C ranged from 20 to 50 Å in diameter and gave the largest hydrogen chemisorption per weight of platinum loaded.

The present paper will report a good parallelism between the amount of hydrogen chemisorption and the catalytic activity of the zeolite-supported platinum catalyst.

Experimental

Catalyst Preparation. The zeolite-supported platinum catalysts were prepared by ion exchange of zeolite 13 Y, followed by calcination in the air and reduction in a hydrogen stream. The catalysts of the Pt-NaY and Pt-NH_4Y types used in this study were prepared in just the same ways as those in the previous work. The catalyst of the Pt-CaY type were prepared in the same way as above except for the pretreatment of the zeolite 13 Y with $CaCl_2$ aqueous solution to replace Na^+ with Ca^{2+}. This treatment was carried out before the ion exchange of the zeolite with $Pt(NH_3)_4{}^{2+}$.

Dehydrogenation of Cyclohexane. The experiment was carried out by the use of the pulse-technique. In the reactor (4 mm in diameter), 8 mg of powder of 0.24 wt% Pt-NaY, calcined at a specified temperature in the air, was placed and then reduced in a hydrogen stream at 500°C for 3 hr. After the catalyst temperature has been lowered to 280—320°C, 1 μl of cyclohexane was injected into the large amount of hydrogen stream that continuously flowed down the catalyst bed. The flow rate of hydrogen stream was 60 ml/min, and the pressure was 240 mmHg (gauge). The product stream was analyzed by gas chromatography (column: tricresyl phosphate on cellite, 2.0 m in length). The hydrogen was supplied from a commercial cylinder after purification over Deoxo catalyst and molecular sieve 5A.

For accurately evaluating the relative rate of a reaction by the use of the pulse technique, it is essential to avoid the use of a catalyst in a temperature range where a prolonged adsorption of the reactant or of the product on the carrier takes place. The preferred range of temperature was determined in the following way. Into a reactor with 8 mg of the zeolite 13Y (NaY type, no platinum loaded), 1 μl of cyclohexane or benzene was injected at temperatures ranging from 200 to 340°C; the changes in the height and width of the peak of gas chromatogram were then obtained as is shown in Fig. 1. This figure suggests that a reaction temperature higher than 280°C should be employed.

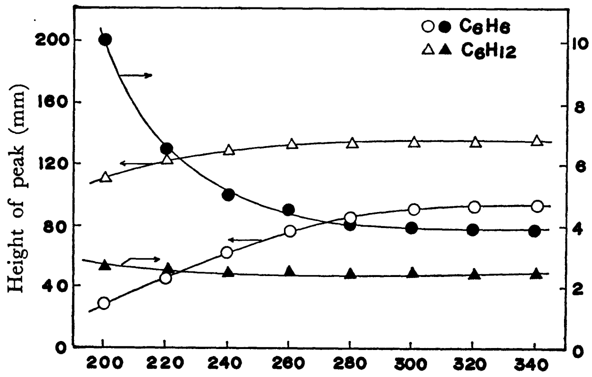

Fig. 1. Adsorption of cyclohexane and benzene on zeolite 13Y.

Hydrodemethylation of Toluene. In a reactor (8 mm in diameter), 0.1 g of a powdered catalyst was placed; 1 μl of toluene was then injected into a large excess amount of hydrogen stream, the flow rate of which was 40 ml/min and the pressure of which was 220 mmHg (gauge). The product stream was analyzed by gas chromatography (column: dinonyl phthalate on cellite, 1.0 m in length). The reaction temperature above 420°C was found to be preferred in the same way as in the cyclohexane experiment.

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[1] H. J. Maat and L. Moscou, Third International Congress on Catalysis, Section 2, Paper 5 (1964).

[2] T. A. Dorling and R. L. Moss, *J. Catal.*, **5**, 111 (1966).

[3] H. E. Swift, F. E. Lutinsky, and H. H. Tobin, *ibid.*, **5**, 285 (1966).

[4] J. A. Cusmans, G. W. Dembinski, and J. H. Sinfelt, *ibid.*, **5**, 471 (1966).

[5] T. Kubo, H. Arai, H. Tominaga, and T. Kunugi, This Bulletin, **45**, 607 (1972).

Results and Discussion

Dehydrogenation of Cyclohexane. The conversions of cyclohexane to benzene remained nearly constant for the first ten injections of cyclohexane at 10 min intervals. Therefore, the average of the conversions in the first ten injections was regared as indicating the catalyst activity. In Fig. 2 the cyclohexane dehydrogenation activities of the Pt-NaY catalyst at 300°C are plotted against the catalyst calcination temperatures in the air. The change in the amount of hydrogen adsorbed on the catalyst (at 25°C, 0.1 mmHg) is also plotted in the figure. This suggests that the active site for dehydrogenation of cyclohexane is closely connected with the adsorption site of hydrogen.

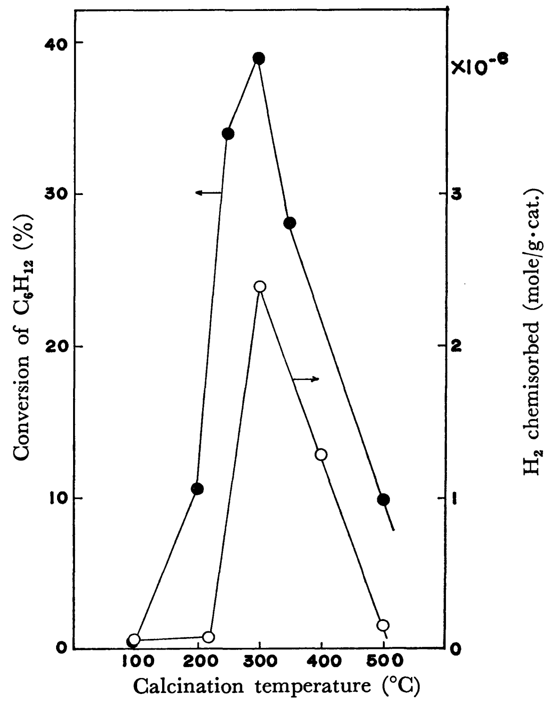

Fig. 2. Dehydrogenation of cyclohexane over 0.24wt% Pt-NaY at 300°C.

In our previous report,[5] it has been suggested that the amount of hydrogen adsorption on the zeolite-supported platinum catalyst depends upon the size of the platinum particles, which is a function of the calcination temperature of ion exchanged zeolite. These results show that the catalyst with fine platinum particles, which are less than 20Å in diameter and which have little hydrogen adsorptive capacity, have little activity to convert cyclohexane to benzene. Based on pseudo-first order kinetics with respect to the concentration of cyclohexane, apparent activation energies for the dehydrogenation were obtained for the different catalysts, as is shown in Table 1. All these activation energies were at 31±3 kcal/mol except for that over the catalyst calcined at 200°C in the air. Furuoya and Shirasaki[6] studied sintering mechanism of palladium on silica-alumina and found that the lattice defect of palladium was mainly determined by the condition of hydrogen reduction and was independent of the condition of previous calcination in air.

Table 1. Apparent activation energies in dehydrogenation of cyclohexane over 0.24wt% Pt-NaY catalyst (280—300°C)

(Reduction of the catalysts in a hydrogen stream was carried out at 500°C for 3 hr.)

Run No.	Calcination temp., °C	Activation energy, kcal/mol
1-1	100	—
1-2	200	19
1-3	250	29
1-4	300	31
1-5	350	34
1-6	400	29
1-7	500	32

In view of these findings, it is considered that the active sites of these catalysts are similar in their quality for dehydrogenation of cyclohexane, and that the difference in the catalytic activities can be attributed to the variation in the effective surface area of the platinum particle.

Hydrodemethylation of Toluene. Hydrodemethylation of toluene over zeolite-supported platinum catalyst of the Pt-NaY type was studied. The activity of the catalyst rapidly decreased with the first ten injections of toluene at 10 min intervals; then it reached a nearly constant level, as is shown in Fig. 3.

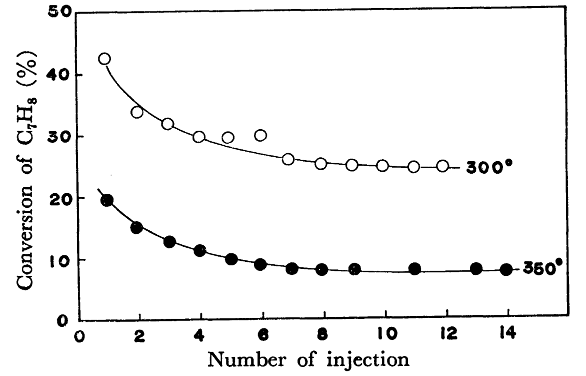

Fig. 3. Hydrodemethylation of toluene over 0.24wt% Pt-NaY at 500°C. Change of activity against the number of injection.

—○— Calcined at 300°C in the air

—●— Calcined at 350°C in the air

All of the catalysts of the Pt-NaY type used in this study showed a similar decline in their catalytic activities. This is considered to come from the deposition of carbonaceous materials on platinum particles because a grey color was found to develop over the catalyst used. After a constant conversion had been attained, the conversion of toluene was taken as a

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6) I. Furuoya and T. Shirasaki, *Kogyo Kagaku Zasshi*, **72**, 1223 (1969).

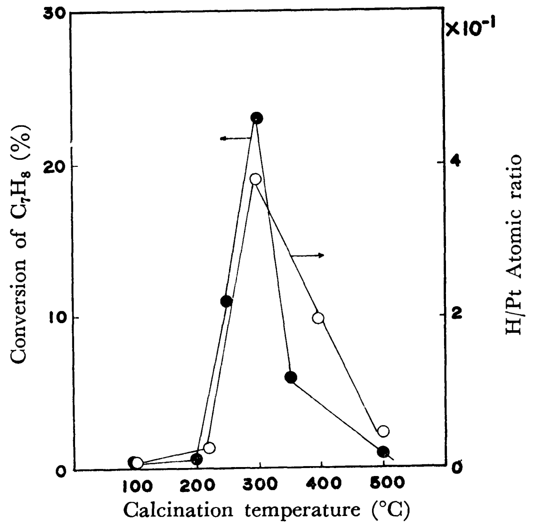

Fig. 4. Hydrodemethylation activity of 0.24wt% Pt-NaY at 500°C against the calcination temperature.

measure of the activity of the respective catalyst. This is plotted against the calcination temperatue in Fig. 4, where the amounts of hydrogen adsorption on the catalyst are also indicated.[5] The figure shows that hydrodemethylation activities of the catalysts are as well correlated with the amounts of hydrogen adsorption as are the cyclohexane dehydrogenation activities. The apparent activation energies for toluene hydrodemethylation were found to lie in the range from 38 to 41 kcal/mol.

Associated with the repeated injection of toluene, a decrease in the activities of the Pt-CaY type catalysts was observed as in the case of the Pt-NaY type catalysts. The hydrodemethylation activity, when a constant level was attained, of the Pt-CaY type catalyst at 500°C is shown as a function of the calcination temperature in the air in Fig. 5. The catalyst calcined at 200°C showed the maximum activity. The characteristic feature of the effect of the calcination temperature was similar to that on the catalysts of the Pt-NaY type.

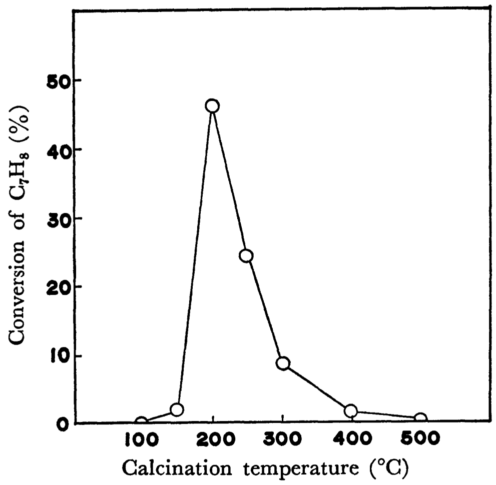

Fig. 5. Hydrodemethylation of toluene over 0.2wt% Pt-CaY at 500°C against the calcination temperature.

In the case of the Pt-NH_4Y type catalysts, no decrease in the initial activity was observed, as is shown in Fig. 6. This makes sharp contrast to the catalysts of the Pt-NaY and Pt-CaY types. The surface proton on the Pt-NH_4Y type catalysts, formed by the decomposition of ammonium ion, might accelerate the cracking of the carbonaceous materials, thus preventing their accumulation. Figure 7 shows the characteristic change in the catalytic activities of the Pt-NH_4Y type catalysts as a function of the calcination temperature. This should be discussed in view of the change in the structure of the zeolite during calcination in the air. That is, the NH_4Y zeolite is transformed by calcination into the decationized type through the HY type, while the structures of the NaY and CaY zeolites are unchanged. At any rate, a good parallelism between the amount of hydrogen

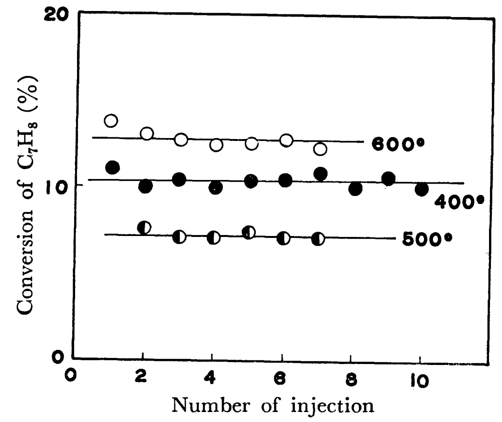

Fig. 6. Hydrodemethylation of toluene over 0.28wt% Pt-NH_4Y at 500°C. Change of the activity against the number of injection.

—●— Calcined at 400°C in the air
—◐— Calcined at 500°C in the air
—○— Calcined at 600°C in the air

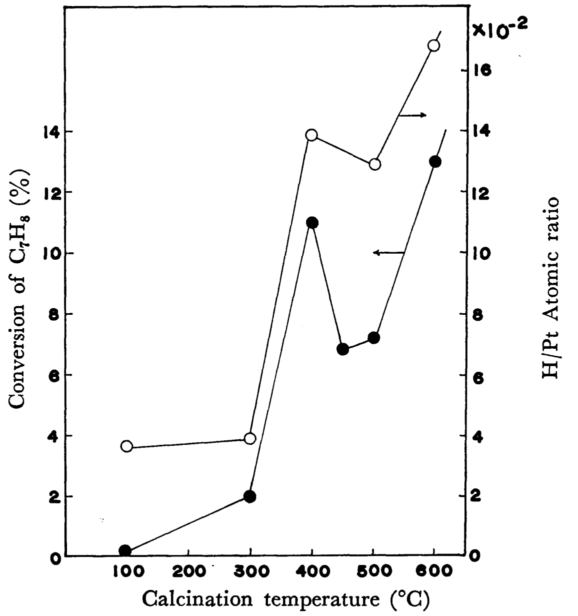

Fig. 7. Hydrodemethylation activity of 0.28wt% Pt-NH_4Y at 500°C against the calcination temperature.

adsorption and the catalytic activity for hydrodemethylation is found to hold. The apparent activation energies for the respective catalysts are shown in Table 2. These experimental facts suggest that the growth of platinum is less favored in the decationized structure of zeolite.

Table 2. Apparent activation energies in hydrodemethylation of toluene over 0.28wt% Pt-NH_4Y catalysts (420—500°C)
(Reduction of the catalysts in a hydrogen stream was carried out at 500°C for 3 hr.)

Run No.	Calcination temp., °C	Activation energy, kcal/mol
2-1	100	—
2-2	300	41
2-3	400	36
2-4	450	37
2-5	500	38
2-6	600	33

Our previous study using electron microscope indicated that the presence of oxygen in the calcination procedure played an important role in the aggregation of platinum, and that the heating of ion exchanged zeolites in a non-oxidizing atmosphere, namely, in a nitrogen or hydrogen stream, had an adverse effect on the growth of platinum particles in the subsequent calcination in the air. The effect of this pretreatment on the Pt-NH_4Y type catalyst is shown in Fig. 8. The hydrodemethylation activity of the catalyst which was pretreated in a nitrogen stream before reduction in the air exhibited a slight activity. The platinum cation or atom may be stabilized on the zeolite by pretreatment in a nitrogen or hydrogen stream at 400—600°C and does not migrate on the surface during the subsequent calcination in the air to form platinum particles. Consequently, the platinum catalyst manufactured by reduction in a hydrogen stream has an ability for neither gas adsorption nor catalytic activity.

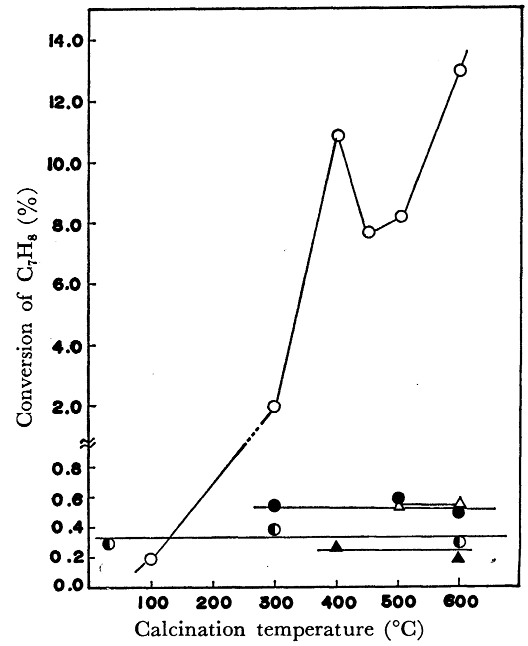

Fig. 8. The effect of pretreatment before calcination in the air and reduction in a hydrogen stream.
—○— Not pretreated.
—◐— Pretreated at 600°C in a nitrogen stream.
—●— Pretreated at 400°C in a nitrogen stream.
—△— Pretreated at 500°C in a nitrogen stream.
—▲— Pretreated at 500°C in a hydrogen stream.

The controlling factors were investigated in preparation of a zeolite-supported platinum catalyst active for hydrogen participating reactions. The most active catalyst, the platinum of which is properly dispersed on the carrier, can be obtained by calcining in the air at a specific temperature prior to reduction in a hydrogen stream. The catalytic activities are in good parallelism with their hydrogen adsorption abilities.