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Dehydrogenation of Cyclohexane on Alumina-Supported Rhodium Catalysts. Effect of Oxidation-Reduction Treatment on the Catalytic Activity

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The cyclohexane dehydrogenation and H_2 chemisorption on Rh/Al_2O_3 catalysts have been studied as a function of reduction temperature (at 373 - 773 K), preceded by O_2 treatment at 673 K. The catalytic activity increased by a factor of 5 after high-temperature reduction at 773 K, while there was almost no change in the H_2 chemisorption capacity with varying the reduction temperature.

Recently attention has been focussed on the effect of H_2 pretreatment on the catalytic and chemisorption properties of supported metal catalysts since the observation of SMSI phenomenon.1) Apart from the drastic effect of catalysts supported on SMSI oxides (TiO_2,2) $Nb_2O_5$3)), it has been reported that high-temperature reduction (HTR; e.g., at 773 K) caused a moderate suppression in catalytic activities, as well as chemisorption capacity, even for catalysts supported on non-SMSI oxides (Ni/SiO_2,4) Rh/SiO_2,5) $Pt/Al_2O_3$6,7)). We report here an anomalous behavior in the activity of cyclohexane dehydrogenation on Rh/Al_2O_3 catalysts.

Two 0.5 wt% Rh/Al_2O_3 catalysts were used in this study: (1) Japan Reference Catalyst (JRC)-A4-0.5Rh (No.15, prepared from $RhCl_3$); (2) JRC-A4-0.5Rh (No.31, prepared from $Rh(NO_3)_3$).8) The catalysts were treated in O_2 at 773 K for 1 h before use. The activity measurements were performed in a pulse reactor similar to that described in Ref.3. Purified He gas was used as the carrier gas (flow rate, 60 cm^3/min) and a pulse (1 cm^3) of a mixture gas (C_6H_{12}, 3.9%; He balance) was injected by a jacketed switching valve purged with He. The O_2 impurity level of the carrier gas was less than 0.05 ppm. Several pulses were introduced until reproducible analyses were obtained. The reaction rate was calculated from the conversion and a residence time (assumed to be the catalyst bed volume ratioed to the carrier flow rate),3) and expressed in molecules converted per total Rh atoms per s. Hydrogen chemisorption measurements were carried out by a conventional volumetric adsorption apparatus.7) Unless otherwise stated, the catalysts were treated in O_2 at 673 K for 1 h followed by H_2 reduction for 1 h at a given temperature (373 - 773 K) before each activity or chemisorption measurement.

Figure 1 shows the activities and the chemisorption values (H/Rh) for the two Rh/Al_2O_3 catalysts as a function of the reduction temperature. There was almost no change in the H_2 chemisorption capacity (H/Rh = ca. 1) with increasing the reduction temperature. The high H/Rh values indicate that both catalysts are highly dispersed. In contrast, the activity of cyclohexane dehydrogenation (i.e.,

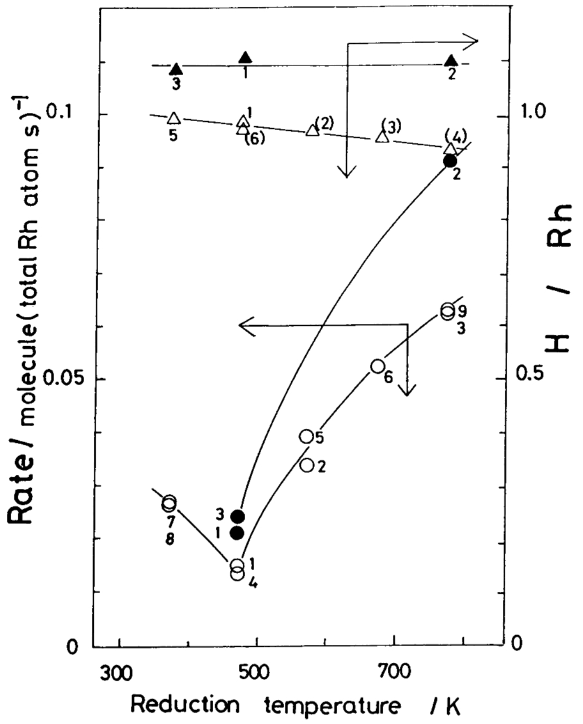

Fig.1. The rate of cyclohexane dehydrogenation at 435 K and the amount of H_2 chemisorption (atomic ratio of H/Rh) as a function of catalyst reduction temperature. The rate is represented by circles and the H/Rh value by triangles. Open symbols indicate JRC-A4-0.5Rh (No.15); filled symbols indicate JRC-A4-0.5Rh (No. 31, Cl free). The numbers in the figure indicate the order of the sequential oxidation-reduction treatments. The numbers in parentheses mean that the O_2 treatment at 673 K was not performed in the pretreatment step: the catalyst was reduced in H_2 at a given temperature followed by evacuation in vacuo at 723 K.

benzene formation) after HTR at 773 K was about 5 times higher than after low-temperature reduction (LTR) at 473 K. It may be noted that the activity after LTR at 373 K was slightly higher than that after LTR at 473 K. The activity variations can be restored reproducibly by repeated oxidation and reduction treatments, as shown in Fig.1. The present result may be the first example to show that HTR of supported metal catalysts resulted in an increase of the activity of a hydrocarbon reaction. The effect of residual Cl (which might be present in the catalyst No.15) may not be important because there was no difference in the catalytic behavior between the samples (Nos. 15 and 31) from different precursors. It may be suggested that Rh surface microstructure can be altered reversibly by the oxidation-reduction treatments,[5] and such morphological changes may affect the activity of the cyclohexane dehydrogenation.

Although we have no detailed interpretation in the present stage, the observed phenomenon, which was quite reproducible and reversible, deserves further attention.

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