Shape-selective Hydrogenation of Olefins with a Rhodium-zeolite Catalyst derived from the Carbonyl Cluster

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A Rh^0_x-NaY zeolite catalyst, which is prepared by decarbonylation of the carbonyl cluster formed in zeolite cavities *via* water-gas shift reaction, shows high shape selectivities for hydrogenation of olefins.

Recently, in attempts to prepare highly selective heterogeneous catalysts, considerable efforts have been expended in the immobilization of homogeneous metal complex catalysts with inorganic supports having intercrystal space such as clay[1,2] and zeolite.[3,4] However there has been little success in achieving high selectivities by zeolite catalysts, because it is not easy to introduce catalytically active metal species selectively into the cavities of zeolite. Recently a new preparation of zeolite-encapsulated π-allyl-rhodium complexes has been reported,[3] however a detailed study[4] on the shape selectivities in olefin hydrogenation showed that the practical use requires selective poisoning of metal sites on the external zeolite surface, indicating that the selective entrapment of the metal species inside the cavities may be incomplete.

In the course of our study to prepare transition metal clusters in zeolite cavities, we have found a new method for entrapment of metallic rhodium in zeolite cavities *via* decarbonylation of rhodium carbonyl clusters prepared by water-gas shift reaction in the cavities. Here we report the shape-selective hydrogenation of olefins by the Rh^0_x-zeolite catalyst.

A Rh^{III} ion-exchanged zeolite, $[Rh(NH_3)_6]^{3+}$/NaY (Rh content, 1.5 wt%), obtained from the usual reaction between $[Rh(NH_3)_6]Cl_3$ and 13NaY zeolite (SK-40; channel diameter 8—9 Å), was dried at 110 °C and then calcined at 400 °C for 5 h. Treatment of the zeolite with wet carbon monoxide (80 kg/cm^2) at 130 °C gave a pink Rh carbonyl cluster, $Rh_m(CO)_n$/13 NaY (**1**). The i.r. spectrum showed the presence of terminal carbonyls at 2090 and bridging carbonyls at 1770 cm^{-1}, indicating formation of a Rh carbonyl cluster.[5] The zeolite (**1**) showed an activity for the hydroformylation of olefins similar to that of type III recently reported by Davis *et al.*[6] Decarbonylation of (**1**) with hydrogen (1 atm) at 120 °C for 24 h yielded grey powder (**2**) of Rh^0_x/13NaY which exhibited no i.r. absorption due to carbonyls at all. The zeolite (**2**) catalysed hydrogenation of various olefins with rates depending on the size/shape of olefin molecules. The hydrogenation

$Rh_m(CO)_n$/13NaY
(**1**)

Rh^0_x/13NaY
(**2**)

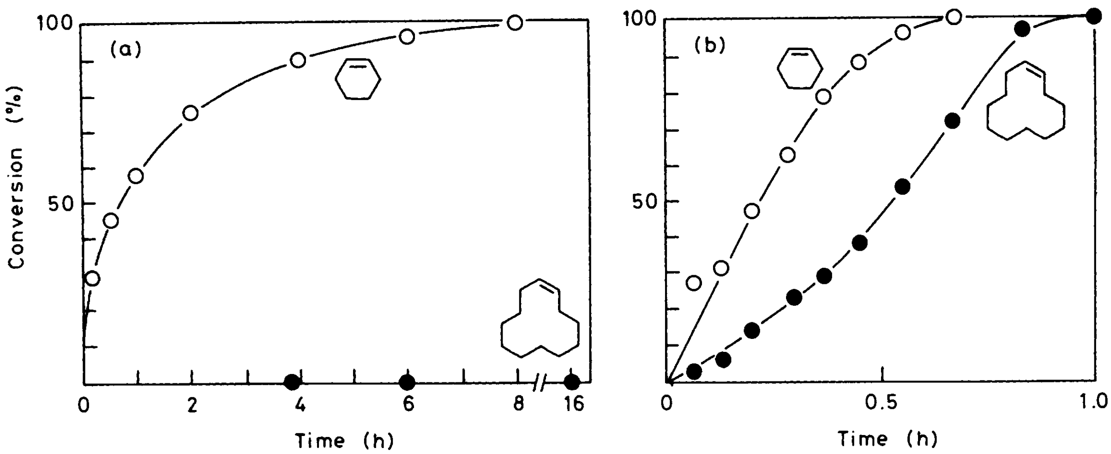

Figure 1. Competitive hydrogenation between cyclohexene (○) and cyclododecene (●): substrate, 5 mmol each; hexane 20 ml. (a) Catalyst (**2**), 50 mg, 50 °C; (b) 5% Rh/C, 20 mg, 30 °C.

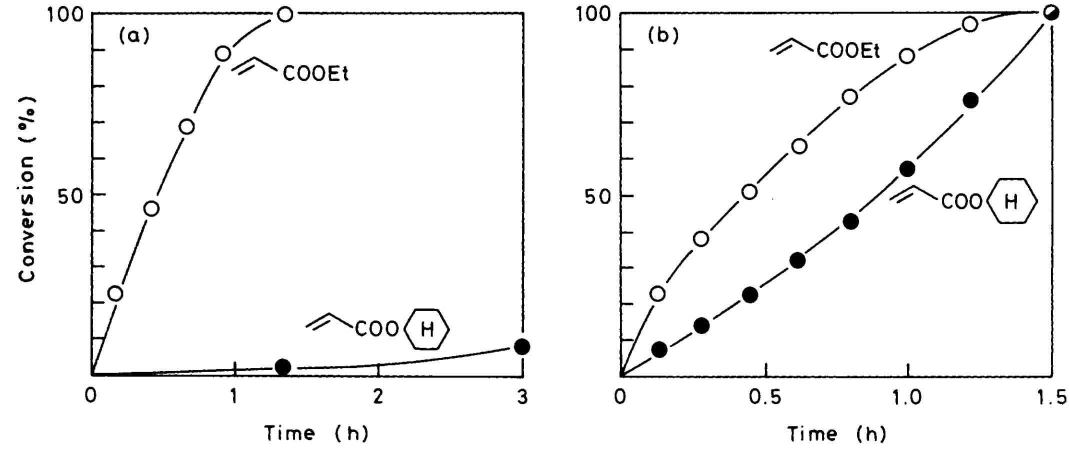

Figure 2. Competitive hydrogenation between ethyl acrylate (○) and cyclohexyl acrylate (●): substrate, 5 mmol each; hexane 20 ml. (a) Catalyst (**2**), 30 mg, 30 °C; (b) 5%Rh/C, 9 mg, 20 °C.

was carried out in hexane at 50 °C under atmospheric pressure of hydrogen without any additives like catalyst poisons.[4] The rates were measured on the basis of H_2 uptake and the yield of hydrogenated products (by g.l.c.). For example, the relative rates decreased in the order, hex-1-ene ≈ oct-1-ene ≈ cyclohexene > cyclo-octene ≫ cyclododecene. However, evaluation based on relative rates does not reflect the exact shape selectivities of catalysts, since the rates for hydrogenation even with rhodium on charcoal catalyst (Engelhart 5%Rh/C; average particle size of Rh, 40—50 Å; average pore diameter of the charcoal, 20—40 Å) depend strongly not only on steric congestion about the double bond, but also on a bulky group remote from the double bond (see, Figures 1b and 2b). We have evaluated, therefore, the selectivity of catalyst (**2**) on the basis of the comparison with Rh/C in the competitive hydrogenation of two kinds of olefins in a single medium. Representative results are shown in Figures 1 and 2. In the competitive reaction between cyclohexene and cyclo-octene, they were hydrogenated at the same rate by Rh/C catalyst, whereas by catalyst (**2**) cyclohexene was hydrogenated five times faster than cyclo-octene. Figure 1 shows clearly that cyclododecene was not hydrogenated by (**2**) even after the hydrogenation of cyclohexene was completed. Figure 2 shows the competitive hydrogenation between two acrylates, revealing that (**2**) may distinguish the molecular size of substrates.

The results obtained above would indicate the location of the active rhodium species inside the zeolite cavities and catalyst (**2**) may be practically used for shape-selective hydrogenation attributed to the molecular sieve nature of the zeolite support.

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