Deactivation of External Acid Sites of H-Mordenite with Ceria Modification in the Isopropylation of Biphenyl

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Cerium modification of H-mordenite was highly effective for the deactivation of acid sites on external surfaces in the isopropylation of biphenyl. The selectivity for 4,4'-diisopropylbiphenyl (4,4'-DIPB) over unmodified H-mordenite decreased with the increase of reaction temperature because of the isomerization of 4,4'-DIPB at the external acid sites. The isomerization was effectively prevented by the ceria modification of H-mordenites.

Many workers have studied the functionalization of polynuclear aromatics such as biphenyl and naphthalene as key components of advanced materials such as heat resistant and liquid crystalline polymers. Shape-selective catalysis using zeolite is useful for manufacturing symmetrically alkylated polynuclear aromatics.[1-14] We have described that highly dealuminated H-mordenites are effective for the shape-selective isopropylation of biphenyl.[1-7] However, the decrease of the selectivity of 4,4'-DIPB was observed with the increase of reaction temperature[6] or with the decrease of propylene pressures.[3,4] These phenomena were explained by the isomerization of 4,4'-DIPB to 3,4'-DIPB at the external acid sites.[1,6] Therefore, the deactivation of external acid sites is essential for the prevention of the isomerization and other non-selective catalysis. Many workers have proposed the deactivation of external acid sites of zeolites.[12-14] We previously found that the external acid sites of H-mordenite were effectively deactivated by ceria modification.[12] In this paper, we describe the prevention of the isomerization of 4,4'-DIPB in the isopropylation of biphenyl over ceria-modified H-mordenites.

H-mordenite (HM, SiO_2/Al_2O_3=128) was obtained from Tosoh Corporation, Tokyo, Japan. Ceria-modified H-mordenite (Ce(x)HM; x: cerium wt% on HM) was prepared by impregnation from ethanol solution of cerium nitrate followed by drying and calcination at 550 °C for 10 h in air stream just before use.[12] The amounts of catalyst were based on the amounts of H-mordenite before the modification. Reaction and analytical procedures were described in previous papers.[4-6]

The effects of reaction temperature on the selectivity of 4,4'-DIPB in the isopropylation of biphenyl under 0.8 MPa of propylene are shown in Figure 1. The isopropylation proceeded shape-selectively over unmodified H-mordenite at moderate temperatures such as 250 °C. However, the selectivity of 4,4'-DIPB was decreased with the increase of reaction temperature, and the selectivity of 3,4'-DIPB increased with the decrease of that of 4,4'-DIPB. On the other hand, the high selectivity of 4,4'-DIPB was observed in encapsulated products inside the pores even at such a high temperature as 300 °C.[6] We have proposed that the decrease of the selectivity was due to the isomerization of 4,4'-DIPB at the external acid sites, and not to the lack of shape-selective catalysis inside the pores.[6]

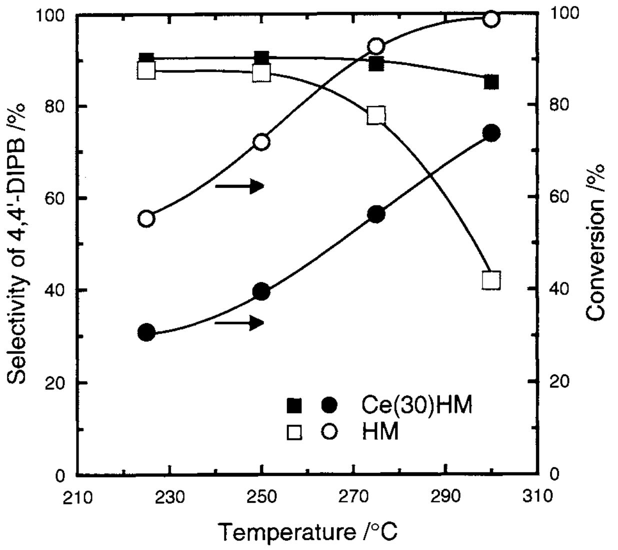

Figure 1. Effects of reaction temperature on the isopropylation of biphenyl over unmodified and ceria-modified H-mordenites. Reaction conditions: biphenyl, 200 mmole; catalyst 1 g (as unmodified HM); propylene pressure, 0.8 MPa; period, 4 h.

Over ceria-modified H-mordenite, Ce(30)HM, the selectivity of 4,4'-DIPB was high even at such a high temperature as 300 °C, and the isomerization of 4,4'-DIPB was effectively prevented. It was almost constant during the reaction, although catalytic activity was decreased. Neither significant formation of 3,4'-DIPB was confirmed in the isomerization of 4,4'-DIPB at 300 °C under propylene pressure of 0.8 MPa. These results show that the formation of 4,4'-DIPB occurs inside the pores of H-mordenite, and that the isomerization of 4,4'-DIPB at the external acid sites is retarded by ceria modification.

Figure 2 summarizes the effects of temperature on the isomerization in the isopropylation of 4,4'-DIPB over unmodified and ceria-modified H-mordenites under 0.8 MPa of propylene. The isopropylation of 4,4'-DIPB was not extensive under our conditions. Over unmodified H-mordenite, no significant isomerization of 4,4'-DIPB was observed below 250 °C, whereas 4,4'-DIPB was extensively isomerized to 3,4'-DIPB with the formation of IPBP isomers above 275 °C.[6] These changes were ascribed to the isomerization of 4,4'-DIPB to 3,4'-DIPB at the external acid sites because the selectivity of 4,4'-DIPB in encapsulated products inside the pores kept high even at high temperatures as 300 °C.[6] On the other hand, no significant

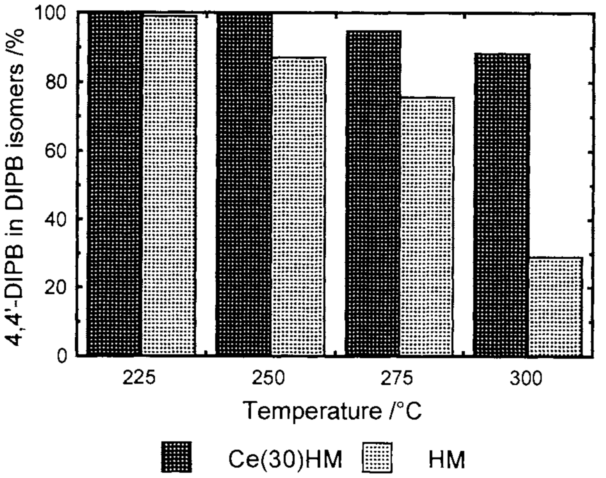

Figure 2. Effects of reaction temperature on the isomerization of 4,4'-DIPB under isopropylation condition over unmodified and ceria-modified H-mordenites. Reaction conditions: 4,4'-DIPB 100 mmole; catalyst 1g (as unmodified HM); propylene pressure, 0.8 MPa; period, 4 h.

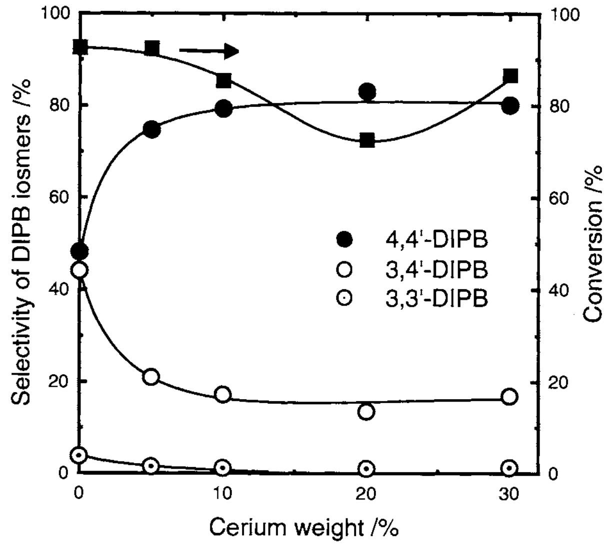

Figure 3. Effects of cerium amounts on the selectivity of 4,4'-DIPB in the isopropylation of biphenyl over ceria modified H-mordenites. Reaction conditions: biphenyl, 200 mmole; catalyst 1g (as unmodified HM); propylene pressure, 0.8 MPa, temperature, 300 °C; period, 4 h.

isomerization of 4,4'-DIPB occurred at every temperature over ceria-modified H-mordenite. These results show that the isomerization occurs at the external acid sites of H-mordenite and is effectively prevented with ceria modification.

The effects of ceria amount on the selectivity of 4,4'-DIPB at 300 °C are summarized in Figure 3. The selectivity was only 50 % for the unmodified H-mordenite. However, it was enhanced by ceria modification, and reached to 80 % by the modification with 10 wt.% cerium against H-mordenite although the small decrease of catalytic activity was accompanied. Similar deactivation of the external acid sites was also described in the isopropylation of naphthalene.[12] However, the effectiveness was not so significant as compared to the results in this paper. These differences should be due to difference of the ease of the isomerization of products.

We described previously that the cracking of bulky 1,3,5-triisopropylbenzene was completely prevented by ceria modification of H-mordenites, and that no significant decrease of adsorption of bulky molecules, such as naphthalene and 2,6-diisopropylnaphthalene were observed over ceria-modified H-mordenites.[12] These results show that ceria is highly dispersed on the external surface of HM with the minimum blockage of the pores, and that external acid sites are effectively deactivated. The prevention of the isomerization of 4,4'-DIPB described in this paper can also be explained by the deactivation of external acid sites of H-mordenite with ceria modification.

In conclusion, the isomerization of 4,4'-DIPB effectively suppresses by ceria modification, and the shape-selective formation of 4,4'-DIPB occurs inside pores even at high reaction temperatures. The ceria modification is a potential method for the deactivation of external acid sites of H-mordenites. Further aspects of the ceria modification will be described in the near future.

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