



The isopropylation of diphenyl ether over H-mordenite catalysts

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ABSTRACT

The isopropylation of diphenyl ether (PE) was examined over dealuminated H-mordenite (MOR) under 0.8 MPa of propene at 175–350 °C. 4,4'-Diisopropyldiphenyl ether (4,4'-DIPPE) was selectively formed at low and moderate reaction temperatures (175–250 °C). The selectivities for 4,4'-DIPPE decreased with increasing reaction temperature, and resulted in the formation of thermodynamically more stable 3,4'- and 3,3'-DIPPE at high temperatures (300–350 °C). The selectivities for DIPPE isomers in encapsulated products had similar features to the selectivities of bulk products. The shape-selective isopropylation of PE consecutively occurs at low and moderate reaction temperatures: 4-isopropyldiphenyl ether (4-IPPE) forms preferentially from PE, and then rapidly convert to 4,4'-DIPPE. However, the isomerization of 4,4'-DIPPE occurred on internal acidic sites in the channels as well as on external acidic sites at high temperatures. MOR channels were large enough for the isomerization of 4,4'-DIPPE at high temperatures because of the fluctuations of zeolite structure and organic molecules.

These features of the isopropylation of PE were quite different from the isopropylation of biphenyl (BP), where no isomerization of 4,4'-diisopropylobiphenyl occurred inside the channels. These differences were due to the conformation of the transition states between PE and BP in MOR channels. Flexible conformation of 4,4'-DIPPE also enabled the isomerization inside the channels.

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1. Introduction

Shape-selective reactions occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically confined environments of the pores and channels of zeolites [1–6]. If all of catalytic sites are located inside channels and small enough to accommodate both the reactants and products, the fate of the reactants and the formation probability of the products are determined by molecular size and configuration of the pores, as well as by the characteristics of its catalytic center. That is, only a reactant molecule whose dimensions are less than a critical size can enter the pore and react at the catalytic site. Furthermore, only molecules that can diffuse out through the pore will appear as products. However, if the space of zeolite pore and channels are wide enough to accommodate the transition states of bulkier isomers, the catalysis depends on the natures of the product molecules, resulting in the formation of bulky molecules under kinetic control and stable molecules under thermodynamic control.

We have discussed shape-selective alkylation of biphenyl (BP) [3–15] and naphthalene (NP) [3,5,6,17–23] over many types of zeolite. Among the zeolites, H-mordenite (MOR) was one of the most effective catalysts for shape-selective isopropylation of BP [3,4,6–16] and NP [3,5,6,17,24–26]. We proposed that the selectivities for the least bulky 4,4'-diisopropylobiphenyl (4,4'-DIPB) and 2,6-diisopropylnaphthalene (2,6-DIPN) were determined by the exclusion of bulky isomers through steric interaction of zeolite channels. In other words, effective exclusion of bulky isomers by the channels at their transition states resulted in shape-selective formation of the least bulky isomers 4,4'-DIPB and 2,6-DIPN from BP and NP, respectively [3–6,8–15,17–23]. However, the catalysis occurred under kinetic and thermodynamic control if the channels could not effectively exclude the bulky isomers [3–6,9–12,14,15,21–23].

Diphenyl ether (PE) can take a more flexible conformation inside the zeolite channels than BP because the oxygen of PE works as a spacer. However, up to now, there has been only one short paper on the isopropylation of PE over MOR by Lee et al. [27]. We have thus been interested in the isopropylation of PE over MOR to understand the mechanism of shape-selective catalysis in zeolite channels. In this work, we report the details of the isopropylation of PE over MOR, and discuss how the catalysis occurs in these channels.

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2. Experimental

2.1. H-mordenites

MOR ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 10, 19, 30, 73, 110, 206, \text{ and } 230$)¹ were obtained from Tosoh Corporation, Tokyo, Japan, and calcined at 550 °C in an air stream just before use. The properties of these MOR are in our previous publication [17].

2.2. Synthesis of substrates and authentic samples

4-Isopropylidiphenyl ether (4-IPPE), 3-diisopropylidiphenyl ether (3-IPPE), 4,4'-diisopropylidiphenyl ether (4,4'-DIPPE), 3,4'-diisopropylidiphenyl ether (3,4'-DIPPE), 3,3'-diisopropylidiphenyl ether (3,3'-DIPPE), 2,4'-diisopropylidiphenyl ether (2,3'-DIPPE), and 2,3'-diisopropylidiphenyl ether (2,3'-DIPPE) were synthesized from corresponding phenols and bromobenzenes according to an analogous procedure for the synthesis of 2-methoxydiphenyl ether [28]. The details of the synthetic procedures are shown in Supporting Information.

2.3. Isopropylation of PE

The isopropylation of PE was carried out in a 100-ml SUS-316 autoclave using propene as alkylating reagent. Typical conditions were 8.51 g (50 mmol) of PE, 250 mg of MOR, 0.8 MPa of propene pressure, and 4 h of operation period at 175–350 °C. The autoclave was purged with nitrogen before heating, and heated to reaction temperature. Propene (0.8 MPa) was, then, supplied to the autoclave, and temperature and pressure were kept constant throughout the reaction. After cooling, the products were separated from the catalyst by filtration. The solution (approximately 1.5 ml) taken from the combined filtrate and washings was diluted with toluene (1.5–6.0 ml), and an aliquot was subjected to the analysis by gas chromatography (Shimadzu GC-14C or GC-18A equipped with an Ultra-1 capillary column (25 m × 0.2 mm; film thickness: 0.25 μm; Agilent Technologies Co. Ltd., MA, USA)). The products were identified by comparison with authentic samples, and confirmed by using a Shimadzu GC-MS-5000 Gas Chromatograph-Mass Spectrometer equipped with an Ultra-1 capillary column.

The analysis of encapsulated products in the catalyst after the reaction was carried out as follows. The catalyst was separated by filtration, washed with 200 ml of acetone, and dried at 110 °C for 12 h. A 50 mg of the resulting catalyst was carefully dissolved using 3 ml of aqueous hydrofluoric acid (47%) at room temperature. This solution was basified with solid potassium carbonate, and the organic layer was extracted three times with 20 ml of dichloromethane. After removal of the solvent *in vacuo*, the residue was dissolved in 5 ml of toluene, and GC analysis was done according to the same procedure as for bulk products.

The stabilities of the products during the dissolution of the catalyst used for the reaction were confirmed by the change in the products distribution without and with hydrofluoric acid treatment.

Thermogravimetric analysis (TGA) of the MOR used for the reaction was carried out on a Shimadzu DTG-50 analyzer with a programmed rate of 10 °C/min in an air stream.

The yield of every product in the isopropylation of PE was calculated on the basis of PE used for the reaction, and the selectivity for each isomer of isopropylidiphenyl ether (IPPE) and diisopropylidiphenyl ether (DIPPE) is expressed as a percentage of each IPPE and DIPPE isomer among the total IPPE and DIPPE isomers. The

selectivity for DIPPE isomers in encapsulated products was also calculated in a similar manner to that for bulk products.

3. Results and discussion

3.1. Influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of MOR on the isopropylation of PE

Fig. 1 shows the influence of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of MOR on the isopropylation of PE under 0.8 MPa of propene at 250 °C, where MORs with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of higher than 20 were prepared by the dealumination [17]. The isopropylation yielded mixtures of IPPE, DIPPE, and triisopropylidiphenyl ether (TIPPE) isomers (Fig. 1a). The conversion of PE initially increased with $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 10 to 128; and, then decreased with further dealumination. The formation of IPPE and DIPPE isomers initially increased with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio; however, further increases in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio decreased the yield of DIPPE isomer, accompanying the increase in IPPE isomers. These results indicated that the catalytic activity at $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 10 to 128 was rapidly enhanced by the dealumination, while the catalytic activity decreased by further dealumination due to the decreased acidic sites. The rapid increase in catalytic activity was due to the decrease in coke formation, as discussed later.

Fig. 1b shows the influence of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of MOR on the selectivity for DIPPE isomers. MOR(10) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 10 gave the lowest selectivities for 4,4'-DIPPE, leading to the formation of bulky 2,3'-DIPPE ($x = 2, 3, 4$). However, the selectivities for 4,4'-DIPPE were remarkably improved up to 80% over MOR(128) with 128 of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

TGA profiles of the catalysts after reaction are shown in Fig. 2. The peaks due to coke-formation were observed at approximately 580 °C. The coke formation was maximized at the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30, and then decreased with the increased ratio (12.8%, 7%, and 7.2% for the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 30, 128, and 202 based on weight loss between 350 °C and 650 °C). Severe coke-formation occurred during the catalysis in their one-dimensional channels of the MOR with ratios of less than 30, while the further dealumination caused the decrease in coke-formation.

The catalytic activities were enhanced by increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio up to 128 due to the decrease in coke-formation; however, further dealumination declined the catalytic activities due to decreased acidic sites for the catalysis, even if coke-formation decreased. Low selectivities over MOR with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were most likely because of non-selective catalysis at the external acid sites, free from choking the channels by coke-formation. These results indicate that the appropriately dealuminated MOR had high potential for shape-selective formation of 4,4'-DIPPE, although the dealumination caused a decrease in acid sites and the formation of meso-pores. These results resemble the isopropylation of BP and NP: the highest catalytic activities were found over the highly dealuminated MOR [3–6,8,17]. From these findings, we chose MOR(128), with 128 of $\text{SiO}_2/\text{Al}_2\text{O}_3$, for further investigation.

3.2. Influence of reaction temperature on the isopropylation of PE

Catalytic activity increased with increased reaction temperature in the isopropylation of PE under 0.8 MPa of propene (Fig. 3). The yield of DIPPE isomers increased with increasing the temperature, reaching a maximum at 275 °C, and then decreased with further increases in the temperature. In contrast, the yield of IPPE was almost the same levels to 250 °C, with a minimum at 275 °C, and then increased again with further increase in the temperature.

¹ The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of MOR expresses in parenthesis.

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