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Preparation of [Fe]-SSZ-24 through the isomorphous substitution of [B]-SSZ-24 with iron, and its catalytic properties in the isopropylation of biphenyl

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ABSTRACT

[Fe]-SSZ-24, a ferrosilicate with AFI topology, was prepared through an isomorphous substitution of [B]-SSZ-24 with iron, and applied for the isopropylation of biphenyl (BP) to understand the mechanism of shape-selective catalysis. The substitution of [B]-SSZ-24 with an aqueous solution of a limited amount of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ effectively gave [Fe]-SSZ-24, and its XRD gave clear patterns of AFI topology without the peaks assigned to Fe_2O_3 . [Fe]-SSZ-24 exhibited enhanced catalytic activity for the isopropylation of BP. Shape-selective formation of 4,4'-diisopropylbiphenyl (4,4'-DIPB) occurred at moderate temperatures (250–300 °C); however, the decreases of the selectivity for 4,4'-DIPB occurred at high temperatures (325–350 °C). On the other hand, the selectivities for 4,4'-DIPB in encapsulated products remained almost constant (*ca* 75%), irrespective of the reaction temperature and the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratios. The differences in the selectivities for 4,4'-DIPB between bulk and encapsulated products indicate that shape-selective formation of 4,4'-DIPB occurs in the [Fe]-SSZ-24 channels, and these channels prevent the isomerization of 4,4'-DIPB, even at 350 °C. These results suggest that the channels of SSZ-24 can discriminate 4,4'-DIPB from other possible DIPB isomers at their transition states although high reaction temperatures cause isomerization at external acid sites.

Large pore molecular sieves of AFI topology, [Fe]-SSZ-24, [Al]-SSZ-24, MgAPO-5, ZnAPO-5, and SAPO-5, gave similar levels of selectivities for 4,4'-DIPB in the isopropylation of BP. These results indicate that the framework of AFI topology primarily controls shape-selective formation of 4,4'-DIPB, although catalytic activities of the materials were dependent on acidic properties.

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1. Introduction

Large pore molecular sieves (LPMS) including zeolites, metallocates, and metallophosphates are the most promising microporous crystals for achieving highly shape-selective catalysis because their pores are uniformly distributed and because they have dimensions that allow both organic reactants and products to enter, to be accommodated, and to leave [1–5]. Among them, LPMS with 12- and 14-membered ring (12- and 14-MR) entrances are expected for the catalysts of the alkylation of polynuclear aromatics [3–20]. For example, dealuminated H-mordenite (MOR) selectively gave 4,4'-diisopropylbiphenyl (4,4'-DIPB) in the isopropylation of biphenyl (BP) [3,5–8]. It has been of great interest to elucidate the catalytic features of the LPMS pores because confined circumstances of the materials highly influence shape-selective catalysis. Recently, we studied the alkylation of BP over various zeolites with one-dimensional 12-MR and 14-MR pore entrances

and over three-dimensional zeolites with 12-MR pore entrances from the aspects of steric restriction at the transition states of the product isomers in the channels [9–17].

SSZ-24 is a high-silica LPMS isostructural with $\text{AlPO}_4\text{-5}$ (AFI topology) with 12-membered ring cylindrical channels and pore entrances of 0.72 nm radii [21]. Zones et al. first synthesized SSZ-24 in its pure-silica form using 1-trimethylammonioadamantane as a structure-directing agent (SDA) [22]. The borosilicate version ([B]-SSZ-24) was subsequently synthesized using a calcined form of boron-substituted zeolite β ([B]-BEA) as the boron and silicon sources [23]. Lobo and Davis also reported the synthesis of [B]-SSZ-24 using N(16)-methylasparteinium bromide $[\text{MeSPA}]^+\text{Br}^-$ as the SDA and sodium borate as the source of boron, and they converted to [Al]-SSZ-24 by an isomorphous substitution with aluminum nitrate [24]. More recently, we developed a new method of [Al]-SSZ-24 by phase transformation of zeolite β ([Al]-BEA) using $[\text{MeSPA}]^+\text{OH}^-$ as the SDA [25].

It is important to understand how the zeolite properties, such as structure of channels and acidity, influences shape-selective catalysis. In particular, we have been interested in the catalytic properties of isostructural LPMS with AFI topology in the isopropylation of BP,

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because they have slightly bigger pore entrances and channels compared to MOR. We have studied the isopropylation of BP over LPMS with AFI topology, [Al]-SSZ-24, MgAPO-5, ZnAPO-5, and SAPO-5, and discussed that the topology is a key factor in shape-selective formation of 4,4'-DIPB [18–20]. It is also important to elucidate the influences of acidic properties of zeolites on shape-selective catalysis. We consider that [Fe]-SSZ-24 is an appropriate candidate to study the influences of acidity on shape-selective catalysis in AFI channels, because [Fe]-SSZ-24 has AFI topology with weak acidity.

In this paper, we studied the preparation of [Fe]-SSZ-24 by an isomorphous substitution of [B]-SSZ-24 with iron, and applied it for the isopropylation of BP to elucidate the relation between the acidic and catalytic properties and to determine the role of topology and acidity in shape-selective catalysis through comparison to other isostructural LPMS with AFI topology.

2. Experimental

2.1. Synthesis of [Fe]-SSZ-24

[B]-SSZ-24 was synthesized by hydrothermal conditions using [MeSPA]⁺OH⁻ according to a procedure in the literature [23]. The typical gel composition is as follows SiO₂:[MeSPA]⁺OH⁻:NaOH:B₂O₃:H₂O = 1:0.2:0.1:0.04:50. SiO₂ (Carb-O-Sil M5) 0.608 g, [MeSPA]⁺OH⁻ 2.9125 g, Na₂B₄O₇·10H₂O 0.0766 g, 32 wt.% NaOH solution 0.0791 g, water 6.5474 g, and [B]-BEA (SiO₂/B₂O₃ = 50) 0.0125 g as seeds were placed in Teflon container, and resultant gel was stirred during 3 h. Then, the gel was transferred to Teflon-lined autoclave, heated at 175 °C during 6 d. After the crystallization was completed, the autoclave was cooled to room temperature. The obtained BEA zeolite was collected, washed thoroughly with water, and dried overnight at room temperature. The resultant zeolites were heated in a flow of air (50 ml/min) with temperature programmed rate of 2 °C/min up to 650 °C, and calcined for 6 h under an air stream (50 ml/min). [B]-SSZ24 with 53.0 of SiO₂/B₂O₃ was obtained. [B]-SSZ-24 (1.0 g) was then deboronated by stirring with 100 ml of 0.01N hydrochloric acid for 1 d. Then, resulting [B]-SSZ-24 after calcination at 650 °C was converted to [Fe]-SSZ-24 according to analogous method for the transformation of [B]-SSZ-24 to [Al]-SSZ-24 [24]. [B]-SSZ-24 was heated at 80 °C with an aqueous Fe(NO₃)₃ solution (1:0.5:50 (weight ratio) [B]-SSZ-24:Fe(NO₃)₃·9H₂O:H₂O) for 18 h with stirring. After cooling the mixture, the solid was filtered and washed two times with 0.5 mol/l hydrochloric acid. Then, the resultant sample was dried at 40 °C overnight and calcined at 550 °C for 6 h. The samples with n times repetitions of the substitution with Fe(NO₃)₃/[B]-SSZ-24 = 0.5 were abbreviated Fn (n = 1–5). Thus, F1, F3, and F5 were used as catalysts. The SiO₂/Fe₂O₃ ratios of F1, F3, and F5 were 55, 38, and 28, respectively.

Isomorphous substitution of [B]-SSZ-24 with the ratio of [B]-SSZ-24:Fe(NO₃)₃·9H₂O:H₂O (1:2.0:50 weight) was also examined to know the influence of the co-precipitation of ferric hydroxide on the zeolite. The obtained solid was filtered and washed two times with water. Then, the resultant sample was dried at 40 °C overnight and was calcined at 550 °C for 6 h. The samples of the zeolites with Fe(NO₃)₃/[B]-SSZ-24 = 2.0 were abbreviated Cn (n = 1–5).

The textual properties of [Fe]-SSZ-24 prepared by isomorphous substitution of [B]-SSZ-24 are summarized in Table 1.

2.2. Isopropylation of BP

The isopropylation of BP was carried out in a 100-ml SUS-316 autoclave under propene pressure. Typical reaction conditions were 3.9 g of biphenyl (25 mmol) and 0.125 g of the catalyst with 0.8 MPa propene pressure at 250–350 °C for 4 h. An autoclave

Table 1
Textural properties of [Fe]-SSZ-24 zeolites.

	SiO ₂ /B ₂ O ₃	SiO ₂ /Fe ₂ O ₃	Surface area (m ² /g)	Pore volume (cm ³ /g)
Calcined	53	–	379	0.16
Deboronated	361	–	343	0.14
F1	–	53	421	0.21
F3	–	38	261	0.10
F5	–	28	191	0.067
C3	–	6.5	380	0.15
C5	–	3.1	327	0.14

containing BP and the catalyst was purged with nitrogen before heating. After reaching the reaction temperature, propene was introduced to the autoclave, and the reaction was started by agitation. The pressure was kept constant throughout the reaction. After cooling the autoclave and release of excess propene, the catalysts were filtered off, and the bulk products were diluted with toluene. The products were analyzed by a Gas Chromatograph (GC-14C or GC-18A, Shimadzu Corporation, Kyoto, Japan) equipped with an Ultra-1 capillary column (25 m × 0.2 mm, 0.25 μm thickness, Agilent Technologies, MA, U.S.A.) and confirmed by a Shimadzu Gas Chromatograph-Mass Spectrometer (GC-MS-5000) using the same type column.

The yield of each product was calculated on the basis of the amount of starting BP, and the selectivities for each isopropylbiphenyl (IPBP) and diisopropylbiphenyl (DIPB) isomers were expressed according to the total amounts of each IPBP and DIPB isomers, respectively.

The analysis of the encapsulated products in the catalyst used for the reaction was carried out as follows. The catalyst was filtered off, washed with 200 ml of acetone, and dried at 110 °C for 12 h. Then, 50 mg of the resultant catalyst was carefully dissolved in 3 ml of aqueous hydrofluoric acid (47%) at room temperature. This solution was basified with solid potassium carbonate, and was extracted three times with 20 ml of dichloromethane. After removing the solvent *in vacuo* from the collected organic phases, the residue was dissolved in 5 ml of toluene and was subjected to a GC analysis following the same procedure as for the bulk products.

2.3. Characterization of the zeolites

Crystal structures of the zeolite were determined by powder X-ray diffraction using a Shimadzu XRD-6000 with Cu Kα radiation (λ = 1.5418 Å). An elemental analysis was performed by inductive coupled plasma atomic emission spectroscopy on a JICP-PS-1000 UV (Leeman Labs Inc., CA, USA). Scanning electron microscopy (SEM) was recorded by using an S-4300 FE-SEM microscope (Hitachi Corporation, Tokyo, Japan). N₂ adsorption measurements were performed on a Belsorp 28SA (Bel Japan, Osaka, Japan). Ammonia-temperature programmed desorption (NH₃-TPD) was measured using a TPD-66 apparatus (Bell Japan). Here, the catalyst was evacuated at 400 °C for 1 h, and ammonia was adsorbed at 100 °C, followed by further evacuation for 1 h. Then, the sample was heated from 100 to 710 °C at a rate of 10 °C/min under a helium stream. A TG analysis was performed using a Shimadzu TG-DTG-50 analyzer with a temperature-programmed rate of 10 °C/min in an air stream. The adsorption of *o*-xylene was measured by a gravimetric method using a microbalance at 25 °C and after the evacuation of the sample at 500 °C.

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