Journal of Molecular Catalysis A: Chemical 367 (2013) 23–30

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Isopropylation of biphenyl over ZSM-12 zeolites

Anand Chokkalingam[a], Hiroaki Kawagoe[b], Seiji Watanabe[b], Yasuhiro Moriyama[b], Kenichi Komura[b], Yoshihiro Kubota[b,c], Jong-Ho Kim[d], Gon Seo[d], Ajayan Vinu[a,*], Yoshihiro Sugi[a,b,**]

[a] Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Qld 4072, Australia
[b] Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
[c] Department of Materials Science and Engineering, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan
[d] School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Republic of Korea

ARTICLE INFO

Article history:
Received 19 September 2012
Received in revised form 16 October 2012
Accepted 17 October 2012
Available online 30 October 2012

Keywords:
ZSM-12
Particle size
Biphenyl
Isopropylation
Shape-selective catalysis

ABSTRACT

ZSM-12 zeolites, ZSM-12L and ZSM-12S, with MTW topology were synthesized by using methyltriethylammonium bromide (MTEABr) and tetraethylammnoium bromide (TEABr) as structure directing agents (SDA), respectively, for the isopropylation of biphenyl (BP) using propene as an alkylating agent. The particle sizes of the ZSM-12L and ZSM-12S were in the range of 5–10 μm and less than 0.5 μm, respectively. The selectivities for 4,4′-diisopropylbiphenyl (4,4′-DIPB) were 60–70% for ZSM-12L and 40–50% for ZSM-12S at lower temperatures below 275 °C, and rapidly decreased with further increase in temperatures to less than 20% at 350 °C over both zeolites. The kinetic controlled catalyses on external acid sites at lower temperatures were resulted in the formation of bulkier isomers, 2,*x*′-DIPB (*x*:2,3,4). The decreases in the selectivity for 4,4′-DIPB occurred by the isomerization of 4,4′-DIPB to stable isomers, 3,4′- and 3,3′-DIPB on external acid sites at higher temperatures. These catalyses were decreased remarkably over ZSM-12LD prepared by the dealumination of ZSM-12L with EDTA-3Na, because of effective removal of external acid sites.

The isopropylation of BP over ZSM-12 zeolites was moderately shape-selective for the formation of 4,4′-DIPB at appropriate temperatures, particularly over ZSM-12L and ZSM-12LD. The formation of 4,4′-DIPB occurred primarily near pore-entrances but not deep in the channels. ZSM-12 channels are less effective for the selective formation of 4,4′-DIPB than MOR channels.

1. Introduction

Zeolites are the most promising microporous crystals for achieving highly shape-selective catalysis because of their uniform distribution of pores and channels. They have dimensions that allow both organic reactants and products to enter, to be accommodated, and to leave [1–8]. Large-pore molecular sieves (LPMS) with 12- and 14-membered ring (12- and 14-MR) entrances have been extensively used as the catalysts for the alkylation of bulky polynuclear aromatics [4–25]. In particular, 4,4′-diisopropylbiphenyl (4,4′-DIPB) and 2,6-diisopropylnaphthalene (2,6-DIPN) have been selectively produced over dealuminated H-mordenite (MOR) from biphenyl (BP) and naphthalene (NP), respectively [6–10,20–25]. It has been of great interest to elucidate the catalytic features of the LPMS with different type of pores and channels from the selectivities of the least bulky products because confined circumstances in the materials highly influence shape-selective catalysis. Recently, we have studied the alkylation of BP over zeolites with one-dimensional 12- and 14-MR pore-entrances and over three-dimensional zeolites with 12-MR pore-entrances, and proposed that shape-selective catalysis occurs by the differences of steric restriction with channels at the transition states of the product isomers [4–18]. We have been interested in the zeolites which have smaller channels than MOR to elucidate what are optimal structures for the shape-selective formation of 4,4′-DIPB.

ZSM-12 zeolites with MTW topology have the smallest pore-entrances (0.56 nm × 0.6 nm) among 12-MR zeolites with straight channels. The channels are smaller than those of MOR and SSZ-24 with AFI topology, but larger than those of ZSM-5 with MFI topology of 10-MR entrances [26]. We expected that ZSM-12 channels should offer higher shape-selective natures than MOR and SSZ-24 channels in the alkylation of BP and NP because ZSM-12 channels are expected to have severer steric restriction than MOR channels. In this paper, we examined the isopropylation of BP over ZSM-12 with different particle sizes, and discussed the differences in shape-selective catalyses by the different type of zeolites.

* Corresponding author. Tel.: +61 7 334 64122.
** Corresponding author at: Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan. Tel.: +81 47 343 3539; fax: +81 47 343 3539.
E-mail addresses: a.vinu@uq.edu.au (A. Vinu), ysugi@gifu-u.ac.jp (Y. Sugi).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2012.10.018

2. Experimental

2.1. Preparation of ZSM-12 zeolites

2.1.1. ZSM-12 with tetraethylammonium bromide (ZSM-12L)

ZSM-12L was synthesized using tetraethylammonium bromide (TEABr) as a structure-directing agent (SDA) according to previous literature [27]. The molar gel composition was $1SiO_2$:0.18$[TEA]^+$:0.18NaOH:0.008Al_2O_3:7.8H_2O. The typical procedures are as follows: $NaAlO_2$ 0.98 g, TEABr, 20 g, H_2O 60 g, and SiO_2 (Ludox HS-40) 75 g were added to the solution of NaOH 3.5 g in water 25 g in 500 mL PP bottle. Subsequently, the resulting solution was sonically agitated for 40 min, and kept the gel at 100 °C for 90 days. A small quantity of water was added in the gel during heating to keep the water level constant. The resultant solid products were filtered, washed several times with water, and dried at 110 °C. Then, the solid was heated in a flow of air (50 mL/min) with a temperature-programmed rate of 2 °C/min up to 550 °C, and calcined for 7 h. Calcined samples were converted to H-form by using 20 mL of 1 M solution of ammonium nitrate per gram of a sample for 12 h at 80 °C. This procedure was repeated three times, and the zeolites were heated in a flow of air (50 mL/min) with a temperature-programmed rate of 2 °C/min up to 550 °C, and calcined for 7 h.

2.1.2. ZSM-12 with methytriethylammonium bromide (ZSM-12S)

ZSM-12S was synthesized using methytriethylammonium bromide (MTEABr) as a structure-directing agent (SDA) according to previous literature [28]. The molar gel composition was $1SiO_2$:0.17$[MTEA]^+$:0.25NaOH:0.01Al_2O_3:25H_2O. The typical procedures are as follows: Ludox S-40, 4.187 g (SiO_2: 28.9%) was added to the solution of MTEABr, 1.686 g and $Al(NO_3)_3{\cdot}6H_2O$, 0.1502 g with a continuous stirring. pH of the mixture was adjusted to 10 by adding H_2SO_4 (97%) and stirred for 1 h. Resulting gel was heated in Teflon autoclave at 150 °C for 10 days. The solid products were filtered, washed several times with water, and dried at 110 °C. Post synthesis treatments were done by the same way as ZSM-12L.

2.1.3. The dealumination of ZSM-12L

Calcined ZSM-12L (1.0 g) was heated in 20 mL of 0.1 M aqueous solution of trisodium hydrogen ethylenediaminetetraacetate hydrate (EDTA-3Na) with stirring at 80 °C for 12 h [29]. The resulting zeolite was heated to 550 °C in air-stream of 50 mL/min with a programmed rate of 2.5 °C/min, and calcined at 550 °C for 7 h. The calcined ZSM-12L was heated with the equal weight of ammonium sulfate in water during 3 h under reflux. Finally, dealuminated H-ZSM-12L (ZSM-12LD) was obtained by the calcination at 550 °C for 7 h.

2.2. Isopropylation of BP

The isopropylation of BP was carried out in a 100 mL SUS-316 autoclave under propene pressure. The reaction conditions were as follows: BP: 3.86 g (25 mmol); catalyst: 125 mg; propene pressure: 0.8 MPa; operating time: 4 h; and reaction temperature: 200–350 °C. The autoclave was purged with nitrogen, and heated to the reaction temperature. Subsequently, the reaction was started with agitation by introduction of propene to the autoclave, and the temperature and pressure were maintained throughout the reaction. After cooling the autoclave, the products were separated from the catalysts by filtration, and washed well with toluene. The filtrates and washings were combined, and an approximately 1.5 mL portion of the solution was diluted with toluene (1.5–6.0 mL). The products were analyzed on a gas chromatograph (GC-14C and/or GC-18A; Shimadzu Corp., Kyoto, Japan) equipped with an Ultra-1 capillary column (25 m × 0.2 mm; film thickness: 25 μm; Agilent Technologies Co. Ltd., MA, U.S.A.).

The yield of each product was calculated according to the amount of BP used in the isopropylation of BP, where the sensitivities were normalized by carbon number of each product. The selectivity for isopropylbiphenyl (IPBP) and diisopropylbiphenyl (DIPB) isomers was expressed as a percentage of each IPBP and DIPB isomer among the total possible IPBP and DIPB isomers.

The analysis of encapsulated products in the catalyst used for the reaction was carried out as follows. The catalyst was filtered off, washed well with 200 mL of acetone, and dried at 110 °C for 12 h. 50 mg of the resulting catalyst was dissolved carefully using 1 mL of aqueous hydrofluoric acid (47%) at room temperature. This solution was basified with solid potassium carbonate, and organic layer was extracted three times with 20 mL of dichloromethane. After removal of the solvent *in vacuo*, the residue was dissolved in 1 mL of toluene. GC analysis was done according to the same procedure as for bulk products. The products are classified as BP, IPBP, DIPB, and triisopropylbiphenyls (TriIPB) isomers.

2.3. The stability of 4,4′-DIPB

The stability of 4,4′-DIPB was examined at 300 °C under propene pressure following the procedures of the isopropylation of BP. The products analyses were carried out by the same procedures as in the isopropylation of BP. The products were classified as 4,4′-DIPB, isomerized DIPB, IPBP, and TriIPB isomers.

2.4. Characterization of catalysts

Phase purity and crystallinity of the zeolites were determined by using a powder X-ray diffractometer (Shimadzu XRD-6000) with Cu Kα radiation (λ = 0.15418 nm). Elemental analysis was performed using inductively coupled plasma spectroscopy (JICP-PS-1000UV, Leeman Labs Inc., NH, U.S.A.). The crystal size and the morphology of the sample were observed by scanning electron microscopy using a Philips XL30 apparatus (Philips Electronics Japan, Tokyo, Japan). Nitrogen adsorption measurements were carried out on a BELSORP 28SA (BEL Japan Inc., Osaka, Japan). Acidity measurements were performed by temperature programmed desorption of ammonia (NH_3-TPD) on a BEL TPD-66 apparatus (BEL Japan). The amounts of acid sites were calculated from desorbed NH_3 from the sample to gas phase based on calibrated amounts of NH_3.

3. Results and discussion

3.1. Properties of the ZSM-12 zeolites

Typical properties of ZSM-12 zeolites used in this study are shown in Table 1. SiO_2/Al_2O_3 ratios are 75.5 for ZSM-12L and 65.3 for ZSM-12S, respectively. Fig. 1 shows the XRD patterns of the ZSM-12 zeolites synthesized by the two procedures. Amorphous phases were not observed for both ZSM-12 zeolites; however, the crystallinity of the ZSM-12L is much higher than that of ZSM-12S.

SEM images of the samples are shown in Fig. 2. Particle size of the ZSM-12L (5–10 μm) is much larger than that of ZSM-12S (less than 0.5 μm).

Textural parameters of the ZSM-12S and ZSM-12L are given in Table 1. Specific surface area of ZSM-12S was much higher than that of ZSM-12L. In addition, the external surface area, and pore volume of ZSM-12S calculated by *t*-plot method were also higher as compared to those of ZSM-12L. These results also support the fact that ZSM-12L has much higher crystallinity than ZSM-12S. These differences in particle size and crystallinity are highly influenced in surface and channel structures, resulting in different features in catalytic properties in this work.

Table 1
Textual properties of ZSM-12 zeolites.[a]

	SiO_2/Al_2O_3	Surface area ($m^2\ g^{-1}$)[b]	Surface area ($m^2\ g^{-1}$)[c]	External surface area ($m^2\ g^{-1}$)[c]	Pore volume ($mm^3\ g^{-1}$)[c]	Peak temperature (NH3-TPD) (°C)	Acid amount ($mmol\ g^{-1}$)
ZSM-12L	75.5	173.8	236.3	6.0	65.8	332	0.29
ZSM-12S	65.3	220.9	299.0	34.4	83.9	324	0.29
ZSM-12LD	78.6	166.8	224.9	9.3	61.0	338	0.30

[a] Sample: H-form.
[b] BET method.
[c] *t*-Plot method.

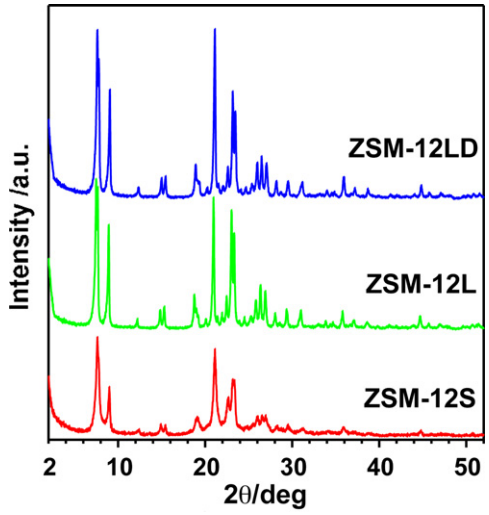

Fig. 1. XRD patterns of ZSM-12. (a) ZSM-12S; (b) ZSM-12L; and (c) ZSM-12LD.

Temperature programmed desorption of NH_3 (NH_3-TPD) of both the ZSM-12 zeolites displays two peaks, *l*-peak and *h*-peak, where *h*-peak is correlated to Brønsted acid sites from tetrahedral aluminum cations. Peak temperatures of *h*-peak indexed to acidity were at almost the same temperatures for both the samples as shown in Table 1. The amounts of acid sites calculated from area of *h*-peak is 0.29 $mmol\ g^{-1}$ for both the ZSM-12L and ZSM-12S. However, the acid strength of the ZSM-12 zeolites is much weaker than that of MOR zeolites [29].

ZSM-12L was dealuminated by EDTA-3Na at 80 °C for the deactivation of external acid sites. No changes in the XRD pattern were observed after the dealumination as shown in Fig. 1. Textual and acidic properties also remained those of original ZSM-12L by the dealumination as shown in Table 1. These results indicate that the dealumination removes almost only the acid sites at the external surface because EDTA-3Na cannot enter the pores of ZSM-12L.

3.2. Isopropylation of BP over ZSM-12 zeolites

Fig. 3 shows the effects of reaction temperatures on the isopropylation of BP over ZSM-12L. The conversion of BP increased with increasing reaction temperatures, and reached around 80% at around 250–275 °C as shown in Fig. 3a. The yields of IPBP and DIPB isomer also increased with an increase in temperatures. IPBP isomers were the principal products at low and moderate temperatures below 250 °C. The yield of DIPB isomers increased with a concomitant decrease of the yield of IPBP isomers with increasing the temperature. The yield of IPBP increased again with the decrease in the yield of DIPB isomers at further high temperatures as 350 °C. The formation of TriIPB isomers was gradually increased with the increase in the temperatures up to 10–15% at 300–350 °C.

Fig. 3b shows the effects of the temperature on the yield of IPBP isomers. 4-IPBP was a predominant isomer at the lower temperatures below 275 °C. However, the yield of 4-IPBP was decreased from around 30% at 200 °C to 10% at 325 °C. On the other hand, the yields of 3-IPBP remained almost constant with the increase in the temperature up to 300 °C. These results indicate that 4-IPBP was predominantly formed from BP and preferentially consumed by the formation of 4,4′-DIPB without significant isomerization to 3-IPBP. The rate of the formation of DIPB isomers, such as 3,4′-DIPB, from 3-IPBP was much slower as compared to that of the formation of 4,4′-DIPB from 4-IPBP. A further increase in the temperature from 300 to 350 °C makes a significant increase in the yield of 3-IPBP; however, the yield of 4-IPBP remained almost constant. These results mean that the increase of the yield of 3-IPBP is due to the de-alkylation of DIPB isomers to IPBP isomers in addition to the isomerization of 4-IPBP to 3-IPBP. The yield of 2-IPBP was less than 7%, and gradually decreased with the increased temperatures.

The effects of the temperature on the yield of DIPB isomers are shown in Fig. 3c. The yield of 4,4′-DIPB was rapidly increased with increased temperatures, and reached a maximum at 275 °C.

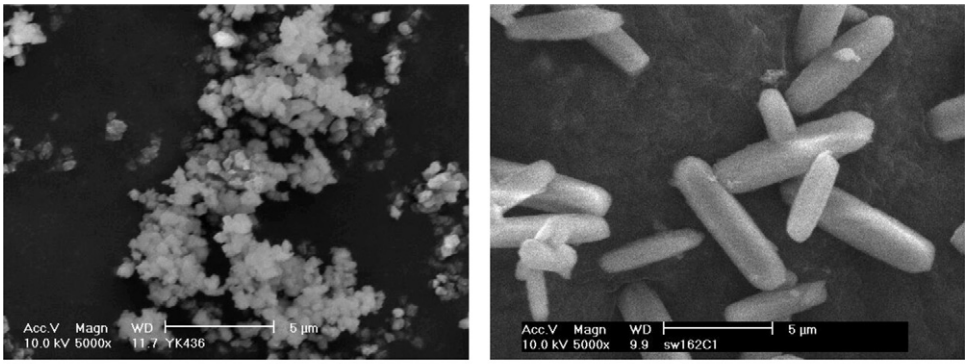

Fig. 2. SEM images of as-synthesized ZSM-12.

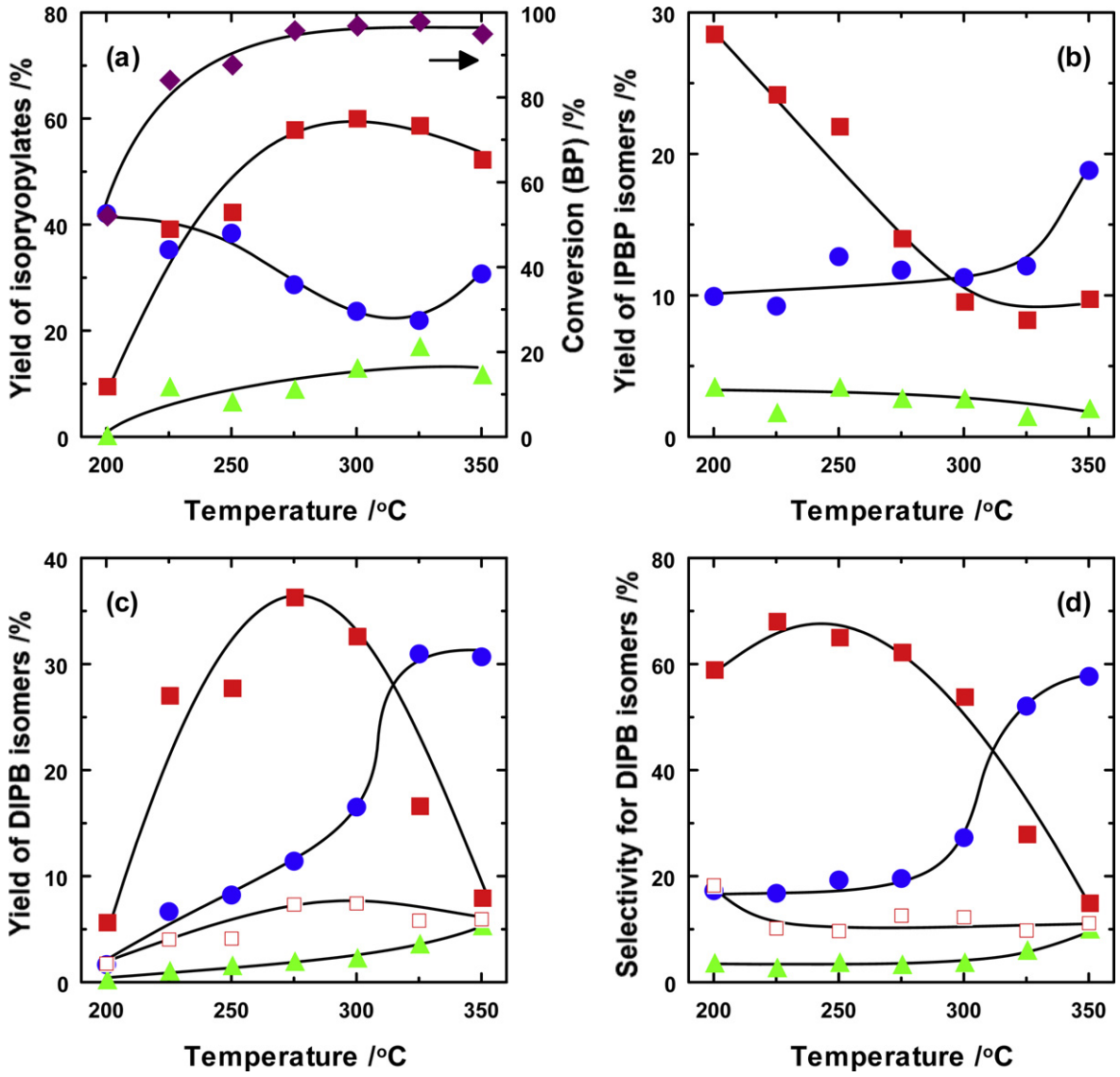

Fig. 3. Effects of reaction temperature on the isopropylation of BP over ZSM-12L. (a) Yield of isopropylates. (b) Yield of IPBP isomers. (c) Yield of DIPB isomers. (d) Selectivity for DIPB isomers. Reaction conditions: BP: 3.86 g (25 mmol); catalyst: ZSM-12L, 125 mg; propene pressure: 0.8 MPa, period: 4 h. Legends: (a) (●) IPBP; (■) DIPB; (▲) TriIPB; and (◆) conversion. (b) (■) 4-IPBP; (●) 3-IPBP; and (▲) 2-IPBP. (c) and (d) (■) 4,4′-DIPB; (●) 3,4′-DIPB; (▲) 3,3′-DIPB; and (□) 2,*x*′-DIPB.

These increases suggest that 4-IPBP preferentially participates in the formation of 4,4′-DIPB because the increase in 4,4′-DIPB corresponds well to the decrease the formation of 4-IPBP. However, a further increase in temperature caused a decrease in the yield of 4,4′-DIPB with a concomitant increase in the yield of 3,4′-DIPB. The yield of 3,4′-DIPB was then saturated at 325–350 °C. The yield of 2,*x*′-DIPB (sum of 2,2′-, 2,3′- and 2,4′-DIPB) was gradually increased with increasing the reaction temperature and reached a maximum at 275–300 °C, whereas remained almost constant at further higher temperatures. The yields of 3,3′-DIPB were increased at high temperatures although they were less than 5%.

Fig. 3d shows the effects of the temperature on the selectivity for DIPB isomers. The selectivity for 4,4′-DIPB was 60% at 200 °C, increased up to 70% at 225–250 °C; however, then rapidly decreased with a threshold of 275 °C by the increase in the temperature, accompanying the increase in the selectivity for 3,4′-DIPB. Gradual decrease in the selectivities for 2,*x*′-DIPB occurred with the increased temperatures from 20% at 200 °C to 10% at 250–350 °C. Further, the selectivities for 3,3′-DIPB were increased with increasing the temperatures from 300 °C, although they were less than 10%.

These features over ZSM-12L suggest that moderately shape-selective formation of 4,4′-DIPB occurred at low and moderate temperatures, although some kinetic controlled reactions, probably at the external sites, were accompanied at lower temperatures as 200 °C, leading to the formation of 2,*x*′-DIPB. However, thermodynamic controlled catalyses occurred at higher temperatures, resulting in the isomerization of 4,4′-DIPB to 3,4′-DIPB.

Fig. 4 shows the effects of reaction temperatures on the isopropylation of BP over ZSM-12LD which was prepared by the dealumination of ZSM-12L to reduce the catalysis at external acid sites. The catalytic activity was decreased by the dealumination, particularly at the lower temperatures from 200 to 275 °C (Fig. 4a). The yield of IPBP isomers was increased with increasing the temperatures. Among IPBP isomers, the yield of 4-IPBP was maximized at around 250 °C, and then, decreased with the increase in the temperatures, whereas the yield of 3-IPBP was spontaneously increased with the increase in temperature (Fig. 4b). The yield of DIPB isomers was increased to 30% with increasing the

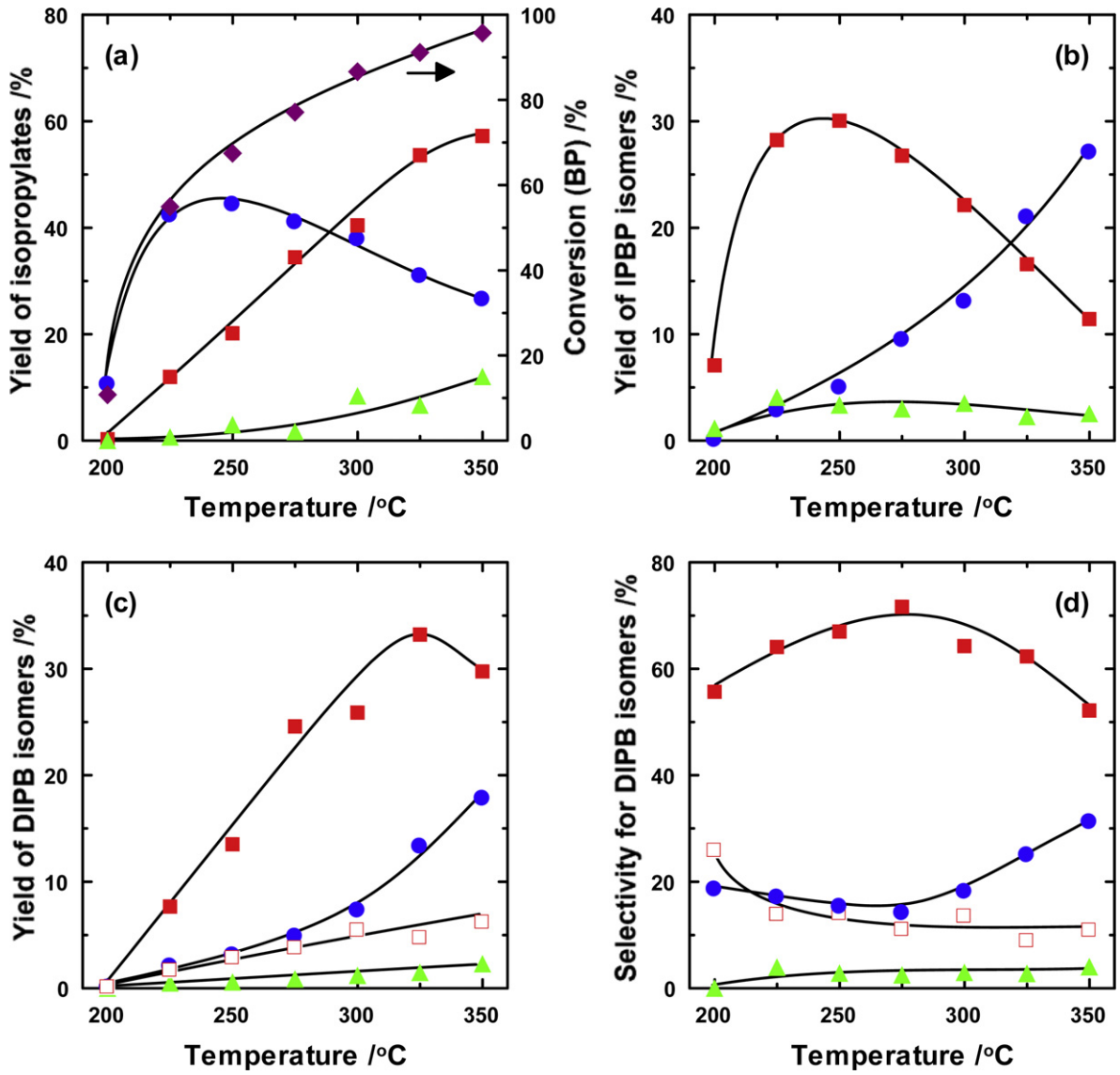

Fig. 4. Effects of reaction temperature on the isopropylation of BP over ZSM-12LD. (a) Yield of isopropylates. (b) Yield of IPBP isomers. (c) Yield of DIPB isomers. (d) Selectivity for DIPB isomers. Reaction conditions and legends: see Fig. 3.

temperature to 300 °C (Fig. 4a). The yield of 4,4′-DIPB was maximized at 325 °C, and then decreased at 350 °C, whereas, the yield of 3,4′-DIPB was increased spontaneously with the increase in the temperature (Fig. 4c). The formation of TriIPB isomers was gradually increased to 10% with the increase in the temperature to 350 °C. ZSM-12LD gave the similar results to ZSM-12L although the catalytic activities were slightly decreased, particularly at lower temperatures.

Fig. 4d shows the effects of reaction temperature on the selectivity for DIPB isomers over ZSM-12LD. The selectivity for DIPB was significantly improved by the dealumination, particularly at high temperatures. The selectivity for 4,4′-DIPB was increased 55% at 200 °C to 70% at 275 °C, and then, gradually decreased to 56% at 350 °C. These results show that the selectivities for 4,4′-DIPB were improved particularly at 250–350 °C by the dealumination of ZSM-12L, and that ZSM-12 channels had the moderately shape-selective natures for the formation of 4,4′-DIPB even at high temperatures.

The formation of bulky isomers and the isomerization of 4,4′-DIPB at the external acid sites were effectively decreased by the dealumination. However, the external acid sites were not completely deactivated by the dealumination with EDTA-3Na, resulting in the occurrence of some non-selective reactions.

The isopropylation of BP over ZSM-12S were examined to know the effects of external acid sites because ZSM-12S has larger external surface than ZSM-12L due to smaller particle size as shown in Table 1. Fig. 5 shows the influences of reaction temperature on the isopropylation of BP over ZSM-12S. Catalytic activity of ZSM-12S was increased with the increased temperatures, and the conversion was reached 80% at 275 °C although ZSM-12S was less active than ZSM-12L at lower temperatures (Fig. 5a). 4-IPBP was a principal product at lower temperatures; however, decreased with the increased temperatures. The yield of 3-IPBP was spontaneously increased with the increase in temperature; however, the yield of 2-IPBP was decreased with the temperature (Fig. 5b). The yield of DIPB increased with increasing the temperatures up to 300 °C, accompanying the decrease in the yield of IPBP isomers, and further increase in temperature resulted in the saturation of the yield of DIPB isomers. The yield of 4,4′-DIPB was maximized at 300 °C, and further increase in temperature decreased the yield of 4,4′-DIPB with the increase in those of 3,4′-DIPB (Fig. 5c). The yield of TriIPB isomers increased spontaneously up to 20% at 350 °C.

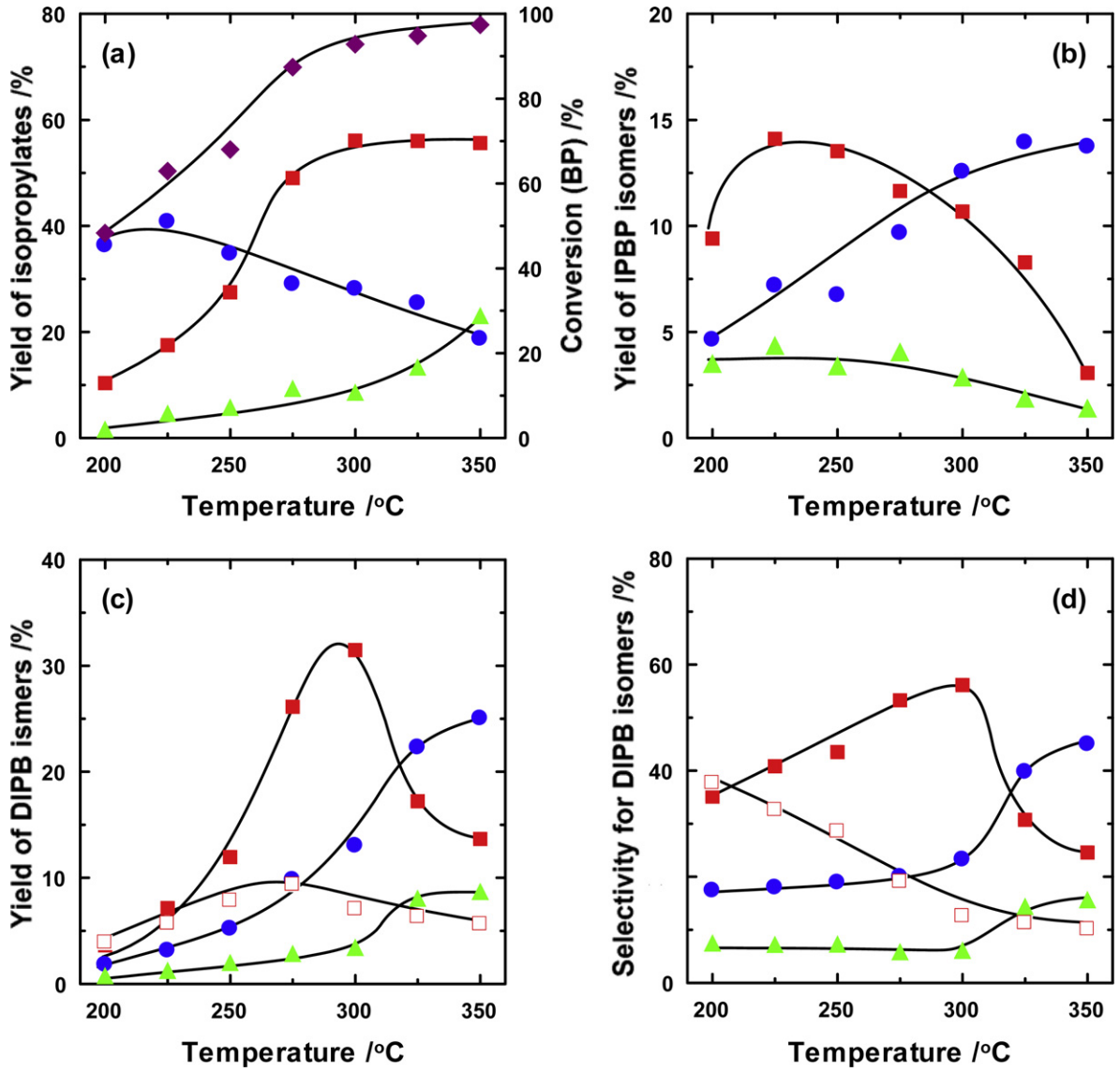

Fig. 5. Effects of reaction temperature on the isopropylation of BP over ZSM-12S. (a) Yield of isopropylates. (b) Yield of IPBP isomers. (c) Yield of DIPB isomers. (d) Selectivity for DIPB isomers. Reaction conditions and legends: see Fig. 3.

These catalytic behaviors of ZSM-12S were fundamentally similar to those of ZSM-12L although the catalytic activities were lower than ZSM-12L, particularly at lower temperatures.

Fig. 5d shows the effects of the temperature on the selectivity for DIPB isomers. ZSM-12S had lower selectivity for 4,4′-DIPB than ZSM-12L. The selectivity was gradually increased with temperatures; reached a maximum, 55% at 300 °C; and then, decreased to around 20% with a threshold of 300 °C by the increase in the temperature. The selectivities for 3,4′- and 3,3′-DIPB remained almost constant from 200 °C to 300 °C; however, rapidly increased with compensation of the selectivity for 4,4′-DIPB at further higher temperatures. The selectivity for 2,*x*′-DIPB was decreased with the increase in the temperature from 35% at 200 °C to 5% at 350 °C. The increase in the selectivity for 4,4′-DIPB corresponded to the decrease in the selectivity for 2,*x*′-DIPB formed by the kinetic controlled reaction at the external acid sites.

The yield of 4,4′-DIPB was maximized at 300 °C, and the increase in temperature decreased the yield of 4,4′-DIPB with concomitant increase in those of 3,4′-DIPB. These trends in DIPB isomers resembled the results over ZSM-12L. The formation of 2,*x*′-DIPB was more extensive for ZSM-12S compared to ZSM-12L. These catalytic properties are due to their active acid sites at the external surfaces. Actually, these acid sites were decreased by the dealumination of ZSM-12L, although, unfortunately, we could not deactivate completely them.

Fig. 6 shows the effects of reaction temperature on the stability of 4,4′-DIPB over ZSM-12 zeolites at 300 and 350 °C under 0.8 MPa of propene pressure. The consumption of 4,4′-DIPB over ZSM-12S was much more significant than that over ZSM-12L, and increased with increasing the temperature. The decrease in the selectivity for 4,4′-DIPB at high temperatures is due to the isomerization to stable isomers. The differences in stability for 4,4′-DIPB by the contact with ZSM-12L and ZSM-12S are due to the availability of the external acid site by the difference of particle sizes. However, the isomerization to DIPB isomers was remarkably decreased over ZSM-12LD because of the deactivation of external acid sites. These results suggest that the similar decrease in the yield and selectivity for 4,4′-DIPB occurred during the isopropylation of BP.

Fig. 7 shows the effects of reaction temperature on the products composition of encapsulated products contained in ZSM-12L,

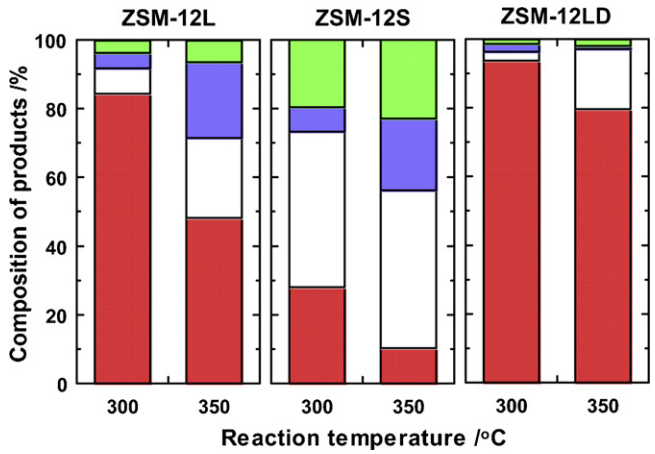

Fig. 6. The stability of 4,4′-DIPB over ZSM-12L, ZSM-12S, and ZSM-12LD under propene pressure. Reaction conditions: 4,4′-DIPB: 2.95 g (12.5 mmol); catalyst: 125 mg; temperature: 300 and 350 °C; propene pressure: 0.8 MPa, period: 4 h. Legends: (■) 4,4′-DIPB; (□) isomerized DIPB; (■) IPBP; and (■) TriIPB.

ZSM-12S, and ZSM-12LD used for the isopropylation of BP at 250 and 300 °C. BP was principal component of the encapsulated products in both ZSM-12 zeolites, although the conversions of BP were 70–90% over these zeolites. IPBP and DIPB were only less than 40%, and afforded almost the same composition irrespective of the temperatures. DIPB isomers were only 10–15% for ZSM-12L, 20% for ZSM-12S, and around 10% for ZSM-12LD. These results of encapsulated products of ZSM-12 zeolites were quite different from those of MOR: DIPB isomers contain high amounts in the encapsulated products of MOR in the isopropylation of BP [10]. We can suggest that the different features between ZSM-12 and MOR are due to less availability of ZSM-12 channels for the isopropylation of BP, and that principal catalytic sites are near pore-entrances.

3.3. Mechanistic aspects of the Isopropylation of BP over ZSM-12 zeolites

We have studied the relation between the selectivity for 4,4′-DIPB and pore structure of zeolites, and found that the steric restriction of zeolite at the transition state of the product isomers, resulting in the formation of the least bulky products [4–7]. The catalysis is kinetic and thermodynamic controlled, resulting in the predominant formation of bulky products and/or of thermodynamically stable isomers, if zeolite channels are wide enough to allow the accommodation of the bulky isomers. The features suggest that the confined structures of zeolite channels are important for shape-selective catalysis. We have considered that a little bit narrow channels of ZSM-12 compared to MOR can achieve the highly shape-selective catalysis.

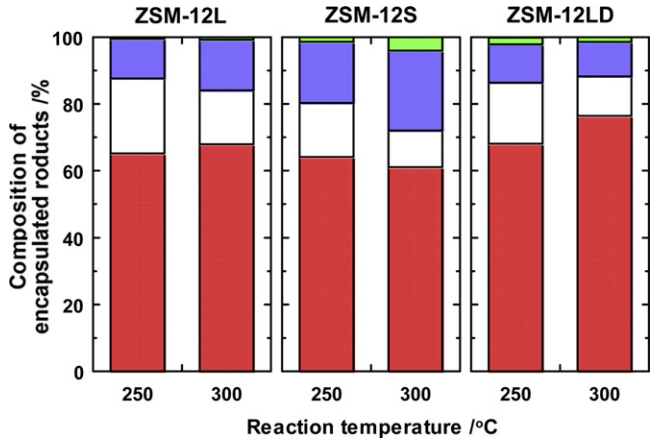

Fig. 7. Effects of reaction temperature on the distribution of encapsulated products in the isopropylation of BP over ZSM-12. Reaction conditions: see Figs. 3–5. Legends: (■) BP; (□) IPBP; (■) DIPB; and (■) TriIPB.

The isopropylation of BP over a ZSM-12 zeolite consecutively occurred in two steps as shown in Figs. 3–5: BP to IPBP isomers, and IPBP to DIPB isomers. The formation of 4-IPBP occurred predominantly from BP, and 4-IPBP was consumed preferentially to 4,4′-DIPB in the second step at moderate temperatures. These results indicate that the moderately shape-selective catalysis occurs in ZSM-12 channels.

The selectivities for 4,4′-DIPB was 60–70% for ZSM-12L and 35–50% for ZSM-12S at the reaction temperatures between 200 and 300 °C. Further, the dealumination of ZSM-12L improved the selectivities particularly at high temperatures. These results indicate that ZSM-12 channels have high potential for the shape-selective formation of 4,4′-DIPB: the restriction by the channels can differentiate 4,4′-DIPB from other bulky isomers at the transitions states. However, the selectivities for 4,4′-DIPB were rapidly decreased to around 20% at 350 °C for ZSM-12L and ZSM-12S by the thermodynamic controlled isomerization of 4,4′-DIPB, once formed in ZSM-12 channels, to 3,4′-DIPB at the external acid sites. The formation of bulky DIPB isomers, 2,*x*′-DIPB also occurred at low temperatures. The formation of bulky 2,*x*′-DIPB indicates the participation of kinetic controls. The latter two reactions occurred at the external acidic ites, because these isomers were preferentially formed for ZSM-12S compared to ZSM-12L. The increased formation of 4,4′-DIPB over ZSM-12LD supports the formation of 2,*x*′- and 3,4′-DIPB occurred at the external acidic sites.

The selectivities for 4,4′-DIPB were highly influenced by the particle sizes. The differences are ascribed to external acid sites, because ZSM-12S has higher external surfaces (Table 1). The external acid sites enhanced kinetic controlled catalysis at lower temperatures, and the isomerization of 4,4′-DIPB at higher temperatures, resulting in the decrease in the selectivity for 4,4′-DIPB, particularly over ZSM-12S. These reactions were decreased over ZSM-12LD after the dealumination of ZSM-12L with preferential removal of external acid sites without changes of textural properties.

The encapsulated products over ZSM-12S and ZSM-12L show that a large amount of BP remained unchanged in ZSM-12 channels although the conversions of BP were 70–90% at 300 °C (Fig. 7). These are quite different results compared to the isopropylation over MOR: most of BP disappeared over MOR even at 250 °C, resulting preferential formation of DIPB isomers, particularly 4,4′-DIPB [10]. These results indicate that large differences in the availability of the channels between ZSM-12 (S and L) and MOR: ZSM-12 channels, particularly deep from pore-entrances, cannot work fully as active sites, probably due to deficient supply of propene in addition to narrow channels, and that the channels are not enough wide to diffuse out/out BP, IPBP, and DIPB isomers, either. We can conclude that the shape-catalysis occurred at the acidic sites in the channels near from pore-entrances, although further studies are necessary on these aspects.

It is interesting to compare the roles of channels of SSZ-24, MOR, and ZSM-12, with 12-MR straight channels in the isopropylation of BP. Their widths of channels decrease in the order: SSZ-24 > MOR > ZSM-12 [26]. MOR gave higher selectivities than SSZ-24 because MOR channels have more effective steric interaction at the transition state of 4,4′-DIPB. However, MOR channels still allow the formation of bulkier isomer, 3,4′-DIPB, because the highest selectivities for 4,4′-DIPB are as high as 85–90% [10–12]. We expected that the ZSM-12 zeolites can differentiate more severely 4,4′-DIPB from the other bulkier isomers, particularly,

3,4′-DIPB, at their transition states than MOR, because ZSM-12 has the smallest channels among 12-MR zeolites. However, unexpectedly, the selectivities for 4,4′-DIPB over ZSM-12 zeolites were lower than those of MOR. The results of ZSM-12 zeolites indicate that the channels afford moderately shape-selective formation of 4,4′-DIPB although the non-selective catalysis, particularly the formation of 2,*x*′-DIPB, occurred at the external acid sites. The formation of 4,4′-DIPB occurred primarily in the channels, probably near the pore-entrances, not so deep in the channels as discussed above. We consider that ZSM-12 channels are moderately shape-selective to fit transition states to 4,4′-DIPB for a highly shape-selective catalysis. However, the channels are a little bit narrow for the isopropylation of BP to occur only inside them, and to exclude them at the external acid sites. It is important that the appropriate steric restriction at the transition states of the bulky isomers by the zeolite channels excludes bulky products for the selective formation of the least bulky products [4–6,9–18].

4. Conclusion

The isopropylation of BP was examined over ZSM-12 zeolites, ZSM-12L and ZSM-12S, with MTW topology synthesized by using methyltriethylammonium bromide (MTABr) and tetraethylammnoium bromide (TEABr) as structure directing agents (SDA), respectively, to clarify their roles in shape-selective catalysis.

The isopropylation of BP over ZSM-12L and ZSM-12S afforded the selectivities for 4,4′-diisopropylbiphenyl (4,4′-DIPB) in 60–70% and 40–50%, respectively, at lower temperatures below 275 °C. These results indicate that ZSM-12 channels have the shape-selective natures to afford the moderately selective formation of 4,4′-DIPB. However, the decrease in the selectivities for 4,4′-DIPB occurred with an increase in temperatures over both ZSM-12 zeolites. These decreases are ascribed to the isomerization to stable 3,4′- and 3,3′-DIPB at the external acids sites. The dealumination of ZSM-12L improved the selectivity for 4,4′-DIPB at higher temperatures because of effective removal of external acid sites.

The encapsulated products for ZSM-12 zeolites indicate that BP remains unreacted in large amounts inside the channels even at high temperatures: the channels for ZSM-12, particularly deep from pore-entrances, do not work fully as active sites, probably due to deficient supply of propene in addition to their narrowness

These results of the isopropylation of BP show that ZSM-12 channels are moderately shape-selective, and that the channels are a little bit narrow to fit transition states to 4,4′-DIPB for a completely shape-selective catalysis. We propose that the shape-selective catalyses occur primarily near the pore-entrances, not so deep in the channels.

Acknowledgements

A part of this work was financially supported by Grant-in-Aids for Scientific Research ((B) 16310056, (B) 19061107, and (C) 21510098), the Japan Society for the Promotin of Science (JSPS). A. Vinu thanks the Australian Research Council for the future fellowship and the University of Queensland for the start-up grant.

References

[1] S.M. Csicsery, Zeolites 4 (1984) 202–213.
[2] P.B. Venuto, Microporous Mater. 2 (1994) 297–411.
[3] N.Y. Chen, W.E. Garwood, F.G. Dwyer, Shape-Selective Catalysis in Industrial Applications, 2nd ed., Marcel Dekker, New York, 1996.
[4] Y. Sugi, Y. Kubota, in: R.J. Spivey (Ed.), Catalysis, vol. 13. A Specialist Periodical Report, Royal Society of Chemistry, 1997, pp. 55–84.
[5] Y. Sugi, Y. Kubota, T. Hanaoka, T. Matsuzaki, Catal. Surv. Jpn. 5 (2001) 43–56.
[6] Y. Sugi, J. Chin. Chem. Soc. 57 (2010) 1–13.
[7] Y. Sugi, J. Jpn. Petrol. Inst. 53 (2010) 263–275.
[8] C. Song, J.M. Garćes, Y. Sugi, in: C. Song, J.M. Garćes, Y. Sugi (Eds.), Shape-Selective Catalysis: Chemical Synthesis and Hydrocarbon Processing, ACS Symposium Series 738, American Chemical Society, Washington, 1999, pp. 1–17.
[9] T. Matsuzaki, Y. Sugi, T. Hanaoka, K. Takeuchi, T. Tokoro, G. Takeuchi, Chem. Express 4 (1989) 413–416.
[10] Y. Sugi, S. Tawada, T. Sugimura, Y. Kubota, T. Hanaoka, T. Matsuzaki, K. Nakajima, K. Kunimori, Appl. Catal. 189 (1999) 251–261.
[11] A. Ito, H. Maekawa, H. Kawagoe, K. Komura, Y. Kubota, Y. Sugi, Bull. Chem. Soc. Jpn. 80 (2007) 215–223.
[12] Y. Sugi, H. Maekawa, A. Ito, C. Ozawa, T. Shibata, A. Niimi, C. Asaoka, K. Komura, Y. Kubota, J.-Y. Lee, J.-H. Kim, G. Seo, Bull. Chem. Soc. Jpn. 80 (2007) 2232–2242.
[13] H. Maekawa, T. Shibata, A. Niimi, C. Asaoka, K. Yamasaki, H. Naiki, K. Komura, Y. Kubota, Y. Sugi, J.-Y. Lee, J.-H. Kim, G. Seo, J. Mol. Catal. A: Chem. 279 (2008) 27–36.
[14] Y. Sugi, H. Maekawa, S.A.R. Mulla, A. Ito, C. Naitoh, K. Nakagawa, K. Komura, Y. Kubota, J.-H. Kim, G. Seo, Bull. Chem. Soc. Jpn. 80 (2007) 1418–1428.
[15] Y. Sugi, H. Maekawa, Y. Hasegawa, A. Ito, R. Asai, D. Yamamoto, K. Komura, Y. Kubota, J.-Y. Lee, J.-H. Kim, G. Seo, Catal. Today 131 (2008) 413–422.
[16] Y. Sugi, H. Maekawa, H. Naiki, K. Komura, Y. Kubota, Bull. Chem. Soc. Jpn. 81 (2008) 1166–1174.
[17] Y. Sugi, H. Maekawa, Y. Hasegawa, H. Naiki, K. Komura, Y. Kubota, Bull. Chem. Soc. Jpn. 81 (2008) 897–905.
[18] Y. Sugi, H. Maekawa, Y. Hasegawa, A. Ito, R. Asai, D. Yamamoto, K. Komura, Y. Kubota, J.-H. Kim, G. Seo, Catal. Today 132 (2008) 27–37, 139 (2009) 242.
[19] G.S. Lee, J.J. Maj, S.C. Rocke, J.M. Garces, Catal. Lett. 2 (1989) 243–247.
[20] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, J. Chem. Soc. Chem. Commun. (1991) 39–40.
[21] M. Toba, A. Katayama, G. Takeuchi, S. Niwa, F. Mizukami, S. Mitamura, in: C. Song, J.M. Garćes, Y. Sugi (Eds.), Shape-Selective Catalysis: Chemical Synthesis and Hydrocarbon Processing, ACS Symposium Series 738, American Chemical Society, Washington, 1999, pp. 292–304.
[22] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, Microporous Mater. 5 (1995) 113–121.
[23] C. Song, A.D. Schmitz, J. Jpn. Petrol. Inst. 42 (1999) 275–298, and their previous papers cited in.
[24] R. Brzozowski, W. Tęcza, Appl. Catal. A: Gen. 166 (1998) 21–27.
[25] R. Brzozowski, W. Skupínski, J. Catal. 210 (2002) 313–318.
[26] IZA Structure Commission, http://www.iza-online.org/
[27] S. Ernst, P.A. Jacobs, J.A. Martens, J. Weitkamp, Zeolites 7 (1987) 458462.
[28] E.J. Rosinski, M.K. Rubin, U.S. Patent 3 832 449, 1974.
[29] S.A.R. Mulla, S.B. Waghmode, S. Watanabe, H. Maekawa, K. Komura, Y. Kubota, Y. Sugi, G. Seo, J.-H. Kim, Bull. Chem. Soc. Jpn. 79 (2006) 1451–2146.