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Shape-selective alkylation of biphenyl over metalloaluminophosphates with AFI topology

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Abstract

Metalloaluminophosphates with AFI topology (MAPO-5; M: Mg, Ca, Sr, Ba, and Zn) synthesized by the dry gel conversion (DGC) method were used as catalysts for the alkylation of biphenyl (BP). MgAPO-5 and ZnAPO-5 had high catalytic activities of the isopropylation; however, activities of CaAPO-5, SrAPO-5, and BaAPO-5 were much lower than those of MgAPO-5 and ZnAPO-5. These results suggest that the catalytic activity of MAPO-5 molecular sieves was originated by the acidity due to the isomorphous substitution of M^{2+} for Al^{3+}. The selectivities for 4,4′-diisopropylbiphenyl (4,4′-DIPB) for all MAPO-5 molecular sieves are at the level of 70%. On the basis of various reaction behaviors, the predominant formation of 4,4′-DIBP was considered to be mainly due to the steric restriction on the transition state of the isopropylation to the least bulky isomer inside the channel of MAPO-5 molecular sieves.

The isopropylation of BP over MgAPO-5 and ZnAPO-5 was accompanied by the isomerization of 4,4′-DIPB to thermodynamically more stable isomers, 3,4′-DIPB at the higher temperatures; the decrease in the selectivity for 4,4′-DIPB was observed in both bulk and encapsulated products. These results show that 4,4′-DIPB formed inside channels was isomerized inside the channels in addition to external acid sites. The channels of MAPO-5 molecular sieves are large enough to allow the isomerization of 4,4′-DIPB especially at higher temperatures: this is quite different from those of H-mordenite.

The *sec*- and *tert*-butylations of BP over MgAPO-5 and ZnAPO-5 gave selectively the least bulky isomers, 4,4′-di-*sec*-butylbiphenyl (4,4′-DSBB) and 4,4′-di-*tert*-butylbiphenyl (4,4′-DTBB), respectively. The selectivity for the least bulky isomer increased with increasing the bulkiness of alkylating agents in the order: isopropylation < *sec*-butylation < *tert*-butylation. This order reflects the spatial constraints of the transition sates inside the AFI structure.

Keywords: Metalloaluminophosphate; AFI topology; Shape-selectivity; Biphenyl; Isopropylation

1. Introduction

Ordered microporous aluminophosphates were first synthesized by Wilson et al. in 1982 [1]. Thereafter, many types of aluminophosphate with different micropore size and topology have been synthesized by changing the templates and/or crystallization conditions. However, the main drawback of these molecular sieves as catalytic materials is low acidity because of neutral tetrahedral framework; they only provide low catalytic activity for acid catalysis. An important progress for catalytic materials was the synthesis of silicoaluminophosphates (SAPO) and other metalloaluminophosphates (MAPO) by Flanigen et al. [2,3]. The imbalance of valency by partial replacement of Al^{3+} by divalent cations or P^{5+} by tetravalent cations gives rise to Brønsted acid sites [4]. The addition of metal cations has expanded the number and diversity of the aluminophosphates, giving new properties to the microporous materials [5].

Molecular sieves such as aluminosilicates and metalloaluminophosphates are the most promising microporous crystals

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for achieving highly shape-selective catalysis because their channels are uniformly distributed and have dimensions allowing both the reactants and products with a limited size to enter, to accommodate, and to leave [6,7]. Large-pore molecular sieves are useful in the alkylation of bulky polynuclear aromatics [8–10]. The isopropylation of biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating the shape-selective nature of the molecular sieve [8–10]. The selective formation of the least bulky 4,4′-diisopropylbiphenyl (4,4′-DIPB) should be facilitated over ordered microporous materials if the catalytic sites are sterically restricted. In the previous papers, we described that 4,4′-DIPB has been selectively produced from BP over dealuminated H-mordenite (H-MOR) [8–13]. Other relevant findings have been the shape-selectivity of CIT-5 [14], SSZ-24 [15,16], SAPO-5 [17], and SSZ-31 [18]for the isopropylation of BP. The high selectivity for 4,4′-DIPB suggests that catalytically active sites in H-MOR effectively restrict the transition state to form the least bulky 4,4′-DIPB [8–13]. We proposed the shape-selective isopropylation of BP over these molecular sieves occurred by the restricted transition state mechanism.

Most of previous works on the shape-selective alkylation of polynuclear hydrocarbons have used aluminosilicates as catalysts, and there are only a few works using aluminophosphate molecular sieves [18–21]. It would be interesting to explore the possibilities of shape-selective catalysis by large pore metalloaluminophosphates. Among them, we focused on the MAPO-5 molecular sieves (AFI topology), which are isostructural with SSZ-24 [22]. To demonstrate their shape-selective catalysis over these molecular sieves, we examine the alkylation (isopropylation, *sec*-butylation, and *tert*-butylation) of BP over MAPO-5 molecular sieves (M: Mg, Ca, Sr, Ba, and Zn), and discuss the catalysis in the channels of molecular sieves with AFI topology.

2. Experimental

2.1. Synthesis of MAPO-5 molecular sieves

The synthesis of metalloaluminophosphate with AFI topology (MAPO-5; M: Mg, Ca, Sr; Ba; and Zn) was carried out by the vapor phase transport (VPT) method, a type of dry-gel conversion (DGC) methods [19,20]. The molar composition of the starting gel was $1.0Al_2O_3$–0.10MO –$1.0P_2O_5$–$0.76Et_3N$–$45H_2O$. The typical procedures are shown for the synthesis of MgAPO-5. A 2.05 g of aluminum isopropoxide (5.0 mmol as Al_2O_3) was slurried in water (1.85 g). To this slurry, 1.15 g of 85% phosphoric acid (5.0 mmol as P_2O_5) diluted in water (2.0 g) was added dropwise over a period of 0.5 h with constant magnetic stirring. To the resulting solution, a 0.107 g of magnesium acetate (0.5 mmol as MgO) was added and the stirring was further continued for 0.5 h. The gels thus obtained were dried at 80 °C in an oil bath with continuous magnetic stirring to remove water. Finally, a mixture of 384 mg of triethylamine (3.8 mmol) and 150 mg of water was placed at the bottom of the autoclave so as to be supplied as vapor. The crystallization was carried out by heating the autoclave statically at 175 °C for 24 h in a convection oven. The autoclave assembled for the DGC method is shown in our previous paper [23].

After the crystallization, the products were washed with distilled water, separated by centrifugation, and dried at 100 °C overnight. The as-synthesized samples were calcined in a muffle furnace in a flow of air (flow rate: 50 ml/min) as follows: the temperature was raised from room temperature to 550 °C in 4 h, kept at this temperature for another 7 h, and finally cooled to room temperature in ambient conditions.

Other MAPO-5 molecular sieves were synthesized in a similar manner to MgAPO-5 [19,20].

2.2. Catalytic reaction over MAPO-5 molecular sieves

The alkylation of BP was carried out in a 100-ml SUS-316 autoclave under a constant pressure of alkylating agent. Typical procedures of the isopropylation of BP are as follows: BP (7.7 g, 50 mmol) and MAPO-5 (250 mg) were mixed in an autoclave, which was flushed with nitrogen followed by heating to a desired temperature. Propene was then introduced to the desired pressure (0.8 MPa), and this pressure was maintained throughout the reaction period (4 h). After the reaction, the autoclave was cooled, and the catalyst was filtered and washed with toluene (50 ml). The solution (ca. 1.5 ml) was taken from the total bulk products and diluted with toluene (1.5–6.0 ml). The products obtained after the reaction were identified by gas chromatography–mass spectroscopy (GC–MS; QP5000, Shimadzu Corporation, Kyoto, Japan), and analyzed by a Shimadzu-14A gas chromatograph equipped with an Ultra-1 capillary column (25 m × 0.2 mm; Agilent Technologies, MA, USA).

The conversion of BP and the yield of each products were calculated on the basis of consumed BP. The selectivities for each diisopropylbiphenyl (DIPB) and isopropylbiphenyl (IPBP) isomer are expressed based on total amounts of IPBP and DIPB isomers, respectively.

$$\text{selectivity for a DIPB (IPBP) isomer (\%)} = \frac{\text{each DIPB (IPBP) isomer (mol)}}{\text{DIPB (IPBP) isomers (mol)}} \times 100$$

The products encapsulated inside the catalysts were analyzed as follows: after collection of the bulk products (as mentioned earlier), the catalyst was washed well with 200 ml of acetone, and dried at 110 °C for 12 h. Then 300 mg of resulting catalyst was carefully dissolved in 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 then 10 mg of naphthalene was added as an internal standard. GC analysis was performed similarly to the case of bulk products.

The *sec*- and *tert*-butylations of BP were carried out in a similar manner as the isopropylation using 1-butene and 2-methylpropene as alkylating agents, respectively. Pressures of 1-butene and 2-methylpropene were set at 0.4 MPa.

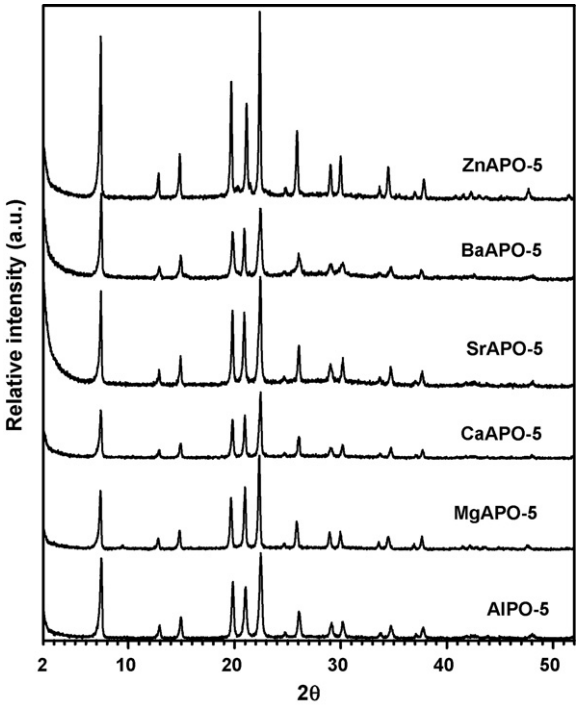

Fig. 1. XRD patterns of MAPO-5 molecular sieves.

2.3. Characterization of MAPO-5 molecular sieves

Crystallinity and phase purity of MAPO-5 molecular sieves were confirmed by powder X-ray diffraction (XRD) measured on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (λ = 0.15418 nm). Crystal size and morphology of the sample were examined by scanning electron microscopy (SEM) by using an S-4300 FE-SEM microscope (Hitachi Corporation, Tokyo, Japan). The bulk composition of MAPO-5 molecular sieves was determined by inductive coupled plasma atomic emission spectroscopy on a JICP-PS-1000 UV spectrometer (Teledyne Leeman Labs Inc., NH, USA). Surface area and porosity measurements were carried out by means of N_2 adsorption on a Belsorp 28SA apparatus (BEL Japan Inc., Osaka, Japan). Acidity of the molecular sieves was measured by temperature-programmed desorption of ammonia (NH_3-TPD) using a BEL TPD-66 apparatus; the sample (10 mg) was evacuated at 500 °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 600 °C at the rate of 10 °C/min in a helium stream. Thermogravimetric (TG) analysis of the used catalysts was performed using a Shimadzu DTG-50 analyzer with the temperature-programmed rate of 10 °C/min in an air stream (30 ml/min).

3. Results and discussion

3.1. Synthesis and properties of MAPO-5 molecular sieves

Metalloaluminophosphates with AFI topology (MAPO-5; M: Mg, Ca, Sr, Ba, and Zn) were synthesized according to previous papers [19,20]. The molar composition of the starting gel was $1.0Al_2O_3$–$0.10MO$–$1.0P_2O_5$–$0.76Et_3N$–$45H_2O$ as described in the Experimental section. MgAPO-5, CaAPO-5, and SrAPO-5 had higher metal content compared to the input ratio; however, metal contents in BaAPO-5 and ZnAPO-5 were lower than that in the input gel. In these MAPO-5 molecular sieves, Al^{3+} is replaced with M^{2+} in the frameworks, and acidity appears due to the resultant deficiency of aluminum. XRD patterns of these MAPO-5 molecular sieves are shown in Fig. 1; all of them had typical patterns corresponding to AFI topology [22]. They consisted of small particles less than 1 μm and their agglomerates of plates or hexagonal prisms.

N_2 adsorption measurement of all the samples gave type-I isotherms indicative of typical microporosities. As shown in Table 1, AlPO-5, MgAPO-5, CaAPO-5, and SrAPO-5 had surface areas higher than 270 m^2/g; however, surface areas of BaAPO-5 and ZnAPO-5 were ca. 200 m^2/g. ZnAPO-5 had a surface area of 216 m^2/g, which is lower than that of MgAPO-5.

MAPO-5 molecular sieves have Brønsted acidity generated by the isomorphous substitution of M^{2+} for Al^{3+}. Two types of peaks, so-called *l*- and *h*-peaks, appeared in NH_3-TPD of MAPO-5 molecular sieves as shown in Fig. 2. The *h*-peaks are due to Brønsted acidity which is active for the acid catalysis. As shown in Table 1, MgAPO-5 and ZnAPO-5 had clear *h*-peaks at 294 and 284 °C, respectively, and their acid amounts were 0.14 and 0.15 mmol/g, respectively. These acid amounts are large enough for solid acid catalysis. On the other hand, CaAPO-5, SrAPO-5, and BaAPO-5 had peaks at 252, 242, and 284 °C. Acid amounts were around 0.01–0.02 mmol/g; they were much lower than those of MgAPO-5 and ZnAPO-5. These results show that acidities of CaAPO-5, SrAPO-5, and BaAPO-5 are much weaker than those of MgAPO-5 and ZnAPO-5. Some of M^{2+} in MAPO-5, particularly, CaAPO-5, SrAPO-5, and BaAPO-5 are possibly outside the frameworks; however, more detailed research should be necessary for clarification of these phenomena.

Table 1
Properties of MAPO-5 molecular sieves

MAPO-5	MO/Al_2O_3[a]	SA (m^2/g)	Pore volume (cm^3/g)	Peak (°C)	Acid amounts (mmol/g)
AlPO-5	–	321	0.12	–	–
MgAPO-5	0.13	351	0.13	294	0.14
CaAPO-5	0.17	276	0.10	252	0.015
SrAPO-5	0.17	307	0.14	242	0.017
BaAPO-5	0.083	216	0.08	242	0.01
ZnAPO-5	0.074	211	0.097	284	0.15

[a] MO/Al_2O_3 of starting gel in the synthesis: 0.1.

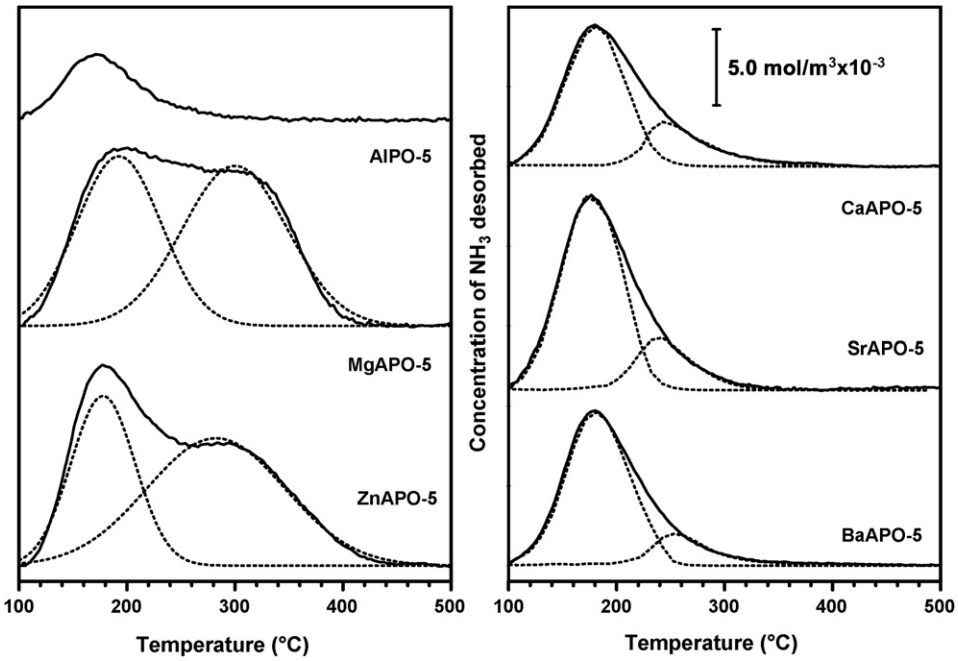

Fig. 2. NH_3-TPD spectra of MAPO-5 molecular sieves.

3.2. Isopropylation of BP over MgAPO-5 molecular sieves

3.2.1. Influence of MgO/Al_2O_3 ratio

Fig. 3 shows the influence of the MgO/Al_2O_3 ratio of MgAPO-5 on the isopropylation of BP. AlPO-5 with no substitution with metal showed no catalytic activity because it had no acidity. MgAPO-5 with MgO/Al_2O_3 ratios in the range of 0.05–0.25 had moderate catalytic activity. The principal products were mixtures of IPBP and DIPB isomers. However, triisopropylbiphenyl (DIPB) isomers were not obtained in large amounts even at higher reaction temperatures. As discussed in a previous paper [19], the acid amount is not always correlated to the MgO/Al_2O_3 ratio. The influences of the ratio on the activity suggest the imperfect substitution of Mg^{2+} for Al^{3+}; some of Mg^{2+} should be present outside of framework of aluminophosphate. However, further research is necessary for elucidation of the detailed mechanism.

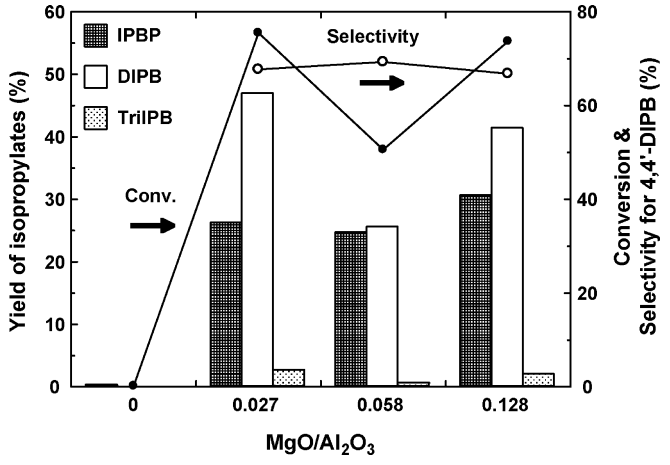

Fig. 3. The influence of MgO/Al_2O_3 ratio of MgAPO-5 on the isopropylation of BP. Reaction conditions: BP, 50 mmol; catalyst, 0.25 g, propene, 0.8 MPa; temperature, 250 °C; period, 4 h.

The selectivity for 4,4′-DIPB was at the level of 70% for all MgAPO-5. These results suggest that shape-selective formation of 4,4′-DIPB is due to the structure of MgAPO-5, and not to the difference in acidity. This selectivity for 4,4′-DIPB over MgAPO-5 is one of the highest selectivities that were ever achieved with zeolites although H-MOR exhibits higher selectivity than MgAPO-5. These high selectivities are ascribed to the shape-selective catalysis in their channels by the restricted transition state mechanism [8–10].

3.2.2. Influence of reaction temperature

Fig. 4 shows the influence of reaction temperature on the isopropylation of BP over MgAPO-5. The conversion of BP increased with the increase in the temperature. The yield of DIPB isomers increased with increasing temperature although the yield decreased when the temperature was increased to 325 °C. In contrast, the yield of IPBP isomers increased slightly with increasing temperature, showed a slight decrease at 300 °C, and then, it again increased when the temperature was increased to 325 °C. The increase in the yield of IPBP isomers and the decrease in the yield of DIPB would be due to the de-alkylation at higher temperatures. The yield of TriIPB isomers increased gradually as a function of temperature.

The influences of reaction temperatures on the yields and the selectivity for IPBP and DIPB isomers are shown in Fig. 5. The influence of temperature on the yield and the selectivity for IPBP isomers are summarized in Fig. 5a. The yield of 4-IPBP increased up to ca. 250 °C, and then decreased rapidly in the range of 260–300 °C. It reached a minimum at 300 °C, and again slightly increased when the temperature was raised to 325 °C; however, the yield of 3-IPBP increased linearly as a function of temperature. The selectivities for 4-IPBP in both bulk and

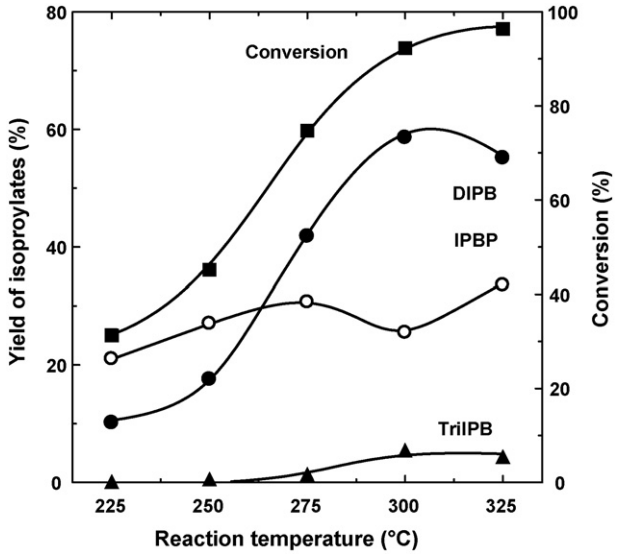

Fig. 4. The influence of reaction temperature on the yield of alkylates in the isopropylation of BP over MgAPO-5. Reaction conditions—catalyst: MgAPO-5 (MgO/Al_2O_3 = 0.13), 0.25 g; BP, 50 mmol; temperature, 225–325 °C; propene, 0.8 MPa; period, 4 h.

encapsulated products decreased in the range of 250–300 °C. These results suggest that the secondary isopropylation of IPBP isomers to DIPB isomers occurs principally through 4-IPBP, and that the isopropylation of 3-IPBP was not rapid.

Fig. 5b shows the influence of temperature on the yields of 4,4′-, 3,4′-, and 3,3′-DIPB. The yield of 4,4′-DIPB increased with increasing temperature, and reached a maximum at 250–300 °C, which decreased with a further increase in temperature, accompanied by the increase in the yields of 3,4′-DIPB and 3,3′-DIPB at higher temperatures than 300 °C. The formation of DIPB isomers with 2-isopropyl groups (2,x′-DIPB: 2,2′-, 2,3′-, and 2,4′-DIPB) was negligible. These results suggest that 4,4′-DIPB was isomerized to 3,4′- and 3,3′-DIPB.

The selectivities for 4,4′-DIPB in bulk and encapsulated products were as high as 60–70% at moderate temperatures; however, they decreased with further increase in reaction temperatures. The decreases in the selectivity for 4,4′-DIPB corresponded to the increase in the selectivities for 3,4′- and 3,3′-DIPB. This trend is consistent with the above-mentioned consideration based on the yields.

Judging from the features of IPBP and DIPB isomers in bulk and encapsulated products, the shape-selective formation of 4,4′-DIPB occurs through 4-IPBP at moderate temperatures inside channels of MgAPO-5; however, 4,4′-DIPB, once formed by the isopropylation inside channels, was isomerized to thermodynamically more stable 3,4′- and 3,3′-DIPB at higher temperatures on the acid sites inside channels as well as on the external acid sites.

3.2.3. Isomerization of 4,4′-DIPB

The isomerization of 4,4′-DIPB under propene pressure was examined over MgAPO-5 in order to find out its total reactivity. Fig. 6 shows the influence of reaction temperature on the isomerization of 4,4′-DIPB under the propene pressure. The influence of temperature on the de-alkylation and isopropylation of 4,4′-DIPB is shown in Fig. 6a. These reactions occurred at higher temperatures. Fig. 6b shows the influence of temperature on the isomerization of 4,4′-DIPB. The yield and the selectivity for 4,4′-DIPB were quite similar to the results of the isopropylation. The selectivities for 4,4′-DIPB decreased with increasing temperatures in both bulk and encapsulated products.

3.3. Isopropylation of BP over CaAPO-5, SrAPO-5, and BaAPO-5 molecular sieves

Fig. 7 shows typical results of the isopropylation of BP over MAPO-5 molecular sieves (M: Mg, Ca, Sr, and Ba). The activities of MAPO-5 molecular sieves were in the order: MgAPO-

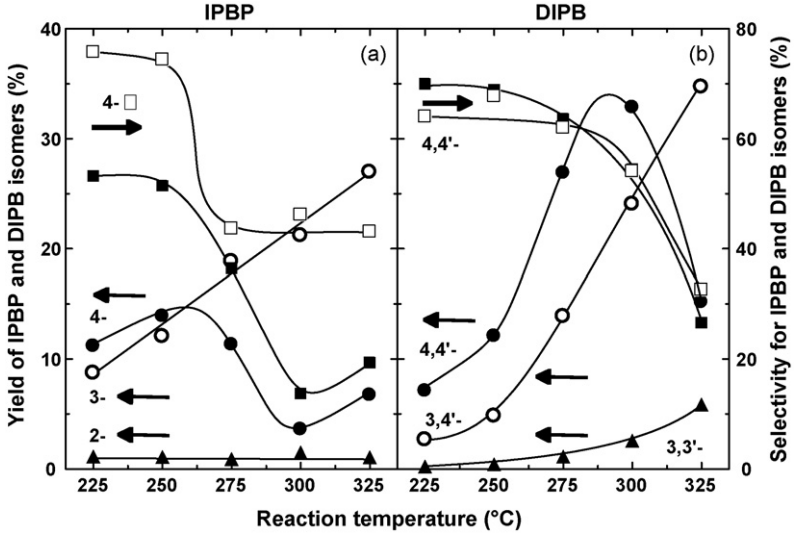

Fig. 5. The influence of reaction temperature on the yield and selectivity for IPBP and DIPB isomers in the isopropylation of BP over MgAPO-5. Reaction conditions: see Fig. 4. Legends—(a) Yield: (●) 4-IPBP; (○) 3-IPBP; (▲) 2-IPBP. Selectivity for 4-IPBP: (■) bulk products; (□) encapsulated products. (b) Yield: (●) 4,4′-DIPB; (○) 3,3′-DIPB; (▲) 3,3′-DIPB. Selectivity for 4,4′-DIPB: (■) bulk products; (□) encapsulated products.

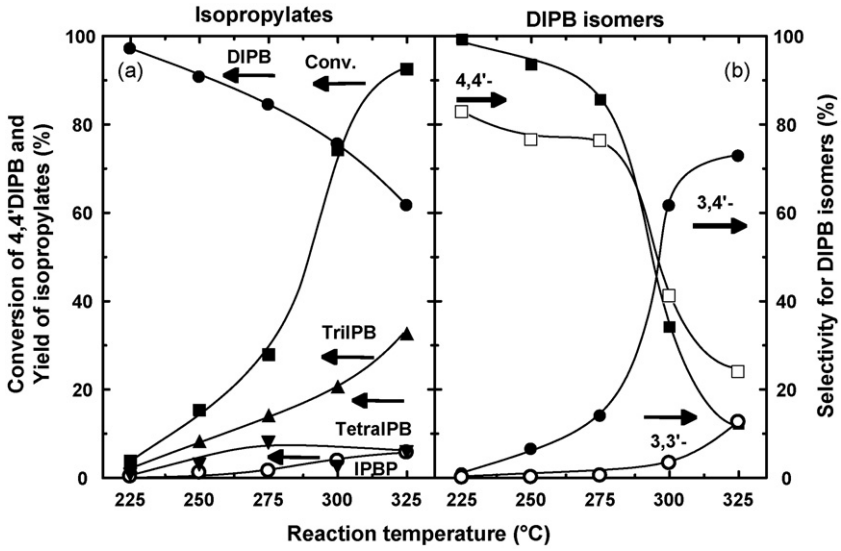

Fig. 6. The influence of reaction temperature on the isopropylation of 4,4′-DIPB over MgAPO-5. Reaction conditions—catalyst: MgAPO-5 ($MgO/Al_2O_3 = 0.13$), 0.25 g; 4,4′-DIPB, 25 mmol; temperature, 225–325 °C; propene, 0.8 MPa; period, 4 h. Legends—(a) Conversion: (■) yield; (●) DIPB; (◯) IPBP; (▲) TriIPB; (▼) TetraIPB. (b) Selectivity for DIPBs in bulk products: (■) 4,4′-DIPB; (●) 3,4′-DIPB; (◯) 3,3′-DIPB. Selectivity for 4,4′-DIPB in encapsulated products: □.

$5 \gg$ CaAPO-5 > SrAPO-5 > BaAPO-5. These activities are due to acid sites generated by heavy alkaline earth metal substitution of the phosphorus sites of AlPO-5 [19] as revealed by the NH_3-TPD peak at 250–350 °C in NH_3-TPD spectra although it was weak for latter three MAPO-5 molecular sieves. The selectivity for 4,4′-DIPB was at the level of 70%. We also observed a similar level of selectivity for 4,4′-DIPB in the isopropylation of BP over SSZ-24 [16] and SAPO-5 [18], which have the same AFI topology as MAPO-5 [22]. These results show that the channels of molecular sieves with AFI topology have the similar level of shape-selectivity for the isopropylation of BP.

3.4. Isopropylation of BP over ZnAPO-5 molecular sieves

The influence of reaction temperature on the isopropylation of BP over ZnAPO-5 is shown in Fig. 8. The conversion of BP increased with the increase in the temperature. The yield of DIPB isomers increased with increasing temperature even up to 325 °C. However, the yield of IPBP isomers remained constant with increasing reaction temperatures. The yield of TriIPB isomers increased gradually at elevated temperatures. ZnAPO-5 showed a trend in catalysis slightly different from MgAPO-5. The reasons for the differences in the catalytic behavior of MgAPO-5 and ZnAPO-5 are unclear at this moment; however, one reason may be the difference in acidic properties.

Fig. 9 shows the influence of reaction temperature on yields and selectivities for IPBP and DIPB isomers. The influences of reaction temperature on the yield and the selectivity for IPBP isomers are shown in Fig. 9a. The yield of 4-IPBP first increased

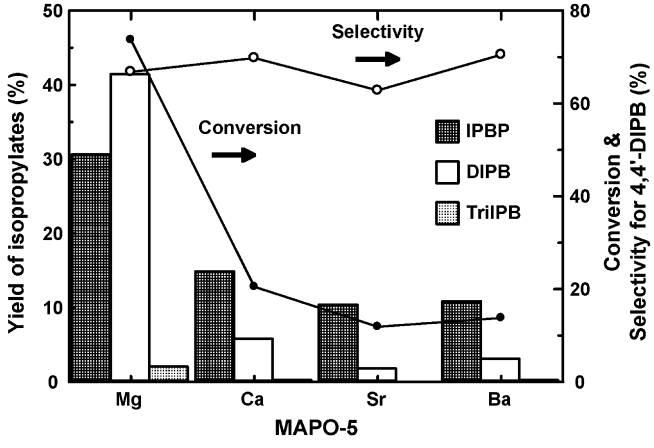

Fig. 7. The influence of metal type of MAPO-5 molecular sieves on the isopropylation of BP. Reaction conditions: MgAPO-5 ($MgO/Al_2O_3 = 0.13$), 0.25 g; BP, 50 mmol; temperature, 250 °C; propene, 0.8 MPa; period, 4 h.

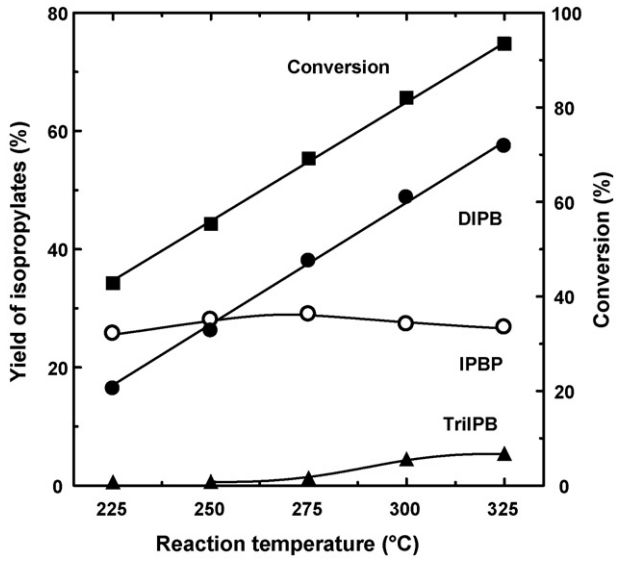

Fig. 8. The influence of reaction temperature on the yield of alkylates on the isopropylation of BP over ZnAPO-5. Reaction conditions: ZnAPO-5 ($ZnO/Al_2O_3 = 0.074$), 0.25 g; BP, 50 mmol; temperature, 225–325 °C; propene, 0.8 MPa; period, 4 h.

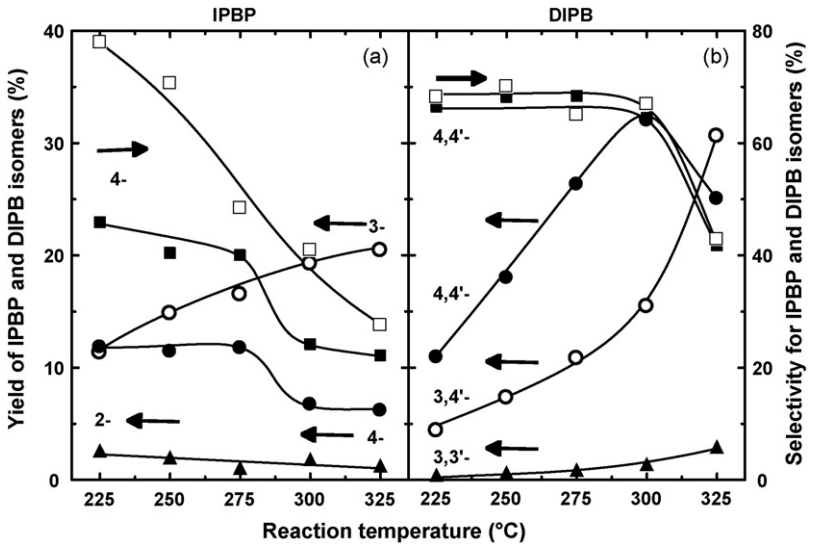

Fig. 9. The influence of reaction temperature on the yield and selectivity for IPBP and DIPB isomers on the isopropylation of BP over ZnAPO-5. Reaction conditions and legends, see Fig. 5.

with increasing temperature up to ca. 250 °C, and then decreased rapidly in the range of 260–325 °C. However, the yield of 3-IPBP increased linearly with increasing reaction temperature. The selectivities for 4-IPBP in bulk and encapsulated products both decreased in the range of 250–325 °C. These results suggest that the secondary isopropylation of IPBP isomers to DIPB isomers occurs through 4-IPBP, and that the isopropylation of 3-IPBP was not rapid.

Fig. 9b shows the influence of reaction temperature on the yield of 4,4′-, 3,4′-, and 3,3′-DIPB. The yield of 4,4′-DIPB increased with increasing temperature, and reached a maximum at 250–300 °C. The yield decreased with a further increase in temperature. The yield of 3,4′-DIPB increased spontaneously with increasing temperature; however, 3,3′-DIPB increased with the decrease in 4,4′-DIPB at higher temperatures than 300 °C. However, 2,x′-DIPB and 3,3′-DIPB were formed in small amounts. The selectivities for 4,4′-DIPB in bulk and encapsulated products were as high as 70% at moderate temperatures; however, they decreased with the further increase in reaction temperatures. The decreases in the selectivities for 4,4′-DIPB resulted in the increase in the selectivities for 3,4′-DIPB and 3,3′-DIPB at higher temperature. These results suggest that 4,4′-DIPB was isomerized to thermodynamically more stable 3,4′-DIPB on the acid sites inside the channels as well as on the external acid sites.

3.5. Coke deposition over MgAPO-5 and ZnAPO-5 molecular sieves in the isopropylation of BP

Fig. 10 shows the TG profiles of MgAPO-5 and ZnAPO-5 used for the isopropylation of BP. The peaks due to coke-combustion appeared at around 500–800 °C. The amounts of coke were 5.3% for MgAPO-5 and 5.5% for ZnAPO-5. These results show that acidic sites on these molecular sieves have comparable strength with those on zeolites, causing coke-deposition.

3.6. The sec- and tert-butylations of BP over MgAPO-5 and ZnAPO-5 molecular sieves

Tables 2 and 3 show the influence of reaction temperature on catalytic activity and the selectivity for 4,4′-di-*sec*-butylbiphenyl (4,4′-DSBB) and 4,4′-di-*tert*-butylbiphenyl (4,4′-DTBB) in the *sec*- and *tert*-butylations of BP over MgAPO-5 and ZnAPO-5. Although the catalytic activities were low, the

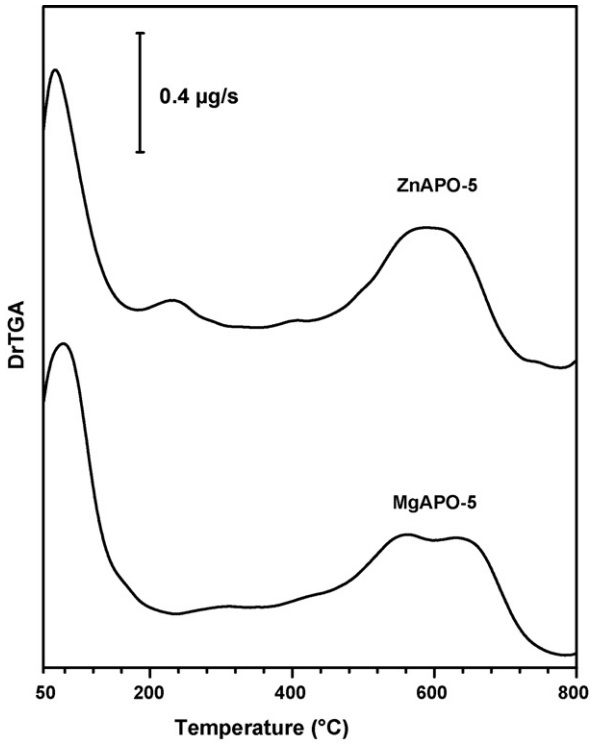

Fig. 10. TG profiles of catalysts used for the isopropylation of BP. Reaction conditions catalyst: MgAPO-5 ($MgO/Al_2O_3 = 0.13$) or ZnAPO-5 ($ZnO/Al_2O_3 = 0.074$), 0.25 g; BP, 50 mmol; temperature, 225–325 °C; propene, 0.8 MPa; period, 4 h.

Table 2
sec-Butylation of BP over MgAPO-5 and ZnAPO-5[a]

	Conversion (%)	Selectivity for *sec*-butylates (%)		Selectivity for DSBB (%)		
		SBBP[b]	DSBB[c]	3,3′-	3,4′-	4,4′-
MgAPO-5	34.6	26.5	73.1	0.3	11.6	87.7
ZnAPO-5	27.7	28.3	71.1	0.3	11.9	87.4

[a] Reaction conditions: BP, 25 mmol; catalyst, 0.125 g (MgAPO-5 ($MgO/Al_2O_3 = 0.13$) ZnAPO-5 ($ZnO/Al_2O_3 = 0.0.074$)); temperature, 250 °C; 1-butene pressure, 0.4 MPa; period, 4 h.
[b] *sec*-Butylbiphenyls.
[c] Di-*sec*-butylbiphenyls.

sec- and *tert*-butylations of BP were highly selective for the formation of the least bulky products, 4,4′-DSBB and 4,4′-DTTB; these selectivities were higher than those in the isopropylation. These differences in the selectivity for 4,4′-dialkylbiphenyl were due to difference in steric constraints of transition states inside the channels.

3.7. Shape-selective catalysis over MAPO-5 molecular sieves

The selectivities for 4,4′-DIPB over all MAPO-5 molecular sieves were at the level of 70%; namely, all MAPO-5 molecular sieves have the same shape-selective nature on the isopropylation of BP. These results show that AFI frameworks of MAPO-5 work in the same manners due to their twelve-membered rings, but not to type of molecular sieves. The differences in catalytic behaviors are due to the acidity originated by difference in their constituents.

It was shown that the isopropylation of BP occurred inside the channel of MAPO-5, and that the transition state to the least bulky isomers, which has the minimal constraints among the isomers inside the channels, leads to the predominant formation of 4,4′-DIPB. However, the selectivity for 4,4′-DIPB over H-MOR was as high as 80–90% [13]. These differences between MAPO-5 and H-MOR are due to the differences in pore diameters: 0.72×0.72 nm for MAPO-5 and 0.67×0.72 nm for H-MOR [22]. These difference in the pore structure is reflected in the discrimination of the transition state to 4,4′-DIPB from those to other isomers. Spatial constraints on the transition state to bulkier DIPB isomers inside the MAPO-5 channels are loose compared to those inside the H-MOR, resulting in lower selectivity for 4,4′-DIPB for MAPO-5 molecular sieves. SSZ-24 [16], SAPO-5 [17], and SSZ-31 [18] with 12-ring straight channels and CIT-5 with 14-ring straight channels [14] have similar levels of the selectivity for 4,4′-DIPB. These molecular sieves have similar levels of pore diameters: 0.56×0.82 nm for SSZ-31 [24] and 0.72×0.75 nm for CIT-5 [22].

The selectivity for 4,4′-DIPB of bulk and encapsulated DIPB isomers decreased at higher temperatures in the isopropylation of BP over MgAPO-5 and ZnAPO-5. The isomerization of 4,4′-DIPB under the pressure of propene also gave a similar decrease in the selectivity for 4,4′-DIPB at high temperatures. These decreases are due to the isomerization of 4,4′-DIPB on acid sites inside channels and also on external acid sites; the channels of MgAPO-5 and ZnAPO-5 are large enough to allow the isomerization of 4,4′-DIPB especially at higher temperatures. The isomerization of 4,4′-DIPB was also observed in the isopropylation of BP over SSZ-24 [13]. However, no isomerization of 4,4′-DIPB was found for SAPO-5 molecular sieves; this is due to its weak acidity compared to other metalloaluminophosphates [5]. These differences in the isomerization are due to their constituents. On the other hand, the selectivity for 4,4′-DIPB in bulk products over H-MOR decreased at higher temperatures; however, the selectivity in encapsulated products remains constant even at higher temperature of 300 °C [13]. These differences suggest that the channels of MAPO-5 molecular sieves impose looser steric restrictions on the formation of bulkier isomers than the MOR channels.

The selectivity for the least bulky 4,4′-dialkylbiphenyl increased in the alkylation of BP over MgAPO-5 and ZnAPO-5 in the order: isopropylation < *sec*-butylation < *tert*-butylation. These differences reflect the differences in spatial constraints in the transition states inside MAPO-5 channels; the predominance of less bulky products increases with the bulkiness of alkylating agents.

Table 3
tert-Butylation of BP over MgAPO-5 and ZnAPO-5[a]

	Conversion (%)	Selectivity for *tert*-butylates (%)		Selectivity for DTBB (%)		
		TBBP[b]	DTBB[c]	3,3′-	3,4′-	4,4′-
MgAPO-5	19.2	10.6	87.3	0.0	0.3	98.9
ZnAPO-5	15.2	9.5	88.9	0.0	0.1	99.3

[a] Reaction conditions: BP, 25 mmol; catalyst, 0.125 g (MgAPO-5 ($MgO/Al_2O_3 = 0.13$) ZnAPO-5 ($ZnO/Al_2O_3 = 0.0.074$)); temperature, 250 °C; 2-methylpropene pressure, 0.4 MPa; period, 4 h.
[b] *tert*-Butylbiphenyls.
[c] Di-*tert*-butylbiphenyls.

4. Conclusion

Metalloaluminophosphates with AFI topology (MAPO-5; M: Mg, Ca, Sr, Ba, and Zn) were used for the alkylation of BP. Among them, MgAPO-5 and ZnAPO-5 had high catalytic activities for the isopropylation while the activities of CaAPO-5, SrAPO-5, and BaAPO-5 were much lower.

The isopropylation of BP occurred inside the channel of MAPO-5 molecular sieves, and the selectivities for 4,4′-DIPB for all MAPO-5 molecular sieves were at the level of 70%. At higher temperatures, the isopropylation of BP over MgAPO-5 and ZnAPO-5 was accompanied by the isomerization of 4,4′-DIPB to the thermodynamically more stable isomer, 3,4′-DIPB; the decrease in the selectivity for 4,4′-DIPB occurred in both bulk and encapsulated products. The 4,4′-DIPB formed inside channels was isomerized on the acid sites inside the channels as well as on the external acid sites. These results show all molecular sieves with AFI topology work in the same manners for the shape-selective catalysis. The catalytic behavior of MAPO-5 molecular sieves is different from that of H-mordenite, which prevents the isomerization inside the pores. The channels of MAPO-5 molecular sieves are large enough to allow the isomerization of 4,4′-DIPB particularly at higher temperatures.

The selectivity for the least bulky 4,4′-dialkylbiphenyls increased in the alkylation of BP over MgAPO-5 and ZnAPO-5 in the order: isopropylation < *sec*-butylation < *tert*-butylation. Inside the AFI channels, the predominance of the least bulky products becomes more obvious in the case of bulkier alkylating agents.

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