



## The alkylation of naphthalene over MCM-68 with MSE topology

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### ABSTRACT

Catalytic activity of MCM-68 zeolite with MSE topology was enhanced by the dealumination in the isopropylation of naphthalene (NP), and maximized at  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ . However, further dealumination accompanies the decrease in catalytic activity. The selectivities for  $\beta,\beta$ -diisopropyl naphthalene ( $\beta,\beta$ -DIPN) were in the level of 50%, and those for 2,6-DIPN were 40% at the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 70–263. The MCM-68 channels have some shape-selective natures in the isopropylation for the formation of  $\beta,\beta$ -DIPN; however, they are too large for selective formation of 2,6-DIPN.

The increase in bulkiness of alkylating agent from propene to 1-butene and 2-methylpropene enhanced the selectivities for  $\beta,\beta$ - and 2,6-dialkyl naphthalene (DAN). The selectivities for  $\beta,\beta$ -di-sec-butyl naphthalene ( $\beta,\beta$ -DSBN) in the sec-butylation and  $\beta,\beta$ -di-tert-butyl naphthalene ( $\beta,\beta$ -DTBN) in the tert-butylation were higher than 90%. Similarly, the selectivities for 2,6-DSBN and 2,6-DTBN increased: 65–75% for 2,6-DSBN in the sec-butylation and 85–98% for the tert-butylation. These results suggest that the differences are due to the steric differentiation of  $\beta,\beta$ -DAN from their isomers and of 2,6-DAN from  $\beta,\beta$ -DAN in the MCM-68 channels, and that the fitting the transition state in the zeolite channels is a key for highly shape-selective catalysis.

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### 1. Introduction

Shape-selective catalyses by zeolites occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environments of the zeolite. The appearance of the shape-selectivity is highly influenced by the structure of zeolites, bulkiness of reagents, etc. If the spaces of zeolite channels are large enough to accommodate the reactants and/or the products, or if the reactants and the products are smaller than the spaces, the catalysis is not operated by restricted transition state selectivity because the formation of transition states from bulky isomers is also allowed. In these cases, the catalysis is controlled kinetically by the reactivity of each position at low temperatures, and by the thermodynamic stability of the products at higher temperatures. These features indicate that the restriction of selective formation of bulky molecules by the channels is one of key factors for shape-selective catalysis, and that it depends on types of zeolites and alkylating agents [1–3].

The isopropylation of polynuclear hydrocarbons, such as naphthalene (NP) and biphenyl (BP) is a typical acid-catalysed reaction for demonstrating shape-selective nature of zeolite. Selective for-

mation of the least bulky 2,6-diisopropyl naphthalene (2,6-DIPN) and 4,4'-diisopropylbiphenyl (4,4'-DIPB) should be facilitated in the isopropylation of NP and BP over zeolites if the steric environments of catalytic sites are properly restricted [4–14]. In the previous papers, we described that 2,6-DIPN was selectively produced from NP over dealuminated H-mordenite (MOR) [9]. Catalytically active sites in MOR channels effectively exclude the transition state of bulky DIPN isomers from the channels, thus resulting in selective formation of the least bulky 2,6-DIPN.

In this paper, we describe the alkylation, i.e., isopropylation, sec-butylation, and tert-butylation of NP over MCM-68 zeolites (Framework Type Code (FTC): MSE) [15–17] with three-dimensional 12-10-10 channel system from points of view how shape-selective catalysis occurs in their channels on the basis of selectivities for  $\beta,\beta$ - and 2,6-dialkyl naphthalene ( $\beta,\beta$ - and 2,6-DAN) among the DAN isomers. The discussion in the paper was based on the selectivities for DAN isomers ( $\beta,\beta$ - and 2,6-selectivities) because they are one of key factors for controlling the catalysis in sterically restricted environments such as zeolites.

### 2. Experimental

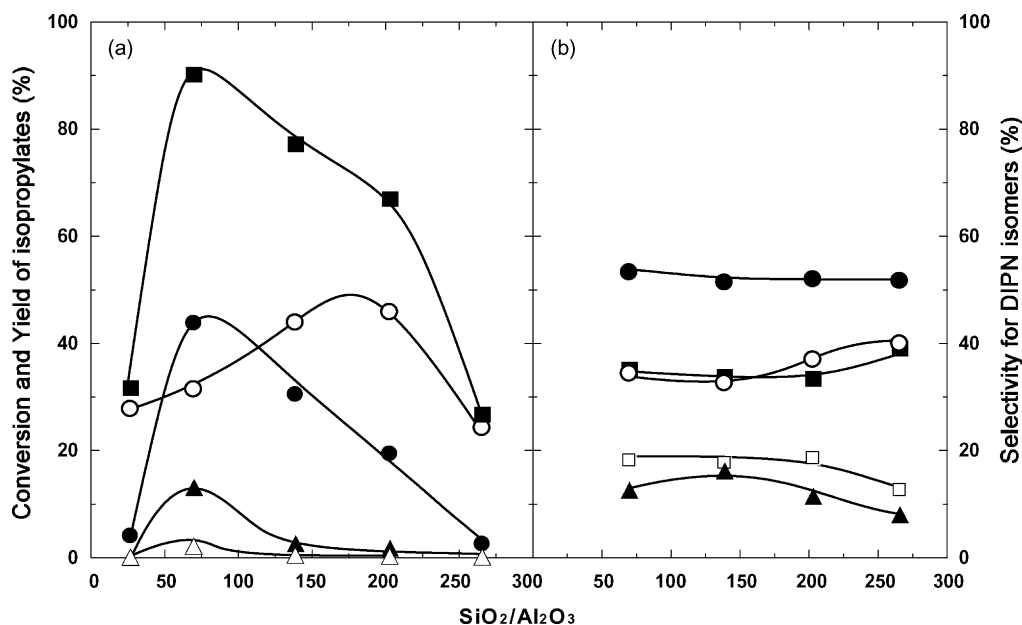
#### 2.1. Catalyst

MCM-68 zeolite (MSE) was synthesized according to our previous papers [16–18]. The dealumination of the calcined sample

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**Fig. 1.** The influence of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of MCM-68 zeolite on the isopropylation of NP. Reaction conditions: NP, 25 mmol; catalyst: MCM-68 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 26–263), 125 mg; propene: 0.8 MPa; period, 4 h. Legends: (a) (■) Conversion, Yield: (○) IPN isomers; (●) DIPN isomers; (▲) TriIPN isomers; (△) Tetra-IPN isomers. (b) Selectivity for DIPN isomers: (■) 2,6-DIPN; (□) 2,7-DIPN; (●) β,β-DIPN; (○) α,β-DIPN; (▲) α,α-DIPN.

(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 20) was carried out by treating with 1N HCl solution (50 mL/g-sample) in a 200-mL round-bottom flask at 50–80 °C for 4–24 h. The obtained SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios were in a range of 70–263. The results of some characterization of the catalysts were shown in our previous paper [18].

## 2.2. The alkylation of NP

The alkylation of NP was carried out in a 100-mL SUS-316 autoclave under our standard conditions [9]. MCM-68 (25 mg) and NP (6.4 g; 5 mmol) were placed in autoclave, flushed with nitrogen, and heated to desired temperature (225–300 °C). An alkylating agent (0.8 MPa of propene, 0.4 MPa of 1-butene, and 0.4 MPa of 2-methylpropene for isopropylation, *sec*-butylation, and *tert*-butylation, respectively) was then introduced to the desired pressure, and agitated for 4 h. The pressure kept constant throughout the reaction. After cooling the autoclave, the products were separated from catalysts by filtration. The solution (*ca.* 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 a gas chromatography (GC-14A or GC-18A, Shimadzu Corporation) equipped with an TC-17 (25 m × 0.25 mm; film thickness: 0.25 μm; GL Sciences, Tokyo) [19]. HP-INNOWax (60 m × 0.25 mm; film thickness: 0.5 μm; Agilent Technologies) was also used for the identification of DAN isomers. The typical gas chromatograms are shown in Supporting information. The product identifications were also referred to the literatures [20–23]. The products were also identified by a Shimadzu GC-MS 5000 Gas Chromatograph–Mass Spectrometer.

The yield of each product is calculated on the basis of the amounts of starting NP, and the selectivities for each 2,6-dialkyl naphthalene (DAN) isomers are expressed on the basis of the total amounts of DAN isomers, respectively.

DAN in isopropylation, *sec*-butylation, and *tert*-butylation to DIPN, DSBN, and DTBN, respectively. β,β-DAN is defined as a mixture of 2,6- and 2,7-DAN isomers, α,β-DAN as 1,3-, 1,6-, and 1,7-DAN isomers, and α,α-DAN as 1,4- and 1,5-DAN isomers.

Thermogravimetric (TG) analysis of the used catalysts was performed on a Shimadzu DTG-50 analyzer with temperature-programmed rate of 10 °C/min in an air stream.

## 3. Results and discussion

### 3.1. Influence of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio on the isopropylation

Fig. 1 shows the influence of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the zeolite on the isopropylation of NP at 250 °C. The conversion and the yield of isopropylates were shown in Fig. 1a. The originally synthesized H<sup>+</sup>-form MCM-68 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 26) has only low catalytic activity for the isopropylation: the products contained almost only isopropyl naphthalene (IPN) isomers and the formation of diisopropyl naphthalene (DIPN) isomers was negligible. However, the catalytic activities were enhanced by the dealumination of the zeolite, and reached maximum at the ratio of 70. The further dealumination to the ratios of 134–263 decreased the catalytic activities: the decrease is due to the decrease in acid amounts by the dealumination [18].

The selectivities for DIPN isomers are shown in Fig. 1b. The selectivities for β,β-DIPN (2,6- and 2,7-), α,β-DIPN (1,3-, 1,6-, and 1,7-), and α,α-DIPN (1,4- and 1,5-) were almost constant in the level of 50–55%, 35–45%, and 10–15%, respectively in the range of 70–263 of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. The selectivities for 2,6- and 2,7-DIPN were in the level of 35–45% and 15–25%, respectively; the selectivities for 2,6-DIPN were slightly increased with the increase in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio accompanying the decrease in the selectivities for 2,7-DIPN. This result means the selectivities for 2,6-DIPN increased slightly with the decrease in the isomerization of 2,6-DIPN to 2,7-DIPN because of the decrease in acid amounts. However, the some shape-selective natures appear for the formation of β,β- and 2,6-DIPN in the MCM-68 channels; however, the differentiation of these isomers was not so strict.

Fig. 2 shows the TG profiles of the catalysts used for the catalysis. The coke-formation in the range of 350–700 °C was particularly

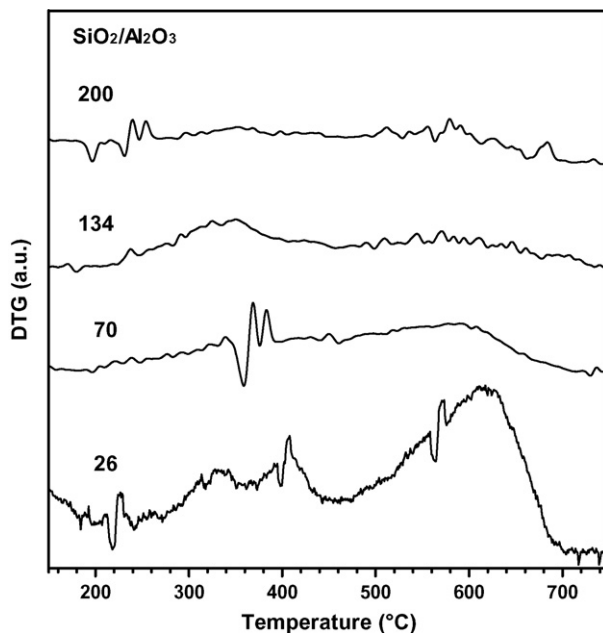


Fig. 2. The influence of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of MCM-68 zeolite on TG profiles of the used catalyst. Reaction conditions: see in Fig. 1.

severe for the zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$ . These results mean highly dense acid sites of originally synthesized MCM-68 zeolite were easily deactivated by the choking the pores due to coke-deposition, resulting in the prevention of the catalysis. The decrease in acid densities by the dealumination reduces the deactivation by choking pores due to the decrease in coke-formation, resulting in the enhancement of catalytic activities. Further dealumination declines the catalytic activities due to the decrease in the acid sites of the zeolite. The increase in catalytic activities of MCM-68 zeolites by mild dealumination is very similar to the cases of MOR [5,6]. However, the catalytic activities of MOR were enhanced by the further dealumination. The differences may be due to the channel structures.

### 3.2. Influence of reaction temperature on the isopropylation

Fig. 3 shows the influence of reaction temperature on the isopropylation of NP over MCM-68 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 134$ ). The catalytic activities were increased with the reaction temperatures (Fig. 3a). Principal products at low temperatures were IPN isomers, and the yield of DIPN was increased with the temperatures. However, the yields of tri- and tetraisopropylnaphthalenes were less than 3% at 300 °C.

The selectivities for thermodynamically stable and less bulky  $\beta,\beta$ -DIPN increased with increasing the reaction temperatures accompanying the decrease in the selectivities for  $\alpha,\beta$ - and  $\alpha,\alpha$ -DIPN, particularly,  $\alpha,\beta$ -DIPN. There are three possibilities for the

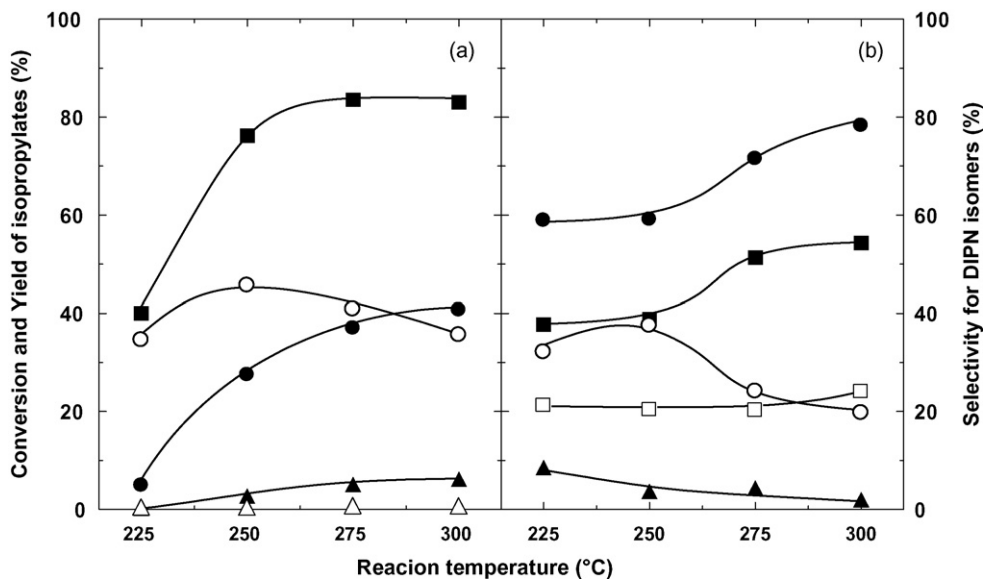
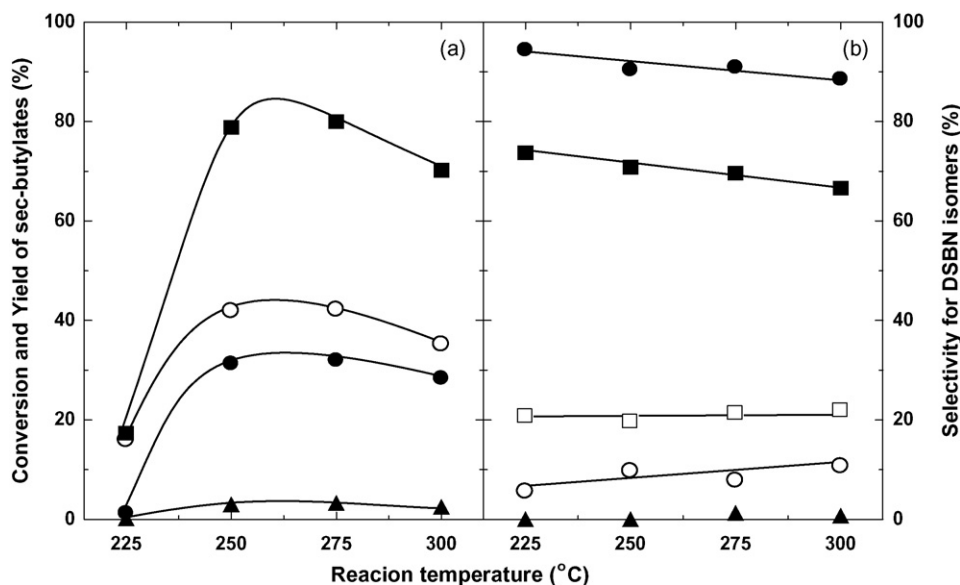


Fig. 3. The influence of reaction temperature on the isopropylation of NP. Reaction conditions: NP, 25 mmol; catalyst: MCM-68 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 134$ ), 125 mg; propene: 0.8 MPa; period, 4 h. Legends: see Fig. 1.



**Fig. 4.** The influence of reaction temperature on the *sec*-butylation of NP. Reaction conditions: NP, 25 mmol; catalyst: MCM-68 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 134$ ), 125 mg; 1-butene: 0.4 MPa; period, 4 h. (a) (■) Conversion. Yield: (○) SBN isomers; (●) DSBN isomers; (▲) TriSBN isomers. (b) Selectivity for DSBN isomers: (■) 2,6-DSBN; (□) 2,7-DSBN; (●)  $\beta,\beta$ -DSBN; (○)  $\alpha,\beta$ -DSBN; (▲)  $\alpha,\alpha$ -DSBN.

change in the selectivities. The first is the enhancement of the formation of thermodynamically more stable  $\beta,\beta$ -DIPN at the high temperatures due to thermodynamic control. The second is the decrease in the isomerization of  $\alpha,\beta$ -DIPN to  $\beta,\beta$ -DIPN. The third is the increase in the shape-selective nature of the zeolites at high temperatures. We consider the first possibility is the most probable, and that it is difficult to understand the difference by third possibility.

The selectivities for 2,6-DIPN increased with the increase in reaction temperature: the selectivities for 2,7-DIPN were almost constant in the range of 225–300 °C; however the selectivities for  $\alpha,\beta$ -DIPN decreased with the increase in reaction temperatures. The increases in the selectivities for 2,6-DIPN were due to formation of thermodynamically more stable 2,6-DIPN and/or the isomerization of less stable isomers to stable 2,6-DIPN.

These results show that the shape-selective natures by the MCM-68 channels in the isopropylation appeared in some extent to differentiate less bulky isomers from their isomers; however, the MCM-68 channels are too large for selective formation of  $\beta,\beta$ - and 2,6-DIPN.

### 3.3. Influence of reaction temperature on *sec*-butylation and *tert*-butylation

As discussed in previous sections, the MCM-68 channels are too large to differentiate highly the less bulky  $\beta,\beta$ -DIPN from  $\alpha,\beta$ - and  $\alpha,\alpha$ -DIPN, and 2,6-DIPN from  $\beta,\beta$ -DIPN. To elucidate shape-selective natures of the channels, we have been interested in steric relation of channels size by changing the bulkiness of the alkylating agent. We examined the alkylation of NP by using bulky alkylating agent, 1-butene and 2-methylpropene.

Fig. 4 shows the influence of reaction temperature on the *sec*-butylation of NP over MCM-68 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 134$ ). The conversion and the yield of *sec*-butylates are increased with the reaction temperatures (Fig. 3a). The principal products were *sec*-butylnaphthalene (SBN) isomers and di-*sec*-butylnaphthalenes (DSBN), and further higher products were negligible even at 300 °C.

The selectivities for DSBN isomers are shown in Fig. 4b. The selectivities for  $\beta,\beta$ -DSBN were higher than 90% in the ranges of 225–300 °C; the selectivities for  $\alpha,\beta$ -DSBN were less than 10%, and

those for  $\alpha,\alpha$ -DSBN were almost negligibly low. These results mean the MCM-68 channels are highly shape-selective for the differentiation of  $\beta,\beta$ -DSBN among DSBN isomers. Although the effective molecular diameters of  $\beta,\beta$ -DSBN are almost the same as that of  $\beta,\beta$ -DIPN, the replacement of isopropyl moieties by *sec*-butyl ones invokes the differences in bulkiness of  $\beta,\beta$ -DSBN and the other bulky  $\alpha,\alpha$ - and  $\alpha,\beta$ -DSBN at their transition states by the interaction with the channels, resulting in the enhancement of the selectivities for  $\beta,\beta$ -DSBN over these zeolites compared to those for  $\beta,\beta$ -DIPN. Thus, the bulky DSBN isomers,  $\alpha,\alpha$ - and  $\alpha,\beta$ -DSBN, are effectively excluded from the channels compared to  $\alpha,\beta$ -DIPN and its bulkier isomers, resulting in the higher selectivities for  $\beta,\beta$ -DSBN.

The selectivities for 2,6- and 2,7-DSBN were also shown in Fig. 4b. The selectivities for 2,6-DSBN were around 70% at all temperatures between 225 and 300 °C, and decreased slightly with the reaction temperatures from 74% at 225 °C to 67% at 300 °C; the selectivity for 2,7-DSBN were also almost constant at around 22–25%. These results mean that MCM-68 channels can differentiate 2,6- and 2,7-DSBN. These selectivities for 2,6-DSBN were much higher than those for 2,6-DIPN in the isopropylation: the steric interaction of *sec*-butyl moieties effectively works although they are almost the same bulkiness in molecular level at the most stable conformation.

These results mean MCM-68 channels were highly selective for the differentiation of  $\beta,\beta$ -DSBN among DSBN isomers; however, the selectivities for 2,6-DSBN were lower than those for  $\beta,\beta$ -DSBN. These results show that steric restriction in the channels are small enough for the formation of  $\beta,\beta$ -DSBN; however, they do not fit completely for the formation of 2,6-DSBN.

Fig. 5 shows the influence of reaction temperature on the *tert*-butylation of NP over MCM-68 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ ). Catalytic activities and the yield of *tert*-butylates are shown in Fig. 5a. Principal products were *tert*-butylnaphthalenes (TBN) and di-*tert*-butylnaphthalenes (DTBN) although the yields of DTBN were lower than those of TBN. The yield of higher products was negligible (Fig. 5a).

The selective formation of  $\beta,\beta$ -DTBN was observed in the range of 225–300 °C, although the selectivities were slightly decreased at the higher temperatures (Fig. 5b). These results mean that the

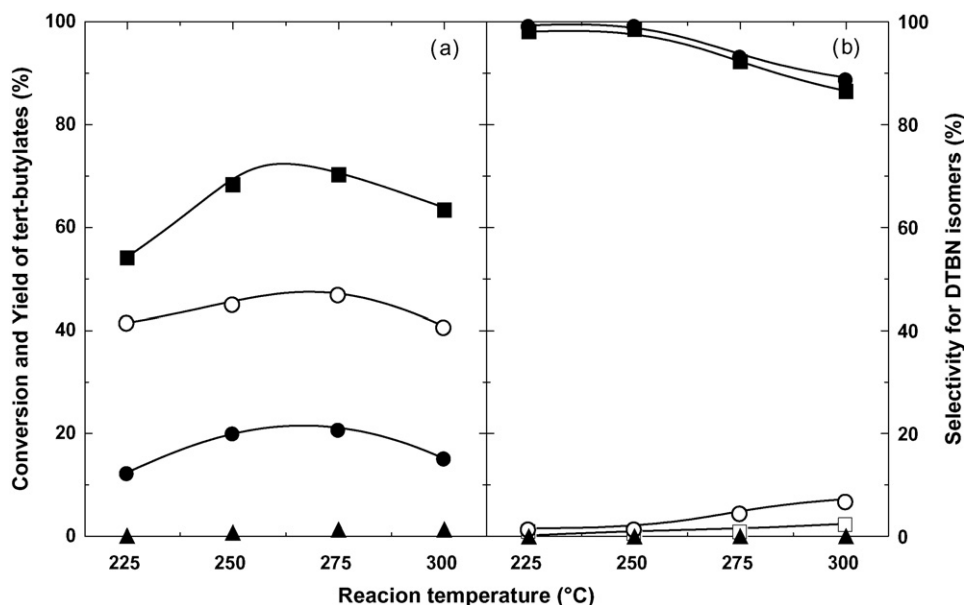


Fig. 5. The influence of reaction temperature on the *tert*-butylation of NP over MCM-68 zeolite. Reaction conditions: NP, 25 mmol; catalyst: MCM-68 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ ), 125 mg; 2-methylpropene: 0.4 MPa; period, 4 h. (a) (■) Conversion. Yield: (○) TBN isomers; (●) DTBN isomers; (▲) TriTBN isomers. (b) Selectivity for DTBN isomers: (■) 2,6-DTBN; (□) 2,7-DTBN; (●)  $\beta,\beta$ -DTBN; (○)  $\alpha,\beta$ -DTBN; (▲)  $\alpha,\alpha$ -DTBN.

MCM-68 channels can differentiate  $\beta,\beta$ -DTBN almost completely from other DTBN isomers. The selectivities for 2,6-DTBN were also 85–98% although they decreased slightly at higher temperatures. These results mean that MCM-68 channels can differentiate 2,6-DTBN from  $\beta,\beta$ -DTBN, and that they fit well the transition states inside the channels.

The results on *sec*-butylation and *tert*-butylation indicate that the MCM-68 channels have the shape-catalysis natures by fitting effectively the channels and bulkiness of the reagents.

#### 3.4. Shape-selective catalysis over MCM-68 channels

MCM-68 is one of three-dimensional zeolites with MSE topology:  $12 \times 10 \times 10$ -MR as shown in Fig. 6 [15]. The 12-MR straight channel of MCM-68 intersects rectangularly with two independent tortuous 10-MR channels, and the super cage in MCM-68 zeolite can be accessible only through 10-MR channels. From these reasons, the channels of MCM-68 zeolite work actually as one-dimensional straight channels for the catalysis with bulky molecules, such as NP and BP. NP and BP cannot be isopropylated over ZSM-5 with 10-MR pore entrance [4,5].

The selectivities for  $\beta,\beta$ - and 2,6-DIPN were around 50–55% and 35–45%, respectively, in the isopropylation of NP at 250 °C over MCM-68 zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$ –263). These results mean the MCM-68 channels have some shape-selective natures for  $\beta,\beta$ -DIPN

among DIPN isomers in the isopropylation; however, they cannot differentiate 2,6-DIPN from  $\beta,\beta$ -DIPN. The selectivities for  $\beta,\beta$ -DIPN and 2,6-DIPN were increased with the reaction temperature: 60–80% for  $\beta,\beta$ -DIPN and 40–55% for 2,6-DIPN, and the increase in these selectivities accompanied by the decrease in the selectivities for  $\alpha,\beta$ -DIPN: 40–20%. These results show that the MCM-68 channels cannot fully differentiate  $\beta,\beta$ -DIPN from DIPN isomers and 2,6-DIPN from  $\beta,\beta$ -DIPN. The increase in the selectivities for  $\beta,\beta$ -DIPN and 2,6-DIPN with the increase in reaction temperature is due to kinetic and thermodynamic controls:  $\alpha,\beta$ -DIPN forms significantly under kinetic control; however, the increase in reaction temperature enhances the formation of  $\beta,\beta$ -DIPN under thermodynamic control.

The increase in the bulkiness of alkylating agent enhanced the differentiation of the product isomers inside the MCM-68 channels. The selectivities for  $\beta,\beta$ - and 2,6-DSBN were 90–95%, and 67–75% in the *sec*-butylation, respectively.

Although effective molecular diameters of  $\beta,\beta$ -DSBN are almost the same as that of  $\beta,\beta$ -DIPN, the difference in steric hindrance between  $\beta,\beta$ - and the other isomers with isopropyl moieties in MCM-68 channels is enhanced by the replacement with *sec*-butyl moieties, resulting in the higher selectivities for  $\beta,\beta$ -DSBN in the *sec*-butylation. Similarly, the selectivities for 2,6-DSBN were higher than those for 2,6-DIPN. The steric hindrance between 2,6- and 2,7-DSBN is larger in the MCM-68 channels than that between 2,6-

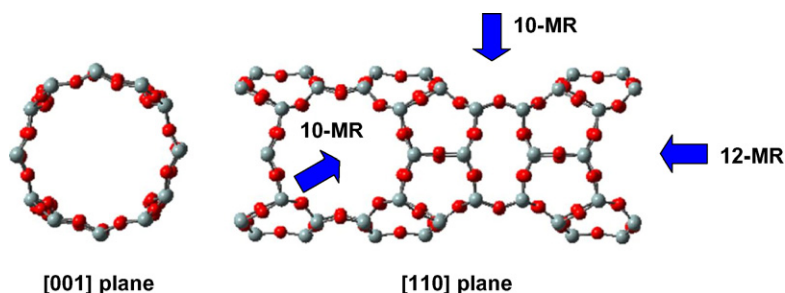


Fig. 6. Model of pore-entrance and channel of MCM-68 zeolite. Drawn on the basis of database in zeolite structure in International Zeolite Association [15].

and 2,7-DIPN, resulting in the improvement in the selectivities for 2,6-DSBN.

The *tert*-butylation of NP occurred with the exclusive formation of  $\beta,\beta$ - and 2,6-DTBN. These results mean that MCM-68 channels allow only the formation of 2,6-DTBN inside the channels, and that the shape-selective alkylation occurs by the differentiation of the least bulky  $\beta,\beta$ - and 2,6-DAN from the other isomers at the transition state inside the channels.

*tert*-Butyl moieties in DTBN isomers also enhance the  $\beta,\beta$ -selectivities in the *tert*-butylation. Thus,  $\alpha,\alpha$ - and  $\alpha,\beta$ -DAN are effectively excluded from the channels by the increase in the bulkiness of alkylating agents in the order: isopropylation < *sec*-butylation < *tert*-butylation.

The high selectivities for  $\beta,\beta$ - and 2,6-DAN were also observed by bulky alkylating agents over three-dimensional zeolites, such as Y (FTC: FAU),  $\beta$  (FTC: BEA), and CIT-1 (FTC: CON) DTBN:  $12 \times 12 \times 12$ -MR for Y and  $\beta$ , and  $12 \times 12 \times 10$ -MR for CIT-1 [12]. The channels of these zeolites are too large for highly differentiating  $\beta,\beta$ - and 2,6-DIPN from the isomers; however, the shape-selective natures appeared in *sec*-butylation and *tert*-butylation [12].

The isopropylation of BP yielded 4,4'-DIPB with high selectivities (60–70%) over MCM-68 with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$  in the range of 200–350 °C [18]. The high selectivities for 4,4'-DIPB are originated from the discrimination of 4,4'-DIPB from the other isomers, particularly 3,4'-DIPB, at their transition states. MCM-68 channels are too large for the differentiation of  $\beta,\beta$ -DIPN from DIPN isomers and 2,6-DIPN from  $\beta,\beta$ -DIPN. The difference in bulkiness between 2,6- and 2,7-DIPN was much small compared to the difference between 4,4'-DIPB and other isomers in the isopropylation of BP. Similar lower selectivities for 2,6-DIPN compared to those for 4,4'-DIPB in the isopropylation were also observed over MOR, SSZ-24 (FTC: AFI), and CIT-5 (FTC: CFI) [9,24,25].

From the results discussed in our current and previous papers [12–14,24–26], it is concluded that the shape-selective alkylation over zeolites is governed by the steric restriction of the transition state in zeolite channels. This means that the zeolites with large channels can be possibly highly selective catalysts if the transition state of the least bulky isomers from the other isomers is appropriately discriminated from their isomers. However, if the channels are too large even for the transition states of bulky molecules, the catalyses occur under kinetic control at lower temperatures and under thermodynamic control at higher temperatures. These considerations can be generally applied for many catalyses in sterically restricted microporous materials.

#### 4. Conclusion

MCM-68 zeolite with MSE topology was applied for the alkylation, i.e., isopropylation, *sec*-butylation, and *tert*-butylation of NP. The dealumination enhanced catalytic activity, and the conversion was maximized at  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ , and further dealumination accompanies the decrease in the activity.

MCM-68 channels have some shape-selective natures for  $\beta,\beta$ -DIPN among DIPN isomers in the isopropylation; however, they cannot differentiate 2,6-DIPN from  $\beta,\beta$ -DIPN. However, the shape-selectivities were enhanced by using the bulky alkylating agents, 1-butene and 2-methylpropene in *sec*-butylation and *tert*-butylation, respectively. The selectivities for  $\beta,\beta$ - and 2,6-DSBN

were 90–95%, and 67–75%, respectively, in the *sec*-butylation. Although effective molecular diameters of  $\beta,\beta$ -DSBN and/or 2,6-DSBN are almost the same as that of  $\beta,\beta$ -DIPN and/or 2,6-DIPN, the difference in steric hindrance between the isomers with isopropyl moieties in MCM-68 channels is enhanced by the replacement with *sec*-butyl moieties, resulting in the enhancement of the selectivities for  $\beta,\beta$ - and 2,6-DSBN. The *tert*-butylation of NP occurred with the exclusive formation of  $\beta,\beta$ - and 2,6-DTBN. These results indicate that MCM-68 channels allow the exclusive formation of 2,6-DTBN.

In conclusion, shape-selective alkylation occurs by the differentiation of the least bulky  $\beta,\beta$ -DAN from their isomers and 2,6-DAN from  $\beta,\beta$ -DAN at transition state inside the zeolite channels.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.09.016.

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