



## The isopropylation of diphenyl ether over H-mordenite catalysts

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### ABSTRACT

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

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

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### 1. Introduction

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

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

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

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## 2. Experimental

### 2.1. H-mordenites

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

### 2.2. Synthesis of substrates and authentic samples

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

### 2.3. Isopropylation of PE

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

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

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

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

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

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

## 3. Results and discussion

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

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

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

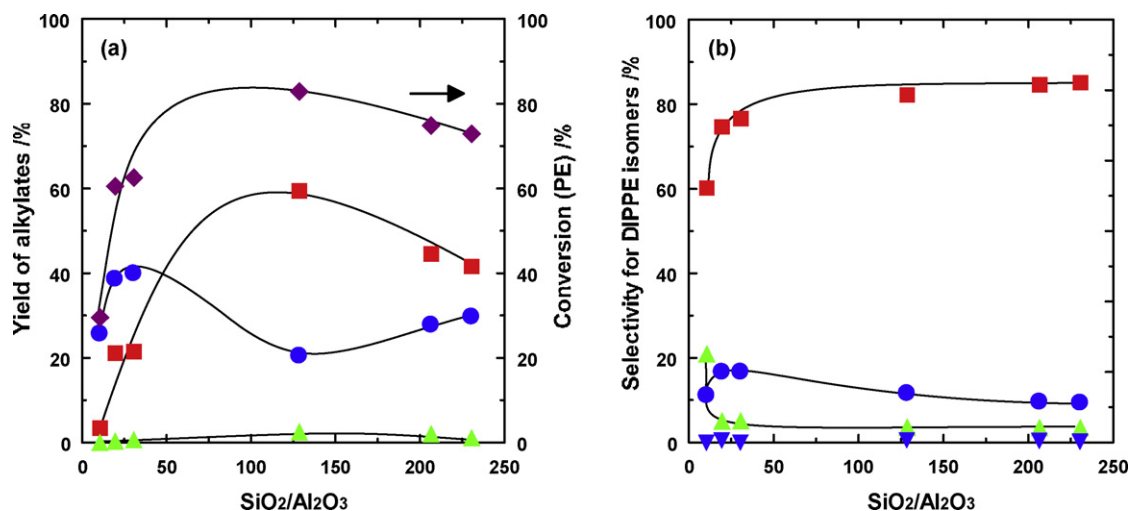
TGA profiles of the catalysts after reaction are shown in Fig. 2. The peaks due to coke-formation were observed at approximately 580 °C. The coke formation was maximized at the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 30, and then decreased with the increased ratio (12.8%, 7%, and 7.2% for the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

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

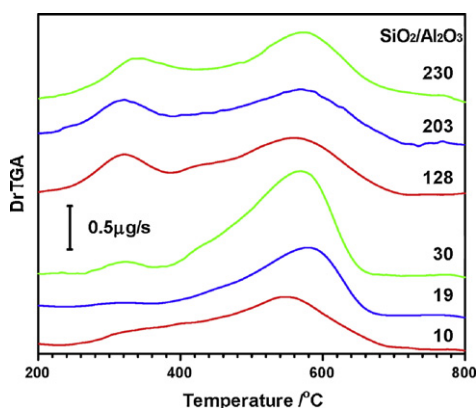
### 3.2. Influence of reaction temperature on the isopropylation of PE

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

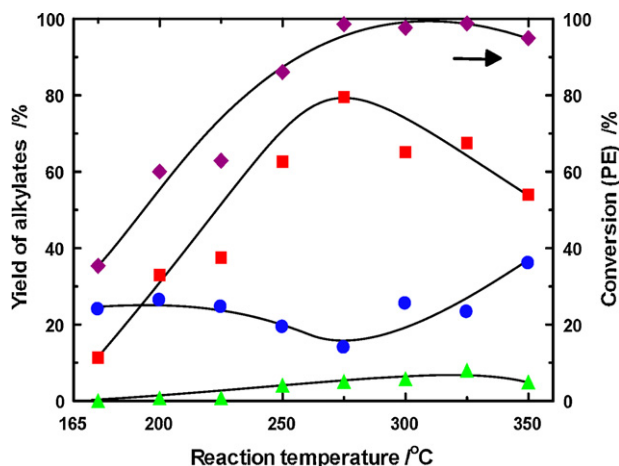
<sup>1</sup> The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of MOR expresses in parenthesis.



**Fig. 1.** Influence of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of MOR on the isopropylation of PE. (a) Yield of alkylates. (b) Selectivity for DIPPE isomers. Reaction conditions: PE: 200 mmol (34.04 g); MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 10–230): 1.0 g; temperature: 250 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a) ■: DIPPE; ●: IPPE; ▲: TIPPE; ◆: conversion (PE). (b) ■: 4,4'-DIPPE; ●: 3,3'-DIPPE; ▲: 3,4'-DIPPE; ▼: 3,3'-DIPPE.



**Fig. 2.** TGA profiles of MOR with Al<sub>2</sub>O<sub>3</sub> ratios of 10–230 used for reactions. Samples: the catalysts used in Fig. 1.



**Fig. 3.** Influence of reaction temperature on yield of alkylates in the isopropylation of PE. Reaction conditions: PE: 25 mmol (4.26 g); MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 128): 0.125 g; temperature: 180–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: see Fig. 1a.

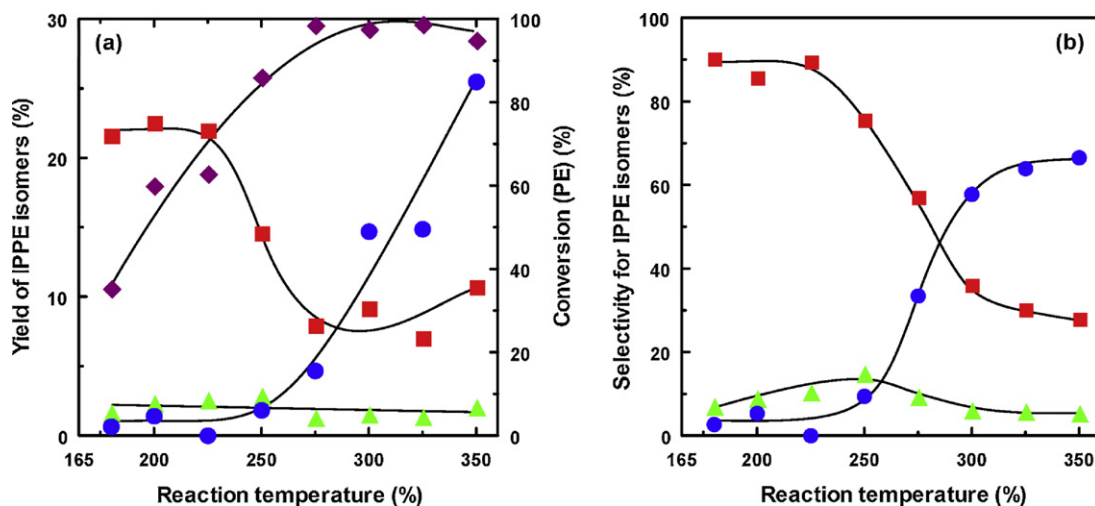
These results indicate that DIPPE isomers were formed through IPPE from PE, and that the increases in IPPE yield along with the decrease in DIPPE yield at high reaction temperatures are due to the de-alkylation reaction.

Fig. 4 shows the influence of reaction temperature on the yield and selectivity for IPPE isomers in the isopropylation of PE. The yield of 4-IPPE was 20–25% at 175–225 °C, then started to decrease to less than 10% at 250–275 °C, and remained almost constant with further increases in temperatures (Fig. 4a). However, the yield of 3-IPPE increased rapidly with increased temperature at 275–350 °C. The yield of 2-IPPE was almost constant in the temperature range. The rapid decrease in 4-IPPE from 200 °C to 275 °C was ascribed to the rapid increase in the formation of DIPPE isomers, particularly of 4,4'-DIPPE because the yield of 3-IPPE was not so much changed (Figs. 3 and 5).

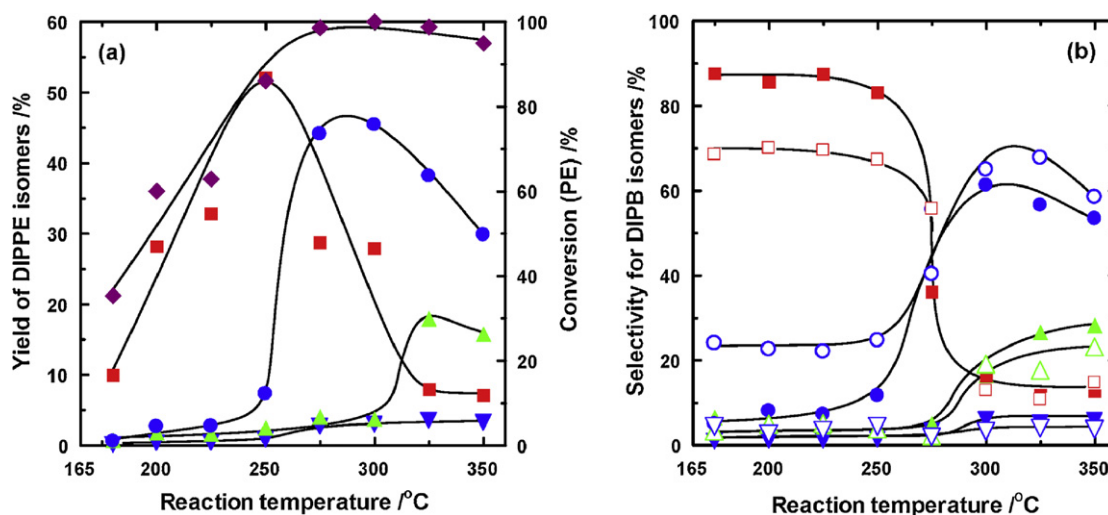
Fig. 4b shows the influence of reaction temperature on the selectivity for IPPE isomers. The changes of selectivities for IPPE isomers of bulk products corresponded to the yield of IPPE isomers with the increase in the temperature as shown in Fig. 4a. The selectivity for 4-IPPE was as high as 80–90% in the range of 175–225 °C, then decreased rapidly with the increase in the selectivity for 3-IPPE, and the selectivities for 4- and 3-IPPE were saturated by further increase in reaction temperature: 60–70% for 3-IPPE and 25–30% for 4-IPPE. The features of IPPE isomers of encapsulated products were similar to that of bulk products (data not given). These results indicate that shape-selective formation of 4-IPPE from PE occurred in MOR channels at low temperatures, particularly below 225 °C. The predominant formation of thermodynamically stable 3-IPPE at high temperatures above 300 °C are probably due to the isomerization of 4-IPPE to 3-IPPE. However, we considered the decrease in 4-IPPE in the range of 225–250 °C were mainly due to its rapid consumption for the formation of DIPPE isomers, particularly, 4,4'-DIPPE in addition to the isomerization. This hypothesis is supported from the difference in yield of 4- and 3-IPPE as in Fig. 4a, and from the high yield and selectivity for 4,4'-DIPB as will be shown in Fig. 5.

Fig. 5 shows the influence of reaction temperature on the yield and selectivity for DIPPE isomers in the isopropylation of PE. The yield of 4,4'-DIPPE was enhanced with increased temperature, reached a maximum at 275 °C, and then, decreased with increases in the yield of 3,4'-DIPPE (Fig. 5a). Further increases in the temperature resulted in increased yield of 3,3'-DIPPE with decreased yield of 3,4'-DIPPE. However, the total yield of DIPPE isomers decreased above 300 °C because of the increase in the de-alkylation (Fig. 3).

These results were confirmed from the selectivities for DIPPE isomers in bulk and encapsulated products (Fig. 5b). The



**Fig. 4.** Effects of reaction temperature on the isopropylation of PE. (a) Yield of IPPE isomers. (b) Selectivities for IPPE isomers. Reaction conditions: see Fig. 3. Legend: (a and b) ■: 4-IPPE; ●: 3-IPPE; ▲: 2-IPPE; ◆: conversion (PE).



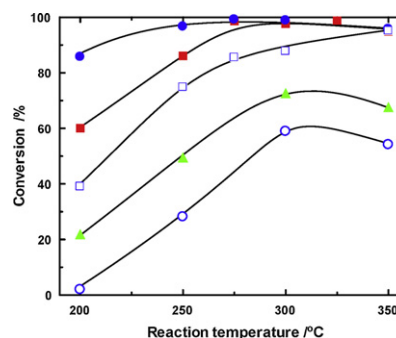
**Fig. 5.** Effects of reaction temperature on the isopropylation of PE. (a) Yield of DIPPE isomers. (b) Selectivities for DIPPE isomers. Reaction conditions: see Fig. 3. Legend: (a) ■: 4,4'-DIPPE; ●: 3,4'-DIPPE; ▲: 3,3'-DIPPE; ▼: 2,x'-DIPPE; ◆: conversion (PE). (b) Bulk products, ■: 4,4'-DIPPE; ●: 3,4'-DIPPE; ▲: 3,3'-DIPPE; ▼: 2,x'-DIPPE. Encapsulated products, □: 4,4'-DIPPE; ○: 3,4'-DIPPE; △: 3,3'-DIPPE; ▽: 2,x'-DIPPE.

selectivities for 4,4'-DIPPE in bulk products were approximately 85% at temperatures below 250°C; however, the increased temperature resulted in increased selectivities for 3,4- and 3,3'-DIPPE and decreased selectivities for 4,4'-DIPPE. The selectivities for 3,4'-DIPPE increased with the temperature from 250°C to 300°C, and the selectivities for 3,3'-DIPPE increased at temperatures above 300°C. A similar dependence of the selectivities for DIPPE isomers was observed in encapsulated products. The selectivities for 4,4'-DIPPE in encapsulated products was approximately 70% at temperatures below 250°C, while the increase in the temperature decreased the selectivities for 4,4'-DIPPE with the increase in 3,4'- and 3,3'-DIPPE isomers. The differences in the selectivities between bulk and encapsulated products indicates that the isomerization of 4,4'-DIPPE occurred at both the internal and external acid sites of MOR. Additionally, we must note the isomerization of 4,4'-DIPPE occurred simultaneously with the de-alkylation of DIPPE isomers, primarily 4,4'-DIPPE (Fig. 3).

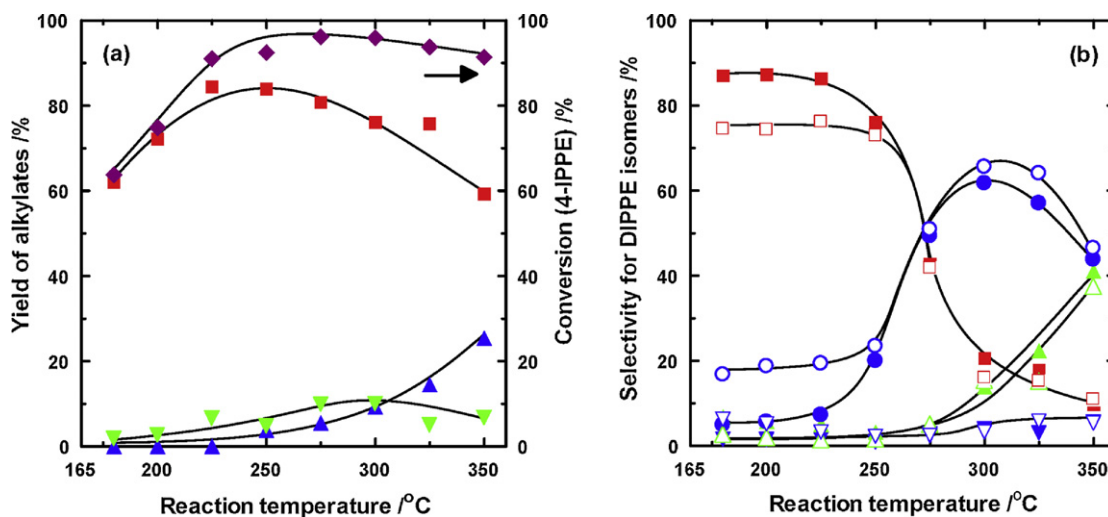
### 3.3. Influence of reaction temperature on the isopropylation of the intermediate products

To clarify their behaviors of the intermediates, 4- and 3-IPPE and 4,4'- and 3,4'-DIPPE during the catalysis under propene

pressure, we investigated the isopropylation using them as starting compounds. Fig. 6 shows the influence of reaction temperature on the consumption rate of PE, 4- and 3-IPPE, and 4,4'- and 3,4'-DIPPE under 0.8 MPa of propene. The rates were in the



**Fig. 6.** Influence of reaction temperature on consumption rate of PE, 4- and 3-IPPE, and 4,4'- and 3,4'-DIPPE. Reaction conditions: PE: 25 mmol (4.40 g), 4- and 3-IPPE, 4,4'-DIPPE and 3,4'-DIPPE: 12.5 mmol (2.65 g for 4- and 3-IPPE; 3.18 g for 4,4'-DIPPE and 3,4'-DIPPE); MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 128): 0.25 g for PE; 0.125 g for others; temperature: 180–350°C; propene pressure: 0.8 MPa; period: 4 h. Legend: ■: PE; ●: 4-IPPE; ▲: 3-IPPE; □: 4,4'-DIPPE; ○: 3,4'-DIPPE.



**Fig. 7.** Influence of reaction temperature on the isopropylation of 4-IPPE. (a) Yield of alkylates. (b) Selectivity for DIPPE isomers. Reaction conditions: 4-IPPE: 25 mmol (5.28 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.125 g; temperature: 180–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a)  $\blacksquare$ : DIPPE;  $\bullet$ : isomerized 3- and 2-IPPE;  $\blacktriangle$ : TIPPE;  $\blacklozenge$ : conversion (4-IPPE). (b)  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE. Encapsulated product,  $\square$ : 4,4'-DIPPE;  $\circ$ : 3,4'-DIPPE;  $\triangle$ : 3,3'-DIPPE;  $\triangledown$ : 2,x'-DIPPE.

order: 4-IPPE > PE > 4,4'-DIPPE  $\gg$  3-IPPE  $\gg$  3,4'-DIPPE. These results showed that 4-IPPE rapidly converted to 4,4'-DIPPE as soon as it was formed from PE, and that 3-IPPE only slowly yielded DIPPE isomers. For DIPPE isomers, 4,4'-DIPPE consumed slower than 4-IPPE, but more rapidly than 3-IPPE. The rate of the consumption of 3,4'-DIPPE was the slowest among the molecules examined. These differences of the rate suggest a consecutive reaction mechanism: PE to 4-IPPE, and 4-IPPE to 4,4'-DIPPE. Further, the order of consumption rates for PE and its products retained even at high temperatures. The details of their behaviors in the isopropylation were summarized in Figs. 7–10.

Fig. 7 shows the influence of reaction temperature in the isopropylation of 4-IPPE. 4-IPPE selectively afforded DIPPE isomers at low temperatures; however, the yield of DIPPE isomers decreased with the further increase in the temperature (Fig. 7a). These results suggested that 4-IPPE, formed from PE, rapidly converted to DIPPE isomers, particularly to 4,4'-DIPPE. On the other hand, the yield of DIPPE reached a maximum at 275 °C, and then decreased with further increases in the temperature, accompanying the de-alkylation and further alkylation. 3- and 2-IPPE were formed by the isomerization of 4-IPPE, and/or by the de-alkylation of DIPPE isomers.

Fig. 7b shows the influence of temperature on the selectivity for DIPPE isomers in bulk and encapsulated products in the isopropylation of 4-IPPE. The selectivity for 4,4'-DIPPE in bulk products was as high as 80% at low and moderate temperatures (200–250 °C); however, it rapidly decreased with increased temperature, above a certain threshold around 275 °C, along with increased selectivity for 3,4'-DIPPE. The decrease in the selectivities for 3,4'-DIPPE and the increase in those for 3,3'-DIPPE occurred with further increase in the temperature at 300–350 °C. Similar features were also observed in the selectivity for DIPPE isomers in encapsulated products. The features are quite similar to the influences of reaction temperature on the selectivity for DIPPE isomers in the isopropylation of PE (Fig. 5b). These results indicated that 4-IPPE was the precursor for the formation of 4,4'-DIPPE. However, the total yield of DIPPE isomers decreased above 300 °C because of enhanced de-alkylation of DIPPE isomers as shown in Fig. 7a.

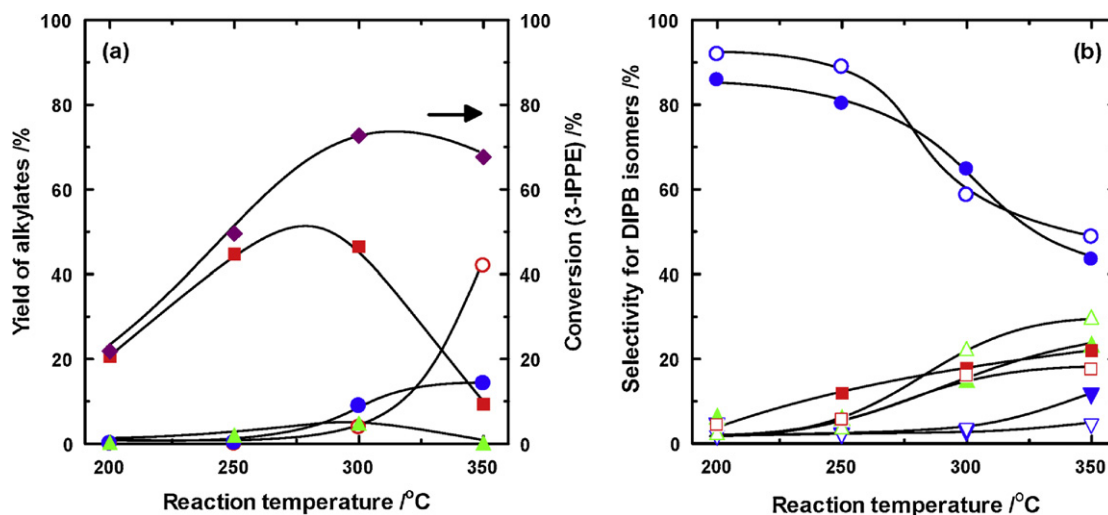
Fig. 8 shows the influence of reaction temperature on the isopropylation of 3-IPPE. DIPPE isomers, particularly 3,4'-DIPPE, were predominantly obtained from 3-IPPE at temperatures below 250 °C, although the rate of the consumption of 3-IPPE was much slower than those of 4-IPPE and PE (Fig. 8a). However, the yield of DIPPE isomers, particularly, 3,4'-DIPPE, decreased with the increased

temperatures along with the formation of PE, IPPE, and TIPPE. These results indicate that the formation of DIPPE isomers is the primary route for 3-IPPE at low and moderate temperatures. However, the de-alkylation to PE and the isomerization to 2- and 4-IPPE increased at high temperatures; particularly, the de-alkylation was the principal reaction at 350 °C even under 0.8 MPa of propene.

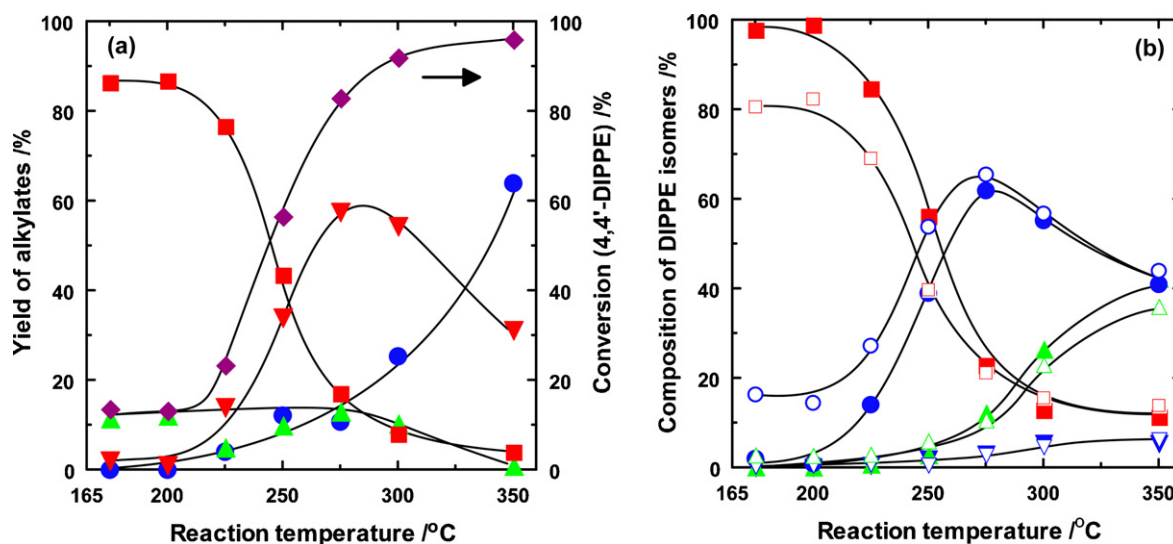
Fig. 8b shows the influence of reaction temperature on the selectivity for DIPPE isomers in bulk and encapsulated products in the isopropylation of 3-IPPE. The selective formation of 3,4'-DIPPE was observed at low temperatures 200–250 °C. However, the selectivity for 3,4'-DIPPE decreased with the increased temperatures, to 50% at 350 °C, resulting in the increase in the selectivities for 3,4'-, 3,3'-, and 2,x'-DIPPE isomers by the isomerization. The selective formation of 3,4'-DIPPE suggest that shape-selective catalysis occurred in the MOR channels because 3,4'-DIPPE is the least bulky isomer among the isomers from 3-IPPE. Similar features in the selectivities for DIPPE isomers were observed in encapsulated products. The isomerization of 3,4'-DIPPE to other DIPPE isomers occurred at the internal and external acid sites of the MOR channels in addition to de-alkylation to PE at high temperatures as shown in Fig. 8a.

Fig. 9 shows the influence of reaction temperature on the isopropylation of 4,4'-DIPPE under propene pressure. The isomerization of 4,4'-DIPPE was not significant at reaction temperatures below 250 °C as shown in Fig. 9a. However, the isomerization occurred rapidly with increases in the temperatures, however, reached maximum at 275–300 °C, and then decreased at higher temperatures. Alternatively, the de-alkylation to IPPE isomers was enhanced with the decrease in the isomerization. Further isopropylation to TIPPE was around 10% at all reaction temperatures.

The selectivities for DIPPE isomers in bulk products were quite similar to those in encapsulated products at the all temperatures (Fig. 9b). No significant isomerization of 4,4'-DIPPE was observed at low temperatures below 225 °C, while the decrease in the selectivity for 4,4'-DIPPE started at 225 °C with the increase in the selectivity for 3,4'-DIPPE. The selectivity for 3,3'-DIPPE increased with the decrease in the selectivity for 3,3'-DIPPE at higher temperatures above 275 °C. The decrease in the selectivity for 4,4'-DIPPE by the isomerization occurred at the both of internal and external acid sites because the similar features were observed in encapsulated products (Fig. 9b). The features are quite similar to the influences of temperature on the selectivity for DIPPE isomers in the



**Fig. 8.** Influence of reaction temperature on the isopropylation of 3-IPPE. (a) Yield of alkylates. (b) Selectivity for DIPPE isomers. Reaction conditions: 3-IPPE: 25 mmol (5.28 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.125 g; temperature: 200–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a)  $\blacksquare$ : DIPPE;  $\bullet$ : isomerized 4- and 2-IPPE;  $\blacktriangle$ : TIPPE;  $\circ$ : PE;  $\blacklozenge$ : conversion (3-IPPE). (b)  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE. Encapsulated product,  $\square$ : 4,4'-DIPPE;  $\circ$ : 3,4'-DIPPE;  $\triangle$ : 3,3'-DIPPE;  $\triangledown$ : 2,x'-DIPPE.



**Fig. 9.** Influence of reaction temperature on the isopropylation of 4,4'-DIPPE. (a) Yield of alkylates. (b) Selectivity for DIPPE isomers. Reaction conditions: 4,4'-DIPPE: 12.5 mmol (3.15 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.125 g; temperature: 200–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a)  $\blacksquare$ : 4,4'-DIPPE;  $\blacktriangle$ : isomerized DIPPE;  $\bullet$ : IPPE;  $\blacktriangle$ : TIPPE;  $\blacklozenge$ : conversion (4,4'-DIPPE). (b)  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE. Encapsulated product,  $\square$ : 4,4'-DIPPE;  $\circ$ : 3,4'-DIPPE;  $\triangle$ : 3,3'-DIPPE;  $\triangledown$ : 2,x'-DIPPE.

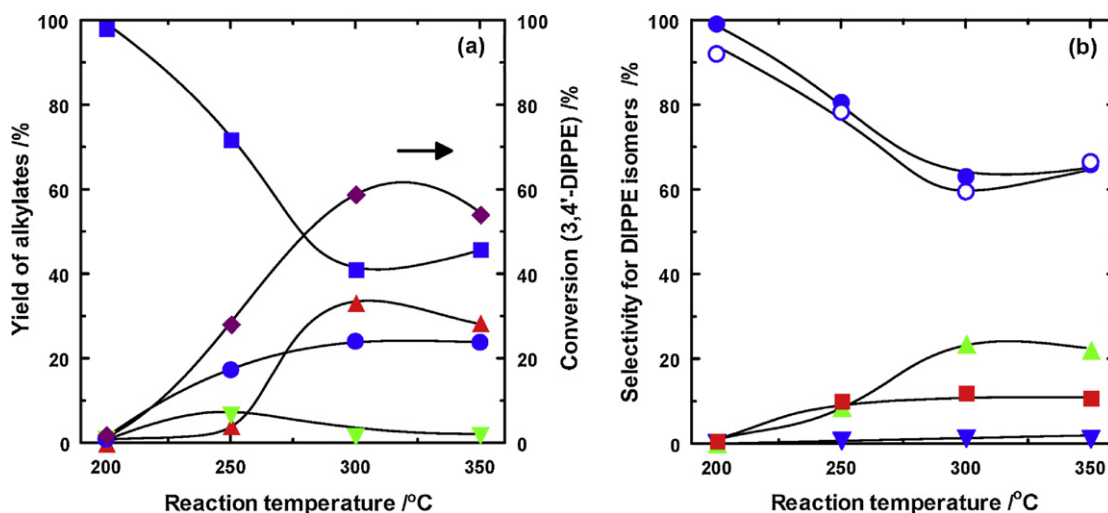
isopropylation of PE (Fig. 5b). We must note that 4,4'-DIPPE plays as key compounds for the shape-selective formation at low temperatures, and for the isomerization and de-alkylation in the isopropylation of PE as shown in Fig. 9a.

Fig. 10 shows the influence of reaction temperature on the isopropylation of 3,4'-DIPPE under propene pressure. The amount of 3,4'-DIPPE decreased with the increase in temperature accompanying the formation of IPPE by the de-alkylation and TIPPE by the further isopropylation, although the rate of consumption of 3,4'-DIPPE was slower than that of 4,4'-DIPPE (see Fig. 6). The isomerization of 3,4'-DIPPE started at 250 °C; however, the amounts of isomerized products and 3,4'-DIPPE was saturated at 300–350 °C (Fig. 10a). However, the de-alkylation and isomerization saturated at high temperatures.

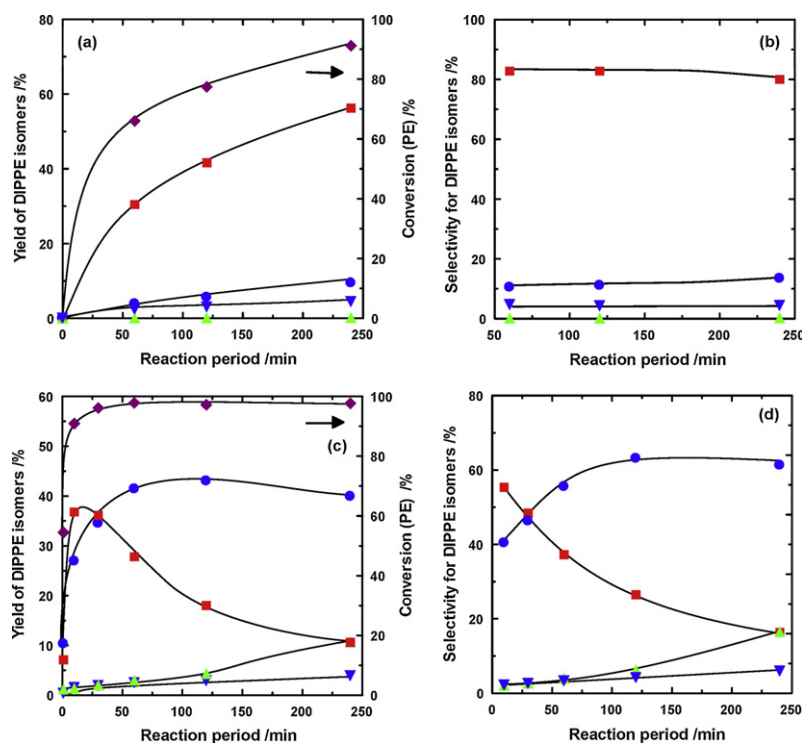
Fig. 10b shows the influence of the selectivity for DIPB isomers on the reaction temperature. Increased temperature enhanced the decrease in the selectivity for 3,4'-DIPPE with increased selectivities for 4,4'-, 3,3'-DIPPE isomers. The temperature dependence on

the selectivity for DIPPE isomers in encapsulated products was similar to that of bulk products as shown in Fig. 10b. These results on 4,4'- and 3,4'-DIPPE indicate that the isomerization of 4,4'- and 3,4'-DIPPE occurred at the internal and external acid sites of the MOR channels.

The results of the isopropylation of 4- and 3-IPPE indicate that 4-IPPE was the principal isomer for the formation of DIPPE isomers, particularly, 4,4'-DIPPE at low and moderate reaction temperatures, while 3-IPPE did not play important role for the formation of DIPPE isomers. These IPPE isomers also isomerized at high temperatures. The de-alkylation of 3-IPPE significantly occurred at high temperatures. Moreover, the differences in temperature dependence between 4,4'- and 3,4'-DIPPE indicate that 4,4'-DIPPE played important key for the isopropylation of PE: 4,4'-DIPPE was formed by the shape-selective catalysis in MOR channels at low temperatures, and 4,4'-DIPPE was isomerized to 3,4'- and 3,3'-DIPPE and de-alkylated to IPPE on the internal and external acid sites at the high temperatures.



**Fig. 10.** Influence of reaction temperature on the isopropylation of 3,4'-DIPPE. (a) Yield of alkylates. (b) Selectivity of DIPPE isomers. Reaction conditions 3,4'-DIPPE: 12.5 mmol (3.15 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.125 g; temperature: 200–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a)  $\blacksquare$ : 3,4'-DIPPE;  $\blacktriangle$ : isomerized DIPPE;  $\bullet$ : IPPE;  $\blacktriangle$ : TIPPE;  $\blacklozenge$ : conversion (3,4'-DIPPE). (b)  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE. Encapsulated product,  $\square$ : 4,4'-DIPPE;  $\circ$ : 3,4'-DIPPE;  $\triangle$ : 3,3'-DIPPE;  $\triangledown$ : 2,x'-DIPPE.

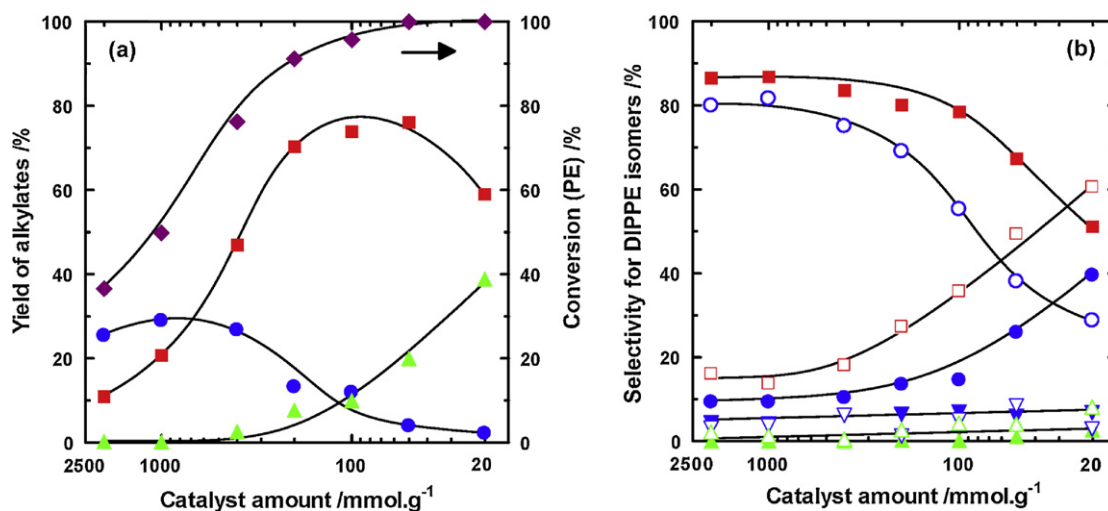


**Fig. 11.** Effects of reaction time on the isopropylation of PE. (a) Yield of DIPPE isomers at 250 °C. (b) Selectivity for DIPPE isomers at 250 °C. (c) Yield of DIPPE isomers at 300 °C. (d) Selectivity for DIPPE isomers at 300 °C. Reaction conditions: PE: 100 mmol (17.02 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.5 g; temperature: 250 °C and 300 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a) and (c)  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE;  $\blacklozenge$ : conversion (PE). (b) and (d) Bulk products,  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE.

#### 3.4. Influence of reaction period on the isopropylation of PE

It is important to clarify what happens on the intermediate products during the isopropylation of PE. Fig. 11 shows the influence of reaction period on the isopropylation of PE at 250 °C and 300 °C. The yields of DIPPE isomers increased with the period without the isomerization at 250 °C (Fig. 11a), and the selectivities for DIPPE isomers were almost constant during the isopropylation (Fig. 11b): 80% selectivity was retained for 4,4'-DIPPE during prolonged reaction period. These results mean that the shape-selective formation

of 4,4'-DIPB occurred inside the MOR channels in typically moderate condition at 250 °C. However, a quite different feature was observed for the reaction at 300 °C (Fig. 11c and d): the preferential formation of 4,4'-DIPPE occurred at very short reaction period; however then, the yield of 4,4'-DIPPE decreased with increasing yield of 3,4'-DIPPE with prolonged reaction period. 3,3'-DIPPE also increased slowly; however, the formation of 2,x'-DIPPE remained constant during the reaction. Corresponding to dependence of reaction period on the yield of DIPPE isomers, the selectivity for 4,4'-DIPPE decreased with period along with increased formation



**Fig. 12.** Influence of amount of MOR(128) on the isopropylation of PE. (a) Yield of alkylates. (b) Selectivities for DIPPE isomers. Reaction conditions: PE: 50 mmol (8.51 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.05–2.5 g; temperature: 250 °C; propene pressure: 0.8 MPa; period: 4 h. Legend: (a)  $\blacksquare$ : DIPPE;  $\bullet$ : IPPE;  $\blacktriangle$ : TIPPE;  $\blacklozenge$ : conversion (PE); (b) Bulk products,  $\blacksquare$ : 4,4'-DIPPE;  $\bullet$ : 3,4'-DIPPE;  $\blacktriangle$ : 3,3'-DIPPE;  $\blacktriangledown$ : 2,x'-DIPPE. Encapsulated products,  $\square$ : 4,4'-DIPPE;  $\circ$ : 3,4'-DIPPE;  $\triangle$ : 3,3'-DIPPE;  $\triangledown$ : 2,x'-DIPPE.

of 3,4'-DIPPE. The selectivity for 3,4'-DIPPE also increased rapidly in the early stages, however, the selectivity for 3,3'-DIPPE increased slowly with increased period. It is interesting that shape-selective formation of 4,4'-DIPPE occurs even at high temperatures as 300 °C inside the MOR channels, particularly in the initial stages. However, 4,4'-DIPPE produced in the channels rapidly converts to 3,4'-DIPPE by the isomerization.

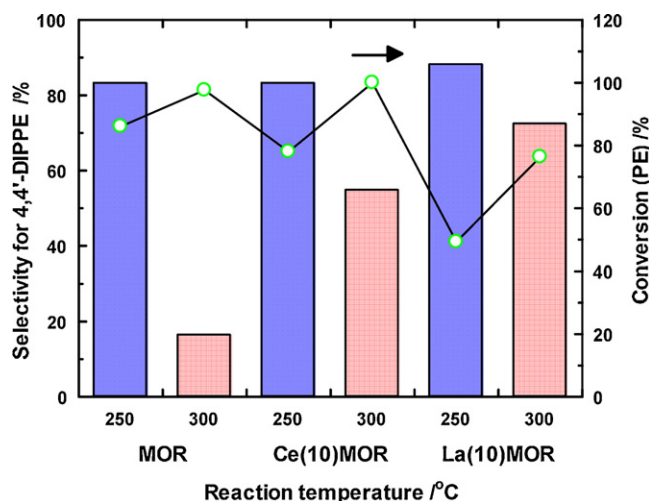
### 3.5. Influence of catalyst amount on the isopropylation of PE

The influence of catalyst amount on the isopropylation of PE at 250 °C was shown in Fig. 12. The increased catalyst amount promoted the formation of higher alkylates, DIPPE and TIPPE. In particular, the yield of TIPPE increased with the decrease of the yield of IPPE isomers by using large amounts of catalyst (Fig. 12a). These results indicate that the isopropylation of PE consecutively produced IPPE, DIPPE, and TIPPE isomers and that the de-alkylation was almost negligible at 250 °C even by using large amounts of catalyst.

Fig. 12b shows the influence of catalyst amount on the selectivity for DIPPE isomers. The use of small amounts of MOR resulted in high selectivity for 4,4'-DIPPE isomers, while the selectivity for 4,4'-DIPPE decreased with catalyst amount despite the reaction at 250 °C. The selectivities for 2,x'-DIPPE were retained almost constant, while the formation of 3,3'-DIPPE was negligibly low. The selectivities for DIPPE in encapsulated products closely resembled those in bulk products although the former was slightly higher than the latter. These differences between bulk and encapsulated products were also found in previous sections discussed on the temperature dependence (see Figs. 3, 7 and 8). These results support the shape-selective formation of 4,4'-DIPPE predominate in the MOR at low and moderate amounts of the catalysts; however, the use of large amounts of catalysts enhance the isomerization of 4,4'-DIPPE at the internal and external acid sites.

### 3.6. Modification of MOR with cerium and lanthanum oxides

The modification of MOR with cerium and lanthanum oxides is effective for the deactivation of external acid sites, as shown in previous papers for the alkylation of BP, NP, and ethylbenzene [29–34]. Here, we examined the modification of MOR(128) with cerium and lanthanum oxides by the impregnation of their nitrates and



**Fig. 13.** Influence of modification of MOR(128) with cerium and lanthanum oxides (10 wt.%) on the isopropylation of PE. Reaction conditions: PE: 25 mmol (4.26 g); MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ): 0.125 g (weight of MOR); temperature: 250 and 300 °C; propene pressure: 0.8 MPa; period: 4 h. Legend:  $\square$ : 250 °C;  $\square$ : 300 °C;  $\circ$ : Conversion (PE).

following calcination at 550 °C to elucidate the role of the external acid sites in the isopropylation of PE. As shown in Fig. 13, the selective formation of 4,4'-DIPPE occurred over unmodified MOR(128) at 250 °C, while the selectivity for 4,4'-DIPPE was less than 20% at 300 °C. The low selectivity was ascribed to the isomerization of 4,4'-DIPPE both at internal and external acid sites as discussed in previous sections.

Modification with cerium oxide retained the catalytic activity at 250 °C, and the selectivity for 4,4'-DIPPE was improved up to 60%. Catalytic activity was declined by the modification with lanthanum oxide; however, the selectivity for 4,4'-DIPPE improved to 75%. These results indicated that the isomerization of 4,4'-DIPPE principally occurred at the external acid sites. Meanwhile, preferential diffusion of 4,4'-DIPPE among the isomers contributed to their coming out to the bulk products from the MOR channels to some extent through modification: pore entrances were unchanged by modification with cerium oxide, while narrowed upon modification with



lanthanum oxide [29–34]. These differences were reflected in the improved selectivity for 4,4'-DIPPE by the modification with the oxides.

### 3.7. Mechanistic aspects of the isopropylation of PE

The results discussed in previous sections indicated that shape-selective formation of the least bulky 4,4'-DIPPE occurred by the discrimination of 4,4'-DIPPE from the other possible isomers at low and moderate reaction temperatures (from 175 °C to 250 °C). These shape-selective catalyses occur through differences in steric restriction of MOR channels (i.e., a “restricted transition state mechanism” proposed for the alkylation of BP and NP) [3–6,8–15,17–23]. However, the selectivities for 4,4'-DIPPE in encapsulated products were lower than those for bulk products in the isopropylation of PE over MOR. These results suggest the possibility of operating a “product selectivity mechanism”: the least bulky 4,4'-DIPPE predominantly diffused from the channels resulting in the improvement of 4,4'-DIPPE in addition to the formation of 4,4'-DIPPE by a “restricted transition state mechanism”.

The results of the intermediates, 4- and 3-IPPE, and the products, 4,4'- and 3,4'-DIPPE with propene suggest their role in the isopropylation in PE. First, the rate of conversion of 4-IPPE was highly rapid compared to 3-IPPE at low and moderate temperatures. This means that 4-IPPE preferentially formed from PE afforded rapidly the DIPPE isomers. However, 3-IPPE has not played important roles on the formation of DIPPE isomers. These differences between 4- and 3-IPPE resulted in the selective formation of 4,4'-DIPPE in the isopropylation of PE and 4-IPPE. Thus, the shape-selective formation of 4,4'-DIPPE occurred in MOR channels at low and moderate reaction temperatures.

The behaviors completely changed with the increase in temperature. 4-IPPE afforded 3,4'-DIPPE as a principal product at 300–325 °C, and the formation of 3,3'-DIPPE increased with the further increase in the temperature. These features are quite similar to the isopropylation of PE. However, 3-IPPE preferentially yielded thermodynamically stable 3,4'- and 3,3'-DIPPE, and the de-alkylation were also enhanced with increased temperature. PE and 4-IPPE gave the similar product distribution. 4,4'-DIPPE disappeared faster than 3,4'-DIPPE. However, the features of the behaviors of the intermediates and products at higher temperatures under propene pressure resembled to each other. That is, the products distribution in the isopropylation of 4-IPPE resembled to that of 3-IPPE, resulting the predominant formation of 3,4'- and 3,3'-DIPPE. 4,4'- and 3,4'-DIPPE also gave similar mixtures of DIPPE isomers in addition to de-alkylation with increasing the temperature, although the reactivities were different from each other. Thus, some of 4,4'-DIPPE converts to TIPPE by further isopropylation; however, the conversion of 3,4'-DIPPE to TIPPE and/or IPPE was slower reactions among the molecules concerned. However, we must remind that the results from the isopropylation of the intermediates or products as a substrate do not always afford the same results as in the isopropylation of PE, because their amounts were varied during the reaction by the conditions.

MOR channels also have high shape-selective natures for the isopropylation of PE at high reaction temperatures as 300 °C as well as at 200–250 °C as shown in Fig. 11. However, they cannot retain high selectivity for 4,4'-DIPPE in the channels, resulting in predominant formation of 3,4'-DIPPE by the isomerization due to the respective thermodynamic stability of the isomers.

Low selectivities for 4,4'-DIPPE at higher reaction temperatures along with major formation of 3,4'- and 3,3'-DIPPE suggest that the MOR channels were large enough for the isomerization of 4,4'-DIPPE. They possibly occurred by the increase in fluctuation of zeolite structure and/or flexible conformation of organic molecules in the channels. Low selectivities for 4,4'-DIPPE suggest

two reasons. The one is the influence of thermodynamic control because the MOR channels were large enough for the formation of thermodynamically stable 3,4'- and 3,3'-DIPPE. The other is the isomerization of 4,4'-DIPPE, which formed in the channels, at the external acid sites because preferential formation of 4,4'-DIPPE was observed at 300 °C in the early stage of the reaction (Fig. 11c and d) and with cerium and lanthanum modification (Fig. 13). These results indicate that straight MOR channels with pore entrances of 0.67 nm × 0.72 nm [35] were small enough for shape-selective formation of 4,4'-DIPPE at low and moderate reaction temperatures, while they fluctuated to allow the isomerization of 4,4'-DIPPE at high temperatures. It is very interesting that small fluctuations of the zeolite structure by increased reaction temperature influenced the shape-selective catalysis. However, further investigations are necessary to clarify the dependence of temperature on the fluctuation of zeolite structures.

The features of the isopropylation of PE over MOR resembled those of BP at low and moderate reaction temperatures. The selective formation of the least bulky isomers 4,4'-DIPPE and 4,4'-DIPB was ascribed to their effective discrimination from the bulky isomers by restriction of the MOR channels in the isopropylation of PE and BP, respectively. However, different features were observed in the isomerization of 4,4'-DIPPE and 4,4'-DIPB over MOR at high reaction temperatures. The isomerization of 4,4'-DIPPE occurred at internal acid sites as well as at external acid sites, resulting in decreased selectivity for 4,4'-DIPPE and increased selectivity for 3,4'- and 3,3'-DIPPE in the both of bulk and encapsulated products. However, the isomerization of 4,4'-DIPB occurred only at the external acid sites in the isopropylation of BP because the selectivity for 4,4'-DIPB in encapsulated products retained high even at high temperatures [8,36]. The differences were ascribed to conformational flexibility of PE, BP, and their products in the MOR channels. PE and its products can take flexible conformations due to the O atom spacer, while BP is a rigid molecule with limited conformations. We believe these differences in the flexibility caused the differences in behavior within the MOR channels, resulting in the isomerization of 4,4'-DIPPE at internal acid sites. The isomerization of 4,4'-DIPPE at high reaction temperatures also suggests the flexibility of the organic molecules in addition to the fluctuation of zeolitic frameworks.

## 4. Conclusion

The isopropylation of PE was examined over MOR as catalyst from aspects of the dealumination, the reaction temperature, the reaction period, the catalyst amount, and the reaction behavior of intermediates 4- and 3-IPPE and products 4,4'- and 3,4'-DIPPE. Appropriate dealumination enhanced the selective formation of 4,4'-DIPPE at low and moderate temperatures (175–250 °C). The selectivities for DIPPE isomers in encapsulated products were very similar to the selectivities of the bulk products. These results indicate that shape-selective isopropylation of PE occurred in two steps: BP selectively formed 4-IPPE, and 4-IPPE rapidly formed 4,4'-DIPPE at low to moderate temperatures.

The selectivity for 4,4'-DIPPE decreased with increasing the selectivities for 3,4'- and 3,3'-DIPPE with the increase in the temperature (275–350 °C) and/or by using a large amount of the catalyst. These decreases are due to the isomerization of 4,4'-DIPPE to 3,4'- and 3,3'-DIPPE at the internal and external acid sites. The MOR channels were large enough for the isomerization of 4,4'-DIPPE due to the fluctuation of the zeolite structure and the organic molecules at high temperatures.

These features of the isopropylation of PE were quite different from the isopropylation of BP, where no isomerization of 4,4'-DIPB occurred inside the MOR channels. These differences were due to

the conformation of the transition states between PE and BP in the channels. Flexible conformation of 4,4'-DIPPE also enabled the isomerization inside the 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.2011.12.004.

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