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Graphical Abstracts

The Isopropylation of Naphthalene with Propene over H-Mordenite: The Catalysis at the Internal and External Acid Sites

Research Highlights

- Mordenite has a shape-selective nature for the isopropylation of naphthalene
- Selective formation of 2,6-diisopropynaphthalene (2,6-DIPN) inside the channels
- Decrease in selectivities for 2,6-DIPN by the isomerization at external acid sites
The Isopropylation of Naphthalene with Propene over H-Mordenite: The Catalysis at the Internal and External Acid Sites

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Isopropylation of NP over MOR [1/1]
Abstract:

The isopropylation of naphthalene (NP) with propene over H-Mordenite (MOR) was studied under a wide range of reaction parameters: temperature, propene pressure, period, and NP/MOR ratio (reciprocal of catalyst amount). Selective formation of 2,6-diisopropylnaphthalene (2,6-DIPN) was observed at reaction conditions, such as at low reaction temperature, under high propene pressure, and/or with high NP/MOR ratio. However, the decrease in the selectivities for 2,6-DIPN was observed at reaction conditions such as high temperature, under low propene pressure, and/or with low NP/MOR ratio. The selectivities for 2,6-DIPN in the encapsulated products were remained high and constant under all reaction conditions. These results indicate that the selective formation of 2,6-DIPN occurs through the least bulky transition state due to the exclusion of the bulky isomers by the MOR channels. The decrease in the selectivities for 2,6-DIPN are due to the isomerization of 2,6-DIPN to 2,7-DIPN at the external acid sites, directing towards thermodynamic equilibrium of DIPN isomers.

Keywords: Mordenite, Naphthalene, Shape-selective Catalysis, Isomerization, External Acid Sites
1. Introduction

Zeolites have been well-recognized as one of the key catalysts in the modern chemical processes [1]. They have strong acids both on internal and external surfaces due to the strains by crystalline structures, and have been widely used as acid catalysts in organic synthetic, petro-chemical, petro-refining, and pharmaceutical processes. Catalytic properties of zeolites are mainly focused on their acidic and porous properties. Some zeolites are expected to offer unique shape-selective catalysis through the interaction of reactants, intermediates, and products with their pores and channels [1-8]. The shape-selective catalysis occurs through molecular recognition of organic molecules in their pores and channels of zeolites which can exclude the bulky reactants, intermediates, and/or products by the steric interaction with them, resulting in the formation of the less bulky products [2,6-8]. They are classified as “reactant selectivity”, “product selectivity”, and “restricted transition state selectivity” mechanisms [2,4-8]. The confined circumstances of the zeolite channels control the steric interaction of the transition states to products; therefore, only zeolites, which preferentially accommodate the less bulky products, can direct the shape-selective catalysis in their pore and channels [2-8].

The alkylation of naphthalene (NP) and biphenyl (BP) has been studied by many
researchers over various zeolites [3-32]. Among the zeolites, H-Mordenite (MOR) offers a typical shape-selective catalysis in the isopropylation of NP [3-14]. We have been interested to clarify where and how the shape selective catalysis occurs during last decades, and indicated that the selective formation of 2,6-DIPN occurs through the least bulky transition state due to the exclusion of the bulky isomers by the MOR channels [12-14].

Recently, Bujis and his co-workers published the doubts whether shape-selective formation of 2,6-DIPN is a myth or reality [33-35]. They claimed that the shape-selective catalysis of whatever kind can be ruled out in the case of MOR by the experimental and the computational works, and that MOR produces usually kinetically controlled mixtures of DIPN which can shift to a direction of thermodynamic distribution at high reaction temperatures. Tasi and Pálinkó supported the claims by their computational studies [36,37]. Against these doubts, Brozozowski severely criticized their findings and doubts because some of the experimental data cannot be explained by kinetics, thermodynamics, and analytical errors, and insisted that the shape-selective diisopropylation of NP over MOR is still there and it is real shape-selective catalysis [38]. Finally, Brozozowski and Bujis jointly published their conclusion that their previously reported data are beyond any doubt which describes
shape-selective formation of 2,6-DIPN over MOR [39]. They further added that the higher ratio of 2,6-DIPN/2,7-DIPN than those predicted for the non-shape-selective catalysts and significantly higher 2,6-DIPN selectivity than the expected for kinetic or thermodynamic product are the clear effects of shape-selective catalysis. However, the discussions in these papers have been based only on the bulk products, and no information has been given about where and how the catalysis occurs. We believe that the discussions should be based on the results under a wide range of reaction conditions because some reaction parameters make crucial changes in the outcome of the products. From these reasons, we recognize the importance to investigate the comprehensive features of the catalysis in wide range of parameters for understanding the origin and the mechanism of the shape-selective catalysis.

We have previously proposed that the encapsulated products are “finger prints of the catalysis” for the explanation of the catalysis in zeolite channels in the isopropylation of NP and BP [4,6,7,12,31,32]. In this paper, we describe the relationships between bulk and encapsulated DIPN isomers from low to high conversions under various reaction parameters in the isopropylation of NP with propene over MOR, and discuss where and how the shape-selective catalysis occurs. We confirmed from the results in current study that the selective formation of
2,6-DIPN occurred by the shape-selective catalysis in the MOR channels, and that the selectivities for 2,6-DIPN are sometimes decreased by the isomerization of 2,6-DIPN to 2,7-DIPN at the external acid sites.

2. Experimental

2.1. Catalysts and reagents

MOR (SiO$_2$/Al$_2$O$_3$ = 128) and FAU (SiO$_2$/Al$_2$O$_3$ = 30) were obtained from Tosoh Corporation, Tokyo, Japan, and calcined at 550 °C in an air stream before use. Some of the physicochemical properties of MOR have been described elsewhere [12,31]. NP was purchased from Aldrich Australia, Sydney, NSW, Australia. Propene was supplied by BOC Australia, North Ryde, NSW, Australia. 2,6- and 2,7-Diisopropynaphthalenes (2,6- and 2,7-DIPN) were purchased from Tokyo Chem. Ind., Ltd. Tokyo, Japan. 2,7-DIPN contains 2,6-DIPN (less than 2 %) and other unidentified impurities (less than 0.5 %). These reagents were used without further purification.

2.2. Isopropylation

The isopropylation of NP was carried out in a 100 ml SUS-316 autoclave with magnetic agitation. The typical conditions are as follows: 50 mmol of NP, 0.25 g of MOR,
propene pressure of 0.35 - 0.90 MPa, reaction temperature of 200 - 300 °C, and the reaction period of 0.1 - 6 h. An autoclave containing NP and MOR was purged with nitrogen before heating. After reaching reaction temperature, propene was introduced into the autoclave with agitation, and the pressure was kept constant throughout the reaction.

After stopping the reaction, the autoclave was quickly cooled to room temperature by immersing in water bath, the catalysts were filtrated off, and then, the bulk products were diluted with toluene and acetone. The products were analyzed by a Shimadzu Gas Chromatograph GC-2010Plus equipped with a TC-17 capillary column (0.25 mm x 60 m; film thickness: 30 μm; GL Sciences, Inc., Tokyo, Japan) by using FID detector. The identification of the DIPN isomers was also conducted by using an HP-INNOWax (60 m x 0.25 mm; film thickness: 0.5 μm; Agilent Technologies, Inc. CA, U.S.A.) (see chromatograms in Fig. S1 of supporting Information of our previous paper [15]), and by using the TC-17 column on a Shimadzu Gas chromatograph-Mass Spectrometer GC-MS 5000. The chromatograms in the paper by Brozozowski were also referred for the identification of DIPN isomers [40].

The analysis of encapsulated products in the catalyst used for the reaction was carried out as follows. The catalyst was washed well with toluene and acetone to
remove the products on external surface, and dried overnight at 60 - 80 °C. A 50 mg of the resultant catalyst was dissolved carefully using 3 mL of aqueous hydrofluoric acid (47 wt.%) at room temperature. After disappearance of solid residues, the solution was basified with solid potassium carbonate, and the organic layer was extracted three times with 2 mL of chloroform. After removal of the solvent in vacuo, the residue was dissolved in aliquot of acetone, and subjected to GC analysis according to the same procedures as for bulk products.

The yield of each product is calculated on the basis of the initial amount of NP, and the selectivities for each isopropynaphthalene (IPN) and diisopropynaphthalene.
(DIPN) isomers are expressed based on the total amounts of IPN and DIPN isomers, respectively. The sums of 2,6- and 2,7-DIPN, of 1,6- and 1,7-, and 1,3-DIPN, and of 1,4- and 1,5-DIPN are expressed as $\beta,\beta$-, $\alpha,\beta$-, and $\alpha,\alpha$-DIPN, respectively (see Scheme 1). The selectivities for 2,6- and 2,7-DIPN in the isomerization of 2,6- and 2,7-DIPN are defined on the basis of the GC counts of 2,6- and 2,7-DIPN in all DIPN isomers.

3. Results and Discussion

3.1. Profiles of the isopropylation of NP over MOR

Figure 1 shows the reaction profile of the isopropylation of NP over MOR based on the NP conversion at 250 °C and under 0.45 MPa of propene pressure. The isopropylation occurred in two consecutive steps: NP to IPN isomers and IPN to DIPN isomers. The selective formation of 2-IPN occurred from NP in the early stages, reached the maximum at 50 – 60 % of the conversion, and then the yield of 2-IPN was decreased at the late stages. However, the yield of 1-IPN, minor isomer, was increased spontaneously with the conversion. These results mean that 2-IPN was selectively formed from NP in the first step, and that resultant 2-IPN works a preferential precursor for DIPN isomers in the second step, resulting in the selective formation of 2,6-DIPN (the least bulky isomer) and 2,7-DIPN (the second least bulky isomer).
However, 1-IPN, minor and bulky isomer, cannot participate in the formation of DIPN isomers even in the late stages.

The selectivities for 2,6-DIPN were remained high and constant: 70 - 75% even at the high conversion. The selectivities for β,β-DIPN were also quite high and constant: 90 - 95 % during the reaction, and those for the bulky DIPN isomers, α,β-DIPN and α,α-DIPN, were totally less than 5 - 10 %. The selective formation of 2-IPN (the least bulky) from NP, and 2,6-DIPN (the least bulky) and 2,7-DIPN (the second least bulky) from 2-IPN occurred by the shape-selective catalysis due to the exclusion of the bulky isomers by the MOR channels. These results suggest that the catalysis was operated by “reactant selectivity” and “restricted transition state” mechanisms in the MOR.

Figure 1. The profile of the isopropylation of NP over MOR. Reaction conditions: NP: 3.20 g (2.5 mmol); MOR (128) 0.25 g (NP/MOR = 100 mmol/g); Temperature: 250 °C; Propene pressure: 0.80 MPa. Period: 0.3 min – 2880 min.
channels [1-8]. In addition, we note that no significant isomerization of 1-IPN to 2-IPN and 2,6-DIPN to 2,7-DIPN occurred during the isopropylation of NP over MOR at the conditions. The similar features of the catalysis were observed in the isopropylation of BP over MOR in our previous works [3,4,6,7,30,31]

We discuss, in the next sections, where and how the selective formation of the least bulky 2,6-DIPN occurs in the isopropylation of NP from the aspects of the selectivities for DIPN isomers in bulk and encapsulated DIPN isomers, and attempt to clarify the roles of internal and external acid sites of H-MOR.

3.2. Effects of reaction temperature and propene pressures in the isopropylation of NP

Figure 2 shows the effects of reaction temperature on the isopropylation of NP under the propene pressure of 0.35 - 0.90 MPa. NP conversion and the yield of DIPN isomers were almost independent on propene pressures at all temperatures as in Figure 2a.

Figure 2b shows the effects of reaction temperature on the selectivities for 2,6- and 2,7-DIPN. The selectivities for 2,6- and 2,7-DIPN were remained almost constant: 68 - 71 % and 23 - 24 %, respectively, at the temperatures lower than 250 °C under the
pressures, 0.35 – 0.90 MPa; however, the selectivities for 2,6-DIPN gradually decreased with the pressure decrease at higher temperatures, 275 and 300 °C. Particularly, a rapid decrease in the selectivities for 2,6-DIPN was observed under the low pressures of 0.35 and 0.45 MPa at 300 °C with concomitant increase in the selectivities for 2,7-DIPN.

DIPN isomers except 2,6- and 2,7-DIPN were totally the less than 5 % under the

**Isopropylation of NP over MOR**

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**Figure 2.** The effects of reaction temperature on the isopropylation of NP over MOR. (a) Conversion; (b) Selectivities for 2,6- and 2,7-DIPN (bulk products); (c) Selectivities for β,β- and α,β-DIPN (bulk products); (d) Selectivities for 2,6- and 2,7-DIPN (encapsulated products). Reaction conditions: NP: 3.22 g (25 mmol); (MOR(128) 0.25 g (NP/MOR = 100 mmol/g); Temperature: 200 - 300 °C; Propene pressure: 0.35 - 0.90 MPa. Period: 120 min. Legends: ■: 0.90 MPa; ●: 0.75 MPa; ▲: 0.60 MPa; ○: 0.45 MPa; □: 0.36 MPa.
The effects of reaction temperature on the selectivities for β,β- and α,β-DIPN are shown in Figure 2c. The selectivities for β,β-DIPN were almost constant: around 90% at all propene pressures although the selectivities for 2,6-DIPN decreased at high temperature as in Figure 2b. The results mean that MOR channels gave β,β-DIPN: the least bulky 2,6-DIPN and the second least bulky 2,7-DIPN by shape-selective catalysis at low and moderate temperatures, and that 2,6-DIPN is isomerized to 2,7-DIPN at high temperatures because β,β-DIPN are the most stable among the DIPN isomers. The equilibrium mixtures of DIPN isomers at 300 °C are composed: 37.4 %, 38.9 %, 20.1%, and 3.6 % for 2,6-, 2,7-, α,β-, and α,α-DIPN, respectively [25].

The effects of reaction temperature on the selectivities for 2,6- and 2,7-DIPN in the encapsulated products under the pressures: 0.35 - 0.90 MPa were shown in Figure 2d. The selectivities for 2,6- and 2,7-DIPN were almost constant at 70 – 85 % and 10 – 15 %, respectively, under all temperatures and pressures. These results clearly indicate that the isopropylation occurs at the acidic sites in the MOR channels, and the no significant isomerization of 2,6-DIPN occurs in the MOR channels at all temperatures. 2,6-DIPN, formed in the channels, is quickly isomerized to 2,7-DIPN at the external acid sites, directing to thermodynamic equilibrium [24]. It should also be noted that the
selectivities for 2,6-DIPN in encapsulated products were a little bit higher than those in bulk products. However, there are still some unclear features why the selectivities for 2,6-DIPN in the encapsulated products were higher than those in bulk products, which trigger to conduct further studies to understand and find out the exact mechanism for differences in the selectivities.

Figure 3 shows the effects of propene pressure on the isopropylation of NP at 200 – 300 °C. The activities were increased with the increase in the temperature, however they were not significantly changed by the pressures (Figure 3a).

The effects of propene pressure on the selectivities for 2,6- and 2,7-DIPN were shown in Figure 3b. The selectivities for 2,6-DIPN were remained high and almost constant: 70 – 80 % at reaction temperatures below 250 °C irrespective of propene pressure; however, they decreased with the decrease in propene pressure at higher temperatures above 275°C; particularly, at 300 °C under low pressures: 0.35 and 0.45 MPa with concomitant increase in the selectivities for 2,7-DIPN. The selectivities for β,β-DIPN were remained almost constant by the change of the pressure, although they were slightly decreased at reaction temperatures of 250 - 300 °C by the increase in the formation of α,β-DIPN (Figure 3c). These results suggest the isomerization of 2,6-DIPN was enhanced at high temperatures, directing towards to the equilibrium of DIPN
The effects of propene pressure on the selectivities for 2,6- and 2,7-DIPN in the encapsulated products are shown in Figure 3d. The selectivities for 2,6- and 2,7-DIPN were almost constant: 70 – 85 % and 10 – 15 %, respectively, at all pressures and temperatures. These results are quite different from the features of the selectivities for 2,6- and 2,7-DIPN in bulk products (Figure 3b). On the other hand, the selectivities for

*Isopropylation of NP over MOR*  
[15/15]
β,β- and α,β-DIPN in the encapsulated products were almost constant: 80 - 90 % and 10 - 20 %, respectively, at all temperatures and pressures (Figure not shown). The selectivities for α,β-DIPN were higher than those from bulk products.

These influences of reaction temperature and propene pressure clearly indicate that the isopropylation of NP occurs in zeolite channels, resulting in selective formation of 2,6-DIPN. However, the decrease in the selectivities for 2,6-DIPN are due to the isomerization of 2,6-DIPN to 2,7-DIPN at external acid sites, not in the MOR channels.

3.3. Effects of reaction period on the isopropylation of NP

Figure 4 shows the effects of reaction period on the isopropylation of NP at 250 and 300 °C under propene pressure of 0.45 and 0.90 MPa. The isopropylation rapidly occurred in the early stages as shown in Figure 4a. The conversions reached 42 % and 60 % within 6 min at 250 and 300 °C, respectively, under 0.45 MPa, and they were increased to 76 % and 95 %, respectively, after 360 min. However, the propene pressure did not influence significantly on the conversion at both temperatures of 250 and 300 °C as similar results in the previous sections.

Figure 4b shows the effects of reaction period on the selectivities for 2,6- and 2,7-DIPN in the bulk products. The selectivities for 2,6-DIPN were remained constant:
70 % during the reaction at 250 °C under 0.45 and 0.90 MPa. These results reveal that the selectivities for 2,6-DIPN were not affected by the deactivation of catalytic active sites at 250 °C even after prolonged period. On the other hand, the selectivities for 2,6-DIPN were slowly decreased after prolonged reaction period at 300 °C under 0.90 MPa, and rapidly under 0.45 MPa, with concomitant increase in the selectivities for
2,7-DIPN. Particularly, the selectivities for 2,6-DIPN were reached to around 50 % at 300°C under 0.45 MPa. However, the selectivities for β,β- and α,β-DIPN were almost constant during the reaction at all reaction temperatures and propene pressures as shown in Figure 4c. These results indicate that the decrease in the selectivities for 2,6-DIPN is due to the isomerization of 2,6-DIPN to 2,7-DIPN, which occurred rapidly even in the early stages of the isopropylation at 300 °C. In addition, we must remind the high propene pressure, 0.90 MPa at 300 °C partly disturbed the isomerization of 2,6-DIPN, probably due to the reasons discussed in previous sections.

Figure 4d summarizes the effects of reaction period on the selectivities for 2,6- and 2,7-DIPN in the encapsulated products. The selectivities for 2,6- and 2,7-DIPN were remained almost constant during the reaction. These results indicate that selective formation of 2,6-DIPN occurred inside the MOR channels irrespective of reaction temperature and propene pressure, and that the decrease in the selectivities for 2,6-DIPN was due to the isomerization to 2,7-DIPN directing towards the equilibrium of DIPN isomers. Further, the isomerization occurred at the external acid sites, not in the MOR channels as discussed in previous section.
3.4. **Effects of NP/MOR ratio on the isopropylation of NP**

The effects of NP/MOR ratio, where the reciprocal of the ratio corresponds to catalyst amount, on the isopropylation of NP are shown in Figure 5. The conversion of NP was enhanced with the decrease in NP/MOR both at 250 and 300 °C; however, the conversion was not significantly influenced by the pressure as previously discussed (Figure 5a).

Figure 5b shows the effects of NP/MOR ratio on the selectivities for 2,6- and 2,7-DIPN. The selectivities for 2,6- and 2,7-DIPN were slowly decreased with decreasing the ratio at 250 °C under 0.45 and 0.90 MPa, and the decrease in the selectivities for 2,6-DIPN occurred rapidly at 300 °C and under 0.45 MPa. However, the selectivities for β,β-DIPN were remained high at all temperatures and pressures (Figures 5c). These results indicate that the decrease in the selectivities for 2,6-DIPN are due to the isomerization to 2,7-DIPN, and that the decreases in the NP/MOR ratio enhance the isomerization of 2,6-DIPN to 2,7-DIPN at both of 250 and 300 °C, whereas the a high propene pressure disturbs the isomerization.

The selectivities for 2,6-DIPN in the encapsulated products were remained almost constant under all reaction conditions even with low NP/MOR ratio of 25 at 300 °C as shown in Figure 5d. These results indicate that the formation of 2,6-DIPN occurred in
the MOR channels irrespective of the NP/MOR ratio, temperature, and/or propene pressure, and that 2,6-DIPN was isomerized to 2,7-DIPN only at the acid sites on external surface of MOR. Similar features of the isomerization of 4′,4′-diisopropylbiphenyl (4,4′-DIPB) were observed in the isopropylation of BP over MOR [3-7,31,32].

**Figure 5.** The effects of NP/MOR ratio on the isopropylation of NP over MOR. (a) Conversion; (b) Selectivities for 2,6-n and 2,7-DIPN (bulk products); (c) Selectivities for β,β- and α,β-DIPN (bulk products); (d) Selectivities for 2,6- and 2,7-DIPN (encapsulated products). Reaction conditions: NP: 1.65 - 3.20 g (12.5 - 25 mmol); MOR (128): 0.125 - 0.25 g (NP/MOR = 25 - 400 mmol/g); Temperature: 250 and 300 °C; Propene pressure: 0.45 and 0.90 MPa. Period: 120 min. Legends: ■: 0.90 MPa, 300 °C; ●: 0.45 MPa, 300 °C; □: 0.90 MPa, 250 °C; ○: 0.45 MPa, 250 °C.
3.5. *Isomerization of 2,6- and 2,7-DIPN under propene pressure*

Figures 6 and 7 show the effects of reaction temperature on the isomerization of 2,6- and 2,7-DIPN, respectively, under propene pressures of 0.45 and 0.90 MPa. The isomerization of 2,6- and 2,7-DIPN: 2,6- to 2,7- and vice versa, was increased with the increase in the temperatures, and particularly significant at the temperatures above 275 °C (Figure 6a). Similar selectivities for 2,6-DIPN were also obtained from the isomerization of both of 2,7-DIPN at 300 °C (Figure 7a). However, the propene pressure does not significantly influence the products distribution at high temperatures. These results indicate that both of 2,6- and 2,7-DIPN were isomerized to approach the mixtures directing towards the equilibrium of DIPN isomers.

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**Figure 6.** The effects of reaction temperature on the isomerization of 2,6-DIPN over MOR. (a) Selectivities for 2,6- and 2,7-DIPN in bulk products. b: Selectivities for 2,6- and 2,7-DIPN in encapsulated products. Reaction conditions: 2,6-DIPN: 0.025 mol; MOR(128): 0.25 g (2,6-DIPN/MOR = 100 mmol/g; Temperature: 200 - 300 °C; Propene pressure: 0.45 and 0.9 MPa. Period: 120 min. Legends: 0.90 MPa: ■: 2,6-DIPN, ●: 2,7-DIPN. 0.45 MPa: □: 2,6-DIPN, ○: 2,7-DIPN.
The effects of reaction temperature on the selectivities for 2,6- and 2,7-DIPN in encapsulated products are shown in Figures 6b and 7b, respectively. The selectivities for 2,6-DIPN were almost constant at 80 – 90 % at all reaction temperatures and propene pressure in the isomerization of 2,6-DIPN. Unexpectedly, the selectivities for 2,6-DIPN in the encapsulated propene pressure were remained almost constant: 70 – 80 % at all reaction conditions in the isomerization of 2,7-DIPN: 2,6-DIPN in the encapsulated products was originated from the 2,6-DIPN contained at about 2 % in 2,7-DIPN samples used. These results mean that MOR channels can adsorb 2,6-DIPN much rapidly than 2,7-DIPN even in the presence of much excess of 2,7-DIPN in

Figure 7. The effects of reaction temperature on the isomerization of 2,7-DIPN over-MOR. (a) Selectivities for 2,6- and 2,7-DIPN in bulk products. (b) Selectivities for 2,6-and 2,7-DIPN in encapsulated products. Reaction conditions: 2,7-DIPN 0.02 mol; MOR(128), 0.2 g (2,7-DIPN/MOR: 100 mmol/g; Temperature: 200 – 300 °C; propene pressure: 0.45 and 0.9 MPa. Period: 2 h. Legends: see as in Figure 6.
reaction mixture, resulting in predominant accommodation of 2,6-DIPN in the MOR channels. The isomerization of 2,6- and 2,7-DIPN occurred at the external acid sites, and did not occur significantly in the channels.

3.6. Isopropylation of NP over FAU.

Figure 8 summarizes the effects of reaction temperature on the selectivities for DIPN of bulk and encapsulated products in the isopropylation of NP over H-Y zeolites (FAU). The features of the bulk and encapsulated products were quite different from those of MOR catalysis. 2,6- and 2,7-DIPN isomers were minor isomers at all temperature range from 150 - 300 °C (Figure 8a). The main products were α,β-DIPN at lower temperatures; however, they were decreased with increasing the temperature accompanying concomitant increase in the formation of β,β-DIPN. The similar low selectivities for 2,6- and 2,7-DIPN can be found in previous papers over large pore zeolites such as FAU and BEA [21-28] and over ordered mesoporous metallosilicates [41-45].

The encapsulated products also had very similar features to the bulk products, although the changes in the selectivities were less significant (Figure 8b). These results show that the re-adsorption of the least bulky 2,6-DIPN is not significant after the
reaction, and the encapsulated products are the “finger prints” to understand the mechanism of the catalysis. These results reveal that the FAU cannot control any transition states of bulky DIPN by the steric interactions with the pores and channels, which obeys kinetic and thermodynamic controls originated by molecular properties of NP as discussed in our previous paper [25].

3.7. Mechanistic aspects of the catalysis over MOR.

The results of the isopropylation of NP over MOR in this study can be summarized as follows:

1. The isopropylation of NP occurred in the two consecutive steps over MOR, 2-IPN

![Figure 8. The effects of reaction temperature on the isopropylation of NP over FAU. (a) Selectivities for DIPN isomers in bulk products. (b) Selectivities for DIPN isomers in encapsulated products. Reaction conditions: NP: 6.44 g (50 mmol); FAU 0.25 g (NP/FAU = 200 mmol/g); Temperature: 150 – 300 °C; Propene pressure: 0.8 MPa. Period: 240 min. Legends: ■: 2,6-DIPN; ●: 2,7-DIPN; ▲: β,β-DIPN; ▼: α,β-DIPN; ◆: α,α-DIPN.](image-url)
is predominantly formed from NP in the first step, and resultant 2-IPN preferentially gives 2,6-DIPN accompanying 2,7-DIPN as a minor isomer. However, 1-IPN, minor and bulky isomer, cannot participate in the formation of DIPN isomers. The selectivities for 2,6-DIPN were remained high and constant at around 70% during the reaction even in the late stages.

2. The selective formation of 2,6-DIPN was observed over MOR in the reaction conditions, such as at low temperatures, with appropriate amount of catalyst, and/or under high propene pressures. The formation of bulky DIPN isomers except 2,6- and 2,7-DIPN were less than 5% under the conditions.

3. The selectivities for 2,6-DIPN in the bulk products were decreased gradually to rapidly with the increase in the temperatures and catalyst amount and with the decrease in the propene pressure, resulting in concomitant formation of 2,7-DIPN.

4. The selectivities for 2,6-DIPN in the bulk products were remained high and constant even after prolonged reaction period at mild reaction conditions such as 250 °C under 0.45 and 0.90 MPa. However, low propene pressure enhanced the decreases in the selectivities for 2,6-DIPN at 300 °C: the decrease in the selectivities gradually occurred under 0.90 MPa at 300 °C; however, rapidly
under 0.45 MPa at 300 °C.

5. The selectivities for 2,6-DIPN in the encapsulated products were remained constant and high over MOR in the wide range of reaction temperature, propene pressure, catalyst amount, and reaction period.

6. The isomerization of 2,6- and 2,7-DIPN was enhanced with increasing the temperatures directing towards the thermodynamic equilibrium, i.e., 2,6-DIPN to 2,7-DIPN and 2,7-DIPN to 2,6-DIPN under propene pressure. The selectivities for 2,6- and 2,7-DIPN were almost in the same levels starting from both of 2,6- and 2,7-DIPN at 300 °C. In addition, the selectivities for 2,6- and 2,7-DIPN in encapsulated products were almost constant with increasing temperatures starting from both of 2,6- and 2,7-DIPN, where 2,6-DIPN in the isomerization of 2,7-DIPN came from 2,6-DIPN contained 2 % in 2,7-DIPN samples as the impurity.

7. The features of the catalysis over FAU were quite different from those over MOR. The less bulky DIPN isomers, β,β-DIPN (2,6- and 2,7-DIPN), were formed as minor products (in almost equal amounts) at all temperatures. The bulkier and thermodynamically unstable isomers, α,β-DIPN (1,3-, 1,6-, and 1,7-DIPN), were principal products in lower temperatures, although they were decreased with
the increase in temperature. In addition, the bulkiest and thermodynamically unstable \( \alpha, \alpha \)-DIPN (1,4- and 1,5-DIPN) was also minor products in both bulk and encapsulated products.

These results clearly show that the isopropylation of NP over MOR occurred in their pore and channels: the shape selective catalysis indeed occurs in the MOR channels. The channels allow the formation of less bulky isomers due to the steric interaction with reactants, intermediates, and products in their confined circumstances: the selective formation of 2,6-DIPN from 2-IPN occurs through the least bulky transition state due to the exclusion of the bulky isomers by the MOR channels. However, FAU channels allow the transition states of the bulky isomers because of the loose steric interaction of their channels: the reactions over FAU are controlled by kinetic and thermodynamic controls due to molecular natures of NP and its products [14]. These differences of MOR and FAU clearly support the shape-selective catalysis in the isopropylation of BP over MOR. In addition, the bulkiness of alkyl moiety of alkylating agent enhanced the selectivities for 2,6-dialkynaphthalenes even over the zeolites with wide pores and channels including FAU in sec- and tert-butylation of NP [7,8,24].

The decrease in the selectivities for 2,6-DIPN was observed in the isopropylation
of NP over MOR under some reaction conditions, however, the selectivities for
2,6-DIPN in the encapsulated products were remained high and constant under all
conditions examined in this study. The results indicate that the decreases in bulk
products are due to the isomerization of 2,6-DIPN, once formed in the channels, to
2,7-DIPN directing, to the equilibrium between DIPN isomers at the external acid sites,
but not inside the channels.

It is interesting why the external acid sites do not work for the isomerization of
2,6-DIPN to 2,7-DIPN at appropriate reaction conditions: low temperatures, high
pressures, and/or low catalyst amounts. We can consider that adsorbed propene on
external acid sites can deactivate the adsorption of 2,6-DIPN, resulting in the
prevention of the isomerization and further alkylation of 2,6-DIPN. However, the vacant
acid sites without propene adsorbed appear easily under reaction conditions: high
temperatures, low propene pressures, and/or high catalyst amounts, and they allow
the adsorption of 2,6-DIPN, resulting in the isomerization of 2,6-DIPN to 2,7-DIPN. On
the other hands, the internal acid sites are not significantly deactivated by the
adsorbed propene due to the steric limitation of the channels, and effectively work as
the catalytic sites for the isopropylation. Similar deactivation at the external acid sites
by propene adsorption was observed in the isopropylation of BP over MOR [6,7,30-32].
The encapsulated products in the isomerization of 2,6- and 2,7-DIPN give us interesting results that 2,6-DIPN can adsorb much faster than 2,7-DIPN in MOR channels even at high temperatures, and the selectivities for 2,6-DIPN in encapsulated products are remained high even at 300 °C in the isomerization of both of 2,6- and 2,7-DIPN. These features support that the isomerization of 2,6- and 2,7-DIPN does not occur in the channels, but at the external acid sites directing towards to the equilibrium of DIPN isomers. In addition, we note that the 2,7-DIPN, once appeared in bulk phase, cannot easily re-enter into the MOR channels during the catalysis.

The selectivities for 2,6-DIPN in encapsulated products were remained high and constant under all reaction conditions in the isopropylation of NP in this study. The results clearly show that the catalytic sites are in the channels. However, they were a little bit higher than those in bulk products. We cannot clearly explain the reason of the higher selectivities for 2,6-DIPN in encapsulated products compared to the bulk products. We can suggest as one of possibilities that the active sites for the bulk products are present near pore mouth of the MOR channels, and their steric interaction is lower than the acid sites in deep channels: the selectivities for 2,6-DIPN in deep acid sites are higher than those for the acid sites near pore-mouth, resulting in higher selectivities for 2,6-DIPN in encapsulated products. However, we cannot exclude
a possibility that preferential re-adsorption of 2,6-DIPN may be occurred during and
after the reaction and/or during the storage of the product samples because 2,6-DIPN
adsorbs much faster than 2,7-DIPN as shown in the isomerization of 2,6- and 2,7-DIPN.
However, these explanations are not definitive and we believe further studies are
necessary for the clarification of the differences.

We observed the isomerization of 4,4′-diisopropylbiphenyl (4,4′-DIPB) in the
isopropylation of BP over MOR [3,4,6,7,31,32]. The isopropylation of BP was highly
selective for the formation of 4,4′-DIPB at moderate reaction conditions; however, the
decrease in the selectivities for 4,4′-DIPB occurred at reaction conditions, such as high
temperature, low propene pressure, and/or large amount of catalyst, resulting in the
increase in the selectivities for bulky and thermodynamically stable 3,4′- and 3,3′-DIPB.
We can consider the selective formation of 2,6-DIPN and 4,4′-DIPB in the
isopropylation of NP and BP, respectively, by shape-selective catalysis in the MOR
channels, and that the decreases in the selectivities for 2,6-DIPN and 4,4′-DIPB are due
to their isomerization directing towards the thermodynamic equilibrium of
corresponding isomers at the external acid sites, and not due to loss of the
shape-selective natures of the MOR channels.

Recently, Bujis and his co-workers claimed the doubts whether shape-selective
formation of 2,6-DIPN is a myth or reality based on the questions that shape-selective catalysis of whatever kind can be ruled out in the case of MOR by the experimental and the computational works: MOR produces usually kinetically controlled mixtures of DIPN which can shift to a direction of thermodynamical distribution at high reaction temperatures [33-35]. They also pointed out the possibilities of analytical errors during products analysis. Tasi and Pálinkó agreed and supported the claims by the computational studies [36,37]. However, Brozozowski severely criticized their findings and doubts because some of the experimental data cannot be explained by kinetics, thermodynamics, and analytical errors, and insisted that the shape-selective diisopropylation of NP over MOR is still there and it is real shape-selective catalysis [38].

Finally, Brozozowski and Bujis jointly made a conclusion that their previously reported data are beyond any doubt which clearly describes shape-selective formation of 2,6-DIPN over MOR [39]. Further, they added that the higher ratio of 2,6-DIPN/2,7-DIPN than those predicted for non-shape-selective catalysts and significantly higher 2,6-DIPN selectivity than the expected for kinetic or thermodynamic product [38].

Our results in this paper support their conclusion by Brozozowski and Bujis [39]. Particularly, the features of encapsulated products clearly indicate that shape-selective isopropylation of NP indeed occurs in the MOR channels, and that the decrease in the
selectivities for 2,6-DIPN is due to the isomerization of 2,6-DIPN, formed in the channels, to 2,7-DIPN at the external acid sites directing towards the equilibrium of DIPN isomers. The catalysis over FAU was not controlled by the steric interaction with their pores and channels, but by the kinetic and/or thermodynamic controls as discussed above. From these differences between MOR and FAU, we can clearly conclude that the selective formation of 2,6-DIPN over MOR occurred by the shape-selective catalysis due to the steric interaction of the transition state with the channels: neither “a myth” nor from the analytical errors.

The acid sites in internal and external surfaces of H-MOR have quite different steric circumstances. 2,6-DIPN, formed on the internal acid sites, was easily isomerized to 2,7-DIPN at the external acid sites directing towards the thermodynamic equilibrium of DIPN isomers. We must remind that the bulk products do not always reflect where the catalysis occurs.

7. Conclusion

The effects of reaction parameters: temperature, propene pressure, reaction period, and catalyst amount on the isopropylation of NP over MOR were examined to understand the steric interaction of NP and its intermediates with the MOR channels.
The formation of 2,6-DIPN was highly selective at appropriate moderate reaction conditions of temperatures, propene pressures, and/or catalyst amounts. The selectivities for 2,6-DIPN in the encapsulated products were remained constant at 70 – 80 % under all reaction conditions. The results revealed that the selective formation of 2,6-DIPN occurs in MOR channels through its least bulky transition states by exclusion of bulky DIPN isomers. However, the decrease in the selectivities for 2,6-DIPN were observed under the severe reaction conditions, such as at high temperatures, under low propene pressure, and/or with the large amounts of catalyst. The decrease in the selectivities for 2,6-DIPN was due to the isomerization of 2,6-DIPN, formed in the channels, to 2,7-DIPN at the external acid sites directing towards the thermodynamic equilibrium of DIPN isomers.

The selective formation of 2,6-DIPN occurred in the MOR channels because the external acid sites are deactivated by the strong adsorption of propene. The vacant acid sites at high temperatures and/or with large amounts of catalyst allow direct contact of 2,6-DIPN, resulting in the isomerization to 2,7-DIPN.

We finally conclude that the selective formation of 2,6-DIPN occurs through the shape-selective catalysis in the MOR channels, and that the decrease in the selectivities for 2,6-DIPN are due to the isomerization of 2,6-DIPN to 2,7-DIPN, directing towards
thermodynamic equilibrium of DIPN isomers. Our results clearly show that the shape-selective catalysis in the isopropylation of NP is “a real scientific phenomenon”: neither “a myth” nor “analytical errors”.

References


Isopropylation of NP over MOR [35/35]


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**Isopropylation of NP over MOR**


Isopropylation of NP over MOR