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Three-step reactions for selective production of 2,6-rich dimethylnaphthalene from 2,7-rich dimethylnaphthalene

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Abstract

Selective production of 2,6-dimethylnaphthalene (2,6-DMN) from 2,7-rich DMN has been investigated, with one-step and successive three-step isomerization containing (i) hydrogenation of 2,7-rich DMN to 2,7-rich dimethyl tetralin, (ii) isomerization of 2,7-rich DMT to 2,6-rich DMT, and (iii) dehydrogenation of 2,6-rich DMT into 2,6-rich DMN, respectively. It was found that the intra-triad isomerization of DMN was possible even at 200 °C, but for the inter-triad isomerization at least 250 °C was required. If the reaction temperature is higher than 300 °C, the yield of 2,6-DMN decreases rapidly due to the side reactions such as dealkylation, cracking and transalkylation. It was also found that 2,6-DMN or 2,6-DMT selectivity were strongly dependant on the Si/Al ratio of H-BEA (or the Brönsted site) and the maximum yield of 2,6-DMN (or 2,6-DMT) was obtained at the Si/Al ratio of 12.5. In the case of DMT, inter- and intra-triads did not show difference in isomerization temperature and were possible even at 180 °C. 14.9% yield of 2,6-DMT was obtained through the three-step isomerization over H-BEA(12.5) at 200 °C, while 10% yield of 2,6-DMN was achieved by one-step isomerization over H-BEA(12.5) at 250 °C.

Keywords: Dimethylnaphthalene; Dimethyltetralin; Isomerization; Hydrogenation; Dehydrogenation; BEA

1. Introduction

Polyethylene naphthalene (PEN) has been known to be one of the representative high-performance thermoplastic polyesters and has new and innovative applications due to the improved gas barrier, thermal and mechanical properties compared with that of polyethylene terephthalate (PET) [1,2]. 2,6-Dialkylnaphthalenes (2,6-DAN) are key intermediates in the synthesis of PEN. Among the various 2,6-DANs, 2,6-DMN is preferred to other dialkyl naphthalenes (i.e., 2,6-diethyl- (2,6-DEN) or 2,6-diisopropylnaphthalene (2,6- DIPN)) because no carbon atoms are lost in the oxidation step. However, large-scale production and commercialization of PEN has been limited due to the high production cost and low availability. Therefore, it has become an important subject to find an efficient process that is able to produce 2,6-DMN in high yield.

DMN has 10 different isomers and can be divided into four different groups of triad as follows depending on the easiness of isomerization:

(A) 1,5-DMN; 1,6-DMN; 2,6-DMN (2,6-group),
(B) 1,8-DMN; 1,7-DMN; 2,7-DNM (2,7-group),
(C) 1,4-DMN; 1,3-DMN; 2,3-DMN (2,3-group),
(D) 1,2-DMN.

Thermodynamically, the isomerization in the triad (intra-triad) is more favorable than that between the triads (inter-triad) because the low activation barrier of CH_3 group shift between α- and β-position in the same aromatic ring is lower than that of β- to β-position [3,4]. Therefore, to produce 2,6-DMN in high yield through isomerization, a catalyst is required, which can make it possible to shift CH_3 groups from β- to β-position through inter-triad isomerization between triads.

Inui et al. reported [5] that medium- and large-pore zeolites, such as ZSM-5, ZSM-11, ZSM-12, BEA, and Y were more effective than large-pore zeolites for the selective production of 2,6-DMN in the methylation of

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methylnaphthalene. This means that there exist an optimum pore size for the selective production of 2,6-DMN without by-product. Recently, BEA zeolite was suggested for the alkylation of two-ring aromatic hydrocarbons due to its strong acidic property and three-dimensional 12-oxygen-member-ring large-pore structure without supercage. Also, based on molecular mechanics and molecular dynamics, MTW was suggested as the most promising candidate for the selective alkylation of naphthalene to 2,6-DMN [6,7].

Recently, to circumvent the difficulties of inter-triad isomerization and obtain high yield of 2,6-DMN from 2,7-DMN, the Chevron cooperation has developed a two-step hydroisomerization/dehydrogenation process [8]. Until now, however, the isomerization of the DMN mixture having 10 isomers has not been studied where inter- and intra-triad isomerization are competitive.

In this work, isomerization of 2,7-rich DMN mixture has been investigated for the selective production of 2,6-DMN through one-step isomerization and three successive step isomerization consisting of (i) hydrogenation of 2,7-rich DMN to 2,7-rich DMT, (ii) isomerization of 2,7-rich DMT to 2,6-rich DMT, and (iii) then dehydrogenation of 2,6-rich DMT into 2,6-rich DMN. Also, the catalytic activity of the intra- and inter-triads isomerization of DMN and DMT are compared at various reaction conditions over H-BEA zeolites.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of Si-MCM-41

The pure silica MCM-41(Si-MCM-41) was prepared using the following gel molar composition [9]: 1.0 CTABr:2.0 NaOH:4.0 SiO_2:400 H_2O, where CTABr denotes cetylmethylammonium bromide. An amount of 30.4 g of Ludox HS-40 colloidal silica (DuPont) as a silica source was mixed with 97 g of 1 M NaOH aqueous solution under vigorous magnetic stirring. Another mixture comprised of 18.2 g of CTABr (Aldrich), 248.6 g of deionized water was prepared during stirring. Both of these mixtures were transferred into a Teflon lined autoclave, stirred for 30 min, and then heated at 100 °C for 2 days for crystallization. To adjust the pH at 10, a certain amount of 5 wt.% acetic acid added to the crystallized solution and heated at 100 °C for 2 days. This pH adjustment was repeated twice. The crystallized solid was filtered, washed with deionized water, dried at 100 °C and finally calcined in air at 550 °C for 10 h.

2.1.2. Preparation of metal-supported catalyst

A series of noble metal-supported zeolite catalysts (5 wt.% Ni and 0.5 wt.% Pd) was prepared by the incipient wetness impregnation with the supports (Si-MCM-41, BEA(25), NaBEA(25), USY(40) and NaY(2.5)) using an aqueous solution containing the desired amount of nickel nitrate (Aldrich) and palladium nitrate (Aldrich) under stirring slowly at room temperature for 12 h. The obtained solid material was filtered, washed with deionized water and dried at 100 °C for 12 h and calcined at 320 °C in an air flow for 2 h.

NH_4-form of H-BEA zeolites (Si/Al = 12.5, 37.5, 75) was used purchased from Zeolyst Corporation after calcining in air at 500 °C for 5 h. The other zeolites were also used as purchased after calcining.

2.2. Characterization of catalysts

For the characterization of physical and chemical properties of catalysts, XRD and in situ FT-IR spectra were carried out. The X-ray diffraction patterns of catalysts were obtained using a Rigaku D-max IIIB X-ray diffractometer with Ni filtered Cu Kα X-ray source. Surface acidity of catalysts was measured by a FT-IR spectrometer (Nicolet AVATAR360) with a resolution of 4.0 cm^{-1}. A self-supported wafer of around 10 mg with a diameter of 10 mm was placed in an in situ infrared cell made of quartz with CaF_2 windows and pretreated in a vacuum system at 500 °C and $P = 10^{-5}$ Torr for 2 h for the dehydration. The background spectra of the samples were obtained after cooling the self-supported wafer to ambient temperature. After heating to 200 °C, the samples were exposed to pyridine vapor and then followed by evacuation for 0.5 h at 200, 300, 400 and 500 °C, respectively. After the thermal treatment, the IR spectra were obtained at ambient temperature. For quantitative comparisons of the peak intensities, all FT-IR spectra were normalized using the area of the overtone lattice vibration bands of the zeolites at 1990 and 1870 cm^{-1} [10,11].

2.3. Catalytic reaction

The catalytic reactions were carried out on an ordinary fixed-bed flow-type reaction apparatus. About 0.5 g of catalyst was loaded into a stainless steel tubular reactor of 6.0 mm inner diameter. The liquid reactant was introduced into the reactor by a micro liquid pump at a weight hourly space velocity (WHSV) of 6 h^{-1}. The catalyst was pretreated at 300 °C in a helium flow for 30 min for dehydration. The isomerization reaction was conducted typically at 100 psig and 100 ml/min helium flow. In both of hydrogenation and dehydrogenation, the catalyst was prereduced in 40 ml/min 5% H_2/He at 300 °C for 2 h and then the reaction was carried out while flowing 40 ml/min hydrogen at 100 psig for hydrogenation and at atmospheric pressure for dehydrogenation, respectively. The products were analyzed with a gas chromatography (HP 5890) equipped with a capillary column: 60 m AT35 + 60 m DB17. The products were identified by a Shimadzu GCMS-QP1000EX gas chromatograph–mass spectrometer. The conversion, product selectivity and product yield were calculated as follows.

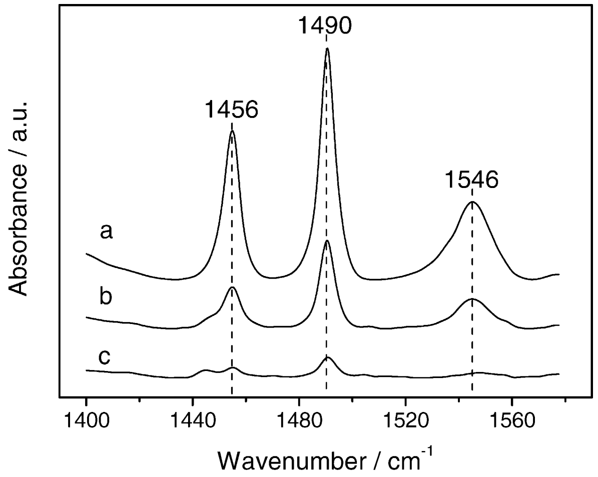

Fig. 1. FT-IR spectra of H-BEA with different Si/Al ratios of (a) 12.5, (b) 37.5 and (c) 75 after adsorption of pyridine at 200 °C.

In the hydrogenation and dehydrogenation, conversion, selectivity and yield were calculated based on the following equation:

$$\text{conversion (\%)} = (W_f - W_p)/W_f \times 100,$$
$$\text{selectivity (\%)} = W_p/W_f \times 100,$$
$$\text{yield (\%)} = \text{conversion (\%)} \times \text{selectivity (\%)}/100,$$

where W_f is the sum of weight % of the DMN (or DMT) in the reactants and W_p is the sum of weight % of the DMN (or DMT) in the products.

In the isomerization, 2,6-DMN (or 2,6-DMT) yield was calculated as follow: yield (%) = $(W_{2,6}\text{-}/W_p) \times (W_p/W_f) \times 100$, where $W_{2,6}$- is the weight % of 2,6-DMN (or 2,6-DMT) in the products.

3. Results and discussion

3.1. Characterization of synthesized catalyst

The XRD patterns of the synthesized mesoporous silicon MCM-41 and noble metal-supported Si-MCM-41 showed strong diffraction peaks near at the 2θ value of 2.5°, 3.8°, 4.4° and 5.7°, which corresponds well with the reference spectra of Si-MCM-41 reported previously [8].

3.2. Acidity of H-BEA with different ratios of Si to Al

The FT-IR spectra of H-BEA with different Si/Al ratios in the region of 1580–1400 cm^{-1} after adsorption of pyridine at 200 °C are shown in Fig. 1. All samples investigated show IR bands at 1456, 1490 and 1546 cm^{-1}. The band at 1490 cm^{-1} could be assigned to the pyridine adsorbed on both Brönsted and Lewis acid sites, while the bands at 1546 and 1456 cm^{-1} to the pyridine molecule protonated by Brönsted acid sites and the pyridine adsorbed on Lewis acid sites, respectively [12]. To quantify the acid site of samples, the peak area of 1546 and 1456 cm^{-1} bands were integrated. The molar extinction coefficient ratio of the bands at 1546 and 1456 cm^{-1} was reported to be 1.5 for the zeolites having a Si/Al ratio of more than 15 [13]. The Brönsted acid sites, Lewis acid sites, and the B/L ratio with different pyridine desorption temperature are shown in Table 1. Depending on the Si/Al ratio, the Brönsted, Lewis acid sites and the B/L ratio of H-BEA after pyridine desorption at 200–500 °C showed big change. As the Si/Al ratio increased, the concentration of Brönsted acid sites and Lewis acid sites increased, which trend was also observed in the case of B/L ratio. It is well known that as the aluminum content increases the amount of acid sites increases but its strength is decreased [14]. As the desorption temperature was increased from 200 to 500 °C, the all samples revealed obvious decrease of Brönsted acid band intensity due to the desorption of pyridine. However, the intensity of the Lewis acid band decreased rather slowly. This indicates that the strength of Brönsted acid is widely distributed ranging from weak to strong, while that of Lewis acid is narrowly distributed [15].

3.3. 2,7-Rich DMN to 2,6-rich DMN by one-step isomerization

3.3.1. Effect of the Si/Al ratios

H-BEA catalysts with three different ratios of Si/Al such as 12.5, 37.5 and 75 are used in the 2,7-rich DMN isomerization reaction at 250 °C. The distribution of isomers in the product is shown in Table 2. Over the all catalysts, the obvious change of composition of the isomers was observed. However, the sum of isomer composition in the each triad group such as 2,7-, 2,6- or 2,3-triad group showed almost

Table 1
Comparison of acid sites and B/L ratios determined by pyridine FT-IR spectra for H-BEA zeolites with different Si/Al ratios[a]

Si/Al	Temperature (°C)											
	200			300			400			500		
	B[b]	L[b]	B/L[c]	B[b]	L[b]	B/L[c]	B[b]	L[b]	B/L[c]	B[b]	L[b]	B/L[c]
12.5	8.1	7.0	1.7	6.0	6.0	1.5	3.2	5.7	0.8	1.0	5.2	0.3
37.5	3.6	3.0	1.8	2.5	2.8	1.3	1.1	2.7	0.5	0.3	2.6	0.2
75.0	0.6	1.0	0.9	0.3	0.8	0.6	0.1	0.7	0.2	0.1	0.6	0.2

[a] The experimental error was less than ±5% of each value.

[b] Where B and L denote the normalized peak area of Brönsted and Lewis acid sites, respectively.

[c] Calculated by the equation of 1.5 × (B/L), where B/L is the absorbance ratio [13].

Table 2
Effect of ratio of Si/Al for isomerization of 2,7-rich DMN to 2,6-rich DMN over H-BEA[a]

Distribution (%)	Si/Al			
	Feed	12.5	37.5	75
2,7-DMN	17.3	16.1	16.1	16.6
1,7-DMN	9.44	11.3	11.2	9.75
1,8-DMN	1.70	1.35	1.60	1.76
2,7-group DMN	28.5	28.7	28.9	28.1
2,6-DMN	3.12	7.07	6.77	5.10
1,6-DMN	10.0	8.34	8.10	8.45
1,5-DMN	5.01	3.42	3.63	5.11
2,6- group DMN	18.2	18.8	18.5	18.8
1,3-DMN	11.9	11.1	11.5	11.5
2,3-DMN	3.76	4.17	4.25	3.84
1,4-DMN	1.84	1.60	1.74	1.85
2,3- group DMN	17.5	16.9	17.5	17.2
1,2-DMN	6.60	6.51	6.50	6.80
Total DMN	70.8	70.9	71.4	70.8
2,6-DMN/Total DMN	4.41	9.97	9.48	7.21
2,6-DMN/2,7-DMN	0.18	0.44	0.42	0.31
2,6-DMN yield (%)	–	9.99	9.57	7.20

[a] Conditions: WHSV $= 6\,h^{-1}$, He $= 100$ ml/min, temperature $= 250\,^{\circ}C$, pressure $= 100$ psig, TOS $= 4$ h.

Table 3
Effect of reaction temperature for isomerization of 2,7-rich DMN over H-BEA (Si/Al = 12.5)[a]

Distribution (%)	Temperature (°C)					
	Feed	200	225	250	275	300
2,7-DMN	17.3	15.8	15.9	16.1	14.9	12.0
1,7-DMN	9.44	10.7	10.7	11.3	10.9	9.21
1,8-DMN	1.70	1.52	1.53	1.35	1.63	0.95
2,7- group DMN	28.5	28.0	28.1	28.7	27.4	22.2
2,6-DMN	3.12	6.80	6.87	7.07	6.80	6.04
1,6-DMN	10.0	7.87	7.29	8.34	7.99	6.61
1,5-DMN	5.01	3.42	3.58	3.42	3.22	2.15
2,6- group DMN	18.2	18.1	17.7	18.8	18.0	14.8
1,3-DMN	11.9	10.7	10.3	11.1	10.6	8.45
2,3-DMN	3.76	4.28	4.07	4.17	4.24	3.25
1,4-DMN	1.84	1.73	1.77	1.60	1.85	1.24
2,3- group DMN	17.5	16.7	16.1	16.9	16.7	12.9
1,2-DMN	6.60	6.25	6.11	6.51	6.35	4.86
Total DMN	70.8	69.1	67.0	70.9	68.5	54.8
2,6-DMN/Total DMN	4.41	9.84	10.3	9.97	9.93	11.0
2,6-DMN/2,7-DMN	0.18	0.43	0.46	0.44	0.46	0.50
2,6-DMN Yield (%)	–	9.60	9.72	9.99	9.61	8.53

[a] Conditions: WHSV $= 6\,h^{-1}$, He $= 100$ ml/min, pressure $= 100$ psig, TOS= 4 h.

no change depending on the Si/Al ratio. This means that one-step isomerization of DMN is favorable in the intra-triad isomers but not between the inter-triad isomers. The isomerization activity of H-BEA was influenced by the Si/Al ratio; the isomerization activity was in the order of H-BEA(12.5) > H-BEA(37.5) > H-BEA(75). The highest 2,6-DMN yield and 2,6-DMN/2,7-DMN ratio of 9.9% and 0.44 were obtained over H-BEA with the Si/Al ratio of 12.5, respectively.

Considering the acidic property of catalysts used, a good correlation between the concentration of acid sites, especially, of Brönsted sites and the 2,6-DMN yield and 2,6-DMN/2,7-DMN ratio was observed. That is, the higher the concentration of Brönsted acid sites, the higher yield of 2,6-DMN and the higher 2,6-DMN/2,7-DMN ratio was obtained. This indicates that the acidity of catalyst plays an important role for the isomerization of DMN.

The above results demonstrate that the intra-triad isomerization can be proceeded over the all of the H-BEA catalyst but its acid strength is not enough to bring the inter-triad isomerization due to the high activation barriers of methyl shift from β- to β-position [3].

3.3.2. Effect of the reaction temperature

The products distribution of one-step isomerization over H-BEA zeolite with the Si/Al ratio of 12.5 in the temperature range of 200–300 °C is compared at Table 3. The isomerization reaction began to occur from 200 °C and as the temperature was increased from 200 to 300 °C, the ratio of 2,6-DMN/2,7-DMN of 0.18 in the feed was increased from 0.43 to 0.50. At 250 °C, the maximum 2,6-DMN yield of 9.9% was obtained and then the 2,6-DMN yield is decreased rapidly due to the by-product formation. The total DMN concentration in products was also decreased at the temperature higher than 250 °C. The intra-triad isomerization of DMN could be proceed from 200 °C but for the inter-triad isomerization of DMN at least 250 °C was required. The yield of 2,6-DMN decreased rapidly at the reaction temperature than 250 °C. This means that even the inter-triad isomerization can be induced at high temperature above 250 °C but it is impossible to exclude the loss of DNM due to the pronounced side reactions such as dealkylation, cracking and transalkylation.

According to the above results, the maximum 2,6-DMN yield of ca. 10% and the 2,6-DMN/2,7-DMN ratio of 0.44 could be achieved by the one-step isomerization using 2,7-rich DMN feed over H-BEA(12.5) at 250 °C. As reported previously, the 2,6-DMN/2,7-DMN ratio of about 1.0 is the maximum obtainable thermodynamically [5,16] and the 2,6-DMN/2,7-DMN ratio of 0.44 is far away from the value at equilibrium condition. Therefore, it could be suggested that the isomerization from 2,7-rich DMN with one-step method over acidic catalysts may not be an efficient way to produce 2,6-DMN in high yield.

3.4. 2,7-Rich DMN to 2,6-rich DMN by three successive steps

3.4.1. Hydrogenation of 2,7-rich DMN to 2,7-rich DMT

The hydrogenation of 2,7-rich DMN to 2,7-rich DMT was carried out at 300 °C over various metal-supported zeolites and its result is shown in Fig. 2. In terms of active metal components and supports, the yield of DMT showed the order of Pd ≫ Ni and Si-MCM-41 > Na-Y > Na-Beta > H-Beta > USY, respectively. Selective hydrogenation of DMN was possible without by-product formation over the

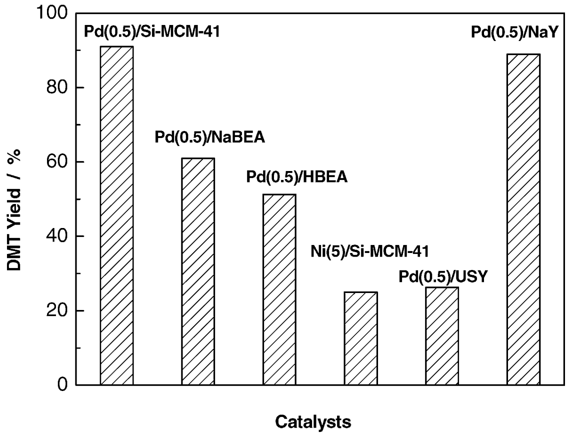

Fig. 2. The DMT yield over various metal-supported zeolite catalysts (WHSV: 2 h^{-1}; H_2: 40 ml/min; temperature: 300 °C; pressure: 100 psig).

Pd/Si-MCM-41 and Pd/Na-Y catalysts and about 96% DMT yield was achieved even at 200 °C without deactivation of catalyst at least for 126 h over 0.5 wt.% Pd/Si-MCM-41 catalyst. It can be suggested that the Pd-containing catalysts with supports of lower acidity and large-pore channels are effective for the selective hydrogenation of DMN to DMT.

3.4.2. Isomerization of 2,7-rich DMT to 2,6-rich DMT

3.4.2.1. Effect of the ratio of Si/Al. To induce inter-triad isomerization, the isomerization of 2,7-rich DMT was carried out at 200 °C over H-BEA zeolites having various Si/Al ratios and the result is shown in Table 4. The H-BEA(12.5) with Si/Al ratio of 12.5 showed the highest isomerization activity among the various Si/Al ratios. The isomerization activity was in the order of H-BEA(12.5) > H-BEA(37.5) > H-BEA(75) same as that of 2,7-rich DMN isomerization activity by one-step method. The 2,6-DMT yield was also increased rapidly from 6.06 to 14.9% as the Si/Al ratio decreased from 75 to 12.5. Interestingly, the 2,6-DMT/2,7-DMT ratio of higher than 1 was also achieved over the H-BEA(12.5) having high concentration of acid sites while that of 0.27 was obtained over the H-BEA(75) with low concentration sites. These experimental results indicate that the 2,6-DMT yield and the 2,6-DMT/2,7-DMT ratio are strongly depended on the acidity of catalysts in the isomerization of DMT.

Different from the isomerization of DMN, obvious change of the product distribution of DMT isomers between the triad groups was observed as well as that of DMT isomers in the triad isomers even over a H-BEA(75) having weak acid sites. This indicates that the alkyl group shift from β- to β-position in the DMT is much easier than that in the DMN because there is no difference in the alkyl group shift between β- to β-position and α- to β-position due to the reduced activation barrier for β- to β-position alkyl group shift. In other words, the probability of intra- and inter-triad isomerization of DMT becomes equal by the hydrogenation of aromatic ring of DMN to cyclohexane.

3.4.2.2. Effect of the reaction temperature. The isomerization of 2,7-rich DMT was carried out at different temperatures over H-BEA with Si/Al ratio of 12.5 (Table 5). The composition of isomers and the distribution of triad group began to show change from 180 °C. As the reaction temperature increased from 180 to 250 °C, the concentration of 2,6-DMT increased rapidly with the decrease of 2,7-DMT

Table 4
Effect of ratio of Si/Al for isomerization of 2,7-rich DMT over H-BEA[a]

Distribution (%)	Si/Al			
	Feed	12.5	37.5	75
2,7-DMT	10.1	6.41	7.09	10.1
1,7- DMT	2.81	2.61	2.78	2.75
1,8-DMT	0.61	1.11	1.43	0.58
2,8-DMT	2.86	2.55	2.85	2.81
2,7-group DMT	16.4	12.7	14.1	16.3
2,6-DMT	2.69	6.71	5.61	2.73
1,6-DMT	3.92	3.35	3.64	3.87
1,5-DMT	4.10	2.96	3.98	4.02
2,5- DMT	3.46	2.68	3.19	3.41
2,6-group DMT	14.2	15.7	16.4	14.0
1,3-DMT	0.41	0.00	0.59	0.35
2,3-DMT	9.09	10.6	10.2	8.91
1,4-DMT	3.99	1.35	1.65	3.81
2,3-group DMT	13.5	11.9	12.4	13.1
1,2-DMT	0.88	0.97	0.95	0.80
Total DMT	44.9	41.2	43.9	44.2
2,6-DMT/2,7-DMT	0.27	1.05	0.79	0.27
2,6-DMT Yield (%)	–	14.9	12.5	6.06

[a] Conditions: WHSV = 6 h^{-1}, He = 100 ml/min, temperature = 200 °C, pressure = 100 psig, TOS = 4 h.

Table 5
Effect of reaction temperature for isomerization of 2,7-rich DMT over H-BEA (Si/Al = 12.5)[a]

Distribution (%)	Temperature (°C)				
	Feed	180	200	225	250
2,7-DMT	10.1	7.54	6.41	6.17	4.58
1,7- DMT	2.81	2.64	2.61	2.53	1.79
1,8-DMT	0.61	0.79	1.11	1.25	2.28
2,8-DMT	2.86	2.75	2.55	2.56	1.95
2,7-group DMT	16.4	13.7	12.7	12.5	10.6
2,6-DMT	2.69	5.17	6.71	5.45	5.12
1,6-DMT	3.92	3.60	3.35	3.19	2.00
1,5-DMT	4.10	3.83	2.96	3.21	1.65
2,5- DMT	3.46	3.13	2.68	2.77	2.07
2,6-group DMT	14.2	15.7	15.7	14.6	10.8
1,3-DMT	0.41	0.46	0.00	0.63	0.00
2,3-DMT	9.09	10.4	10.6	9.60	8.56
1,4-DMT	3.99	1.74	1.35	1.73	1.32
2,3-group DMT	13.5	12.6	11.9	12.0	9.87
1,2-DMT	0.88	0.93	0.97	1.08	1.12
Total DMT	44.9	43.0	41.2	40.2	32.4
2,6-DMT/2,7-DMT	0.27	0.69	1.05	0.88	1.12
2,6-DMT Yield (%)	–	11.5	14.9	12.1	11.4

[a] Conditions: WHSV = 6 h^{-1}, He = 100 ml/min, pressure = 100 psig, TOS = 4 h.

Table 6
Effect of reaction temperature for dehydrogenation of 2,6-rich DMT to 2,6-rich DMN over 0.5 wt.% Pd/Si-MCM-41[a]

Temperature (°C)	Conversion (%) of DMT	Selectivity (%) to DMN	Yield (%) of DMN
350	83.3	95.1	79.2
375	86.4	96.2	83.1
400	98.8	96.5	95.3
400[b]	98.5	96.4	95.0
425	99.1	96.0	95.1
450	99.3	96.2	95.5

[a] Conditions: WHSV $= 6\,h^{-1}$, H_2 $= 40$ ml/min, pressure = atmosphere, TOS = 4 h.

[b] TOS = 10 h.

concentration and the 2,6-DMT/2,7-DMT ratio of 0.27 in the feed also increased from 0.69 to 1.12, respectively, which was higher than that of thermodynamically predicted value. A maximum yield of 2,6-DMN, 14.9% could be obtained at 200 °C and then its yield decreased at higher temperature.

Different from the inter-triad isomerization of DMN, methyl group shift between the adjacent β to β of DMT began to occur even from 180 °C over H-BEA(75) having weak acid site due to the reduced activation barriers β to β transition.

3.4.3. Dehydrogenation of 2,6-rich DMT to 2,6-rich DMN

Finally, to produce 2,6-rich DMN in three-step isomerization, dehydrogenation of 2,6-rich DMT was carried out at different temperatures over 0.5 wt.% Pd/Si-MCM-41 catalyst (Table 6). More than 95% yield of DMN was achieved in the temperature range of 400–450 °C, which is similar to the result reported by Mitsubishi Co. [17], and no deactivation of catalyst was observed at least 15 hrs at 400 °C.

Through the successive three-step isomerization of dehydrogenation → isomerization → dehydrogenation, the 2,6-DMN/2,7-DMN ratio of 1.1 which is higher than the value predicted thermodynamically and ca. 14% of 2,6-DMN yield calculated by (DMT yield of hydrogenation) × (2,6-DMT yield of isomerization) × (DMN yield of dehydrogenation)) were obtained from 2,7-rich DMN feed. From the result, it could be suggested that the three-step isomerization is more effective than the one-step one for the inter-triad isomerization of 2,7-rich DMN to 2,6-DMN.

4. Conclusions

The intra-triad isomerization of the DMN isomers within same triad group was relatively easier than that of inter-triad isomerization. However, in the case of DMT, the inter- and intra-triad isomerization did not show difference in activity. The isomerization activity of DMT or DMN was increased depending on the reaction temperature, but if the reaction temperature was to high, the yield of 2,6-DMN or 2,6-DMT was decreased due to the side reactions such as dealkylation, cracking and transalkylation. Different from the yield, however, the ratio of 2,6-DMN/2,7-DMN (or 2,6-DMT/2,7-DMT) was increased monotonously as the reaction temperature increased.

The selectivity of 2,6-DMN or 2,6-DMT was strongly depended on the acidity of H-BEA zeolite. The more the Brönsted acid sites, the higher the yield of 2,6-DMN or 2,6-DMT was obtained.

For the selective production of 2,6-DMN from 2,7-rich DMN through isomerization, the three-step process of hydrogenation → isomerization → dehydrogenation was more efficient than the direct one-step isomerization.

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