[Regular Paper]

2-Methylnaphthalene Methylation over Aluminosilicate and Ferrisilicate with MTW-type Zeolite Structure and Their Kinetic Analysis

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Aluminosilicate and ferrisilicate with the MTW-type zeolite structure were hydrothermally prepared and used to catalyze the methylation of 2-methylnaphthalene (2-MN) under supercritical conditions in a batch-type reactor. Dimethylnaphthalene (DMN) and 1-methylnaphthalene (1-MN) yields increased with decreasing Si/Al ratio of the zeolite. In contrast, ferrisilicate with the MTW-type zeolite structure (Si/Fe = 100) exhibited higher DMN selectivity and the β,β-DMN fraction in total DMNs was higher than that over aluminosilicate with MTW structure (Si/Al = 100). Kinetic analysis of 2-MN methylation over MTW zeolites was conducted, to obtain the reaction rate constants and apparent activation energies. The activation energy for the methylation of 2-MN over aluminosilicate with MTW structure was 176 kJ mol^{-1}, which was almost the same as that for the ferrisilicate with MTW structure. This indicates that the mechanism for methylation is independent of hetero-atoms species in the MTW zeolite framework. The introduction of Fe atoms into the framework significantly decreased the rate constant for the isomerization of 2-MN compared with that for the methylation of 2-MN. Therefore, ferrisilicate with MTW structure is effective for 2-MN methylation due to the decrease of the isomerization rate.

Keywords
Kinetic analysis, Methylation, MTW-type zeolite catalyst, 2-Methylnaphthalene, Ferrisilicate

1. Introduction

2,6-Dimethylnaphthalene (2,6-DMN) is an important substance as an intermediate of in the production polyethylenenaphthalate (PEN), which possesses superior properties such as gas impermeability and heat resistance to those of polyethyleneterephthalate (PET). However, 2,6-DMN is commercially produced from *o*-xylene and butadiene in a multistep reaction process using an alkali metal catalyst and a large quantity of organic solvent[1]. DMN has 10 different isomers; β,β-DMN (2,6-DMN, 2,7-DMN and 2,3-DMN), α,β-DMN (1,2-DMN, 1,3-DMN, 1,6-DMN and 1,7-DMN) and α,α-DMN (1,4-DMN, 1,5-DMN and 1,8-DMN). The boiling points of these DMN isomers are close to each other[2],[3]; therefore, separation of the isomers requires a large amount of energy. Furthermore, the separation of 2,6- and 2,7-DMN is difficult because the difference in their boiling points is only 0.3 ℃, and they form eutectic crystals when the 2,6-DMN/2,7-DMN ratio is 0.7[4]. To decrease the number of reaction steps and energy consumption thus requires the development of an alternative process for the selective production of 2,6-DMN, and catalysis over zeolites has received much attention for the production of 2,6-DMN.

Zeolite, a crystalline aluminosilicate, has strong acid sites, high surface area and micropores close in size to the molecular diameter of hydrocarbons, which can enable shape-selectivity for specific molecules. Various medium- and large-pore zeolites have been applied for 2,6-DMN synthesis by the methylation of naphthalene or 2-methylnaphthalene (2-MN)[5]~[8]. Although MFI-type zeolite that possesses smaller pores than the molecular size of 2,6-DMN exhibits high β,β-DMN selectivity, conversion of the feedstock is low due to high diffusion resistance. In contrast, MTW-type zeolite possesses pores close in size to β,β-DMN molecules; therefore, MTW-type zeolite are considered to have an advantage for the production of β,β-DMN. In addition, during the methylation of 2-MN over zeolite in the vapor phase, coke formed on the zeolite crystal leads to fast deactivation of the zeolite due to pore blocking. MTW-type zeolite (Si/Al = 100) with different crystal sizes was previously applied for 2-MN methylation under supercritical conditions, and deactivation by coke formation was successfully suppressed. Moreover, kinetic analysis of the methylation (DMN formation)

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and isomerization (1-MN formation) of 2-MN have been achieved[9].

Isomorphous substitution of Al in the zeolite framework by Fe to form a ferrisilicate can weaken the acidity of the zeolite[8],[10]~[12], and it has been reported that ferrisilicate with MFI-type zeolite structure enhances selectivity toward β,β-DMN as the product[8].

The conversion and selectivity of 2-MN methylation is considered to be strongly affected by the relationship between the methylation and isomerization rates over the zeolite catalyst. Accordingly, the present study is focused on the effect of the amount of acid sites and isomorphous substitution of Al by Fe in the MTW-type structure on the 2-MN methylation and isomerization rates. To clarify these factors, nano-sized MTW-type zeolite with various Si/Al ratios (Si/Al = 50, 100, 200, here after Al-MTW) and nano-sized ferrisilicate with MTW-type zeolite structure (Si/Fe = 100, here after Fe-MTW) were hydrothermally prepared and applied for 2-MN methylation under supercritical conditions.

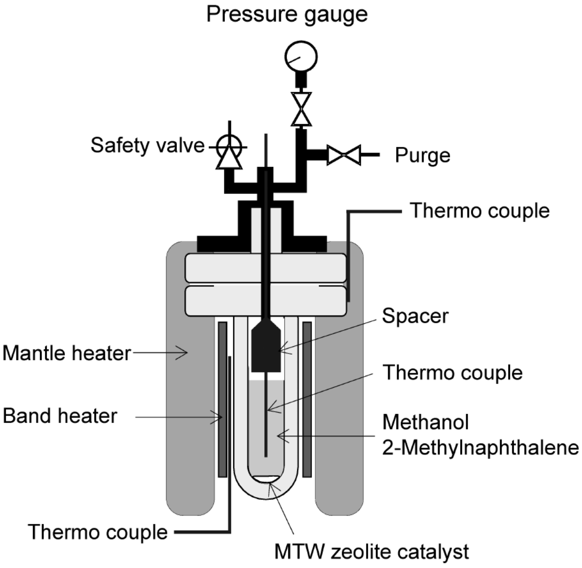


Fig. 1 Experimental Setup of Batch-type Reactor

2. Experimental

2. 1. Synthesis of Al- and Fe-MTW Zeolites

Al- and Fe-MTW were prepared by conventional hydrothermal synthesis. Colloidal silica (Sigma-Aldrich, Co., LLC.), sodium aluminates (Wako Pure Chemical Industries, Ltd.) or iron (III) nitrate monohydrate (Fe source, Wako Pure Chemical Industries, Ltd.) and sodium hydroxide (Wako Pure Chemical Industries, Ltd.) were used as sources of Si, Al (for Al-MTW), Fe (for Fe-MTW) and alkali, respectively. Tetraethylammonium bromide (TEABr, Wako Pure Chemical Industries, Ltd.) was used as organic structure directing agent (OSDA)[13]. The reaction gel composition was $Na_2O : OSDA : SiO_2 : T_2O_3 : H_2O = 10 : 60 : 100 : x : 5555$, where $x = 0.25$ to 1.0 and T = Al or Fe. The resulting solution was sonically agitated for 1 h, poured into a Teflon-sealed stainless steel bottle and then heated at 423 K for 6 days. The precipitates obtained were washed with alcohol, dried at 383 K for 12 h, and calcined at 823 K for 12 h in an air stream to remove OSDA molecules and other adsorbed hydrocarbons. The white powders obtained were treated with NH_4^+ ions (10 % NH_4NO_3 aqueous solution) at 343 K for 9 h to exchange sodium ions on the acid sites for ammonium ions. The resultant powdered zeolites were pelletized, crushed and sieved to yield samples with particles diameters of *ca.* 0.4 mm. Details concerning the preparation of Al-MTW and Fe-MTW have been described previously[13].

2. 2. Characterization of Al- and Fe-MTW Zeolites

The morphology and crystallinity of the obtained samples were analyzed using field emission scanning electron microscopy (FE-SEM; JSM-6500F, JEOL Ltd.) and X-ray diffraction (XRD; Ultima IV, Rigaku Corp.), respectively. Brunauer-Emmett-Teller (BET) surface areas, external surface areas and micropore volumes for the obtained samples were calculated using the BET and *t*-plot methods, respectively, based on nitrogen adsorption isotherms obtained (BELsorp mini, MicrotracBEL Corp.). The Si/T (T = Al or Fe) ratios for the samples were measured using X-ray fluorescence spectroscopy (XRF; supermini, Rigaku Corp.). The acidity and amount of acid sites the samples was evaluated from *ac*-NH_3-temperature programmed desorption (TPD) profile measurements[14].

2. 3. Methylation of 2-MN over MTW-type Zeolites with Different Acid Properties

The methylation of 2-MN over a zeolite catalyst was performed out using a batch-type reactor with a volume of 3.0×10^{-5} m^3 under high-pressure as shown in **Fig. 1**. Prior to the reaction, the catalyst (NH_4^+ form) was activated by calcination at 823 K under an air stream for 1 h.

A mixture of 2-MN and methanol (2-MN : methanol molar ratio = 0.1) with a volume of 2.82×10^{-5} m^3 and 0.5 g of Al-MTW or 1.0 g of Fe-MTW were placed in the reactor. The reactions were conducted at reaction temperatures in the range of 523-583 K and maintained for 90-270 min after the reaction temperature was reached. The pressure in the reactor was 25 MPa, which was monitored with a pressure gauge. Details concerning the experimental procedure have been described previously reported[9].

3. Results and Discussion

3. 1. Characterization of Al- and Fe-MTW Zeolites

Figure 2 shows XRD patterns for the samples obtained with various Si/T ratios. The patterns showed peaks corresponding to the MTW-type zeolite phase and no other phases were observed. The crystallite sizes of the MTW-type zeolite determined from the XRD peaks and the Scherrer equation were 60-80 nm.

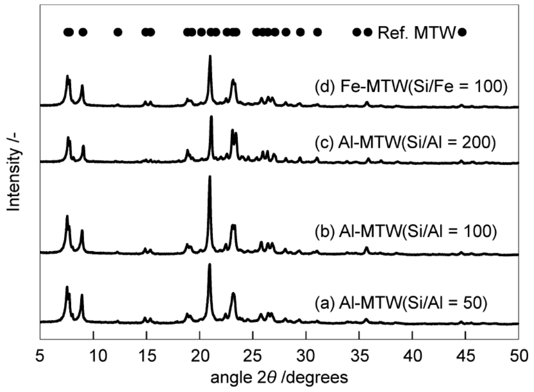


Fig. 2 XRD Patterns for (a) Al-MTW (Si/Al = 50), (b) Al-MTW (Si/Al = 100), (c) Al-MTW (Si/Al = 200), and (d) Fe-MTW (Si/Fe = 100)

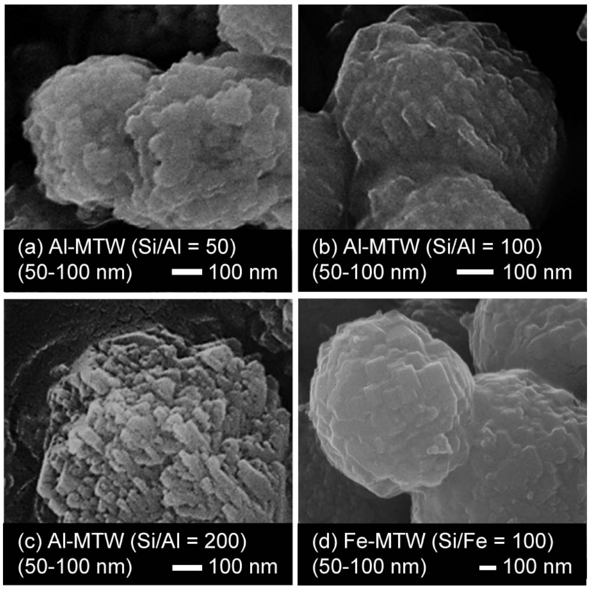


Fig. 3 FE-SEM Micrographs of (a) Al-MTW (Si/Al = 50), (b) Al-MTW (Si/Al = 100), (c) Al-MTW (Si/Al = 200), and (d) Fe-MTW (Si/Fe = 100)

Figure 3 shows FE-SEM images of the obtained samples. Secondary particle aggregates with sizes in the range of 500-1000 nm were formed from primary particles with sizes of approximately 50-100 nm. **Table 1** summarizes the BET surface area (S_{BET}), external surface area (S_{EXT}) and micropore volume (V_{m}) for the zeolites obtained from nitrogen desorption isotherms, and the Si/T ratio determined from XRF measurements. S_{BET}, S_{EXT} and V_{m} for all the zeolites were similar, and were equivalent to those previously reported[15),16)]. Si/T ratios for the zeolites measured by XRF were almost the same as those calculated from the Si and T concentrations in the synthesis solutions.

Figure 4 shows *ac*-NH_3-TPD profiles for the Al-MTW and Fe-MTW. Peaks observed above 600 K for Al-MTW and above 550 K for Fe-MTW are associated with desorption of NH_3 adsorbed on the strong acid sites, which indicates that Al and Fe are present in the MTW-type zeolite frameworks. In contrast, peaks observed below these temperatures were assigned to the desorption of NH_3 weakly held adsorbed or physisorbed on the zeolite surfaces. It was confirmed that NH_3 was desorbed from the strong acid sites of Fe-MTW at lower temperature than Al-MTW, which is consistent with our previous report[13)]. The amounts of strong acid sites estimated from the peak areas of the *ac*-NH_3-TPD profiles are also listed in **Table 1**. The acid sites on

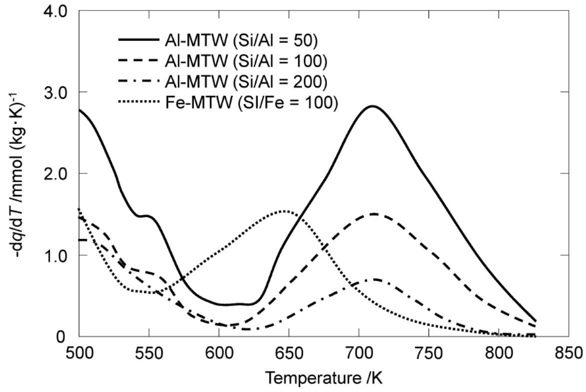
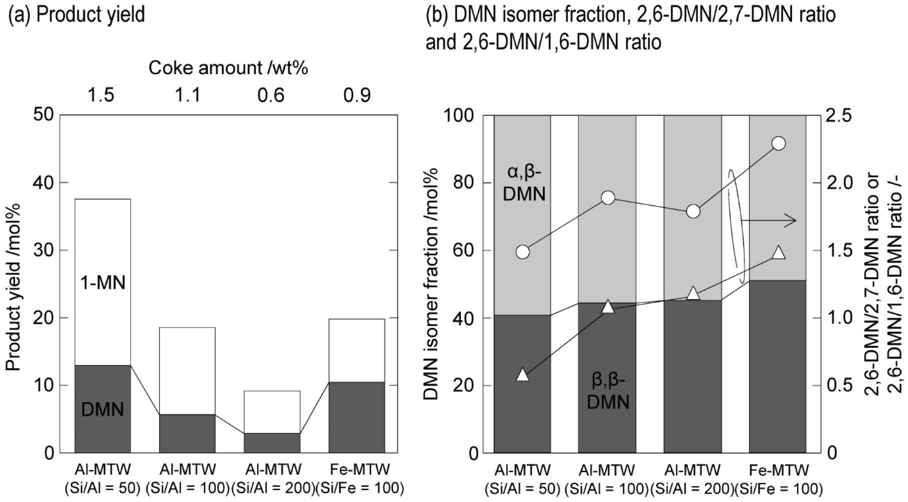


Fig. 4 *ac*-NH_3-TPD Profiles for Al-MTW (Si/Al = 50, 100 and 200) and Fe-MTW (Si/Fe = 100)

Table 1 Micropore Volume, BET Surface Area, External Surface Area, Si/T Ratio, and Amount of Acid Sites for the Al-MTW and Fe-MTW Zeolites

Sample	V_{m} [$cm^3\ g^{-1}$]	S_{BET} [$m^2\ g^{-1}$]	S_{EXT} [$m^2\ g^{-1}$]	Si/T ratio [-]	Amount of acid sites [$mmol\ g^{-1}$]
Al-MTW (50)	0.13	340	40	56	0.28
Al-MTW (100)	0.13	310	45	105	0.15
Al-MTW (200)	0.11	290	30	233	0.07
Fe-MTW (100)	0.13	300	40	102	0.15

V_{m}: micropore volume by the *t*-plot method; S_{BET}: BET surface area by the BET method; S_{EXT}: external surface area by the *t*-plot method.



Reaction conditions: $T = 583$ K, pressure = 25 MPa, time = 0-270 min, catalyst weight = 0.5 g (for Al-MTW) or 1.0 g (for Fe-MTW).

Fig. 5 Effect of Amounts of Acid Sites and Isomorphous Substitution of Al by Fe in the MTW-type Zeolite Framework on (a) the Product Yield and (b) DMN Isomer Fraction, 2,6-DMN/2,7-DMN Ratio and 2,6-DMN/1,6-DMN Ratio; circles: 2,6-DMN/2,7-DMN ratio, triangles: 2,6-DMN/1,6-DMN ratio

Al-MTW decreased with increasing Si/Al ratio. In addition, the amount of acid site amount for Al-MTW with a Si/Al ratio of 100 was almost the same as that for Fe-MTW with a Si/Fe ratio of 100. Moreover, the Si/T ratios estimated from the TPD profiles were close to those determined from XRF measurements.

3. 2. Methylation of 2-MN over MTW Zeolites with Different Acid Properties

To investigate the effect of the amount of acid sites on the product yield, the DMN isomer fractions and the amount of coke formed over the MTW-type zeolites, 2-MN methylation over nano-sized Al-MTW with various Si/Al ratios were conducted at a reaction temperature of 583 K. **Figure 5(a)** shows the product yields of DMN and 1-MN. Trimethylnaphthalene, which can be formed by the methylation of DMN, was not formed during the reaction. The yield of DMN formed by methylation of 2-MN and the yield of 1-MN formed by isomerization of 2-MN increased with the amount of acid sites on Al-MTW. **Figure 5(b)** shows the DMN isomer fractions in the product DMNs. β,β- and α,β-DMN were formed by the methylation of 2-MN, whereas α,α-DMN, which may form by the methylation of 1-MN and/or isomerization of other DMNs, was not formed, regardless of the Si/Al ratio in Al-MTW. The fraction of β,β-DMN in the product DMNs was $>$ 40 mol%, which was higher than that for thermodynamic equilibrium (35-37 mol%)[4], regardless of the amount of acid sites. In contrast, the fraction of β,β-DMN in the product DMNs slightly decreased with increasing amount of acid sites.

The isomerization of 2,6-DMN into 1,6-DMN can easily occur on acid sites because the isomerization of DMN proceeds predominantly between the β-position and α-position[12],[17]. Millini and Perego reported that the energy barrier for α,β-DMN formation within the pores of MTW-type zeolite and it was assumed that it is quite difficult for α,β-DMN to diffuse inside the pores[3]. Therefore, it is considered that the β,β-DMN produced isomerizes into α,β-DMN on the outer surface of the zeolite because the 2,6-DMN/1,6-DMN ratio decreased over Al-MTW with higher a Si/Al ratio, as shown in **Fig. 5(b)**.

The methylation of 2-MN over Fe-MTW was also performed to investigate the effect of different heteroatoms in the zeolites framework. Fe-MTW had lower 2-MN conversion than Al-MTW (100) with the same catalyst loading in the reactor; therefore, twice the weight of Fe-MTW (100) was used for methylation to obtain almost the same 2-MN conversion with Al-MTW (100). Although the 2-MN conversions were similar, Fe-MTW (100) exhibited higher DMN selectivity than Al-MTW (100), which indicates 1-MN formation by isomerization of 2-MN could be suppressed and methylation of 2-MN became the preferred reaction. In addition, Fe-MTW (100) resulted in a higher β,β-DMN fraction ($>$ 50 mol%) in the product DMNs than that over Al-MTW (100). It is known that isomerization activity over zeolite depends on the acid strength[4]~[8],[18]. For this reason, it is considered that isomerizations of reactant/products on the outer surface are suppressed because isomerization activity over Fe-MTW is lower than that over Al-MTW. Therefore, it is considered that the isomerization of β,β-DMN into α,β-DMN over

Fe-MTW(100) is also suppressed as with Al-MTW(100). Furthermore, the 2,6-DMN/2,7-DMN ratio in the DMNs produced over Fe-MTW(100) was > 2.0, which is higher than that obtained over Al-MTW. Komatsu *et al.* reported that the 2,6-DMN/2,7-DMN ratio in DMNs produced over Fe-MFI was also higher than that over Al-MFI8). It is thus considered that isomorphous substitution of Al by Fe in the zeolite framework contributes to an increase in the 2,6-DMN/2,7-DMN ratio.

The amount of coke loaded on the zeolite after the reaction was 1.5, 1.1, 0.6 and 0.9 wt% for Al-MTW (50), Al-MTW (100), Al-MTW (200) and Fe-MTW (100), respectively. These amounts were much lower than those reported under atmospheric reaction conditions (10.2-14.1 wt%)18). The amount of coke loaded on the zeolite increased due to an increase in the amount of acid sites on Al-MTW, which resulted in an increase in 2-MN conversion. In contrast, it seems that the effect of different heteroatoms on coke loading was small.

3. 3. Kinetic Analysis of 2-MN Methylation over Al- and Fe-MTW Zeolites

Because conversion of 1-MN methylation was quite lower than that of 2-MN methylation, it is considered that 2-MN methylation and the isomerization of 2-MN occurred as parallel reactions9). Assuming that methylation and isomerization of 2-MN are first-order reactions with respect to the 2-MN concentration, the reaction rates can be expressed as follows:

Rate of DMN formation

$$r_{\mathrm{DMN}} = k_1 C_{\text{2-MN}} \tag{1}$$

Rate of 1-MN formation

$$r_{\text{1-MN}} = k_2 C_{\text{2-MN}} \tag{2}$$

where r_{DMN} and $r_{\text{1-MN}}$ are the rates (mol kg^{-1} s^{-1}) for methylation and isomerization of 2-MN, respectively. $C_{\text{2-MN}}$ is the concentration of 2-MN (mol m^{-3}), and k_1 and k_2 are the apparent rate constants (m^3 kg^{-1} s^{-1}) for the methylation and isomerization of 2-MN, respectively.

From Eqs. (1) and (2), the consumption rate of 2-MN in the overall conversion is expected to be:

$$-r_{\text{2-MN}} = -(k_1 + k_2) C_{\text{2-MN}} \tag{3}$$

By integrating Eq. (3),

$$\ln\left(\frac{C_{\text{2-MN,0}}}{C_{\text{2-MN}}}\right) = (k_1 + k_2)\frac{W}{V}t \tag{4}$$

where $C_{\text{2-MN,0}}$ is the initial 2-MN concentration (mol m^{-3}), W is the catalyst weight (kg), and V is the volume of reactant (m^3).

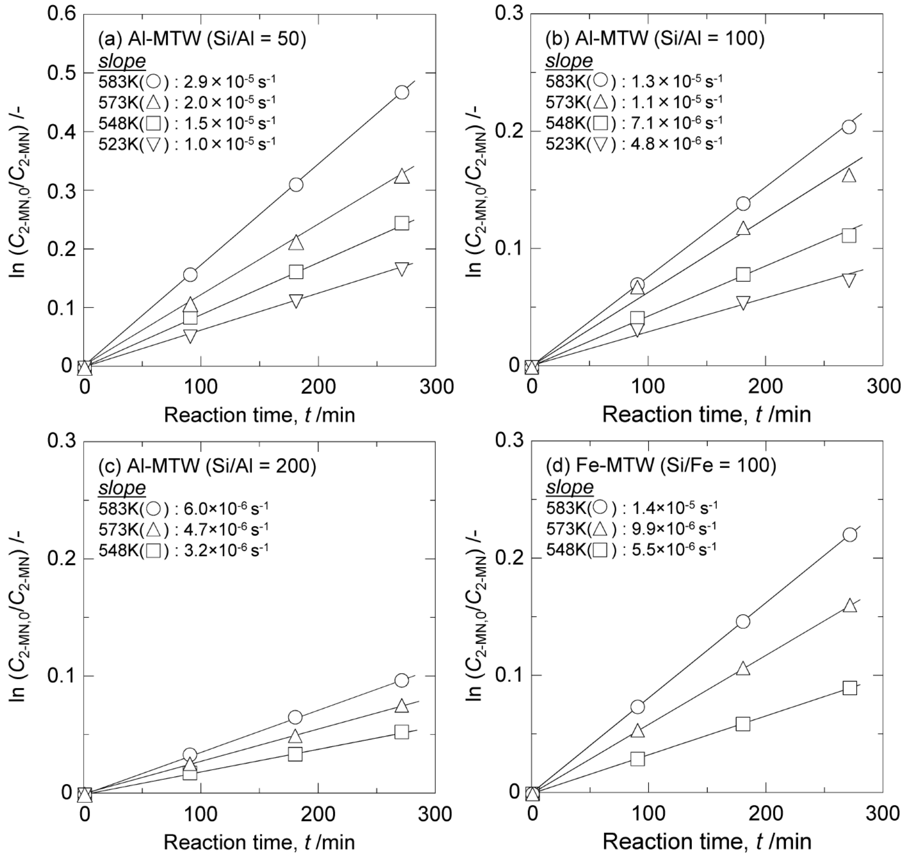
In addition, Eq. (5) was obtained from Eqs. (1) and (3).

$$\frac{C_{\text{2-MN,0}} - C_{\text{2-MN}}}{C_{\mathrm{DMN}} - C_{\mathrm{DMN,0}}} = \frac{k_1 + k_2}{k_1} \tag{5}$$

The methylation of 2-MN over both Al-MTW and Fe-MTW was conducted in the temperature range from 523 to 583 K. **Figure 6** shows the change in ln ($C_{\text{2-MN,0}}/C_{\text{2-MN}}$) with the reaction time, t. Proportional relationships between ln ($C_{\text{2-MN,0}}/C_{\text{2-MN}}$) and reaction time were obtained for both catalysis. This indicates that the effect of coke formation on the kinetics was negligibly small under the reaction conditions. The slope in **Fig. 6** indicates $(k_1 + k_2)W/V$; therefore, the rate constant for methylation (k_1) and isomerization (k_2) could be calculated using the slope and Eq. (5).

Figure 7 shows Arrhenius plots of the rate constants for methylation and isomerization of 2-MN over Al-MTW and Fe-MTW. The rate constants for both 2-MN isomerization and 2-MN methylation over Al-MTW zeolites increased with Al content in the zeolites. In contrast, the apparent activation energies for 2-MN methylation and 2-MN isomerization were 176 kJ mol^{-1} and 26 kJ mol^{-1}, respectively, regardless of the Si/Al ratio in Al-MTW. The apparent activation energy generally becomes half that of the intrinsic activation energy when the reaction is conducted under diffusion-limiting condition19), and it has found that 2-MN methylation over macro-sized Al-MTW has been reported to be approximately half of that over nano-sized Al-MTW due to the effect of diffusion9). Although the rate constant for methylation is enhanced by a decrease in the Si/Al ratio, the apparent activation energy has the same value, regardless of the Si/Al ratio, which indicates that methylation proceeds under reaction-limiting condition, regardless of the Si/Al ratio in the zeolite. Conversely, the Si/Al ratio on the outer surface of the zeolite is considered to affect the rate constant for isomerization because isomerization mainly occurs on the outer surface of the zeolite9). Although the activation energies for 2-MN methylation and 2-MN isomerization over Fe-MTW were also 176 kJ mol^{-1} and 26 kJ mol^{-1}, respectively, the rate constant for methylation was the same while that for isomerization was lower value than over Al-MTW (100). This result indicates that the isomorphous substitution of Al by Fe in the MTW-type zeolite framework maintains the rate of methylation, while the rate of isomerization is decreased.

Figure 8 shows the relationship between 2-MN conversion and the β,β-DMN yield over the Al-MTW and Fe-MTW zeolites. The linear relationship between the β,β-DMN yield and 2-MN conversion for Al-MTW indicated that the β,β-DMN yield is almost the same 2-MN conversions, regardless of the Si/Al ratio and reaction temperature. The β,β-DMN yield obtained by 2-MN methylation over Fe-MTW was higher than that over Al-MTW for each 2-MN conversion. The isomerization rate was selectively decreased by the isomorphous substitution of Al by Fe in the MTW-type zeolite framework; therefore, it is considered that the isomerization of β,β-DMN into α,β-DMN is also suppressed, which leads to a higher β,β-DMN yield than



Reaction conditions: $T = 523$-583 K, time = 0-270 min.

Fig. 6 Relationship between ln ($C_{\text{2-MN,0}}/C_{\text{2-MN}}$) and Reaction Time t, in the Methylation of 2-MN over Al-MTW (Si/Al = 50, 100 and 200) and Fe-MTW (Si/Fe = 100)

that with Al-MTW.

4. Conclusion

Methylation of 2-MN with methanol over Al-MTW (Si/Al = 50, 100 and 200) and Fe-MTW (Si/Fe = 100) was performed at reaction temperatures in the range of 523 to 583 K under high-pressure reaction conditions. Kinetic analysis for 2-MN methylation over these MTW-type zeolites indicated the activation energies for the methylation and isomerization of 2-MN were almost the same for all the catalysis, regardless of the acid properties (Si/Al ratio and acid strength). The mechanism for the methylation and isomerization of 2-MN on acid sites was thus determined to be independent of the acid properties of the zeolites. Conversely, the rate constants for methylation and isomerization of 2-MN increased over Al-MTW with decreasing Si/Al ratio, which led to an increase in the yield of DMN and 1-MN. In contrast, the rate constant for methylation over Fe-MTW was the same value while that for isomerization was lower than that with Al-MTW (Si/Al = 100), which indicates that the isomorphous substitution of Al by Fe in the MTW structure maintains the methylation rate and decreases the isomerization rate. For this reason, the DMN selectivity and β,β-DMN fraction in the DMNs produced with Fe-MTW (100) was higher than those with Al-MTW (100).

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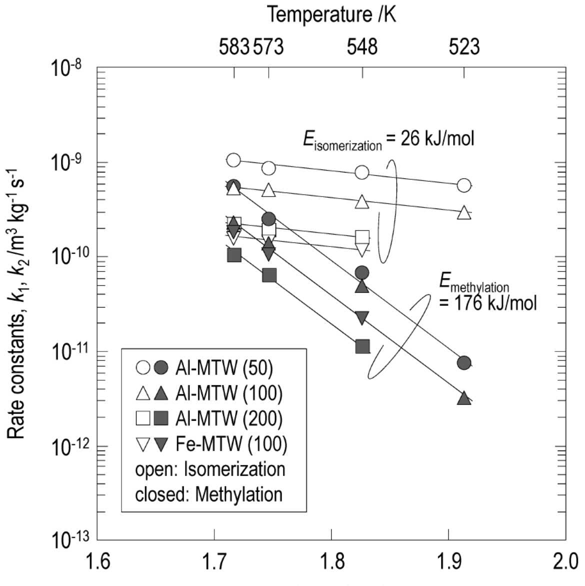

Reaction conditions: T = 523-583 K, time = 0-270 min.

Fig. 7 Arrhenius Plots of Rate Constants for the Methylation and Isomerization of 2-MN over Al-MTW (Si/Al = 50, 100 and 200) and Fe-MTW (Si/Fe = 100)

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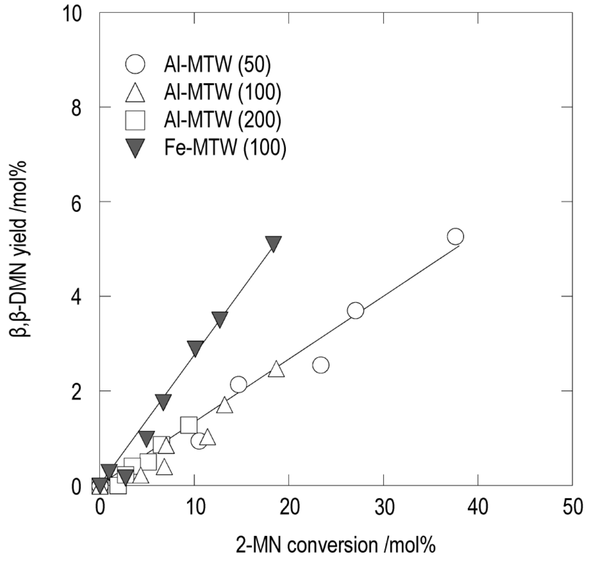

Reaction conditions: T = 523-583 K, time = 0-270 min.

Fig. 8 Relationship between the β,β-DMN Yield and 2-MN Conversion for 2-MN Methylation over Al-MTW (Si/Al = 50, 100 and 200) and Fe-MTW (Si/Fe = 100)

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要　　旨

MTW 型ゼオライト構造を有するアルミノシリケートおよびフェリシリケートを用いた 2-メチルナフタレンのメチル化反応とその速度解析

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MTW 型アルミノシリケートおよびフェリシリケートによる 2-メチルナフタレン（2-MN）のメチル化を高圧条件下で行い，速度解析を実施した。得られたメチル化および異性化の活性化エネルギーは酸量や骨格導入ヘテロ原子種によらず，それぞれ 176 kJ mol^{-1} および 26 kJ mol^{-1} と求まった。Si/Al 比の異なるアルミノシリケートを用いた場合，Al 量の増大に伴いメチル化および異性化の速度定数は向上した。一方，アルミノシリケート（Si/Al＝100）と比較して，フェリシリケート（Si/Fe＝100）のメチル化速度定数は同程度の値を示し，異性化速度定数は大きく低下した。異性化反応が抑制されるため，フェリシリケートは高いジメチルナフタレン（DMN）選択率および β,β-DMN 組成を示した。

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