

Size-Controlled Synthesis of Metallosilicates with MTW Structure and Catalytic Performance for Methanol-to-Propylene Reaction

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Abstract The synthesis of metallosilicates with a MTW structure was achieved using tetraethylammonium bromide methyltriethylammonium chloride (TEABr) and (MTEACl) as organic structure-directing agents (OSDAs). MTW zeolites (Al-MTW, Si-MTW, Fe-MTW and (Al, Fe)-MTW) were obtained by hydrothermal synthesis. The crystal size of the resulting MTW zeolite strongly depended on the type of OSDA, in which the column-like and agglomerated nano-sized crystals could be produced by using MTEACl and TEABr, respectively as an OSDA. Isomorphous substitution of Fe for Si was demonstrated by UV-vis spectra and *ac*-NH₃-TPD profiles. These analyses indicated that Fe atoms were incorporated into the lattice framework and that almost all of the Fe species were welldispersed without forming bulky iron oxide particles. The ac-NH₃-TPD profiles showed that the acid strength of the Fe-MTW zeolite was weaker than that of the Al-MTW zeolite. Al-MTW zeolites with different crystal sizes were applied to methanol-to-propylene reactions. The nanosized Al-MTW zeolite exhibited a longer catalyst life time compared to the macro-sized Al-MTW zeolite. Since decreasing the acid strength of the MTW zeolite inhibited

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excessive reactions followed by the formation of aromatics, the (Al, Fe)-MTW zeolite exhibited higher yields of propylene and butenes and a lower yield of aromatics compared with the Al-MTW zeolite.

Graphical Abstract



Keywords Size-controlled synthesis · Metallosilicate · MTW zeolite · Methanol to propylene reaction

1 Introduction

Zeolites, crystalline microporous aluminosilicates linked through oxygen atoms, possess three-dimensionally connected framework structures constructed from corner sharing TO₄ tetrahedra, where T is any tetrahedrally coordinated cation such as Si or Al. These framework structures are composed of *n*-rings, where *n* is the number of T-atoms in the ring (e.g., 4-, 5-, or 6-rings), and large pore openings of 8-, 10-, and 12- rings that are framed by these small rings. Because zeolites have micropore of a specific diameter almost equal to a diameter of lighter hydrocarbons, zeolites exhibit a remarkable molecular sieve effect for these hydrocarbons. Therefore, zeolites have been widely used as catalysts and adsorbents. Currently, 229 types of zeolites and related structures are recognized [1].

Recently, methanol to olefins and propylene (MTO and MTP, respectively) reaction using zeolite catalysts has attracted much attention because of their potential as alternative processes for the production of the lower olefins from non-petroleum sources [2-5]. MFI zeolites have been widely used for methanol conversion reactions [6-9]. In the production of olefins from methanol, the initial step is dehydration of the methanol to dimethyl ether, followed by the production of light olefins including ethylene and propylene. Moreover, butenes, higher alkenes (C5+ hydrocarbons), paraffin, and aromatics are usually obtained [10]. In the detailed reaction mechanism, the hydrocarbonpool mechanism proposed initially by Dahl and Kolboe [11, 12], and Olsbye et al. suggested the dual-cycle concept consisting of a methyl aromatics route and an olefins methylation/cracking route [13–15].

In this model, propylene and butenes are obtained from the olefins methylation/cracking route, whereas ethylene and aromatics are formed from the methyl aromatics route. Moreover, the aromatics are formed through cyclization of the higher alkenes formed in the olefins methylation/ cracking route [16]. Since propylene is mainly formed from the olefins methylation/cracking route, suppression of alkenes cyclization followed by the formation of aromatics leads to high propylene selectivity.

Wang et al. reported that the MTO reaction is a spacedemanding process and the size of key reactive hydrocarbon-pool intermediates for the MTO process is between 5.7 and 6.0 Å [17]. Because the channel intersection of MFI zeolite provides sufficient volume for the intermediates, MFI zeolite is a promising candidate for olefins production from methanol. However, its strong acidity leads to cyclization and intermolecular hydride transfer reactions to form paraffin and aromatics [14, 18-20]. In order to increase the yield of propylene from methanol, suppression of cyclization of intermediates is necessary. It is well known that the strength of Brønsted acid sites can be modulated by isomorphic substitution of Si for trivalent atoms other than Al [21, 22]. The substitution of Al for Fe in the zeolite framework (e.g., LTA, MFI, and MOR zeolites) has been reported [23–28] and highly selective production of light olefins from methanol was achieved using Fe containing MFI zeolite (Fe-MFI) [26-28]. On the other hand, since the channel intersection for MFI have a critical dimension of nearly 9.0 Å [29], it provides enough volume for cyclization reaction by which higher alkenes can be converted into aromatics [14, 30].

As described above, the suppression of the alkenes cyclization followed by the formation of aromatics is a desirable approach to increase propylene selectivity. MTW zeolite, which was first reported by Rosinski and Rubin in 1974 [31], possesses one-dimensional 12-ring pores $(5.6 \times 6.0 \text{ Å})$, so MTW zeolite provides pore space for the reactive hydrocarbon-pool intermediates in the MTO reaction. Although the pore size of MTW zeolite is larger than that of MFI zeolite, it is smaller than the critical dimension of channel intersection for MFI zeolite. The non-intersecting one-dimensional structure of MTW zeolite provides insufficient volume for cyclization reaction, which is expected to suppress cyclization reactions, leading to high propylene selectivity. In contrast, although isomorphous substitution of other hetero atoms in the MTW zeolite framework [32] has been reported by Zhi et al., there are few reports concerning methanol-to-olefins reactions over MTW zeolite [17, 33].

In this study, the substitution of Fe for Al in the MTW structure was demonstrated using TEABr and MTEACl as organic structure-directing agents (OSDAs). Metallosilicates with MTW structures (Al-, Si-, Fe-, and (Al, Fe)-MTW zeolites) could be obtained using these OSDAs. We found that the crystal size of the MTW metallosilicate depended on the type of OSDA, and nano-crystalline MTW zeolite could be obtained using TEABr. These zeolites were applied to the methanol-to-propylene (MTP) reaction as catalysts, and the effects of the crystal size and physico-chemical properties of the prepared MTW zeolites on catalytic stability and product selectivity during the MTP reaction was examined.

2 Experimental

2.1 Synthesis of Metallosilicates with MTW Structure

Raw materials used included the following: colloidal silica (Sigma-Aldrich, Co., LLC.) as a Si source, and sodium aluminate (Wako Pure Chemical Industries, Ltd.) and/or iron (III) nitrate enneahydrate (Wako Pure Chemical Industries, Ltd.) as T (T = Al and/or Fe, respectively) sources. Sodium hydroxide (Wako Pure Chemical Industries, Ltd.) was used as an alkali source. A variety of OSDAs, including alkylammonium ions, alkylamines, and nitrogen-containing polymers, direct the crystallization of the MTW zeolite, but the most commonly used OSDAs include tetraethyl and methyltriethylammonium cations, TEA and MTEA, respectively [34]. In this study, tetraethylammonium bromide (TEABr, Wako Pure Chemical Industries, Ltd.) or triethylmethylammonium chloride (MTEACl, Tokyo Chemical Industry Co., Ltd.) was used as an OSDAs source.

A series of Al-, Si-, Fe-, and (Al, Fe)-MTW zeolites with different Si/T ratios (T = Al and/or Fe) was prepared by hydrothermal synthesis under static conditions. An aqueous solution containing Si, T sources and OSDA was prepared. The synthetic gel composition was 10 Na₂O: x OSDA: 100 SiO₂: y T₂O₃: 5555 H₂O, where (x,y) = (20,0) to (60,1). The (x,y) value was adjusted depending on the amount of OSDA and T source, respectively, added to the synthetic gel. Scheme 1 shows the synthetic procedure of MTW zeolites. The order of Si and T source addition is different in synthetic procedure A from that of B.

For both procedures, the synthetic gel was transferred to a Teflon-sealed stainless steel bottle, and hydrothermal treatment was carried out at 423 K for a designated period in an oven under static conditions with autogenous pressure. After hydrothermal treatment, the product was separated from the liquid by centrifugation, followed by washing of the solid with distilled water and 2-propanol and then drying overnight at 383 K. The OSDA was removed by calcination in a muffle furnace at 823 K for 12 h in air.

2.2 Characterization of Metallosilicate with MTW Structure

The crystallinity and phase purity of each zeolite crystal was examined using X-ray diffract meter (XRD, JEOL JDX). The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F). BET area was measured using nitrogen adsorption at 77 K (BEL Japan, Inc., Belsorp mini). The composition of the samples (Si/T atomic ratio) was determined using X-ray fluorescence analysis (XRF, Rigaku Supermini 200). Acidity was determined from *ac*-NH₃-TPD profiles [35]. UV–vis diffuse reflectance spectra were measured using a JASCO V-670 unit, in the wavelength range from 200 to 700 nm.

2.3 Methanol-to-Propylene Reaction

The MTW zeolite powders used for the MTP reaction were pelletized, crushed and sieved to yield samples ca. 300 μ m in diameter. The Si/T ratio of samples used for the MTP reaction was 100. The MTP reaction was carried out using a fixed bed reactor under a N₂ stream at 723 K and atmospheric pressure. The methanol was introduced to the reactor using syringe pump. The introduced methanol was vaporized by passage of preheater at 423 K. The partial pressure of methanol was 23.5 kPa. The weight ratio of the catalyst [g] to the methanol feed rate [g h^{-1}] was in the range from 0.1 to 0.2 h. The composition of the exit gas was measured using on-line gas chromatography (GC-2014, Shimadzu Co., Ltd.) using a Porapak-Q column with a thermal conductivity detector (TCD), and a Gaskuropack 54 and SP-1700 column with a flame ionization detector (FID). The conversion of each reaction was calculated based on the amount of methanol transformed to reaction products, excluding dimethyl ether. The amount of coke deposited on each catalyst after the MTP reaction was measured by thermogravimetry (TGA-50, Shimadzu Co., Ltd.).

3 Results and Discussion

3.1 Synthesis of Al-MTW Zeolites and Effects of Gel Compositions

Table 1 shows the compositions of the synthetic gels and the characteristics of the products. Synthetic procedure A was employed in preparation of Al-MTW zeolites. Figures 1 and 2 show X-ray diffraction patterns and SEM photographs of the prepared samples at different Si/Al ratio using TEABr (Al01, Al02, Al03) and MTEACl (Al04, Al05, Al06) as OSDAs, respectively. The hydrothermal time was 6 days. As shown in Fig. 1, all prepared samples showed peaks corresponding to a MTW zeolite structure. Though the BET areas of these samples showed almost the same values of approximately 330 m²/g, the XRD pattern of the prepared samples depended on the type of OSDA. The MTW zeolite prepared using TEABr (Al01, Al02, Al03) exhibited an XRD pattern with a larger half-width compared to that of the samples prepared using MTEACl (Al04, Al05, Al06), indicating that the crystal morphology is deferent.

The effect of the type of OSDA on the crystal size and morphology of the prepared MTW zeolites is shown in Fig. 2. The crystal size of the prepared MTW zeolites depended strongly on the type of OSDA, regardless of the Si/Al ratio. When using MTEACl, columnar grain growth on a macro order was observed. In contrast, the use of TEABr resulted in agglomeration of small crystals of ca. 50 nm in diameter.

The difference in crystal morphology was attributed to different nucleation and growth rates of the zeolite crystal during hydrothermal synthesis. To investigate this in detail, changes in the crystallinity of MTW zeolites with hydrothermal time were examined. The intensity of the XRD pattern increased with hydrothermal time. After 6 days, well-crystallized MTW zeolites were obtained, and no further improvement in the pattern was observed. Accordingly, this sample was used as a standard to



Scheme 1 Synthetic procedure of MTW zeolites

calculate the crystallinity of all synthesized samples. Figure 3 shows the changes in crystallinity of the MTW zeolites with synthesis time. In MTEACl, the peaks corresponding to MTW zeolite appeared after 3 days, and the crystallinity gradually increased with hydrothermal time. In TEABr, a long induction period of approximately 4 days was required to form zeolite nuclei, and the crystallinity increased dramatically to reach almost 100 % for 1 day, considering that the smaller crystals but higher in the amount of nuclei is reason for longer induction period, leading to formation of nanocrystal. When using MTEACl, nucleation occurred at an initial stage, followed by crystal growth. Because crystal growth occurred mainly during hydrothermal synthesis, columnar macro-sized MTW zeolites could be obtained. In contrast, when using TEABr, a burst of nucleation occurred after a long induction period, which caused rapid crystallization of MTW zeolites that produced only nano-sized MTW zeolites.

3.2 Synthesis of Metallosilicate with MTW Structure

The synthesis of metallosilicates with a MTW structure (Si-MTW, Fe-MTW, and (Al, Fe)-MTW) was conducted hydrothermally at different Si/T ratio (Si/T = 50 to ∞). The hydrothermal time was 6 days. The synthetic gel conditions and characteristics of the products are listed in Table 2.

The synthesis of Si-MTW was conducted at different OSDA/Si ratios using TEABr (Si01, Si02). Although the prepared samples showed peaks corresponding to the MTW zeolite structure, an amorphous phase was mainly formed at an OSDA/Si ratio of 0.2. In contrast, well-crystallized Al-MTW zeolites were obtained at an OSDA/Si ratio of 0.2 (see Table 1; Fig. 1). The presence of aluminum in a synthetic gel stabilizes the OSDAs during hydrothermal treatment [36, 37]. In the synthesis of metallosilicates with a MTW structure, the OSDAs were not stable without aluminum, leading to the formation of an amorphous phase at low OSDA/Si ratios. Therefore, greater OSDA/Si ratios were required to obtain pure Si-MTW zeolite compared to Al-MTW zeolite. During the preparation of Fe-MTW zeolite, a high OSDA/Si ratio was employed to achieve greater crystallinity of the MTW phase.

In the preparation of Fe-MTW zeolites, the effect of the synthetic procedure on crystal structure and the incorporation of Fe atoms was examined. Fe-MTW zeolites were prepared at a Si/Fe ratio of 100 by using TEABr and employing synthesis procedures A and B; the products are denoted as samples Fe01 and Fe02, respectively. The XRD patterns of Fe01 and Fe02 exhibited the typical MTW structure. However, the XRD patterns did not provide conclusive evidence of isomorphous substitution of Fe for Si in the MTW framework.

The color of the prepared sample acts as a simple indicator of whether bulk iron oxide exists in the sample [38]. The color of the calcined samples Fe01 and Fe02 were brown and completely white, respectively. The brown color of sample Fe01 indicated that it contained aggregated iron oxide clusters. For sample Fe02, the white color was retained after calcination, indicating that no bulk iron oxide apparently existed. On the basis of all the above evidence, it was not concluded that isomorphous substitution of Fe for Si in the crystalline lattice of MTW zeolite had been

Run	Si/Al ratio (gel)	OH/Si	OSDA/Si	Synthesis time (day)	OSDA source	Phase	Si/Al ratio (product)	BET area (m ² /g)
AL01	50	0.2	0.2	6	TEABr	MTW	65	345
AL02	100	0.2	0.2	6	TEABr	MTW	122	343
AL03	200	0.2	0.2	6	TEABr	MTW	234	324
AL04	50	0.2	0.2	6	MTEACI	MTW	62	319
AL05	100	0.2	0.2	6	MTEACI	MTW	149	325
AL06	200	0.2	0.2	6	MTEACI	MTW	222	316
AL07	50	0.2	0.2	1	TEABr	Amorphous	_	-
AL08	50	0.2	0.2	2	TEABr	Amorphous	_	-
AL09	50	0.2	0.2	3	TEABr	Amorphous	_	-
AL010	50	0.2	0.2	4	TEABr	Amorphous	_	-
AL011	50	0.2	0.2	5	TEABr	MTW	_	344
AL012	50	0.2	0.2	10	TEABr	MTW	_	338
AL013	50	0.2	0.2	1	MTEACl	Amorphous	_	-
AL014	50	0.2	0.2	2	MTEACl	Amorphous	_	-
AL015	50	0.2	0.2	3	MTEACl	Amorphous + MTW	_	82
AL016	50	0.2	0.2	4	MTEACl	MTW	_	210
AL017	50	0.2	0.2	5	MTEACl	MTW	_	301
AL018	50	0.2	0.2	10	MTEACl	MTW	-	280

Table 1 Composition of synthetic gel and product characteristics of Al-MTW zeolites

Fig. 1 X-ray diffraction patterns of Al-MTW zeolites with different Si/Al ratios obtained using a TEABr and **b** MTEACl

(a) Using TEABr



demonstrated. These are necessary but not sufficient conditions to prove the occurrence of isomorphous substitution, and consequently other characterization techniques must be used to assess the incorporation of the Fe atoms into framework positions.

Characterization by UV-vis spectra and ac-NH₃-TPD profiles was applied to determine the nature and distribution of iron species in the prepared samples. Figure 4 shows the UV-vis spectra of Fe01 and Fe02. For comparison, the spectrum of a sample with mechanically mixed Fe₂O₃ and SiO₂ is also shown. Bands between 200 and 300 nm are typically attributed to isolated Fe³⁺ species, either tetrahedrally coordinated in the zeolite framework or with higher coordination. Octahedral Fe³⁺ ions in small oligonuclear $Fe_x^{3+}O_y$ complexes give rise to broad bands between 300 and 450 nm, and bands above 450 nm are characteristic of Fe³⁺ ions in large iron oxide aggregates [39]. The UV-vis spectrum of Fe01 showed a charge transfer band between 200 and 300 nm, as well as broad absorption bands of comparatively low intensity at







Fig. 3 Crystallization kinetics of Al-MTW zeolites during synthesis with TEABr (*circle*) and MTEACl (*triangle*)

wavelengths higher than 450 nm, indicating the presence of octahedral Fe^{3+} ions in small oligonuclear $Fe_x^{3+}O_y$ complexes (possibly iron oxide). In contrast, the UV–vis spectrum of Fe02 displayed a band at 200–300 nm, with no contribution above 450 nm, indicating that the majority of Fe^{3+} species in the samples were well isolated. This result demonstrates that no iron oxide particles were formed in Fe02.

Figure 5 shows the *ac*-NH₃-TPD profiles of Fe01 and Fe02. The peaks at desorption temperatures above 550 K were associated with desorption of NH₃ adsorbed on strong acid sites, whereas peaks below 550 K were assigned to NH₃ weakly held or physically adsorbed on zeolite crystals. Since these strong acid sites could have been generated only by protons associated with trivalent atoms in lattice positions, the presence of strong acid sites was

Table 2 Composition of synthetic gel and product characteristics of MTW metallosilicates

Synthetic gel						Product					
Run	Procedure	Si/Al ratio	Si/Fe ratio	OH/Si	OSDA/ Si	Synthesis time (day)	OSDA source	Phase	Si/Al ratio	Si/Fe ratio	BET area [m2/g]
Si01		_	_	0.2	0.2	6	TEABr	Amorphous + MTW	_	_	_
Si02		-	_	0.2	0.6	6	TEABr	MTW	_	_	-
Si03		-	_	0.2	0.6	6	MTEACl	MTW	_	_	-
Fe01	А	-	100	0.2	0.6	6	TEABr	MTW	_	88	302
Fe02	В	-	100	0.2	0.6	6	TEABr	MTW	_	88	352
Fe03	В	-	50	0.2	0.6	6	TEABr	Amorphous	_	_	-
Fe04	В	-	200	0.2	0.6	6	TEABr	MTW	_	165	-
Fe05	В	-	100	0.2	0.6	6	MTEACl	MTW	_	68	248
Fe06	В	-	50	0.2	0.6	6	MTEACl	Amorphous	_	_	-
Fe07	В	-	200	0.2	0.6	6	MTEACl	MTW	_	161	-
AlFe01	В	200	200	0.2	0.6	6	TEABr	MTW	235	183	304
AlFe02	В	200	200	0.2	0.6	6	MTEACl	MTW	233	163	-



Fig. 4 UV-vis spectra of Fe-MTW (Si/Fe = 100) prepared using TEABr by synthetic procedure A and B, corresponding to *a* Fe01 and *b* Fe02, and *c* mechanically mixed Fe₂O₃ and SiO₂



Fig. 5 *ac*-NH3-TPD profiles of Fe-MTW prepared using procedure A and procedure B, corresponding to Fe01and Fe02, respectively

strong evidence of isomorphous substitution of Fe for Si in the MTW framework. Fe01 exhibited only one NH₃ desorption peak, this result clearly shows that Fe01 possessed no strong acid sites, indicating that Fe atoms were not incorporated into the MTW framework. In contrast, Fe02 exhibited two NH₃ desorption peaks, and the presence of strong acid sites demonstrated the incorporation of Fe atoms into the MTW framework. These results indicated that the synthetic procedure was an important factor affecting efficiency in the incorporation of Fe atoms into the MTW framework.

In accordance with procedure A, the synthetic gel became a red-brown color after addition of the Fe source, indicating that agglomerated ferric hydroxide had been formed during synthetic gel preparation. In procedure B, the synthetic gel became a yellow-brown color after addition of the Fe source, which indicated that the Fe species were adsorbed on the zeolite synthetic gel as ions state. Because the Fe species were added to the synthetic gels in which Si species was well dispersed, the formation of ferric hydroxide was suppressed by interaction of Fe and Si species, leading to incorporation of Fe atoms into the MTW framework.

MTW zeolites containing Fe atoms were prepared at different Si/Fe ratios and with different OSDAs employing synthetic procedure B. Figure 6 shows the XRD patterns of samples prepared at different Si/T ratios using TEABr (Fe02, Fe03, Fe04, AlFe01, Si02) and MTEACl (Fe05, Fe 06, Fe07, AlFe02, Si03) as OSDAs. No peaks corresponding to the MTW zeolite structure were observed in samples prepared at Si/Fe ratios below 50, indicating that the addition of an excess amount of the Fe source (iron (III) nitrate enneahydrate) suppressed the formation of MTW zeolite structure were observed in samples prepared at Si/Fe ratios corresponding to the MTW zeolite structure were observed in Si/Fe ratios above 100, regardless of the type of OSDA.

The crystal morphologies of the prepared metallosilicates with a MTW structure were obtained using FE-SEM. As shown in Fig. 7, the crystal size of metallosilicates with a MTW structure depended strongly on the type of OSDA and nano-sized zeolites could be synthesized using TEABr. The dependence of the crystal morphology of Si-, Fe-, and (Al, Fe)-MTW zeolites on the type of OSDA was similar to that of Al-MTW, indicating that the type of OSDA was the most important factor affecting the crystal morphology and size of the MTW zeolite. The samples prepared by TEABr and MTEACl were denoted as nano-MTW and macro-MTW, respectively.

Figure 8 shows the *ac*-NH₃-TPD profiles of the nano-Al, Fe-, and (Al, Fe)-MTW zeolites (Al02, Fe02, AlFe01). The Si/T ratio of these samples was 100. The NH₃ desorption peak was shifted to lower temperatures in the order: Al-MTW > (Al, Fe)-MTW > Fe-MTW, indicating that the acid strength depended on the type of heteroatom. Since the acid amount of these samples is almost the same, these samples were applied to MTP reaction as catalysts, and catalytic performance was measured.

3.3 Methanol-to-Propylene Reaction

3.3.1 Effect of Crystal Size on Catalyst Lifetime

The effects of the crystal size and acidity of the MTW zeolite on the MTP reaction were examined. Before the reaction, the zeolite catalysts underwent ion-exchange in an NH₄NO₃ aqueous solution to prepare the H-type counterpart of each zeolite. The MTP reaction was conducted over Al-MTW (Si/Al = 100) with different crystal sizes at 723 K with a *W/F* ratio of 0.1 h to clarify the effect of crystal size on catalytic performance. Figure 9 shows the changes in conversion with time on stream over the nano-



Fig. 7 SEM photographs of MTW zeolites obtained using a TEABr and b MTEACl

Al-MTW and macro-Al-MTW. As shown in Fig. 9, conversion dramatically decreased with time on stream in the macro-Al-MTW. In contrast, the nano-Al-MTW maintained the initial conversion after 260 min. The amounts of coke formed on the macro- and nano-Al-MTW during the MTP reaction were 5.9 and 0.9 wt%, respectively. Although the nano-Al-MTW possessed physical/chemical properties (i.e., BET area, acid amount, acid strength) similar to those of the macro-Al-MTW, the changes in conversion and the amount of coke deposition were different, indicating that the crystal size of the catalyst strongly affected the catalyst lifetime and catalytic performance.

Because the diffusion length of the reactant and products was assignable to the crystal size, the residence time of the reactant and products inside the zeolite channels becomes



Fig. 8 *ac*-NH₃-TPD profiles of nano-Fe-MTW, nano-(Al, Fe)-MTW, nano-Al-MTW. Si/T ratio of samples is 100

longer in the macro crystal, so that the excessive reactions to form aromatics and coke tended to proceed in the macro-Al-MTW. In the nano-Al-MTW, larger external surface area and smaller diffusion resistance of reactant/product within the micropore resulted in stable activity.

3.3.2 Effect of Zeolite Acidity on Product Yield

Since acid strength affects the progress of the methanol conversion reaction, the effect of acidity on catalytic performance was investigated using the nano-Fe-MTW and



Fig. 9 Changes in conversion with time on stream for MTP reaction over Al-MTW with different crystal sizes

nano-Al-MTW as catalysts. The MTP reaction was conducted at 723 K with a *W/F* ratio of 0.1 h. The Si/T ratio of these catalysts was 100. For comparison, Al-MFI zeolite with crystal size of approximately 100 nm (nano-Al-MFI, Si/Al = 100) was applied to MTP reaction at 723 K with a *W/F* ratio of 0.1 h. It was confirmed that the *ac*-NH₃-TPD profiles of the nano-Al-MFI is similar to that of the Nano-Al-MTW, indicating that the two zeolites possessed almost same acid amount and acid strength. The detailed preparation method of nano-Al-MFI was explained in our previous study [40].

Figure 10 shows the product yield after 20 min for the MTP reaction at 723 K. As shown in Fig. 10, the nano-Al-MFI exhibited higher aromatics and ethylene yield and lower propylene yield compared to the nano-Al-MTW. Because channel intersection of the MFI zeolite provides enough volume for cyclization reactions, higher alkenes was converted into aromatics [14, 30], leading to high yield of aromatics due to greater contribution of the methyl aromatics route. Aromatics and ethylene were formed to a slight extent in the nano-Fe-MTW and nano-Al-MTW, indicating that the formation of aromatics was effectively suppressed due to the non-intersecting one-dimensional structure of the MTW zeolite.

However, the initial conversion using the nano-Fe-MTW was as low as 72 C-mol% and yield of C5+ hydrocarbons was higher than that of the reaction using the nano-Al-MTW, indicating that the weak acidity of the nano-Fe-MTW was not enough to crack the C5+ hydrocarbons. In order to increase the yields of propylene and





Fig. 10 Product yield of exit



Fig. 11 Changes in methanol conversion, product selectivity and olefin composition with time on stream over nano-(Al, Fe)-MTW

butenes from the cracking of C5+ hydrocarbons, the nano-(Al, Fe)-MTW, which possesses strong and weak acid sites ascribable to Al and Fe, respectively, was applied to the MTP reaction. In order to obtain the same amount of Fe and Al within the reactor, a W/F ratio of 0.2 h was employed.

As shown in Fig. 10, the nano-(Al, Fe)-MTW gave higher yields of propylene and butenes compared to the nano-Al-MTW, and the total yield reaching more than 70 C-mol%. In addition, the aromatics and ethylene yields of the nano-(Al, Fe)-MTW were lower than those of the nano-Al-MTW and the C5+ hydrocarbons yield of the nano-(Al, Fe)-MTW was lower than that of the nano-Fe-MTW, indicating that the introduction of weak acid sites in the Al-MTW led to suppression of the formation of aromatics while retaining cracking ability. Figure 11 shows the changes in conversion, product selectivity and olefin composition with time on stream over the nano-(Al, Fe)-MTW. The conversion remained at approximately 98 C-mol% during the reaction. Moreover, the product yields and olefin selectivity were also stable, indicating that the nano-(Al, Fe)-MTW possesses high catalytic stability.

Therefore, although MTW zeolite possesses one-dimensional pore, it was concluded that the pore size was sufficiently large for the olefins methylation/cracking route to produce propylene and that the co-existence of Al and Fe in the MTW zeolite framework was effective in increasing the yields of propylene and butenes.

4 Conclusion

A series of Al-, Si-, Fe-, and (Al, Fe)-MTW zeolites were synthesized using TEABr and MTEACl as OSDAs. The crystal size and morphology were founded to depend on the type of OSDA, nano-sized MTW zeolites obtained using TEABr, regardless of variations in the T site atom. The synthetic procedure is an important factor affecting efficiency in the incorporation of Fe atoms into the framework. The isomorphous substitution of Fe for Si was demonstrated using UV-vis spectra and ac-NH₃-TPD profiles. These analyses showed that Fe atoms were incorporated into the lattice framework and that almost all of the Fe³⁺ species was well dispersed without forming bulky iron oxide particles. In addition, the ac-NH₃-TPD profiles demonstrated that the acid strength of the Fe-MTW zeolite was weaker than that of the Al-MTW zeolite. In the methanol-to-propylene reaction, the nano-Al-MTW zeolite exhibited a longer catalyst lifetime than the macro-Al-MTW zeolite. Accordingly, the nano-sized zeolite is considered a promising material for increasing the external surface area as well as decreasing the diffusion resistance of the reactant within the micropore, which improves the catalytic activity and catalyst lifetime. Moreover, employing the nano-(Al, Fe)-MTW zeolite during the MTP reaction gave higher yields of propylene and butenes in conjunction with lower yields of aromatics and ethylene, compared with the nano-Al-MTW zeolite, indicating that the cyclization of C5+ hydrocarbons was suppressed while retaining cracking ability. The nano-(Al, Fe)-MTW zeolite, which possesses a non-intersecting one-dimensional structure and contains strong and weak acid sites derived from Al and Fe atoms, respectively, is responsible for the greater contribution of the olefins methylation/cracking route, leading to the high yields (above 70 C-mol%) of propylene and butenes.

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