1. Introduction

"MSE" is one of the known “framework type codes (FTCs)” approved by International Zeolite Association (IZA) \(^1\). The IZA recommendation is that the FTC should be in bold text, but plain text is used here for simplicity. MCM-68 is a typical zeolite with the MSE framework (“type material” of MSE) first synthesized by Mobil researchers \(^2\). UZM-35 \(^3\) and YNU-2 \(^4\) are related materials with the same MSE topology.

Organic structure-directing agents (OSDAs) are used in syntheses of MSEs, incorporating the organic cation N,N,N’,N’-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrolidinium (TEBOP\(^2\)) as shown in Fig. 1 (left) for the syntheses of MCM-68 and YNU-2, and Me\(_2\)Pr\(_2\)N\(^+\) (Fig. 1, right) for UZM-35. The MSE is an example of a new multi-dimensional framework with a 12-10-10-ring pore system, which contains a straight 12-ring channel (Fig. 2(a)) that intersects with two independent tortuous 10-ring channels as well as an 18-12-ring supercage (Fig. 2(b)) accessible only through the 10-ring channels \(^5\). This framework also possesses eight distinct T-sites \(^1\) \(^5\). Zeolites of this type in \(H^+\)-form are known to exhibit unique catalytic properties \(^6\) \(^7\) and are potentially useful as shape-selective catalysts for the alkylation of aromatics \(^8\) \(^9\), disproportionation of ethylbenzene and bifunctional isomerization of \(n\)-alkanes \(^10\) as well as for the production of propylene by...
paraffin cracking). Post-synthetic dealumination is very important to fabricate high-performance catalysts for these processes. These materials can function as hydrocarbon traps without dealumination. In addition, Fe-containing MCM-68 prepared by a direct hydrothermal method (Fe-HMCM-68) or by impregnation of MCM-68 with different iron precursors (FeOCl/HMCM-68, FeCl3/HMCM-68) act as the catalysts for Friedel-Crafts-type benzylaion of toluene. Titanium-substituted MCM-68 has demonstrated superior performance as an oxidation catalyst to TS-1 ([Ti]-MFI) for the oxidation of phenol and olefins using H2O2 as the oxidant.

The original synthesis of MCM-68 was possible only under hydrothermal conditions using TEBOP2+ as the OSDA. The gel composition window for the successful crystallization of pure MCM-68 is very narrow and the Si/Al ratio of the product is limited to the range of 9 to 12. The synthesis of MCM-68 also requires a prolonged crystallization period of more than 10 days. Changes to the chemical composition of the product through the direct crystallization of a pure MSE phase is difficult to achieve, and tends to instead generate other phases such as BEA, MTW or MOR. We have previously succeeded in overcoming this limitation by utilizing the steam-assisted crystallization (SAC) method with some post-synthetic modification to obtain a pure-silica version of MSE (YNU-2). This process requires a crystallization period of ca. 5 days. We were subsequently successful in the synthesis of an Al-rich MSE-type zeolite (YNU-3) with a Si/Al molar ratio of approximately 7, requiring a relatively short crystallization period of only 3 days, via the hydrothermal conversion of an FAU-type zeolite. However, the use of TEBOP2+ as an OSDA was still necessary, and the efficiency of crystallization as well as the phase-selection was sensitive to the synthesis conditions in all cases. These findings indicate the difficulty of the MSE synthesis even with the use of an OSDA.

MSE-type zeolites were also successfully synthesized under OSDA-free conditions. The as-synthesized Al-rich products were stabilized and dealumminated by steaming treatment followed by heating in a nitric acid solution. The steaming treatment probably causes Si-migration during the steaming process is suggested.

In this review article, we summarize the advances in the preparation and utilization of solid acid catalysts based on various MSE-type zeolites for the selective production of light olefins, especially propylene, from petroleum and non-petroleum resources.

2. Various Techniques for the Preparation of Solid Acid Catalysts Based on MSE-type Zeolites

2.1. Conventional Hydrothermal Synthesis

The first synthesis of MCM-68 was achieved under hydrothermal conditions by using TEBOP2+ (I–) as an OSDA, and this is still the most typical route to MCM-68. A typical gel composition is 1.0SiO2–0.1TEBO2+ (I–)2–0.375KOH–0.1Al(OH)3–30H2O and the gel is kept statically at 160 °C for 16 d to give the desired product. This method has the disadvantages of the very narrow gel-composition window for the successful crystallization of pure MCM-68 and limited Si/Al ratio of 9-12, as well as difficulty in changing the chemical composition of the product through the direct crystallization of a pure MSE phase resulting in other phases such as *BEA, MTW, or MOR.

2.2. Hydrothermal Conversion Using FAU-type Zeolite as a Precursor

The requirement for a crystallization period of 14 days or more during the conventional synthesis of MCM-68 is an important issue to be resolved, although the synthesis of the UZM-35 zeolite, which has an identical topology to MSE, can be synthesized in 5-9 days by using a processing temperature of 175 °C with Me3PzN˚OH as the OSDA. A promising strategy to accelerate the crystallization of a certain zeolitic phase is hydrothermal conversion. Since the first report of the hydrothermal conversion of zeolite A (LTA) into sodalite (SOD) and zeolite P (GIS), this alternative method has attracted considerable attention. Hydrothermal conversion of a low density zeolite into a high-density zeolite is possible; for example, they transformed zeolite Y (FAU) transformed into SSZ-13 (CHA) and [B]-beta (*BEA) into [B]-SSZ-24 (AFI), [B]-SSZ-31 (*STO), or [B]-SSZ-33 (*CON) (I–)2_0.375KOH_0.1Al(OH)3_30H2O and (I–)2 as an OSDA. A promising strategy to change the chemical composition of the product through the direct crystallization of a pure MSE phase resulting in other phases such as *BEA, MTW, or MOR.

More recently, rapid crystallization of various zeolites was achieved from an FAU-type zeolite in the presence of a specific OSDA, including the successful transformation of the FAU phase into *BEA, RUT, CHA, LEV, MTN, and OFF phases. Synthesis of CHA-type zeolite from LEV-type zeolite was also reported. Locally ordered aluminosilicate species resulting from the decomposition and dissolution of FAU-type zeolites under hydrothermal conditions may be present in the synthetic media, and that assembling such aluminosilicate species with the aid of OSDAs leads to the observed increased rates of crystallization. Rapid crystallization of an MSE-type zeolite was achieved by using an FAU-type zeolite and TEBOP2+ (I–) as the starting material and OSDA, respectively. The aluminum-rich MSE-type zeolite successfully obtained...
from the FAU-type zeolite has special physicochemical features, so is referred to as [Al]-YNU-3. [Al]-YNU-3 with Si/Al ratio as low as 7 has been successfully synthesized in a remarkably short crystallization period of only 3 days by the hydrothermal conversion of an FAU-type zeolite, presumably by the assembly of 4-ring aluminosilicate oligomers supplied by the double 6-ring (D6R) components of the FAU framework with the aid of TEBOP\(^{24}\) and seed crystals. In another example of the use of a specific zeolite, FER was used as the precursor and the hydrothermal synthesis was carried out by rotating the autoclave at 60 rpm\(^{48}\).

2.3. OSDA-free Synthesis

A working hypothesis was proposed for the seed-assisted, OSDA-free synthesis of zeolites on the basis of the results of the OSDA-free syntheses of beta, mordenite, and ferrierite\(^{49}\). This hypothesis involves structural consideration of the common composite building units (CBUs) between the seed zeolite and the zeolites obtained from seed-free gels. By applying this hypothesis, seed assisted, OSDA-free syntheses of ZSM-5, ZSM-11, and ZSM-12 were successfully performed\(^{49,50}\). Furthermore, an alternative successful route to the OSDA-free synthesis of ZSM-12 (CBU: bik, jbw, mtw, cas) was accomplished with the aid of beta seeds based on considering the combination of the CBUs in the beta seeds (mtw) and the gel-yielding ZSM-5 (cas) when no seeds were added. This working hypothesis was applied to the crystallization of MSE phase without the use of any OSDA. As a result, fine tuning of the starting gel including alkaline contents enabled the seed-assisted, OSDA-free synthesis of MSE-type zeolite (designated as MSE\(_{\text{OSD}}\))\(^{23}\), and the optimal ratio of K/[Na + K] was found to be 0.067. Accordingly, syntheses were carried out by adding the calcined MCM-68 seeds (Si/Al = 11) to OSDA-free (Na, K)-aluminosilicate gels with the molar composition 1.0SiO\(_2\)-0.3Na\(_2\)O-0.3K\(_2\)O-0.01Al\(_2\)O\(_3\)-20H\(_2\)O. Typical crystallization temperature and time were 140 °C and 48 h, respectively. Reproducible synthesis was possible even at increased synthetic scale involving five times larger quantities than the initial investigations (from 30 mmol-SiO\(_2\) to 150 mmol-SiO\(_2\)), affording pure MSE phases in constant yields. The product yields (defined here as the mass of dried product per a total mass of starting silica, sodium aluminate, and seed) were within the range of 20-21 % and quite reproducible under the current synthesis conditions.

The obtained MSE\(_{\text{OSD}}\) was not always stable during the dealumination by acid-treatments (see Section 3.1.2).

3. Post-synthetic Modification for Catalytic Application

This section discusses dealumination by acid-treatment as an important part of post-synthetic modification.

3.1. Dealumination of MSE-type Zeolite

3.1.1. Direct Dealumination by Acid-treatment

Zeolite samples are specified in this article by including their Si/Al molar ratio in parentheses following the name of zeolitic material; for example, the MCM-68 with Si/Al = 10 is designated as MCM-68(10). MCM-68 zeolites with high Si/Al molar ratios can be prepared by treating the parent MCM-68(10) with acid solution to remove framework aluminum species\(^{35}\). In practice, the samples were heated at 80-100 °C in diluted nitric acid with 1-6 mol L\(^{-1}\) for 2-24 h, resulting in the formation of MCM-68(47), MCM-68(69), MCM-68(98), MCM-68(134), MCM-68(159), MCM-68(215), and MCM-68(308). These products were used to catalyze the DTO reactions (Section 4.2.) and a typical catalyst MCM-68(64.5) for the hexane cracking reaction was similarly derived from MCM-68(11). Dealuminated MCM-68 maintains the MSE framework after acid treatment indicating that the framework of MCM-68 was quite stable against acid treatment. The particle size of ion-exchanged MCM-68 zeolites was about 100 nm and no change in morphology or particle size was observed. The N\(_2\) adsorption-desorption of MCM-68 followed typical type I isotherms, and their BET surface areas and micropore volumes were unchanged before and after acid treatments (BET surface areas: 490-560 m\(^2\) (g-cat.)\(^{-1}\), micropore volume: 0.181-0.188 cm\(^3\) (g-cat.)\(^{-1}\), indicating that the dealumination process did not change the porosity of MCM-68. The use of nitric acid with higher concentrations gave the MCM-68 with higher Si/Al ratios as well as a smaller number of acid sites according to the temperature-programmed desorption of ammonia (NH\(_3\)-TPD) profiles. Therefore, the MCM-68 products with different Si/Al ratios showed no significant differences in X-ray diffraction (XRD) patterns, scanning electron microscope (SEM) images and N\(_2\) adsorption isotherms, and the physical properties such as framework and pore structures were similar except for the number of acid sites. The controllable Si/Al ratio of MCM-68 with maintained framework structure is a valuable feature for a solid acid catalyst. Dealumination of MCM-68 allowed selective removal of the external acid sites with reduced Al content, as demonstrated by the catalytic behavior in the cracking of 1,3,5-trisopropylbenzene (TIPB) or cumene over dealuminated MCM-68.

[Al]-YNU-3 was also dealuminated but the maximum Si/Al ratio was ca. 70, and a typical sample used for the cracking catalyst was denoted YNU-3(69.4)\(^{22}\).

3.1.2. Dealumination via Ion Exchange, Steam Treatment, and Acid Treatment

In many cases, framework aluminum atoms are readily removed by liquid phase nitric acid treatment at 80-100 °C to give dealuminated MCM-68 with the frame-
work intact. In contrast, direct dealumination by acid-treatment of MSE(DSADAF) (typical Si/Al is 6-7 corresponding to 14-16 Al sites/unit cell) causes significant collapse of the framework. Steam treatment of an NH$_2$-form was found to be an effective method to avoid this collapse. MSE(DSADAF) underwent ion exchange with an NH$_4$NO$_3$ solution at 80 °C to give the NH$_4$-form. Steam treatment of this NH$_4$-form typically used the steam (7.3-12.3 kPa) at 700 °C for 24 h and no framework collapse was observed, whereas the Si/Al ratio (based on ICP data) of the sample did not increase. Subsequent HNO$_3$ treatment resulted in a remarkable increase in the Si/Al ratio even though the steam treatment of MSE(DSADAF)(66.9) denoted as MSEOSDAF(66.9).

Migration of Si(OH)$_3$ is considered to take place during steam-treatment to repair site defects by condensation reactions between Si(OH)$_3$ and silanols$^{41,19}$. The Q$^3$ signals seen in the $^{29}$Si MAS NMR spectra were significantly smaller than expected based on the initial aluminum amounts in the as-synthesized MSEOSDAF sample.

3. 2. Loading of Various Species on MSE-type Zeolite

3. 2. 1. Modification with La$^{12}$

The lanthanum oxide was loaded on dealuminated MCM-68 by impregnation using a solution of La(NO$_3$)$_3$·6H$_2$O (0.25 g) in ethanol (40 mL), and this mixture was stirred for 1 min. The whole mixture was evaporated using a rotary evaporator and the residue was calcined in air at 500 °C.

3. 2. 2. Modification with Phosphate Species$^{52}$

Phosphate-loaded MCM-68 zeolites were prepared from proton forms of MCM-68 with Si/Al molar ratios of 10 and 60. For phosphorus impregnation, 0.5 g of zeolites were suspended in aqueous solution of (NH$_4$)$_2$HPO$_4$ (0.21 mol L$^{-1}$, 1.0 mL) at room temperature for 30 min. Then, phosphate-modified MCM-68 was dried at 100 °C for 2 h and calcined at 550 °C for 4 h to obtain the proton form of MCM-68. In this paper, the phosphate-modified MCM-68(60) is designated as P/MCM-68(60). The number in parentheses is the Si/Al molar ratio.

4. Catalytic Reaction

4. 1. Hexane Cracking over Various MSE-type Zeolites

Hexane cracking was investigated as a typical example of the conversion of petroleum resources.

Numbers 8, 10, and 12 indicate 8-, 10-, and 12-ring pores, respectively.

Fig. 3 Schematic Diagrams of the Pore-systems of (a) MSE, (b) MFI, (c) MOR, and (d) *BEA Frameworks

4. 1. 1. Effects of Dealumination and Reaction Temperatures on the Catalytic Cracking of Hexane

Schematic illustrations of MCM-68 (MSE), ZSM-5 (MFI), mordenite (MOR), and beta (*BEA) are shown in Fig. 3. Figure 4 shows the conversions and product distributions after cracking reactions for 5 min at 450, 500, 550 and 600 °C catalyzed by MCM-68(12), MCM-68(51), ZSM-5(45), mordenite(45), and beta(41) (the values in parentheses are Si/Al ratios). The product distributions for hexane cracking over various zeolite catalysts as well as the effect of reaction temperature on hexane conversion after 5 min of time-on-stream are given. Pyrolysis (thermal cracking) had almost negligible contribution at 500 °C and was about 2 % and 5 % at 550 °C and 600 °C, respectively. High conversion was maintained at all temperatures in the case of ZSM-5(45).

Conversion significantly decreased especially at higher temperatures just after the reaction started in the case of beta(41) and mordenite(45). Coke may have covered the active sites, causing the loss of catalytic activities. Although MCM-68(12) exhibited adequate catalytic activity at temperatures lower than 550 °C, the catalytic activity at 600 °C was less than that at lower reaction temperatures. This deactivation was probably caused by the large amount of coke (132 mg-coke (g-cat.)$^{-1}$ after 70 min) formed on the catalyst.

In contrast, dealuminated MCM-68(51) showed a gradual increase in the initial catalytic activity with increase in the reaction temperature from 450 to 600 °C. ZSM-5(45), which is one of the conventional catalysts used for alkane cracking, showed a gradual increase in the initial catalytic activity with increasing temperature. The resistance to coke formation of dealuminated MCM-68(51) (only 22 mg-coke (g-cat.)$^{-1}$ after 70 min,
and about 1/10 of that of MCM-68(12)) was as high as that for ZSM-5(45) (14 mg-coke (g-cat.)⁻¹ after 70 min), probably due to its potentially moderate acidity similar to ZSM-5 and a lower density of acid sites in the three-dimensional micropore system. Mordenite(45) and dealuminated beta(41) showed gradual increases in the initial activity with increase in the reaction temperature as shown in Fig. 4, but these two catalysts were typically deactivated during 70 min of reaction¹¹, despite similar acid site contents to dealuminated MCM-68(51). In the case of mordenite, the stronger acidity probably causes the coke formation (69 mg-coke (g-cat.)⁻¹ after 70 min) that clogs the one-dimensional 12-ring micropores, resulting in the rapid decrease in catalytic activity for hexane conversion. Despite the milder acidity of dealuminated beta(41) compared with mordenite, MCM-68, and ZSM-5, the polymerization of cracking products and the successive formation of coke components (72 mg-coke (g-cat.)⁻¹ after 70 min) in the three-dimensional 12-ring micropores and their wide intersections may predominantly occur, leading to the significant loss of activity during the reaction. In all the zeolite catalysts tested, selectivity to propylene was fairly constant, even after deactivation due to coking, and slight production of methane and benzene was observed at reaction temperatures higher than 550 °C. Therefore, the following discussion of initial selectivity after 5 min on stream at each temperature focuses on the propylene selectivity. MCM-68(12) had a lower selectivity to propylene of 22 % at 450 °C, but as the reaction temperature increased, the selectivity to propylene gradually increased up to 39 % at 600 °C. Dealuminated MCM-68(51) had a higher selectivity to propylene of 45-50 %, regardless of the reaction temperature from 450 to 600 °C. Such high propylene selectivity up to 45 % was rarely observed in the other zeolite catalysts examined in this study. ZSM-5(45) exhibited selectivity to propylene of 36-37 % at lower temperatures of 450, 500, and 550 °C, but the selectivity to propylene was slightly decreased to 33 % at 600 °C, probably due to the polymerization of propylene and successive re-cracking of the polymerized products. Mordenite(45) showed gradually increased selectivity to propylene from 31 to 45 % as the reaction temperature increased from 450 to 600 °C. The high selectivity of mordenite (45 % propylene selectivity at 600 °C) indicates the potential as a cracking catalyst for the selective production of propylene.

However, dealuminated MCM-68 would be an even more useful cracking catalyst, with high selectivity to propylene at 600 °C, in addition to lower reaction temperatures from 450 to 550 °C. Selectivity to propylene over the dealuminated beta(41) catalyst was relatively low and almost constant at 34-37 %, regardless of the reaction temperature. Thus, dealuminated beta is not suitable as a catalyst for the production of propylene during hexane cracking. MCM-68(12) showed gradually increased selectivity to propylene with increasing reaction temperature. This behavior of MCM-68(12) was quite similar to that of mordenite(45), in which the straight 12-ring channels are predominantly active in hexane cracking. In contrast, the propylene selectivity of dealuminated MCM-68(51) showed no significant change, regardless of the reaction temperature, which is analogous to ZSM-5(45) with interconnected 10-ring channels. We speculate that hexane cracking mainly occurs at the acid sites in the interconnected 10-ring channels of dealuminated

![Fig. 4 Hexane Conversion and Product Distributions in the Catalytic Cracking of Hexane (time-on-stream, 5 min) over (a) MCM-68(12), (b) MCM-68(51), (c) ZSM-5(45), (d) Mordenite(45), and (e) Beta(41)](image-url)
MCM-68(51), whereas hexane cracking predominantly occurs on the acid sites within the straight 12-ring channels of MCM-68(12). This implies that the preferential dealumination of MCM-68 involves the framework Al atoms that face the straight 12-ring micropores. In addition, highly selective formation of propylene over dealuminated MCM-68(51) may take place inside the supercages. Since these supercages are only accessible through the 10-ring micropores, the diffusion of bulky coke precursors into the cages may be obstructed.

The involvement of the cage structures in the MCM-68 may be similar to that of the one-dimensional cage structures in SSZ-35 and MCM-586). Both MCM-68 catalysts before and after dealumination were regenerated after reaction at 600°C to show almost the same performance as the initial catalysts12).

Utilizing this characteristic, we obtained the following results12) with MCM-68(22), MCM-68(52), and MCM-68(130). MCM-68(22) had high activities for both TIPB and cumene cracking reactions. In contrast, MCM-68(52) converted less TIPB, despite having some intact acid sites, as confirmed by the high conversion of cumene. MCM-68(130) converted no TIPB but achieved moderate conversion of cumene. These results strongly imply that the framework Al species on the external surfaces of MCM-68 samples were selectively removed by HNO3 treatment, whereas the framework Al was retained on their internal surfaces.

From the macroscopic viewpoint, heavy coke deposition tends to take place on external surface rather than inside pores12,53). To obtain the information about the acid sites on the external and internal surfaces, the catalytic properties of MCM-68 with different extent of dealumination were evaluated by comparing the catalytic cracking reactions of two substrates (cumene and 1,3,5-triisopropylbenzene (TIPB)) using a pulse-type reactor.

Catalytic cracking of TIPB should occur only at acid sites on the external surface of MCM-68 catalyst, as TIPB molecules are much larger than the pore diameters of the 12-ring and 10-ring micropores within the MSE framework. In contrast, cumene molecules, which are much smaller than TIPB molecules, can penetrate the 10-ring micropores in the MSE framework. Therefore, catalytic cracking of cumene occurs at the acid sites on both the external and internal surfaces of MCM-68 catalysts54).

Utilizing this characteristic, we obtained the following results12) with MCM-68(22), MCM-68(52), and MCM-68(130). MCM-68(22) had high activities for the hexane cracking process, but was gradually deactivated by coke deposition. Non-dealuminated MCM-68(11.0) and YNU-3(7.4) were deactivated very rapidly caused by heavy coking, showing conversions and product distributions similar to those of thermal cracking (Figs. 5(a)-5(c)). MCM-68(64.5), one of the dealuminated versions of MCM-68, exhibited adequate catalytic activity for the hexane cracking process, but was gradually deactivated.
lanthanum oxide (La-modification). Decr
than that over YNU-3(69.4). Looking at the product proved by modification of the external surfaces with selectivity at the point of 70 % hexane conversion shown in again likely caused by the large amount of coke conversion with this catalyst was always much higher compared to MCM-68(64.5) (Fig. 4). 1.3 Effect of Modification of External Surface

The reaction conditions: catalyst weight = 100 mg; temperature = 650 °C; W/F = 19.6 g-cat. h mol⁻¹; partial pressure of hexane = 5 kPa; CH₄/Ar gas flow rate = 40.0 cm³(NTP) min⁻¹.

Fig. 6 Effect of La-modification on the Catalytic Cracking of Hexane

ally deactivated until the hexane conversion at 305 min was below 50 % (Fig. 5(d)). This deactivation was again likely caused by the large amount of coke (33.4 mg-coke (g-cat.)⁻¹ after 305 min of reaction) formed on the catalyst. In contrast, YNU-3(69.4), one of the dealuminated versions of YNU-3 maintained its initial catalytic activity after 305 min and showed a minimal coke formation (1.8 mg-coke (g-cat.)⁻¹ at 305 min) (Fig. 5(e)). Surprisingly, MSEOSDAF(66.9), the dealuminated version of MSEOSDAF, showed much improved catalytic activity and comparatively less coke formation (3.3 mg-coke (g-cat.)⁻¹ at 305 min). Hexane conversion with this catalyst was always much higher than that over YNU-3(69.4). Looking at the product selectivity at the point of 70 % hexane conversion at 650 °C, MSEOSDAF(66.9) exhibited higher selectivity to propylene (ca. 44 %; the same level as the less active YNU-3(69.4) and lower BTX selectivity (1 %) compared to MCM-68(64.5) (ca. 41 % and 3 %, respectively) (Fig. 5(f)). Propylene yield over MSEOSDAF (66.9), the stabilized, dealuminated version of MSEOSDAF, was much higher than over other MSE-type catalysts at any point in the reaction (Fig. 4), indicating that optimally modified MSEOSDAF may be a viable candidate for application as a long-lived paraffin-cracking catalyst for the selective production of propylene.

4.1.3 Effect of Modification of External Surface with Lanthanum Oxide (La-modification)

Catalytic performance of MCM-68 catalyst was improved by modification of the external surfaces with lanthanum oxide (La-modification). Decrease in activity was observed for MCM-68(50) at 650 °C as shown in Fig. 6, although high propylene selectivity was maintained. Significant coke formation was again considered to be the main cause of the loss of activity. This problem was eliminated by La-modification of the external surfaces based on previous successful examples of modification of ZSM-5 and mordenite with La or other rare-earth oxides. In fact, hexane conversion of over 80 % was maintained using 10 wt% La/MCM-68(50), with greatly suppressed coke formation; the coke amount after reaction was 27 mg (g-cat.)⁻¹ for the modified catalyst while 68 mg (g-cat.)⁻¹ for unmodified MCM-68(50). At the same time, high selectivity to propylene (> 40-45 %) was maintained. Cracking of TIPB catalyzed by 10 wt%La/MCM-68(50) clearly showed that most external acid sites are covered. Conversely, cumene cracking over 10 wt% La/MCM-68(50) indicated that the active sites are intact inside micropores. La/MCM-68(50) samples were calcined at different temperatures (500 °C and 600 °C) just before the reaction, and complete deactivation of external surfaces was achieved for the catalyst loaded with 10 wt% La when calcined at 600 °C, although calculations at these temperatures had essentially the same effect in hexane cracking. Therefore, covering the external acid site could thus suppress the decrease in activity. In addition, judging from the unchanged product distributions, the reaction probably proceeds inside the micropore of MCM-68. The micropore volumes based on the N₂ adsorption isotherms hardly decrease with higher La-loading up to 10 wt%[20]. The micropore volume slightly decreases with La-loading of 20 wt%, suggesting that La species start entering into the pores. Therefore, in a limited range (up to 10 wt% La loading), we excluded the major possibility of the introduction of La into zeolitic micropores.

4.2 Dimethyl Ether-to-olefin (DTO) Reaction over MCM-68

DTO reaction was investigated as an example of the conversion of non-petroleum resources.

4.2.1 Effect of Dealumination

Investigation of the DTO reaction to determine the effect of dealumination found higher yields of propylene (37 C-%) and butenes (22 C-%) with lower yield of ethylene, lower paraffins, and aromatics (1.2, 0.8, and 2.1 C-%, respectively) over MCM-68(134) at 400 °C, whereas production of ethylene and aromatics as well as coke deposition were predominant over parent MCM-68(10) (Table 1) [21]. Such extreme change in the product distributions from parent MCM-68(10) to dealuminated MCM-68(134) is probably due to the persisting acid sites with moderate acid strength within the micropore that mainly cause lower yield of ethylene and lower coke formation during DTO reaction. The distribution of the acid sites may be important. Schematic illustrations of approximate estimates of the density and location of acid sites are shown in Fig. 7. Assumed Si/Al ratios before and after dealumination are around 10 and 50-100, respectively. An extremely
numbers greater than 6. On the other hand, optimization for the DTO reaction. The large number of acid sites on parent MCM-68(10) produced more C2, C3 and C4 paraffins, aromatics, and hydrocarbons with carbon number 25) was obtained in the DTO reaction over dealuminated MCM-68 with sufficient acid sites for the propylene conversion. The reaction temperature from 400 to 500 °C. Here, we have compared the catalytic performance of dealuminated MCM-68(60) with phosphate-modified MCM-68(60) (designated as P/MCM-68(60)). Comparisons of the activity and selectivity over MCM-68(60) and P/MCM-68(60) in the DTO reactions are presented in Figs. 8. When the contact-time, W/F, (g h mol−1) was 20, complete conversion of dimethyl ether to hydrocarbons over MCM-68 and P/MCM-68(60) was achieved with contact time W/F of 20 g h mol−1. To compare the product selectivity, the conversion level was tuned at around 95 % by decreasing the catalyst loading from 100 to 50 mg (Table 2). The product selectivity and DME conversion in the DTO reactions over MCM-68(60) and P/MCM-68(60) are also shown in Figs. 8(d) and 8(e), respectively. Phosphate modification of MCM-68(60) slightly reduced the conversion since more unreacted methanol and dimethyl ether were observed in the DTO reaction over P/MCM-68(60) compared with that over MCM-68(60). The selectivity to light olefins, except ethylene, was greatly increased by phosphate modification, whereas the selectivities to aromatics (benzene, toluene, xylenes, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, pentamethylbenzene and hexamethylbenzene) and light paraffins (ethane, propane, butane and isobutane) were decreased by phosphate modification. The product distributions were definitely different for the DTO reaction using 100 mg of MCM-68(60) and P/MCM-68(60) (Fig. 8). Using MCM-68(60), the increase in catalyst loading from 50 to 100 mg significantly increased the yield of ethylene and aromatics, particularly for pentamethylbenzene and hexamethylbenzene (Figs. 8(a) and 8(d)). Using P/MCM-68(60), the increase in catalyst loading increased the yield of propylene from ca. 40 to ca. 50 C-%, whereas the yields of aromatics and ethylene did not drastically change.

Table 1 Effect of Si/Al Ratio of MCM-68 Catalyst on the DTO Reaction and Comparison with ZSM-5 Catalyst (time-on-stream = 125 min)\(^a\)

<table>
<thead>
<tr>
<th>Catalyst(^b)</th>
<th>Conv.(^c) [%]</th>
<th>Product yield(^d) [C-%]</th>
<th>M.B.(^e) [C-%]</th>
<th>Content of coke(^f) [mg-coke g-cat.–1](^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH C1 + C2 + C3</td>
<td>C2 =</td>
<td>C3 =</td>
<td>C4 =</td>
</tr>
<tr>
<td>MCM-68(10)</td>
<td>100</td>
<td>0</td>
<td>16.8</td>
<td>6.5</td>
</tr>
<tr>
<td>MCM-68(47)</td>
<td>100</td>
<td>13.0</td>
<td>7.1</td>
<td>13.9</td>
</tr>
<tr>
<td>MCM-68(69)</td>
<td>100</td>
<td>0</td>
<td>7.1</td>
<td>5.8</td>
</tr>
<tr>
<td>MCM-68(134)</td>
<td>98.2</td>
<td>&lt;0.1</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>MCM-68(159)</td>
<td>96.3</td>
<td>4.4</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>MCM-68(215)</td>
<td>98.0</td>
<td>2.0</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>MCM-68(308)</td>
<td>94.5</td>
<td>3.9</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>ZSM-5(153)</td>
<td>8.1</td>
<td>21.1</td>
<td>19.9</td>
<td>7.8</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: catalyst weight = 100 mg; W/F = 20.0 g-cat. h mol\(^{-1}\); pellet size = 500-600 μm; He gas flow rate = 40 cm\(^3\)(NTP) min\(^{-1}\); partial pressure of DME = 4.9 kPa; reaction temperature = 400 °C. Pretreatment conditions: 550 °C, 1 h, air flow rate = 40 cm\(^3\)(NTP) min\(^{-1}\).

\(^b\) Values in parentheses are Si/Al ratios determined by ICP-AES analysis.

\(^c\) DME conversion = [1 - (C-atoms of DME\(_{\text{output}}\))/(C-atoms of DME\(_{\text{input}}\))] × 100.

\(^d\) Product yield = ([C-atoms of the product]/[C-atoms of DME\(_{\text{input}}\] - [C-atoms of DME\(_{\text{output}}\]) × [DME conval(C-%)].

\(^e\) Material balance = (total C-atoms of products and DME\(_{\text{output}}\))/(C-atoms of DME\(_{\text{input}}\]) × 100.

\(^f\) Propylene-to-ethylene molar ratio in the products.

\(^g\) Catalysts used in DTO reaction for 305 min were analyzed by thermogravimetry. The weight loss observed from 300 to 700 °C in a thermogravimetric analysis was ascribed to coke.

![Fig. 7 Rough Estimation of Acid-site Distribution in MCM-68](a) before and (b) after Dealumination.

high propylene/ethylene (P/E) molar ratio (greater than 25) was obtained in the DTO reaction over dealuminated MCM-68 compared with ZSM-5 with a similar Si/Al molar ratio (P/E molar ratio ca. 8). The P/E molar ratio in the DTO reaction catalyzed by dealuminated MCM-68 is also extensively controllable by changing the reaction temperature from 400 to 500 °C.

### 4.2.2. Effect of Phosphate Modification of MCM-68 on DTO Reaction

In the previous section, we described the effect of Si/Al molar ratio of MCM-68 on the catalytic performance for the DTO reaction. The large number of acid sites on parent MCM-68(10) produced more C2, C3 and C4 paraffins, aromatics, and hydrocarbons with carbon numbers greater than 6. On the other hand, optimization of the number of acid sites by acid treatment gives MCM-68 with sufficient acid sites for the propylene production in the DTO reactions\(^{18,51}\). Such optimization suppresses the undesirable consecutive reactions from the light olefins. Here, we have compared the catalytic performance of dealuminated MCM-68(60) with phosphate-modified MCM-68(60) (designated as P/MCM-68(60)).
To clarify the effect of treatment with phosphate on the acidity of MCM-68, MCM-68 with the Si/Al molar ratio of 84, which contains fewer acid sites than MCM-68(60), was used for the DTO reaction under the same reaction conditions (shown in Figs. 8(c) and 8(f)). Using MCM-68(84), the yields of propylene and butenes were increased and the yields of aromatics and paraffins were decreased. These findings agree well with our previous research into the catalytic performance of MCM-68 with various Si/Al molar ratios\(^{18,51}\). On the other hand, there is slight difference in product distributions, and the reaction over P/MCM-68(60) resulted in higher yields of propylene and butenes compared to that over unmodified MCM-68. Furthermore, the propylene/ethylene (P/E) ratio in the products significantly increased with phosphate modification (from 16 to 42). These results indicate that the content of certain active sites, which may be responsible for the formation of aromatics (especially pentamethylbenzene and hexamethylbenzene) and ethylene, was decreased by phosphate impregnation on MCM-68(60). Olefin aromatization is one of the most undesirable side reactions in the DTO reaction. P/MCM-68(60) showed decreased aromatic selectivity compared with MCM-68(60) and MCM-68(84), probably due to fewer strong Lewis acid sites, which are known to catalyze aromatization and hydrogen transfer reactions.
The spent catalysts were characterized by thermogravimetry-differential thermal analysis (TG/DTA) to determine their coke contents. A distinct weight loss, accompanied by an exothermic DTA peak, was observed at the temperature range of around 300-700 °C, mainly related to combustion of the carbonaceous material deposited on the catalysts during the DTO reactions. The amount of coke deposited on P/MCM-68(60) was lower than that on MCM-68(60) (Table 2). These results indicate that phosphate impregnation of MCM-68 catalyst could improve the tolerance for coke deposition during the DTO reaction. Coke, which should be considered as a mixture of hydrogen deficient residues, originates mainly from aromatics, so the aromatization and hydrogen transfer reactions are highly important contributors to coke deposition. The enhanced durability to coke deposition during DTO reaction over P/MCM-68(60) is probably due to the decrease in number of stronger Lewis acid sites, which take part in the formation of aromatics from the conversion of dimethyl ether. Conversely, the low ethylene selectivity observed over P/MCM-68(60) is probably due to the changes in number of strong Brønsted acid sites because the formation of ethylene is to proceed through carbenium cations formed by the cracking reactions of intermediates. Bleken et al. reported catalytic results of the MTO reaction over SSZ-13 and SAPO-34 catalysts. The high P/E ratios in products were obtained when catalyzed by SSZ-13, which has the same topology and the number of acid sites, but is slightly more acidic due to the framework composition. They concluded that the differences in acid strength might affect the product distribution in the MTO reactions. The energy level of the primary carbenium ions is higher than that of the secondary and tertiary carbenium ions, so the formation of ethylene, which requires formation of primary carbenium ions, will proceed more readily in the presence of the stronger acid sites on the catalysts. Although we could not obtain a reliable evidence of any decrease in the number of strong Brønsted acid sites on MCM-68 resulting from by phosphate modification, we believe that the high P/E ratio in products obtained over P/MCM-68 is probably due to a decrease in the number of strong Brønsted acid sites.

### Table 2 Effect of Phosphate-modification (time-on-stream = 125 min)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Product yield [%]</th>
<th>M.B. [%]</th>
<th>Content of coke [mg-coke g-cat⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH C1 + C2 + C3</td>
<td>C3 =</td>
<td>C4 =</td>
<td>C5 + C6 =</td>
</tr>
<tr>
<td>MCM-68(60)</td>
<td>96.2</td>
<td>4.0</td>
<td>1.3</td>
<td>2.2</td>
</tr>
<tr>
<td>P/MCM-68(60)</td>
<td>96.7</td>
<td>6.7</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>MCM-68(84)</td>
<td>93.1</td>
<td>4.7</td>
<td>0.8</td>
<td>2.6</td>
</tr>
</tbody>
</table>

a) Reaction conditions: catalyst weight = 100 mg; W/F = 20.0 g-cat. h mol⁻¹; pellet size = 500-600 μm; He gas flow rate = 40 cm³(NTP) min⁻¹; partial pressure of DME = 4.9 kPa, reaction temperature = 400 °C. Pretreatment conditions: 550 °C, 1 h, air flow rate = 40 cm³ (NTP) min⁻¹.

b) Values in parentheses are Si/Al ratios determined by ICP-AES analysis.

c) DME conversion = 1 - (C-atoms of DMEinput - C-atoms of DMEoutput) / C-atoms of DMEinput × 100.

d) Product yield = (C-atoms of products)/(C-atoms of DMEinput - C-atoms of DMEoutput) × [DME conv. (C-%)]

e) Material balance = (total C-atoms of products and DMEinput) / C-atoms of DMEinput × 100.

f) Propylene-to-ethylene molar ratio in the products.

g) Catalysts used in DTO reaction for 35 min were analyzed by thermogravimetry. The weight loss observed from 300 to 700 °C in a thermogravimetric analysis was ascribed to coke.

### 4.2.3. Effect of Ce-modification of MCM-68

Based on the positive effect of La-modification in the case of the hexane cracking reaction (section 4.1.3.), some special procedure of Ce-modification was also found to effectively enhance the catalytic performance for the DTO reaction. Although MCM-68 calcined at 800 °C after dealumination showed low catalytic activity due to loss of crystallinity, Ce-modification of dealuminated MCM-68 enhanced the stability. By successive calcination at 800 °C, selective and long-lived catalyst for the DTO reaction was generated, and the propylene yield was as high as 46 % as shown in Fig. 9.

### 5. Conclusion

Recent examples of synthesis, post-synthetic modification, and catalytic application of MSE-type zeolites, microporous silicates with a 12-10-10-ring micropore system, are presented. Unmodified Al-rich MCM-68(12) suffered significant deactivation due to coke formation, whereas dealuminated MCM-68(51) exhibited adequate catalytic activity and resistance to coke formation for hexane cracking from 450 to 600 °C. Dealuminated MCM-68(51) also had higher selectivity to propylene of 45-50 % compared to ZSM-5(45) and other zeolite catalysts tested at the reaction temperatures of 450 to 600 °C. At higher reaction temperature (650 °C), La-modification was effective for avoiding heavy coke formation to maintain catalytic activity and selectivity to propylene.

Dealumination by post-synthetic acid treatment was usually effective to realize enhanced catalytic perfor-
mance of various MSE-type catalysts for hexane cracking, even at temperatures as high as 650 °C. The dealumination behaviors during post-synthetic acid treatments as well as the properties of the products differed depending on the synthetic technique. The dealuminated version of various Al-rich MSE-type zeolites showed high levels of coking resistance in addition to a significant yield of propylene in the hexane-cracking reaction, and the order of catalytic performance after post-synthetic modification was as follows: conventional MCM-68 < MSE synthesized by hydrothermal conversion of an FAU-type zeolite (YNU-3) < MSE synthesized under OSDA-free conditions (MSEOSDAF). The Al-rich MSE products obtained in this study, especially YNU-3 and MSEOSDAF, are promising parent materials for industrial applications as highly selective and long-lived catalysts.

Dealumination of MCM-68 by post-synthetic acid treatment using nitric acid allowed selective removal of only the external acid sites with reduced Al content, proven by the unique behavior in the cracking of TIPB or cumene over dealuminated MCM-68.

In the DTO reaction at 400 °C, the higher yields of propylene (37 C-%) and butenes (22 C-%) were obtained with lower yields of ethylene, lower paraffins, and aromatics (1.2, 0.8, and 2.1 C-%, respectively) over dealuminated MCM-68(134), whereas the formation of ethylene and aromatics as well as coke deposition were predominant over parent MCM-68(10). Drastic changes in the product distributions from parent MCM-68(10) to dealuminated MCM-68(134) were probably due to the persisting acid sites with a moderate acid strength within the micropores that mainly cause lower yield of ethylene and a decrease in coke content during the DTO reaction. In other words, dealumination of parent MCM-68 may selectively remove both the stronger Brønsted acid sites which produce ethylene and the Lewis acid sites which cause hydrogenation/dehydrogenation and aromatization of olefins into paraffins and aromatics. An extremely high P/E molar ratio (greater than 25) was obtained in the DTO reaction over dealuminated MCM-68 as compared to ZSM-5 with a similar Si/Al molar ratio (P/E molar ratio was ca. 5), and the P/E molar ratio in the DTO reaction catalyzed by dealuminated MCM-68 was also widely controllable by changing the reaction temperature from 400 to 500 °C. The present findings in this paper suggest that dealuminated MCM-68 catalyst is effective for the highly selective production of propylene from dimethyl ether, and the dealumination treatment of zeolite catalysts can modify the acid site distribution in the zeolite framework to obtain desirable acid catalytic properties.

MCM-68(60) and phosphate-loaded MCM-68(60) zeolites were synthesized by the post-synthetic treatment of hydrothermally synthesized MCM-68(10). The results obtained from the DTO reactions indicate that the P/MCM-68(60) is an effective catalyst for the selective production of light olefins such as propylene and butenes. Impregnation of MCM-68 with phosphate efficiently changed the product distributions in the DTO reaction. The DTO reaction over P/MCM-68(60) achieved almost 70 C-% selectivity to propylene and butenes with ca. 50 C-% selectivity to propylene. Moreover, the phosphate modification improved the resistance to coke deposition and decreased the selectivity toward aromatics and ethylene, probably due to

![Diagram](image-url)
the selective decrease in the number of acid sites on the external surface of MCM-68 as confirmed by the TIPB and cumene cracking reactions. Furthermore, phosphate modification decreased the number of strong Lewis acid sites by covering them, providing the resultant catalyst P/MCM-68(60) with high resistance to coke deposition during the DTO reaction. The high P/E ratio over P/MCM-68(60) is probably due to the removal of strong Brønsted acid sites with phosphate modification.

MCM-68 catalyst modified with Ce was resistant to thermal treatment at 800°C, whereas dealuminated, unmodified MCM-68 was significantly damaged by the same thermal treatment. Ce-modified MCM-68 after calcination at 800°C was not only a robust material but also a very active, selective, and long-lived catalyst in the DTO reaction. The maximum propylene yield was as high as 46%. Therefore, this catalyst would be tolerable to deterioration during the reaction under severe hydrothermal conditions.

Acknowledgment

This work was financially supported in part by the Japan Science and Technology Agency (JST) for the project of Creation of Innovative Functional Materials with Advanced Properties by Hyper-nano-space Design in the CREST program (project code: JPMJCR1423), by Adaptable and Seamless Technology Transfer (A-STEP, AS231Z03507C) from Japan Science and Technology Agency (JST), by the New Energy and Industrial Technology Development Organization (NEDO), and by Grant-in-Aid for Scientific Research (nos. 13199071 and 23760741).

References


要 旨

MSE 型ゼオライト触媒を用いた軽質オレフィンの高選択的な合成

高選択的にプロピレンを得ることを目的として、酸素 12-10-10型微孔ミクロ孔を有する MSE 型ゼオライト触媒の調製手法の開発を進めている。本稿では石油および非石油資源の転換のための触媒開発の事例を概説する。調製過程を工夫することで、ヘキサのクラッキングでの触媒特性を向上しつつ MSE 型ゼオライトを得ることができた。La 修飾はクラッキング触媒としての特性を高めるのに有効な手法である。また、MSE トポロジーからなる MCM-68 の酸点分布を制御するために、リン酸水素二アンモニウムを含浸担持して焼成することで、リン修飾 MCM-68 を調製した。ジメチルエーテルからオレフィンを得る（DTO）反応では、リン修飾や希土類修飾によってプロピレンとブテンへの高選択性を観察し、プロピレン／エチレン比が飛躍的に向上した。これらの修飾処理を経ると高い炭素析出耐性も示されたことから DTO 反応の触媒の長寿命化を図ることができたと言える。

J. Jpn. Petrol. Inst., Vol. 60, No. 6, 2017