



Remarkable enhancement of catalytic activity and selectivity of MSE-type zeolite by post-synthetic modification



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ABSTRACT

Besides conventional MCM-68, Al-rich MSE-type zeolites with a 12-10-10-ring micropore system were successfully synthesized in a remarkably short crystallization period by some different synthetic methods: (1) hydrothermal conversion of an FAU-type zeolite with the aid of the dipyrrolidinium-type organic structure-directing agent (OSDA) and (2) hydrothermal synthesis without using any OSDA with the aid of seed crystals. The dealumination behaviors during post-synthetic acid treatments as well as the properties of the products differed depending on the synthetic method. The dealuminated version of each Al-rich MSE-type zeolite showed a high level of coking resistance in addition to a significant yield of propylene in the hexane-cracking reaction, and the MSE synthesized under OSDA-free conditions showed the best catalytic performance among three different MSE-type zeolites after post-synthetic modification. The Al-rich MSE products obtained in this work are promising parent materials for industrial applications as highly selective and long-lived catalysts.

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1. Introduction

The properties of zeolites depend on the method of preparation including starting gel composition and synthesis conditions. For example, the synthesis using organic structure-directing agent (OSDA) usually gives high-silica zeolites, while OSDA-free synthesis gives materials with much lower silica contents [1]. Even in the synthesis using an OSDA, Al-rich (relatively low-silica) zeolite sometimes crystallizes under some conditions. In all cases, some post-synthetic modifications are necessary for preparing catalysts that have appropriate amount of active sites, proper hydrophobicity, and stability. As pointed out by Valtchev et al. [2], the widening window of post-synthetic options enables the preparation of zeolites with application-specific properties. We have found that zeolites with MSE topology (the “type material” is MCM-68) offer interesting examples of the OSDA-assisted and OSDA-free syntheses, post-synthetic modifications, and catalytic applications. Although framework type codes are to be described in boldface (e.g. **MSE**) according to the International Zeolite Association [3],

they will be expressed without using boldface hereafter for simplicity.

MSE is a new type of three-dimensional zeolite framework with a $12 \times 10 \times 10$ -ring ($12 \times 10 \times 10R$) channel system [3]. This framework has a characteristic structure in which a straight 12R channel intersects with two independent tortuous 10R channels and, in addition, possesses an $18R \times 12R$ supercage which is accessible only through 10R channels [4]. Zeolites with this type of framework (e.g. MCM-68) are known to exhibit unique acid catalytic properties [5,6] and are potentially useful as shape-selective catalysts for the alkylation of aromatics [7–9] as well as for the production of propylene by naphtha cracking [10]. Their use as hydrocarbon traps has also been reported [11]. In addition, Ti-substituted MCM-68 has demonstrated performance superior to that of TS-1 ([Ti]-MFI) for the oxidation of phenol and olefins with H_2O_2 as an oxidant [12].

MCM-68, a typical MSE-type zeolite, has been synthesized under hydrothermal conditions using *N,N,N',N'*-tetraethyl-*exo,exo*-bicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium diiodide ($TEBOP^{2+}(I^-)_2$) as the OSDA [4,7,13–15]. The gel composition window for the successful crystallization of pure MCM-68 is very narrow and the Si/Al molar ratio of the product is limited to the range of 9–12. We have previously succeeded in overcoming this limitation by utilizing the steam-assisted crystallization (SAC)

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[16–19] to obtain a precursor of pure-silica version of the MSE topology (YNU-2P) or its stabilized microporous version (YNU-2) [14,20]. Even so, the current requirement for a crystallization stage spanning 14 days or more during the synthesis of MCM-68 had remained an important unresolved issue. This has recently been solved in some ways, parts of which are reported in this paper. It should be noted that the MSE-type zeolite has also been synthesized as UZM-35 by charge density mismatch [21] with a simple OSDA, dimethyldipropylammonium [22]. In addition, continuous efforts to avoid using TEBOP²⁺ are being made by ExxonMobil researchers [23].

The main target product in this work is propylene (propene), which is an important synthetic intermediate for petrochemicals and functional organic materials. Currently, worldwide propylene production comes from steam cracking (ca. 70%), refinery fluid catalytic cracking (FCC) (ca. 28%), and other deliberate processes (ca. 2%) such as propane dehydrogenation and metathesis [24,25]. It is well known that propylene yield in the fluid catalytic cracking (FCC) processes has been enhanced using zeolite Y (FAU topology [3]) and ZSM-5 zeolite (MFI topology [3]) catalysts by the control of the synthetic parameters, post-synthetic treatment such as steaming, and further modification with alkaline-earth or rare-earth metals. Over the past decade, new types of zeolite materials with large (12-ring; 12R) or extra-large (>12R) micropores have been synthesized and tested as FCC catalysts or as their additives [10]. Based on the various results, zeolite frameworks with multi-dimensional 10R or 12R micropores would be suitable for propylene production in the FCC process, and the zeolite catalyst with MSE topology is a promising candidate. The cracking of *n*-alkane, especially *n*-hexane, is often examined as a model reaction for the FCC catalytic test [26–30].

In this study, we focus on the remarkable enhancement of catalytic properties of some different versions of MSE-type materials for hexane cracking by post-synthetic treatments.

2. Experimental

2.1. Chemicals and materials

The commercially available reagents were used as-received without further purification. The suppliers and cautions are described in each section when necessary.

2.2. Synthesis of MCM-68 as a conventional MSE-type zeolite

MCM-68 zeolite was synthesized as follows: colloidal silica (Ludox HS-40, DuPont, 40 wt% SiO₂, 6.01 g, 100.0 mmol), deionized water (40 mL), and Al(OH)₃ (Pfaltz & Bauer, 780 mg, 10.0 mmol) were mixed in a 180-mL Teflon beaker and stirred for 10 min. Aqueous KOH solution (5.93 mmol g⁻¹, 6.32 g, 37.5 mmol) was added to the solution and stirred for further 30 min. Then, TEBOP²⁺(I⁻)₂ (10.0 mmol) was added as an OSDA and the mixture was stirred for another 4 h. The resulting mixture with a molar composition: 1.0SiO₂-0.1TEBOP²⁺(I⁻)₂-0.375KOH-0.1Al(OH)₃-30H₂O was taken into a 125-mL Teflon-lined autoclave and kept statically at 160 °C for 16 days in a convection oven. After cooling the autoclave to room temperature, the solid obtained was separated by centrifuging, washed several times with deionized water, and dried overnight. The as-synthesized MCM-68 zeolite was obtained as white powder (6.04 g).

To remove the OSDA occluded in the pore, the as-synthesized MCM-68 was kept in a muffle furnace, and heated stepwise as follows: the temperature was raised from room temperature to 650 °C under 1 °C min⁻¹ of the ramping rate and maintained at the same temperature for 10 h. Finally, the sample was cooled

to room temperature to give a calcined sample as white powder (Si/Al = 11–12).

2.3. Synthesis of MSE-type zeolite (YNU-3) via hydrothermal conversion of FAU-type zeolite [15]

A typical synthetic procedure of the hydrothermal conversion of FAU-type zeolite (Tosho, HSZ-360HUA; Si/Al = 6.7) is as follows: deionized water (40 mL) and aqueous KOH solution (5.93 mmol g⁻¹, 6.32 g, 37.5 mmol) were mixed in a 125-mL Teflon beaker. To this mixture, TEBOP²⁺(I⁻)₂ (5.58 g, 10.0 mmol) was added and stirred for 30 min, and then as-synthesized [Al]-MCM-68 (0.30 g, 5.0 wt% of FAU-type zeolite) was added as the seed crystal. Finally, FAU-type zeolite (6.01 g) was added and the mixture was stirred for another 4 h. The resulting mixture with a molar composition: 1.0(SiO₂-Al₂O₃)-0.1TEBOP²⁺(I⁻)₂-0.375KOH-30H₂O was taken into a 125-mL Teflon-lined autoclave and kept statically at 160 °C for 5 days in a convection oven. After cooling the autoclave down to room temperature, the precipitated solid was separated by centrifugation, washed thoroughly with deionized water, and dried overnight to give the as-synthesized MSE-type zeolite (6.38 g) as a white powder. This material is denoted as-synthesized YNU-3 [15] to distinguish from conventional MCM-68 because of its unique properties. After removing the OSDA occluded in the pore from the as-synthesized YNU-3 in the same way as that for MCM-68, a calcined YNU-3 sample was obtained as a white powder (Si/Al = ca. 7).

2.4. Synthesis of MSE-type zeolite under OSDA-free conditions [25,31]

Aqueous solutions of NaOH (6.32 mmol g⁻¹; 12.68 g, 84.06 mmol) and KOH (5.96 mmol g⁻¹; 996 mg, 5.94 mmol) were mixed with distilled water (43.84 g, 3.00 mol) in a Teflon cup and sodium aluminate (Al/NaOH = 0.77; 443 mg) was dissolved in the mixture. The resulting clear solution was transferred to a mortar and calcined MCM-68 seeds (901 mg) were added. After the entire mixture was homogenized using a mortar and pestle for 10 min, Cab-O-Sil M5 (9.01 g, 150 mmol) was added and the combined ingredients were again homogenized in the same manner for 20–30 min. The mixture was then transferred to a 60-mL stainless steel autoclave and subjected to hydrothermal treatment at 140 °C for 44 h under static conditions and autogenous pressure. The product was subsequently filtered, washed thoroughly with hot distilled water, and dried at 60 °C to obtain pure MSE_{OSDAF} (2.16 g). The yield was 21% (see Section 3.1).

2.5. Ion-exchange of MSE-type materials into their ammonium forms

Ion exchange from the calcined sample to its NH₄ form was carried out using NH₄NO₃ solution as follows: NH₄NO₃ (4.0 g) and the calcined sample (2.0 g) were suspended in H₂O (100 mL) in a 250-mL polypropylene bottle. The bottle was capped tightly and allowed to stand at 80 °C for 24 h with occasional purge of pressure and careful shaking. After cooling down, the sample was separated by filtration, and washed with deionized water. This process was repeated twice. The sample was filtered, washed thoroughly with water, and dried overnight at room temperature to give MCM-68 in NH₄ form (MCM-68.cal.IE), YNU-3 in NH₄ form (YNU-3.cal.IE), and the NH₄-form of MSE_{OSDAF} (MSE_{OSDAF}-IE). Then, the NH₄ form zeolites were again calcined in a muffle furnace. The temperature was raised from room temperature to 550 °C over a period of 4 h and kept at the same temperature for 6 h to give MCM-68 in H-form (MCM-68.cal.IE.cal, Si/Al = 11), YNU-3 in H-form (YNU-3.cal.IE.cal, Si/Al = 7.4), and MSE_{OSDAF}.IE.cal (Si/Al = 7.3).

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