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Seed-assisted, OSDA-free synthesis of MTW-type zeolite and "Green MTW" from sodium aluminosilicate gel systems

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ABSTRACT

Recently, the seed-assisted methods have provided a new route for the organic structure-directing agent (OSDA)-free synthesis of industrially useful zeolites under environmentally-friendly conditions. In this paper, the various parameters are investigated in the OSDA-free synthesis of MTW-type zeolite by the hydrothermal treatment of sodium aluminosilicate gel with the aid of calcined ZSM-12 seed crystals prepared using tetraethylammonium hydroxide (TEAOH). More importantly, the green production of MTW-type zeolite referred as "Green MTW" is achieved for the first time, by using the product of OSDA-free synthesis as seeds. The X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and solid-state ^{27}Al MAS NMR results exhibit better crystallinity of MTW-type zeolite and Green MTW than those of calcined ZSM-12 seeds. MTW-type zeolite is not obtained when seeds are absent in the initial reactant gel while ZSM-5 (MFI-type zeolite) and/or mordenite (MOR-type zeolite) are formed. The results of thermogravimetric (TG) analysis of hydrated samples confirm the enough micropore volume in MTW-type zeolite whereas nitrogen adsorption–desorption measurements of MTW-type zeolite and Green MTW show nitrogen adsorption capacity lower than that of the seeds, which might be attributed to the partial pore blocking in the one-dimensional channel systems of the MTW framework.

1. Introduction

Zeolites are crystalline microporous aluminosilicates with tetrahedrally-coordinated framework structures incorporating well-defined channel systems and cavities. Because of their outstanding solid-acid and adsorption–desorption properties for organic and inorganic molecules, zeolites have been widely used as catalysts and adsorbents in industry [1–4]. ZSM-12 is the type material with the framework of MTW with one-dimensional, non-interpenetrating 12-ring pores (with the size of 5.6×6.0 Å^2 along *b*-axis), which was first reported by Rosinski and Rubin in 1974 [5–9]. Since then, ZSM-12 has attracted much attention because of its excellent catalytic properties in the cracking of hydrocarbons or in other petroleum refining processes [10–14]. The conventional synthesis of ZSM-12 has been achieved by the hydrothermal treatment of sodium aluminosilicate mixtures containing tetraalkylammonium cations such as methyltriethylammonium bromide (MTEABr), tetraethylammonium hydroxide (TEAOH) or tetraethylammonium bromide (TEABr) as an organic structure-directing agent (OSDA) [5,15–20]. In these syntheses, it has been recognized that OSDAs are indispensable for the formation of MTW framework structure. For the practical applications, the mass commercialization of ZSM-12 requires large amount of expensive OSDAs which causes high cost in the whole synthesis process. Moreover, the calcination at high temperature is required to remove all the residual OSDAs in the channels, and such process results in the large consumption of energy as well as the mass generation of harmful product. Therefore, an alternative route to realize environmentally-friendly, OSDA-free synthesis of ZSM-12 is strongly desired.

In recent years, it is widely recognized that the OSDA-free syntheses of industrially useful zeolites such as ZSM-34 [21], beta [22–26], ZSM-5 [27] and RTH-type zeolite [28] could be achieved by the addition of calcined zeolite seed crystals to the initial OSDA-free reactant gels, followed by the hydrothermal treatment. Very recently, we have succeeded in the OSDA-free synthesis of MTW-type zeolite by the addition of the conventional calcined ZSM-12 seeds to the OSDA-free (lithium, sodium) aluminosilicate gel [29]. It was found that the presence of calcined ZSM-12 seeds as well as lithium cations played a crucial role for the crystallization of MTW-type zeolite in the synthesis system. Unfortunately, the crystallization area of the highly crystalline, pure MTW-type zeolite in the system was very limited in a narrow range. Since most of the conventional ZSM-12 zeolites were preferentially synthesized from the initial sodium aluminosilicate mixture prepared with higher Si/Al ratios [5,15–17,19,20], it is desired to synthesize MTW-type zeolite in more simple OSDA-free system prepared with higher Si/Al region than the previous (lithium, sodium) aluminosilicate system [29]. In addition, our previous study [25,26] have

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shown that sodium aluminosilicate gel systems provided much more favorable conditions for the seed-assisted crystallization of beta. Because MTW as well as beta are categorized as pentasil zeolites, it seems more effective to synthesize MTW-type zeolite from the seeded sodium aluminosilicate gel systems.

In this paper, OSDA-free synthesis of highly crystalline, pure MTW-type zeolite has been studied by the addition of calcined ZSM-12 seeds to the OSDA-free sodium aluminosilicate gel with wide range of chemical compositions and optimized synthesis conditions were found. To the best of our knowledge, we have succeeded in the synthesis of "Green MTW" for the first time, by the use of the obtained MTW-type zeolite as seeds. The synthesis of Green MTW provides the basis for the environmentally-friendly process for the production of MTW-type zeolite, which is essential from the viewpoint of green chemistry. The detailed synthesis conditions as well as the characterizations of MTW-type zeolite and Green MTW obtained by seed-assisted, OSDA-free syntheses are reported.

2. Experimental section

2.1. Materials

The following raw materials were used as provided: Cab-O-Sil® (Grade M5, Cabot), as a silica source, sodium aluminate ($NaAlO_2$, Wako) as an aluminum source and sodium hydroxide solution (NaOH, 50 w/v% in water, Wako) as an alkali source. For the synthesis of ZSM-12 seeds, colloidal silica (LUDOX HS-40, 40 wt.% in water, DuPont) was used as a silica source and tetraethylammonium hydroxide (TEAOH, 35 wt.% in water, Aldrich) was used as an OSDA.

2.2. Synthesis of calcined ZSM-12 seeds

ZSM-12 seed crystals were synthesized by the hydrothermal treatment of aluminosilicate solution containing TEAOH with the following chemical composition: $0.0125Na_2O:0.125TEA_2O:0.0125Al_2O_3:SiO_2:13H_2O$. The initial reactant solution was prepared as follows; initially, sodium aluminate and TEAOH were dissolved in distilled water and then, colloidal silica was added to the solution and the mixture was stirred to obtain a clear solution. Here, the total weight of all aluminosilicate solution was adjusted to 12 g. The mixture was transferred to a 23 mL Teflon-lined stainless steel autoclave and was then subjected to the hydrothermal treatment at 160 °C for 120 h in an oven under static condition with autogeneous pressure. After the hydrothermal treatment, the product was recovered by filtration, washed thoroughly with hot distilled water and dried at 60 °C. The residual TEA cations in the zeolite were removed completely by the calcination under dry air flow condition at 550 °C for 10 h. The characterization of the seeds was performed as the calcined form.

2.3. Seed-assisted, OSDA-free synthesis of MTW-type zeolite and Green MTW

OSDA-free synthesis of MTW-type zeolite was carried out by adding calcined ZSM-12 seeds to the OSDA-free sodium aluminosilicate gel with the following chemical compositions: $xNa_2O:yAl_2O_3:SiO_2:zH_2O$, where $x = 0.1–0.2$, $y = 0.0083–0.05$, and $z = 8.25–13.3$ (see Table 1 for details). The initial sodium aluminosilicate gel was prepared as follows; sodium aluminate was dissolved in distilled water, followed by the addition of aqueous NaOH to obtain a clear solution. Then, calcined ZSM-12 seeds (Si/Al = 47.3) and Cab-O-Sil were slowly added together to the solution, which was mixed using a mortar and pestle to obtain a homogeneous gel. Here, the adding amount of calcined ZSM-12 seeds was 1–10 wt.% relative to the silica source, and the total weight of all sodium aluminosilicate gel was adjusted to 18 g. Subsequently, the seeded sodium aluminosilicate gel was transferred to a 60 mL stainless-steel autoclave and subjected to the hydrothermal treatment at 165 °C for different periods of time under static condition with autogeneous pressure. After the hydrothermal treatment, the product was recovered by filtration, washed thoroughly with hot, distilled water and dried at 60 °C. The obtained solid products were characterized as their as-synthesized forms. The solid yield (g/g × 100%) of the resulting product was defined as the ratio of the weight of dried solid product to the dry weight of SiO_2, $NaAlO_2$ and calcined ZSM-12 seeds in the initial sodium aluminosilicate gel. The obtained products were denoted as MTW-No. 1 to MTW-No. 13, respectively (see Table 1).

In the synthesis of Green MTW, three different MTW-type zeolites (MTW-No. 7, MTW-No. 11 or MTW-No. 12 in Table 1) obtained from seed-assisted, OSDA-free synthesis were selected as seeds, and added to the initial sodium aluminosilicate gels with different compositions (see Table 2 for details). Other procedures were the same as those for the seed-assisted, OSDA-free synthesis as described above. The adding amount of MTW-type zeolite seeds was 10 wt.% relative to the silica source. The obtained products were denoted as GMTW-No. 1 to GMTW-No. 5, respectively (see Table 2) and characterized as their as-made forms.

2.4. Characterizations

Powder X-ray diffraction (XRD) patterns of the solid products were collected using a Mac Science MO3XHF22 diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm, 40 kV, 30 mA) from 5° to 40° with 2θ. The scanning step was 0.02° at the scanning speed of 2° per min. The crystallinity of the solid products was calculated by comparing the intensity of the diffraction peak at $2\theta = 20.8°$ ($hkl = 310$) to that of fully-crystallized MTW-type zeolite (MTW-No. 7) or Green MTW (GMTW-No. 5), respectively. Elemental analyses of the ZSM-12 seeds and the products were performed by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Varian Liberty Series II) after dissolving them in hydrofluoric acid or potassium hydroxide solution. The crystal size and morphology of the seeds and products were observed by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). Solid-state ^{27}Al MAS NMR spectra were collected with a JEOL CMX-300 spectrometer. ^{27}Al MAS NMR spectra were recorded at the resonance frequency of 78.3 MHz, a pulse width of 1.0 μm and a recycle delay of 5 s. For ^{27}Al MAS NMR measurement, samples were spun at 10 kHz in standard 4 mm zirconia rotors. Prior to the measurements, all samples were finely ground and hydrated in a desiccator with saturated ammonium chloride solution for 72 h at room temperature. Here, 1 M aluminum nitrate was used as standard references of chemical shift (at 0 ppm) for the ^{27}Al MAS NMR. Nitrogen adsorption–desorption measurements of the Na- and H-form zeolite products were performed on Quantachrome Autosorb-1 at −196 °C. Prior to the nitrogen adsorption–desorption measurements, all samples were degassed at 400 °C for 4 h under vacuum. The ion-exchange was carried out in 1 M ammonium chloride solution at 80 °C under stirring for 12 h, and repeated twice. The H-form sample was obtained by the calcination of ion-exchanged NH_4-form sample (MTW-No. 7) under dry air flow condition at 500 °C for 4 h. The obtained sample was denoted as HMTW-No. 7. According to the chemical analysis, the Si/Al and Na/Al ratios of the HMTW-No. 7 were 16.7 and 0.01, respectively. Thus, almost all of the sodium cations in the MTW framework were successfully exchanged to protons. Thermogravimetric (TG) analyses of hydrated products, which were prepared by leaving them for 7 days in a desiccator with saturated ammonium chloride solution at room temperature were carried out on