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Direct crystallization of **CHA**-type zeolite from amorphous aluminosilicate gel by seed-assisted method in the absence of organic-structure-directing agents

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ABSTRACT

Highly crystalline **CHA**-type aluminosilicate zeolites with the Si/Al ratio of around 4–5 were successfully synthesized by a seed-assisted method in the absence of organic-structure-directing agents (OSDAs); a method for so-called "OSDA-free synthesis" of the **CHA** zeolite has been newly developed. In this OSDA-free system, in addition to the seeds with the **CHA** topology, a judicious use of potassium or cesium cations together with sodium cations is a crucial key to the crystallization of the amorphous aluminosilicate gel into the **CHA** structure. The Si/Al ratio of the **CHA** zeolite was increased by decreasing the total amount of alkali cations added and/or the use of cesium cations in place of potassium ones. Furthermore, the employment of the amorphous aluminosilicate gel containing boron species led to the formation of the **CHA** zeolite with a high Si/Al ratio of 6.1 compared with the synthetic chabazite crystallized through the interzeolite conversion of the **FAU** zeolite (Si/Al: 2.0). The catalytic performance of the prepared **CHA** zeolites was also evaluated. In the methanol-to-olefins reaction, the catalyst life was improved by increasing the Si/Al ratio of the **CHA** zeolite.

1. Introduction

In the last two decades, zeolites with 8-membered ring (8-MR) channels have attracted much attention because they exhibit high selectivities to ethene and propene in the methanol-to-olefins (MTO) reaction due to the limitation of the size of the products imposed by the small pores [1]. Among the 8-MR zeolites, aluminosilicate zeolite SSZ-13 and silicoaluminophosphate zeotype material SAPO-34 with the **CHA** topology are well-known as an excellent catalyst for the MTO reaction; they provide high yields of light olefins with a long catalyst life [2–7]. The catalyst life can be improved by decreasing the framework Al species [5].

SSZ-13, the high-silica **CHA**-type aluminosilicate zeolite, is directly synthesized from an amorphous aluminosilicate gel by using *N*,*N*,*N*-trimethyladamantammonium hydroxide (TMAdaOH) as an organic-structure-directing agent (OSDA) [8]. However, from the viewpoint of the development of simple, economical and environmentally benign processes for zeolite synthesis, the method for the OSDA-saving or -free synthesis of the zeolite has been highly desirable. In preparing the **CHA**-type aluminosilicate zeolite, the reduction in the amount of TMAdaOH and the use of inexpensive OSDAs such as benzyltrimethylammonium hydroxide have been extensively investigated [9–11].

By contrast, the **CHA**-type aluminosilicate zeolite is formed in nature as "chabazite" mineral, and it has been easily synthesized through the interzeolite conversion of the **FAU** zeolite without using OSDAs [12]. However, the obtained **CHA** zeolite has a high Al content; the Si/Al atomic ratio is below 3. Our target in this study is to develop the direct synthesis method of the **CHA** zeolite from an amorphous aluminosilicate gel without using any OSDAs to control the Si/Al ratio in the product.

Since Xiao and his co-workers reported the OSDA-free synthesis of beta zeolite from an amorphous aluminosilicate gel by adding seed crystals of beta zeolite [13], the OSDA-free synthesis of zeolites from amorphous aluminosilicate gels has been widely studied for beta zeolite [14–17], ZSM-5 [18–20], **RTH**-type zeolite [21,22], **MTW**-type zeolite [23,24], **LEV**-type zeolite [25] and ferrierite [26–28]. The crystallization process from a sodium aluminosilicate gel in the absence of OSDAs has been also studied for clarifying the relation between synthesis conditions and product structures [29]. In the OSDA-free synthesis of zeolites, alkali metal cations (lithium, sodium, potassium, rubidium and cesium cations) as well as seed crystals strongly affect the nucleation and crystallization processes. Moreover, the cooperation of alkali cations can play an important role in the crystallization of the target zeolites in the

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absence of OSDAs. **MTW**-type zeolite was crystallized from an aluminosilicate gel containing sodium and lithium cations together with the seed crystals, while the initial gel without lithium cations was transformed to **MFI** zeolite [30]. In the synthesis of ferrierite, potassium cations contribute toward the formation of building units of ferrierite, while sodium cations leads to the crystallization by ordering the building units [26]. However, the effect of the cooperation of alkali cations on the crystallization of zeolites has not been well-studied in the OSDA-free synthesis of zeolites; furthermore, there are few previous reports on the use of alkali cations as mineralizers except for sodium and potassium cations for the synthesis of zeolites. It is expected that the associative employment of alkali cations would lead to the promotion of the diversification of the OSDA-free zeolite synthesis in the presence of seed.

Here we report a method for directly crystallizing an amorphous aluminosilicate gel into the **CHA**-type aluminosilicate zeolite in the absence of OSDAs. The crystallization process of the **CHA** zeolite in the absence of OSDAs has been clarified. The effects of the cooperation of alkali cations on the crystallization as well as the chemical composition of the **CHA** zeolite were also investigated in detail. We also investigated the effect of the addition of $Na_2B_4O_7$ as a boron source into the starting aluminosilicate gel on the structural properties because the occupation of framework by B^{3+} instead of Al^{3+} should lead to an increase in the Si/Al ratio. Finally, the synthesized **CHA** zeolites were used as an acid catalyst for the MTO reaction.

2. Experimental

2.1. Synthesis of ***CHA***-type aluminosilicate zeolite in the absence of OSDAs

First, sodium-type Al-containing SSZ-13 ([Al]-SSZ-13) as seed crystals was hydrothermally synthesized at 150 °C for 5 days by using *N,N,N*-trimethyladamantammonium hydroxide (TMAdaOH) as an OSDA in the presence of NaOH, according to the previous report [8]. Then as-synthesized [Al]-SSZ-13 was calcined at 600 °C for 10 h to remove the OSDA. In this study both as-synthesized and calcined [Al]-SSZ-13 samples were used as seed crystals.

In typical preparation of an amorphous aluminosilicate gel for the **CHA** zeolite synthesis, $NaAlO_2$ (Al/NaOH = 0.79, Kanto Chem. Inc.) as an aluminum source was added to an aqueous solution containing NaOH (97%, Wako) and KOH (85%, Wako) to form a clear solution. Fumed silica (Cab-O-Sil M5, Cabot) as a silica source was added to the mixture. The molar composition of the prepared gel was 1 SiO_2: 0.05 Al_2O_3: 0.40 Na_2O: 0.09 K_2O: 100 H_2O. After adding the seed crystals, the amorphous gel was transferred into a Teflon-lined stainless steel vessel with a volume of 20 mL and hydrothermally treated at 170 °C with tumbling at 20 rpm. The obtained product was recovered by filtration, washed with deionized water, and dried at 100 °C. For the purpose of varying the Si/Al ratio in the final product, CsOH (99.9%, Aldrich) instead of KOH was used and the composition of the starting gel was extensively investigated. Furthermore, $Na_2B_4O_7$ (99.5%, Aldrich) as a boron source was added to the aluminosilicate gel.

2.2. Characterization

XRD patterns were collected on a Rint-Ultima III (Rigaku) using a Cu-Kα X-ray source (40 kV, 40 mA). Nitrogen adsorption–desorption measurements were conducted at −196 °C on a Belsorp-mini II (Bel Japan) instrument. Prior to the measurement, the sample was evacuated at 350 °C for 2 h. The BET (Brunauer–Emmett–Teller) specific surface area (S_{BET}) was calculated from the adsorption data. Elemental analyses of the samples (Si/Al ratio) were performed on an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000). Profiles of temperature-programmed desorption of ammonia (NH_3-TPD) were recorded on a BELCAT (BEL Japan) apparatus. Typically, the sample was pretreated at 500 °C in He (50 mL min^{-1}) for 1 h and then was cooled to adsorption temperature of 100 °C. Then, 10% NH_3 in He was allowed to make contact with the sample; subsequently, the sample was evacuated to remove weakly adsorbed NH_3. Finally, the sample was heated from 100 to 610 °C at a ramping rate of 10 °C min^{-1} with the He flow (50 mL min^{-1}) passed through the reactor. A thermal conductivity detector was used to monitor desorbed NH_3. Field-emission scanning electron microscopic (FE-SEM) images of the powder samples were obtained on an S-5200 (Hitachi) microscope.

2.3. Methanol-to-olefins reaction

For the use of the OSDA-free **CHA**-type zeolites for the methanol-to-olefins (MTO) reaction, the sodium-type zeolites were converted into the proton-type ones by repeated ion-exchange using 1 M ammonium nitrate solution (3 times) and subsequent calcination at 550 °C for 2 h.

The MTO reaction was carried out in a 0.25 in. (OD) quartz tubular flow microreactor loaded with 100 mg of 50/80 mesh zeolite pellets without a binder. The catalyst was calcined at 500 °C for 1 h prior to the reaction, and then the reactor was cooled to 350 °C. The partial pressure of methanol was set at 5 kPa. He gas was used as a carrier. The catalyst weight to the flow rate ratio ($W/F_{\text{-methanol}}$) was 34 $g_{\text{-cat}}$ h $(mol_{\text{-methanol}})^{-1}$, which corresponded to the weight hourly space velocity of methanol (WHSV) of 0.93 h^{-1}.

The reaction products were analyzed with an on-line gas chromatograph (Shimadzu GC-2014) with a flame ionization detector and a capillary column (HP-PLOT 30 m × 0.53 mm, 6 μm film thickness). The selectivities to the products were calculated based on the carbon numbers.

3. Results and discussion

3.1. Crystallization of ***CHA***-type zeolite from amorphous aluminosilicate gel in the absence of OSDAs

A TG-DTA measurement revealed that as-made [Al]-SSZ-13 contained 20 wt.% $TMAda^+$; thus the employment of 20 wt.% as-made [Al]-SSZ-13 as a seed in the absence of OSDAs corresponds to the addition of 4 wt.% $TMAda^+$ ($TMAda^+/SiO_2$ molar ratio of 0.013) to the starting gel. Calcined [Al]-SSZ-13 exhibited an XRD pattern typical of the **CHA** structure (Fig. 1a). The Si/Al ratio of [Al]-SSZ-13 was 7.7. The FE-SEM image in Fig. 4 shows that [Al]-SSZ-13 was composed of cubic crystals with one side about 0.25 μm in length.

The synthesis conditions of the **CHA** zeolite in the absence of OSDAs and the obtained products are summarized in Table 1. When as-made [Al]-SSZ-13 was used as a seed, the product synthesized with NaOH alone was the **MOR** zeolite (Sample 1, Fig. 1b). It was found that the zeolite with the **CHA** topology was successfully synthesized by increasing the H_2O/SiO_2 ratio to 200 in the starting gel with the much smaller $TMAda^+$ content ($TMAda^+/SiO_2 = 0.013$) (Sample 2, Fig. 1c) than that used in the conventional synthesis ($TMAda^+/SiO_2 = 0.20$ [8]). This would be ascribed to the suppression of further transformation of the **CHA** zeolite into the **MOR** zeolite by a decrease in the alkalinity.

For the purpose of the OSDA-free synthesis of the **CHA** zeolite, the calcined [Al]-SSZ-13 was used as a seed. A mixture of the **CHA** phase and unknown phases was formed under the same conditions as those for the synthesis of Sample 2 (Sample 3, Fig. 1d). The pure **CHA** zeolite was successfully obtained from the amorphous gel