



Synthesis of phosphorus-modified small-pore zeolites utilizing tetraalkyl phosphonium cations as both structure-directing and phosphorous modification agents

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ABSTRACT

A rational strategy for the synthesis of phosphorus-modified small-pore zeolites by utilizing tetraalkyl phosphonium cations as both a structure-directing agent and a phosphorous modification agent was developed. Initially, we investigated the hydrothermal conversion of FAU zeolites as a starting silica/alumina source in the presence of tetraalkyl phosphonium cations with different structures. Various types of zeolites, including small-pore zeolites with 8-MR windows such as LEV, GIS, AEI, and CHA zeolites, were obtained. Next, we applied the dual-template method with a mixture of the N-containing organic structure-directing agent (OSDA) *N,N,N*-trimethyl-1-adamantammonium cation and the P-containing OSDA tetraethyl phosphonium cation to the synthesis of phosphorus-modified zeolites with small pores, especially CHA zeolites. Using this method, the proportion of P-containing OSDA/N-containing OSDA in as-synthesized CHA zeolites can be easily controlled. After the calcination of the as-synthesized zeolites, CHA zeolites with different degrees of phosphorus modification were easily obtained without significant pore occlusion or toxification of catalytically active sites. The phosphorus-modified CHA zeolite had high thermal stability and retained its structure even after calcination at 1050 °C for 1 h. In addition, in the selective catalytic reduction of NO_x with NH₃, the Cu-loaded phosphorus-modified CHA zeolite exhibited NO conversion above 90%, even after hydrothermal treatment at 900 °C for 8 h, indicating extremely high hydrothermal stability.

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1. Introduction

Microporous aluminosilicate zeolites, which have attractive structural features in terms of their selective separation, storage, and conversion of suitable chemicals, are important industrial materials vital both environmentally and commercially [1–3]. Among them, small-pore zeolites with 8-membered ring (8-MR) windows, such as CHA, AEI and LEV zeolites (where the three characters indicate the framework type) have received considerable attention. They have been utilized as catalyst supports for the selective catalytic reduction (SCR) of NO_x by ammonia for air

purification [4–7], economical separation membranes for dehydration of aqueous organic solutions [8–11] and gas separation [12–14], and alcohol conversion catalysts for production of light olefins [15–18]. Therefore, significant effort has been made to synthesize small-pore zeolites having new framework structures and beneficial physicochemical properties through the use of complex organic structure-directing agents (OSDAs) [19–21], organotemplate-free seed-assisted synthesis [22–25], and other novel synthetic strategies [26–30].

It is well recognized that P-containing OSDAs such as tetraalkyl phosphonium cations, phosphazenes, and aminophosphonium cations, as well as conventional N-containing OSDAs including quaternary ammonium cations and amines, are effective for zeolite synthesis [31–37]. Very recently, we have investigated a novel synthesis methodology utilizing tetraalkyl phosphonium cations as both a structure-directing agent and a phosphorus modification agent. We succeeded in synthesizing high-silica AEI zeolites with

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Si/Al ratios of 13–20 by hydrothermal conversion of FAU zeolites in a tetraethyl phosphonium hydroxide media [36,37]. OSDAs occluded in zeolitic micropores exhibited different decomposition behaviors when as-synthesized zeolites were calcined. N-containing OSDAs could be completely removed by calcination at high temperatures, resulting in formation of micropores, whereas monomeric and condensed phosphate species were formed in the zeolitic pores by the decomposition/oxidation of P-containing OSDAs during the conventional calcination process. The phosphorus species generated in the zeolitic pores improved the thermal/hydrothermal stability of zeolite. This is due to the presence of highly condensed polyphosphate bound to framework aluminum, resulting in suppression of dealumination [38–40]. As the post-modification of the small-pore zeolites with phosphorus compounds has never been accomplished because of their limited diffusion into the zeolitic pores, the use of P-containing OSDAs as phosphorous modification agents is the most promising method for preparing phosphorus-modified small-pore zeolites with enhanced thermal/hydrothermal stability. However, the formation of condensed polyphosphate species derived from P-containing OSDAs resulted in the blocking of zeolitic pores. The phosphonate species entrapped in the zeolitic cavities could not be completely removed even after severe thermal treatment [36,37], resulting in the reduction of crystallinity.

Consequently, we have now attempted to synthesize P-modified small-pore zeolites using a mixture of N-containing OSDA and P-containing OSDA. It is well known that the dual-template method using two types of OSDAs with different roles in the crystallization process is an efficient zeolite synthesis for formation of hierarchical pore structures [41–43], unique crystalline structures [44–46], and effective catalyst preparations [47–49]. Herein, we used both N-containing and P-containing OSDAs with structure-directing abilities for the synthesis of small-pore zeolites, especially CHA zeolite. Through subsequent calcination treatment at high temperatures the P-containing OSDA decomposed and the phosphorus-modified zeolite was easily obtained, whereas the N-containing OSDA was completely removed to form zeolitic pores. In this study, we initially investigated the potential of tetraalkyl phosphonium cations with different structures for zeolite synthesis. Then, we applied the dual-template method to the synthesis of high-silica CHA zeolite, in which tetraethyl phosphonium hydroxide (TEPOH) and *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH) were used as OSDAs. We also prepared Cu-loaded zeolite catalysts using these phosphorus-modified CHA zeolites and investigated their catalytic performance in the NH_3 -SCR of NO_x .

2. Experimental

2.1. Hydrothermal conversion of FAU zeolites using various tetraalkyl phosphonium cations

Starting FAU zeolites used in this work were prepared according to the procedure in the previous work [17]. NH_4 -Y zeolite (Si/Al = 2.8, Tosoh Co., Japan) was treated by carrying out dealumination involving a combination of steaming at 700 °C and H_2SO_4 (0.40–0.75 M) treatment at 30 °C for 16 h. The XRD pattern of the dealuminated zeolite showed no peaks other than those corresponding to the FAU structure. The particle size of a dealuminated FAU zeolite was 0.2–0.5 μm . The hydrothermal conversion of the FAU zeolites into the different zeolites was conducted as follows: The dealuminated FAU zeolite was thoroughly mixed with an aqueous solution containing sodium hydroxide (>99%, NaOH, Kojundo Chemical Laboratory, Japan) and various tetraalkyl phosphonium hydroxides, such as tetramethyl phosphonium hydroxide (TMPOH), TEPOH, and tetrabutyl phosphonium hydroxide (TBPOH),

as OSDAs. Then, the mixture was placed into a 30 cm^3 Teflon-lined stainless steel autoclave. The alkyl phosphonium hydroxides were prepared from phosphonium chloride, bromide, and iodide salts (Tokyo Chemical Ind. Co., Japan) by treating them with a hydroxide anion exchange resin. The hydrothermal conversion was conducted at 125–170 °C for 3 h–21 days in a convection oven. The solid product was collected by centrifugation and washed thoroughly with deionized water until the pH of the washes was near neutral, then dried overnight at 70 °C. Table 1 lists the hydrothermal synthesis conditions and characteristics of several zeolites obtained.

2.2. Hydrothermal conversion of FAU into CHA zeolites using a mixture of TEPOH and TMAdaOH

We applied the dual-template method using both P-containing and N-containing OSDAs to the hydrothermal conversion of FAU into CHA zeolites. The dealuminated FAU zeolite was thoroughly mixed with an aqueous solution containing sodium hydroxide (NaOH), TEPOH, and TMAdaOH (25 wt%, Sachem Asia Co., Ltd., Japan). Then, the mixture was placed into a 30 cm^3 Teflon-lined stainless steel autoclave. The hydrothermal conversion was conducted at 150 °C for 7 days in a convection oven. The solid product was collected by centrifugation and washed thoroughly with deionized water until the pH of the washes was near neutral, and then it was dried overnight at 70 °C. Table 2 lists the hydrothermal synthesis conditions and characteristics of CHA zeolites obtained. To remove the TEP cations from zeolitic pores and perform modification with phosphorus-containing species generated by decomposition/oxidation of TEP cations, the as-synthesized CHA zeolites were calcined in air at 600 °C for 10 h (a heating rate of 5 °C min^{-1}). Then, the Na cations in the calcined CHA zeolites were removed by ion-exchange with an aqueous solution of NH_4NO_3 (ca. 1.0 mol L^{-1}) at 60 °C for 6 h. The ion-exchange treatment was repeated three times, and the obtained NH_4 form was calcined at 450 °C for 6 h, yielding the H-form.

2.3. Preparation of the Cu-loaded CHA catalyst

The Cu-loaded CHA catalyst was prepared by the impregnation method as follows: An aqueous solution containing a measured amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Kishida Chemical Co. Ltd., Japan) was added to the H-form zeolite and mixed thoroughly in a ceramic mortar. The resultant wet powder was dried at 110 °C, followed by calcination at 550 °C for 1 h.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns of the solid products were collected using a powder X-ray diffractometer (Rigaku Mini-Flex) with graphite-monochromatized Cu $K\alpha$ radiation at 30 kV and 15 mA. The Si/Al, P/Al, and Cu/Al ratios were determined using inductively coupled plasma optical emission spectroscopy (ICP, Seiko SPS7000). The crystal morphology was observed using a Hitachi S-4800 scanning electron microscope (SEM) coupled with an energy-dispersive X-ray (EDX) analyzer. ^{13}C , ^{27}Al , ^{29}Si , and ^{31}P magic angle spinning (MAS) NMR spectra were recorded at 150.88 MHz, 156.33 MHz, 119.17 MHz, and 242.87 MHz, respectively, on a Varian 600PS solid NMR spectrometer, using a 3.2 mm diameter zirconia rotor at a rotation speed of 15 kHz for ^{27}Al and ^{31}P MAS NMR, and a 6 mm diameter zirconia rotor at 7 kHz for ^{13}C and ^{29}Si MAS NMR. The ^{27}Al spectra were acquired using 2.8 μs pulses, a 1 s recycle delay, and 256 scans. The ^{29}Si spectra were acquired using 6.2 μs pulses, a 100 s recycle delay, and 100 scans. The ^{31}P spectra were acquired using 2.35 μs pulses, a 10 s recycle delay, and 8500 scans. $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 3-(trimethylsilyl)propionic-2,2,3,3-

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