



Synthesis of phosphorus-modified AFX zeolite using a dual-template method with tetraethylphosphonium hydroxide as phosphorus modification agent

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ABSTRACT

Hydrothermal conversion of FAU zeolite was carried out in the presence of both 1,1'-(1,4-butanediyl)bis(1-azonia-4-azabicyclo[2,2,2]octane) (Dab-4) cation as a structure-directing agent and tetraethylphosphonium (TEP) cation as a phosphorus modification agent. By optimizing the synthesis parameters such as the TEPOH/SiO₂, [Dab-4](OH)₂/SiO₂, NaOH/SiO₂, and H₂O/SiO₂ ratios in the starting reaction mixtures, we successfully synthesized highly crystalline phosphorus-modified (P-modified) AFX zeolite with truncated hexagonal bipyr- amidal morphology. The P-modification of the AFX zeolite needed a TEP/(Dab-4 + TEP) ratio higher than 0.9 because TEP cations have no structure-directing ability for the AFX phase. The obtained P-modified AFX zeolite with a Si/Al ratio of 5–6 and a P/Al ratio of 0.07–0.2 exhibited high thermal stability compared to the P-free one.

1. Introduction

Small-pore zeolites with 8-ring windows (3–4 Å) and large cavities, such as CHA, AEI, LEV, LTA, KFI, and ERI zeolites, have recently received much attention because they exhibit excellent catalytic performance in methanol-to-olefins (MTO) reactions and the selective catalytic reduction of NO_x with ammonia (NH₃-SCR) [1–9]. As these reactions are performed at high temperatures in the presence of steam, improving the thermal/hydrothermal resistance of zeolites is critical for developing high-performance zeolite catalysts with high catalytic activity and durability. It is well recognized that the synthesis of high-silica zeolites using complex organic structure-directing agents (OSDAs) or removing the framework Al (dealumination) is very effective for preparing zeolite catalysts with high durability, especially due to the suppression of coke deposition.

The impregnation method using P-compounds such as H₃PO₄ and (NH₄)₂HPO₄ is also highly effective for enhancing the thermal/hydrothermal stability of zeolites. However, the post-modification of small-pore zeolites with such P-compounds is not effective because of their limited diffusion into the small pores. To overcome this problem, we have very recently developed a new methodology to synthesize P-modified small-pore zeolites using a dual-template method with a mixture of N- and P-containing OSDAs [10,11]. When calcination is carried out at high temperatures, the P-containing OSDA occluded in zeolitic pores decomposes/oxidizes and the generated phosphorus species can modify the zeolite framework, whereas the N-containing

OSDA gets completely removed to form zeolitic pores. This establishes an effective P-modification method, with an optimum modification degree, without drawbacks such as excess pore blocking and loss of crystallinity, resulting in an enhancement of thermal/hydrothermal stability of small-pore zeolites. The Cu-loaded P-modified CHA and AEI zeolite catalysts prepared using our method exhibited high catalytic activity and durability in the NH₃-SCR reaction [10,11].

In this short communication, we report the synthesis and characterization of P-modified AFX zeolite through the hydrothermal conversion of FAU zeolite using both Dab-4 and TEP as OSDA and the P-modification agent, respectively. Although the AFX zeolite was only synthesized under limited conditions, the material has recently attracted much interest because it possesses remarkably larger cavities (ca. 8 × 13.0 Å) compared to CHA and AEI zeolites [9,12–16].

2. Experimental

2.1. Synthesis of phosphorus-modified AFX zeolite

The starting FAU zeolites used in this study were prepared according to the procedure described in previous research [17]. The NH₄-Y zeolite (Si/Al = 2.8, Tosoh Co., Japan) was dealuminated using a combination of steaming at 700 °C and H₂SO₄ (0.40–0.75 M) treatment at 30 °C for 16 h. The dealuminated FAU zeolites with various Si/Al ratios were thoroughly mixed with an aqueous NaOH solution (NaOH > 99%, Kojundo Chemical Laboratory, Japan),

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Table 1
Synthesis of P-modified AFX from FAU using the dual-template method.

| Run no | Synthesis conditions ^a | | | | | | Product | | | | | |
|--------|-----------------------------------|------------------------|----------------------|-------------------|-----------------------------------|-----------------------|------------|---------|--------------------|-------------------|--|---|
| | Si/Al of FAU | Dab-4/SiO ₂ | TEP/SiO ₂ | TEP/(Dab-4 + TEP) | H ₂ O/SiO ₂ | NaOH/SiO ₂ | Phase | Yield/% | Si/Al ^b | P/Al ^b | BET surface area/m ² g ^{-1c} | Micropore volume/cm ³ g ^{-1d} |
| 1 | 17 | 0.1 | 0 | 0 | 5 | 0.6 | AFX | 39 | 4.0 | 0 | 819 | 0.31 |
| 2 | 17 | 0.05 | 0.1 | 0.67 | 5 | 0.6 | AFX | 25 | 4.0 | 0 | 742 | 0.29 |
| 3 | 17 | 0.01 | 0.18 | 0.95 | 5 | 0.6 | AFX | 26 | 4.0 | 0 | 699 | 0.27 |
| 4 | 17 | 0.03 | 0.27 | 0.9 | 10 | 0.6 | AFX + ANA | | | | | |
| 5 | 17 | 0.03 | 0.27 | 0.9 | 10 | 0.5 | AFX | 35 | 5.0 | 0.07 | | |
| 6 | 17 | 0.03 | 0.27 | 0.9 | 10 | 0.4 | AFX | 40 | 5.7 | 0.07 | 799 | 0.29 |
| 7 | 17 | 0.03 | 0.27 | 0.9 | 10 | 0.3 | FAU + AFX | | | | | |
| 8 | 17 | 0.024 | 0.276 | 0.92 | 10 | 0.4 | AFX | 28 | 5.6 | 0.08 | 807 | 0.30 |
| 9 | 17 | 0.015 | 0.285 | 0.95 | 10 | 0.4 | AFX | 42 | 4.8 | 0.09 | 801 | 0.30 |
| 10 | 17 | 0.006 | 0.294 | 0.98 | 10 | 0.4 | AFX | 44 | 5.6 | 0.20 | 665 | 0.25 |
| 11 | 17 | 0.003 | 0.297 | 0.99 | 10 | 0.4 | AFX + *BEA | | | | | |
| 12 | 30 | 0.006 | 0.294 | 0.98 | 10 | 0.4 | EMT + FAU | | | | | |
| 13 | 50 | 0.006 | 0.294 | 0.98 | 10 | 0.4 | *BEA | | | | | |

^a Temp. = 140 °C, Time = 2 days.

^b Measured by ICP.

^c Determined using the BET method.

^d Determined using the t-plot method.

tetraethylphosphonium hydroxide (TEPOH) and 1,1'-(1,4-butanediyl) bis(1-azonia-4-azabicyclo[2,2,2]octane) dihydroxide ([Dab-4](OH)₂). We prepared TEPOH and [Dab-4](OH)₂ by treating TEPBr (> 98, Tokyo Chemical Ind. Co., Japan) and [Dab-4]Br₂ (> 98, Wako Pure Chemical Industries, Japan) with a hydroxide anion exchange resin DIAION SA10A0H (Mitsubishi Chemical Co., Japan), respectively. Subsequently the mixture was placed in a 30 cm³ Teflon-lined stainless-steel autoclave. The hydrothermal conversion was conducted under static conditions at 140 °C for 2 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, following which it was dried overnight at 70 °C.

To remove the TEP cations from the zeolitic pores and perform modifications with P-containing species generated by the decomposition/oxidation of the TEP cations, the as-synthesized AFX zeolites were calcined in air at 600 °C for 10 h (heating rate was 5 °C min⁻¹). Subsequently the Na cations in the calcined AFX zeolites were removed by ion-exchange with an aqueous NH₄NO₃ solution (ca. 1.0 mol L⁻¹) at 60 °C for 6 h. The ion-exchange treatment was repeated three times, and the obtained NH₄ form was calcined at 450 °C for 6 h, yielding the protonated form.

2.2. Characterization

Powder XRD patterns of the solid products were collected using a powder X-ray diffractometer (Bruker D8 ADVANCE) with graphite-monochromatized Cu K α radiation at 40 kV and 40 mA. The Si/Al and P/Al ratios were determined using a Seiko SPS7000 inductively coupled plasma (ICP) optical emission spectroscope. The crystal morphology was observed using a Hitachi S-4800 scanning electron microscope (SEM) coupled with an energy-dispersive X-ray (EDX) analyzer. We recorded ¹³C, ²⁷Al, ²⁹Si, and ³¹P magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra at 150.88, 156.33, 119.17, and 242.87 MHz, respectively, on a Varian 600 PS solid NMR spectrometer, using a 3.2 mm diameter zirconia rotor at a 15 kHz rotation speed for ²⁷Al and ³¹P, and a 6 mm diameter zirconia rotor at 7 kHz for ¹³C and ²⁹Si MAS NMR. The ²⁷Al MAS NMR spectra were acquired using 2.8 μ s pulses, a 1 s recycle delay, and 256 scans; the ²⁹Si spectra using 6.2 μ s pulses, a 100 s recycle delay, and 100 scans; and the ³¹P spectra using 2.35 μ s pulses, a 10 s recycle delay, and 8500 scans. We used AlK (SO₄)₂·12H₂O, 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt, and ammonium dihydrogen phosphate as chemical shift references for the ²⁷Al, ²⁹Si, and ³¹P MAS NMR, respectively. Prior to the ²⁷Al MAS

NMR measurements, the samples were moisture-equilibrated over a saturated NH₄Cl solution for 24 h. The ¹H-¹³C cross-polarized (CP) MAS NMR spectra were measured using a spinning frequency of 7 kHz, a 90° pulse length of 5.6 μ s, and a cycle delay time of 5 s. The ¹³C chemical shifts were referenced to hexamethyl benzene. Nitrogen adsorption isotherms were obtained at -196 °C using a conventional volumetric apparatus (BELSORP-mini, Bel Japan). Prior to performing the adsorption measurements, the calcined samples (ca. 50 mg) were heated at 400 °C for 10 h under a N₂ flow. The Brunauer–Emmett–Teller (BET) surface area and micropore volume were calculated using the BET method (P/P₀ = 0.05–0.1) and the t-plot method, respectively.

2.3. Thermal stability

The thermal stabilities of P-free and P-modified AFX zeolites obtained using the dual-template method were evaluated using XRD analysis by comparing the change in the intensities of the sample peaks at 2 θ = 11.6, 12.9, 17.9, 20.3, and 21.8° before and after calcination at 600–1000 °C for 1 h in air. The relative crystallinity (RC) was determined as follows:

$$\text{RC (\%)} = \frac{\text{Sum of intensities of the peaks at } 2\theta \text{ after calcination at various temperatures for 1 h}}{\text{Sum of intensities of the peaks at } 2\theta \text{ before calcination}} \times 100$$

$$= \frac{\text{Sum of intensities of the peaks at } 2\theta \text{ at } 11.6, 12.9, 17.9, 20.3, \text{ and } 21.8^\circ \text{ after calcination}}{\text{Sum of intensities of the peaks at } 2\theta \text{ at } 11.6, 12.9, 17.9, 20.3, \text{ and } 21.8^\circ \text{ before calcination}} \times 100$$

3. Results and discussion

3.1. Hydrothermal conversion of FAU into AFX

The powder X-ray diffraction (XRD) pattern of the dealuminated FAU zeolite as a starting material showed no peaks other than those corresponding to the FAU structure, thus indicating high crystallinity without impurity. The SEM images also showed that no amorphous or impurities existed in the dealuminated FAU zeolite and the particle size was 0.2–0.5 μ m. By using the dealuminated FAU zeolite, we attempted to synthesize P-modified AFX zeolites.

To control the degree of P-modification, i.e., the P/Al ratio, in the AFX zeolite obtained by calcination, we carefully tuned the TEPOH/SiO₂ and [Dab-4](OH)₂/SiO₂ ratios in the starting reaction mixtures. Table 1 lists the hydrothermal conversion conditions and characteristics

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