Synthesis of hydrophobic siliceous ferrierite by using pyridine and sodium fluoride

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ABSTRACT

We report for the first time, the successful synthesis of siliceous ferrierites with SiO_2/Al_2O_3 = 138.8–324 by the hydrothermal treatment of aluminosilicate gel with the introduction of pyridine and easy-to-handle sodium fluoride (NaF). It has been found that pure siliceous ferrierites exhibit well-defined plate-like morphologies with sufficient micropore volume. Moreover, in terms of the adsorption of water vapor, siliceous ferrierites ($SiO_2/Al_2O_3 \geqslant 208$) exhibit significantly higher hydrophobicity than commercially available siliceous zeolite (ZSM-5, HSZ-890HOA, SiO_2/Al_2O_3 = 1880). This work provides a promising approach for the preparation of siliceous ferrierites with a simple synthesis system, and this finding will help to broaden the practical applicability of ferrierites.

1. Introduction

A large number of different zeolitic framework structures are known today, and zeolite ferrierite (Framework Type Code: FER) [1,2] is an important pentasil aluminosilicate zeolite with a two-dimensional channel system consisting of an eight-membered ring (8MR) channel (3.5×4.8 Å) along the *b*-axis and a 10MR (4.2×5.4 Å) channel along the *c*-axis [3,4]. Synthetic ferrierite is expected to be a useful material because of its suitability for various industrial applications. For instance, as a catalyst, H-form ferrierite with a high aluminum content (SiO_2/Al_2O_3 = 18) has exhibited superior performance in the skeletal isomerization of linear *n*-butenes to *iso*-butene [5,6]. Moreover, H-form ferrierite with SiO_2/Al_2O_3 = 17.6 has proven to be useful in the selective catalytic reduction (SCR) reaction of nitrogen oxide (NO_x) using ammonia gas [7]. Despite the potential applicability of ferrierite, there are major difficulties when using aluminum-rich ferrierite, namely the deactivation of the catalyst caused by coke formation and dealumination at high temperature in a water vapor environment [8]. For these reasons, the synthesis of high-silica ferrierite (siliceous ferrierite) with higher hydrothermal stability, higher selectivity to organic compounds, and unique catalytic properties compared

with aluminum-rich ferrierite has attracted much attention in recent years [9].

The synthesis of ferrierite with various SiO_2/Al_2O_3 ratios has been extensively studied by many researchers for both fundamental and practical purposes, and the SiO_2/Al_2O_3 ratios in the framework can be tuned by selecting appropriate routes. Aluminum-rich ferrierites with SiO_2/Al_2O_3 ratios of less than 20 have been synthesized by the hydrothermal treatment of Na or (Na,K)-aluminosilicate gels in the absence of organic structure-directing agents (OSDAs) [10–12]. Moreover, aluminosilicate ferrierites with SiO_2/Al_2O_3 ratios in the 20–60 range have been synthesized by introducing a variety of OS-DAs (*i.e.* pyridine, tetrahydrofuran, ethylenediamine, pyrrolidine, tetramethylammonium hydroxide, trimethylamine, or cyclohexyl-amine) [13–17] to the reactant mixtures, although these methods could not increase the SiO_2/Al_2O_3 ratio of the product above 60. On the other hand, one successful method for the preparation of all-silica ferrierite has been achieved that involves the hydrothermal treatment of silicate reactant mixtures containing OSDAs and fluoride ions as mineralizing agents [18–23]. The pioneering work on the synthesis of all-silica ferrierite was undertaken by Kuperman et al. [18], who formed a ferrierite framework from a silicate reactant mixture containing pyridine, hydrogen fluoride (HF), and 1-amino-*n*-propane. Later, Weitkamp and co-workers [23] reported the solvothermal synthesis of all-silica and aluminosilicate (SiO_2/Al_2O_3 = 28–35) ferrierites using pyridine, HF and various alkyl-amines. These important studies allowed us to prepare all-silica and aluminosilicate ferrierites. However, the controllable $SiO_2/$

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Al$_2$O$_3$ ratios of ferrierite products are still limited in a very narrow range, and to the best of our knowledge, there have been no reports on optimized synthesis conditions that yield siliceous ferrierites with SiO$_2$/Al$_2$O$_3$ ratios greater than 60. Moreover, these previous synthesis processes [18–23] still require the use of hazardous HF and various organics in their reactant mixtures, which leads to both high production costs and complex processes, and this has a negative impact on the potential for commercial mass production. Therefore, a much simpler way of synthesizing siliceous ferrierites is highly desirable from both industrial and environmental viewpoints.

This study proposes a new and straightforward synthesis method that provides siliceous ferrierites with a wide range of SiO$_2$/Al$_2$O$_3$ ratios (138.8–324) by using an optimized chemical composition for the reactant mixture, which contains pyridine and easy-to-handle sodium fluoride (NaF), under optimized hydrothermal conditions. The characteristics of the obtained ferrierite products with different SiO$_2$/Al$_2$O$_3$ ratios are reported and discussed in detail.

2. Experimental section

2.1. Materials

The following raw materials were used as provided: sodium aluminate (NaAlO$_2$, Wako Pure Chemical Industries, Ltd.) as the aluminum source, sodium hydroxide solution (NaOH, 1 N, Wako Pure Chemical Industries, Ltd.) and potassium hydroxide solution (KOH, 1 N, Wako Pure Chemical Industries, Ltd.) as alkali sources, Cab-O-Sil® (Grade M5, Cabot) as the silica source, pyridine (99.5 wt%, Wako Pure Chemical Industries, Ltd.) as the OSDA, sodium fluoride (NaF, 99.0 wt%, Wako Pure Chemical Industries, Ltd.) as the fluoride source, and ammonium chloride (NH$_4$Cl, 99.0 wt%, Wako Pure Chemical Industries, Ltd.) for NH$_4^+$ ion exchange. To compare the hydrophobicity of the obtained ferrierites, the commercially available H-form ZSM-5 (framework type code: MFI) with SiO$_2$/Al$_2$O$_3$ = 1880 (HSZ-890HOA, Tosoh Corp.) was used as provided. Siliceous ZSM-5 was chosen for the comparison because FER and MFI topologies have 10MR channels in common and similar micropore volumes (*ca.* 0.12 cm^3 g^{-1}).

2.2. Syntheses and post-treatment

The siliceous ferrierites (SiO$_2$/Al$_2$O$_3$ ⩾ 138.8) were synthesized by introducing pyridine as an organic structure-directing agent (OSDA) and NaF as a mineralizer into aluminosilicate gel with the following procedure. Sodium aluminate and sodium hydroxide solution were mixed with distilled water to obtain a clear solution. Then, pyridine and NaF were added to the clear solution, and mixed thoroughly. Subsequently, Cab-O-Sil was slowly added to the clear solution, and the resulting mixture was homogenized using a mortar and pestle to obtain a pasty gel. The gel compositions and the synthesis conditions are described in detail in Table 1. Subsequently, the obtained gel was transferred to a 60 mL stainless-steel autoclave and subjected to hydrothermal treatment at 165 °C for 96 h in an oven under autogenous pressure while being rotated at 20 rpm. After the hydrothermal treatment, the product was filtered, washed with distilled hot water (*ca.* 80 °C) until the filtrate had an almost neutral pH and dried at 60 °C. The obtained product was calcined at 650 °C for 10 h in a stream of dry air to completely remove the OSDA from the zeolite. The solid yield of the obtained zeolite was defined as the weight ratio percentage (g/g × 100) of the calcined solid product to the sum of the dry SiO$_2$ and NaAlO$_2$ in the starting aluminosilicate gel.

For comparison, ferrierites with SiO$_2$/Al$_2$O$_3$ ratios lower than 99.2 were prepared by different synthesis procedures and conditions as

shown in Table 1. An aluminum-rich ferrierite with a SiO$_2$/Al$_2$O$_3$ ratio of 12.6 was synthesized according to our previous report [11] by the hydrothermal treatment of (Na,K)-aluminosilicate gel (at 165 °C and 20 rpm) without the addition of OSDA or a fluoride source. On the other hand, ferrierites with SiO$_2$/Al$_2$O$_3$ ratios in the 19–99.2 range were prepared by the hydrothermal treatment of Na-aluminosilicate gel with the aid of pyridine as an OSDA. The synthesis procedure was very similar to that of siliceous ferrierites except for the chemical composition of the gel (see Table 1) and the addition of NaF.

To prepare H-form ferrierites, ion exchange was performed by the following procedure. First, NH$_4$-ferrierite was prepared by the ion exchange of the obtained product using 1 M ammonium chloride solution at 60 °C for 8 h. After filtration and washing with distilled water, the same ion-exchange procedures were repeated three times. Finally, the sample was dried at 60 °C followed by calcination at 500 °C for 3 h to prepare H-form ferrierite. The obtained solid products were characterized as H-form. In the following section, the ferrierite products are denoted as FER nos. 1–10 (see Table 1).

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of the products were collected by a powder X-ray diffractometer (Mac Science MO3XHF22) with Cu Kα radiation (λ = 0.15406 nm, 40 kV, 30 mA) at 2θ values of 5–40° with a scanning step of 0.02° at a scanning speed of 2° min^{-1}. The elemental analysis was performed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin–Elmer Optima-3000) after dissolving the solid products in a potassium hydroxide solution. The morphology and crystal size of the products were observed with a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). Solid-state ^{27}Al NMR spectra were recorded on a Bruker AVANCE-400 spectrometer equipped with a 4 mm magic-angle spinning (MAS) probe. The ^{27}Al MAS NMR spectra were observed at a resonance frequency of 104.2 MHz, with a pulse width of 1.0 at the resonance frequency. To obtain a symmetric environment around the aluminum species, all the samples were hydrated in a desiccator with saturated ammonium chloride solution for 24 h at room temperature prior to the ^{27}Al NMR measurements. The samples were spun at 12.5 kHz using standard 4 mm zirconia rotors. The ^{27}Al chemical shifts were referenced to 1 M aluminum nitrate solution (δ_{Al} = 0 - ppm). The pore characteristics of the products were evaluated by performing nitrogen adsorption–desorption measurements using an automatic gas adsorption apparatus (BELSORP-mini, BEL Japan, Inc.) at −196 °C. To evaluate the hydrophilic–hydrophobic character of the products with different SiO$_2$/Al$_2$O$_3$ ratios, the water adsorption measurements were performed using an automatic adsorption measurement apparatus (BELSORP-aqua, BEL Japan, Inc.). Prior to the nitrogen and water adsorption measurements, samples were dehydrated at 400 °C for 4 h in a vacuum.

3. Results and discussion

Table 1 summarizes the chemical compositions of the aluminosilicate gels, the synthesis conditions, and the features of the zeolite products obtained in the present study. Fig. 1 shows the simulated XRD pattern of FER [2,24], and the measured XRD patterns of H-form products (FER nos. 1, 4, 7, and 9). All the products were identified as ferrierite by comparison with the simulated FER pattern, and no impurity phases were observed. FER nos. 2, 3, 5, 6, and 8 in Table 1 also showed a pure FER framework structure (XRD data not shown). The SiO$_2$/Al$_2$O$_3$ and M/Al (M = Na or Na + K) ratios