Preparation of Fluorinated Aluminophosphate Molecular Sieve with Hexagonal Nanoflake Morphology by Ionothermal Method

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A novel hexagonal fluorinated aluminophosphate molecular sieve has been prepared ionothermally using 1-ethyl-3-methylimidazolium bromide as solvent and template provider in the presence of HF. The resulting fluorinated aluminophosphate molecular sieve is hexagonal nanoflakes with a thickness of about 170 nm and has the single-crystal property. Further comparative experiments show that fluoride ions have a strong effect on the morphology and framework of the samples.

Ionic liquids are special molten salts typically containing organic cations and inorganic anions, which have a low melting point (<100 °C), relatively low viscosity, high electric and thermal stability, are good solvents for a wide range of organic and inorganic materials, and, importantly, have negligible vapor pressure.[1,2] These characteristics enable ionic liquids to be widely used as "green" solvent, functional solvent, or catalyst in organic synthesis,[3,4] inorganic preparation,[5,6] electrochemistry,[7,8] as well as other areas.[9,10] Recently, Morris et al. reported a novel method using ionic liquids as the reaction solvent and structure directing agent (SDA) for the preparation of AEL-type aluminophosphate molecular sieve, which is called ionothermal synthesis. It is different from hydrothermal and solvothermal synthesis, which employs a molecular liquid.[11] The predominant advantages of the ionothermal preparation of molecular sieves are that a separate organic template is not required and that the preparation can be carried out at ambient pressure.

Following the discovery of the synthesis of microporous crystalline aluminophosphates, $AlPO_4$-*n*, by Flanigen et al.,[12] Kessler et al. developed the fluorine route to the preparation of metal phosphates with new zeolite-like architectures in the presence of organic template.[13,14] There is evidence that fluoride itself can play a structure-directing role[15–18] and is intimately involved in SDA ordering in certain materials.[19–21] In ionothermal synthesis, the addition of fluoride seems to be important in determining the phase selectivity of the reaction.[11] Here, we report for the first time the ionothermal preparation of a novel nanoflake of fluorinated aluminophosphate with single-crystal structure.

A PTFE-lined autoclave (volume 25 mL) was filled with $Al[OCH(CH_3)_2]_3$ (0.102 g, 0.50 mmol) and H_3PO_4 (0.173 g, 1.50 mmol, 85 wt % in H_2O).[22–24] This mixture was then heated to 50 °C on a hot plate for 2 h to remove excess water and any impurity formed during the reaction. The 1-ethyl-3-methylimidazolium bromide ([Emim]Br) (4.05 g, 21.2 mmol) and HF (0.045 mL, 48 wt % in H_2O) were added, and the mixed solution was kept in an ultrasonic cleaning bath (IMECO Ultrasonic, Bombay, Type I s250, 34 kHz, 250 W). The solution was sonicated for 5 min at 75 °C. The typical composition of the solution was $1Al_2O_3$:$3P_2O_5$:1.26HF:84.80[Emim]Br (molar ratio of reagents). Then the PTFE-lined autoclave was kept at 150 °C for 68 h. After the autoclave had been cooled to room temperature, the product was suspended in distilled water and then washed thoroughly with acetone and distilled water.

The X-ray diffraction (XRD) pattern was acquired in a 2θ range from 6 to 90° on a Bruker D8-ADVANCE X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) images, selected-area electron diffraction (SAED) pattern and energy dispersive spectroscopy (EDS) analysis were taken with an FEI Tecnai G2 20 S-TWIN instrument. The field emission scan electron microscope (FE-SEM) images were obtained on LEO 1530 instrument. Fourier transform infrared (FT-IR) absorption spectra were obtained with a NICOLET 510DX spectrometer.

The XRD pattern of the as-prepared product is shown in Figure S1 (S is referred to Supporting Information). It shows that the product is a new type of crystal with a strong diffraction peak at the 2θ of about 9°. The FE-SEM images (shown in Figures 1a and 1b) display fine hexagonal-plate-like crystals, and the thickness of the crystal is about 170 nm (see Figure S2). Figure 1c reveals the TEM image of one randomly chosen individual flake. A typical SAED pattern (shown in Figure 1d) measured upon a single plate confirms the single-crystal property of the product. The EDS analysis of the product (see Figure S3) demonstrates that the product is composed of Al, P, O, and F with the Al/P/O/F atomic ratio of about 1.3:1:3.8:0.7, indicating that fluoride ions are incorporated into the framework structure. The peaks of C and Cu signals are attributed to the carbon-coated copper grid.

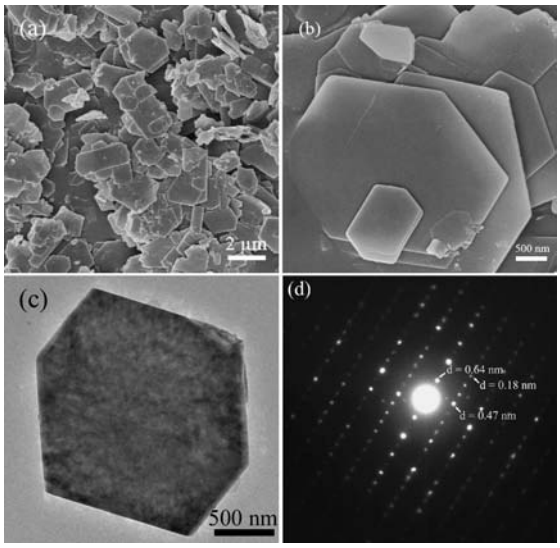

Figure 1. FE-SEM, TEM, and SAED images of the as-prepared product.

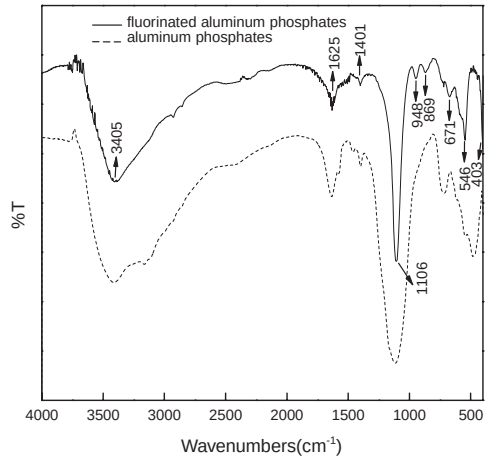

Figure 2. FT-IR spectra of the as-prepared product.

Figure 2 shows the FT-IR spectra of the obtained products (The solid line represents the fluorinated aluminophosphate, while the broken line represents aluminophosphate without fluoride ions.). The absorption bands at 3405 and 1625 cm^{-1} can be assigned to the O–H vibration mode. There exist four bands at 1401, 1106, 671, and 546 cm^{-1}, which are characteristic of aluminophosphate molecular sieves.[25] The asymmetric stretching vibrations of the P–O–Al unit occur at 1401, 1106, and 671 cm^{-1}. The band at 546 cm^{-1} arises from vibration characteristic of the aluminophosphate framework. While the band at 403 cm^{-1} arises from the P–O bending mode. In comparison with those for the no fluoride-substituted microporous aluminophosphates (476 cm^{-1}), the P–O vibration bands for fluorinated aluminum phosphates shift towards lower frequencies. Owing to the presence of fluoride element, there are two more peaks of 948 and 869 cm^{-1}, which are due to the stretching vibrations of Al–F bonds.

In order to investigate the effect of different molar ratio of HF on the framework and morphology of the products, comparative experiments were performed. It was found that without HF and with 0.013-mL HF, neither of the products had specific morphology, while the latter had the trend to form hexagonal morphology (see Figure S4). When the volume of HF was increased to 0.09 mL, even to 0.135 mL, no products were obtained.

Mineralizing agents such as fluoride are known to promote T–O–T (where T represents a tetrahedral atom) bond formation. The presence of fluoride anions would favor the formation of Al–F–Al bondings and prevent the linkage of Al–O–P.[26,27] This would reflect the different complexation constants between fluorides anions and phosphates anions with aluminum, which occurred in hydrothermal system. It has been reported by Parnham and Morris[28] that in ionothermal system, the framework consists of double six-membered rings (D6Rs) of alternating aluminum and phosphorus tetrahedra. These are linked through four-membered rings to produce a three-dimensional pore structure with eight-membered ring windows. Each six-membered ring of the D6Rs contains one octahedral aluminum that connects to octahedral aluminum of another D6R through two bridging fluorines. And thus Al–F–Al bonds were formed, when Al/P/O/F atomic ratio is about 1:1:4:0.3. In this work, we increased the F/Al ratio to 0.63, and the F/Al content of the final product is about 0.54. In comparison with the traditional hydrothermal system,[29] fluoride ions are more effectively incorporated into the framework structure. From the SAED, we could find that about double proportion of fluoride ion existed in the product. While fluoride ions were too much, their negative effect of preventing the linkage of Al–O–P became notable. And thus the framework could not be formed.

A new hexagonal nanoflake of fluorinated aluminum phosphate molecular sieve was successfully prepared using [Emim]Br ionic liquid as both the solvent and the template. According to comparative experiments, it could be found that only with the certain ratio of the precursors can the hexagonal fluorinated aluminophosphate be obtained. Detailed structure and formation mechanism are under investigation.

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