Formation mechanism and catalytic application of hierarchical structured FeAlPO-5 molecular sieve by microwave-assisted ionothermal synthesis

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ABSTRACT

At atmospheric pressure, FeAlPO-5 molecular sieve with hierarchical micro- and meso-porous structure has been ionothermally synthesized by microwave heating with eutectic mixture as the solvent. Among the synthesis parameters investigated, the ratio of P_2O_5/Al_2O_3, aluminum source, and heating methods significantly affected the mesoporosity of FeAlPO-5 molecular sieve. N_2 Physisorption, SEM and TEM characterizations showed that the resultant material possessed inter- and intra-crystalline mesopores simultaneously. The larger intercrystalline mesopores in size resulted from the intercrystalline void space between bar crystals and nanoparticles. The calcination removed the organic species embedded in the crystals of FeAlPO-5 molecular sieve, leading to the formation of smaller intracrystalline mesopores. The catalytic properties of hierarchical FeAlPO-5 molecular sieve were investigated in the hydroxylation of phenol with microporous FeAlPO-5 as a reference. The results showed that the catalytic performance of the former catalyst was superior to the latter.

1. Introduction

Recently, hierarchical zeolites received considerable interest in the zeolite community due to their excellent mass transfer capacity [1–6]. In particular, hierarchical ZSM-5 [7–9], TS-1 [10–12], Beta [13] and Y zeolites [14,15] synthesized by different methods have been applied to some important reactions relevant to industrial process, and exhibited higher catalytic activity compared with their microporous analogues. By contrast, the reports concerning the synthesis of hierarchical structured aluminophosphate molecular sieves are scarce [16–28]. Aluminophosphate molecular sieves are another class of molecular sieves first reported in 1982, which have been used to various reactions as catalysts or catalyst supports [16,29,30]. As was expected, hierarchical structured aluminophosphate molecular sieves also showed superior catalytic performance similar to hierarchical zeolites [16–19]. However, the synthetic procedures of this type of material are relatively complex. In view of the importance of aluminophosphate molecular sieves in catalytic reactions and the complexity of the synthetic methods reported in the literature, it is necessary to develop a facile synthetic method of hierarchical aluminophosphate molecular sieves.

Ionothermal synthesis developed by Morris et al. [31], in which ionic liquids served as both the solvent and template provider, is a novel method that has attracted much interest in the synthesis of zeolitic and other porous materials [32–38]. Owing to the vanishingly low vapor pressure of ionic liquids, synthesis could be carried out under atmospheric pressure, thus eliminating safety concerns associated with high hydrothermal pressure and facilitating the study on the formation mechanism of molecular sieves with in situ technique [39]. From this point of view, to synthesize hierarchical zeolites or aluminophosphate molecular sieves with ionothermal method is desirable.

Microporous FeAlPO-5 molecular sieve, an important redox catalyst, had been used to the alkylation and the selective catalytic reduction of N_2O with CH_4, and exhibited excellent catalytic performance [40–41]. In our previous work, we found that hierarchical FeAlPO-5 molecular sieve with AFI topology, which may be an alternative to microporous FeAlPO-5 for these reactions, can be ionothermally synthesized by microwave heating in eutectic mixture solvent, a related class of ionic liquid [42]. However, the formation mechanism of mesoporosity has not been revealed. In the present work, we aimed to solve this issue by studying the effects of crystallization conditions on mesoporosity and carrying out a series of characterizations, thus providing theoretical basis for the design of other types of hierarchical structured materials. Moreover, the catalytic performance of hierarchical FeAlPO-5

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molecular sieve was investigated in the hydroxylation of phenol with microporous FeAlPO-5 as a reference.

2. Experimental section

2.1. Synthesis of FeAlPO-5

Various hierarchical FeAlPO-5 molecular sieves were synthesized by microwave-assisted ionothermal method in a three-component eutectic mixture solvent consisting of succinic acid, choline chloride and tetraethylammonium bromide. The synthetic procedure of these materials can be found in our previous work [42]. Detailed synthesis conditions and the corresponding product phases were listed in Table 1. In order to understand the role of heating methods for the generation of mesopores, conventional heating method was also employed to synthesize FeAlPO-5 molecular sieve. The sample obtained with conventional heating (denoted as S1.1–1.5$_{conv}$) was prepared from the compositions and crystallization temperature same as those of S1.1–1.5 by microwave heating. As a comparison, microporous FeAlPO-5 [43] catalyst (denoted as S-micropor) was synthesized by direct hydrothermal method according to the literature.

2.2. Characterization

X-ray powder diffraction (XRD) patterns of the synthesized materials were conducted on a D/Max-2400 Rigaku diffractometer with Cu Ka radiation operated at 40 kV and 100 mA. The crystallinities of the samples were calculated on the base of the intensity of the peaks at 2θ of 7.5°, 14.9°, 19.8°, 21.1°, 22.5° and 26.0° [22]. The content of iron in the final product was quantified by a Rigaku JY38S inductively coupled plasma atomic emission spectrometer (ICP-AES). Nitrogen adsorption/desorption studies were conducted on a Micromeritics ASAP 2020 surface area and pore size analyzer at −196 °C. Samples were outgassed at 200 °C for 2 h prior to measurements. Specific surface areas of materials were calculated from the adsorption data obtained at p/p_0 between 0.07 and 0.20, using the Brunauer–Emmett–Teller (BET) equation. The micropore volumes were determined by the t-plot method. The mesopore parameters were determined from adsorption branches by BJH method. Thermogravimetric (TG) and differential thermal analysis (DTA) (Netzsch, STA409) was performed in air at a heating rate of 10 °C/min. The product morphology was obtained from a scanning electron microscopy (SEM JSM-6701F). Transmission electron micrographs (TEM) were obtained on a JEOL JEM-2010 microscope with a point resolution of 0.2 nm at 200 kV. For TEM, the sample was ground, dispersed in ethanol, and deposited on a holey carbon film supported on a copper grid. Diffuse reflectance UV–vis spectra (DR UV–vis) were measured with a spectrometer of Shimadzu UV-240, and BaSO$_4$ was an internal standard sample.

2.3. Catalytic reaction

In a standard reaction, 2 g of phenol and 0.10 g of catalyst were added to 24 mL of deionized water in a two neck flask equipped with a magnetic stirrer and a reflux condenser. After heating the reaction mixture to the temperature of 353 K, 2.22 mL of hydrogen peroxide (H$_2$O$_2$, 30 wt.% aqueous solution) was added through a syringe to the phenol solution containing catalyst (molar ratio of phenol/H$_2$O$_2$ = 1/1). The product distributions were determined by a LC2000 HPLC (Tianmei, Shanghai, China) equipped with a reversed phase C18 column using the methanol/water mixture (40/60, volume ratio) as the mobile phase at the flow rate of 1.0 mL min^{-1} with UV detection at 277 nm.

3. Results

3.1. Effects of P_2O_5/Al_2O_3 and HF/Al_2O_3 ratios on mesoporosity

Hydrofluoric acid (HF) is an extremely useful mineralizer or structure-directing agent for aluminophosphate synthesis. Our previous research had demonstrated that pure FeAlPO-5 molecular sieves cannot be synthesized when no HF was used [42]. In the present work, different amount of hydrofluoric acid was added to the synthetic system in order to study its potential effect on mesoporosity of FeAlPO-5. The N$_2$ adsorption/desorption isotherms and corresponding pore size distributions (PSDs) for the samples synthesized under different P_2O_5/Al_2O_3 and HF/Al_2O_3 ratios (XRD patterns shown in Fig. S1) are presented in Fig. 1 and Figs. S2–6. The pore parameters are summarized in Table 2. Obviously, the samples synthesized at P_2O_5/Al_2O_3 ratio of 1.1 (S1.1–0.5, S1.1–1.0, S1.1–1.5 and S1.1–2.0) are materials with hierarchical micro- and meso-porous structure, and have similar external surface area, mesoporous volumes, and PSDs. They all contain a small mesopore with average pore diameter below 10 nm and a large mesopore beyond 15 nm. As a comparison, the samples prepared with P_2O_5/Al_2O_3 ratio being 2.2 (S2.2–0.5, S2.2–1.0 and S2.2–2.0) exhibit lower mesoporous volumes, and they only possess one kind of mesopore below 10 nm.

Fig. 2 shows the SEM images of two typical calcined samples (S1.1–1.5 and S2.2–0.5). The sample S1.1–1.5 in fact is an agglomerate of bar crystals and nanoparticles, whereas the sample

Table 1
Synthesis conditions and the corresponding products.

Entry	Sample	[a]Al$_2$O$_3$: P$_2$O$_5$: F: Fe$_2$O$_3$: EU(molar ratio)	Product phases	Crystallinity (%)
1	S1.1–0.5	1.0: 1.1: 0.5: 0.4: 62	AFI	68
2	S1.1–1.0	1.0: 1.1: 1.0: 0.4: 62	AFI	68
3	S1.1–1.5	1.0: 1.1: 1.5: 0.4: 62	AFI	78
4	S1.1–2.0	1.0: 1.1: 2.0: 0.4: 62	AFI	79
5	S2.2–0.5	1.0: 2.2: 0.5: 0.4: 62	AFI	100
6	S2.2–1.0	1.0: 2.2: 1.0: 0.4:62	AFI	99
7	S2.2–2.0	1.0: 2.2: 2.0: 0.4: 62	AFI + amorphous	81
8	S1.1–1.5(A)	1.0[b]: 1.1: 1.5: 0.4: 62	AFI	94
9	S1.1–1.5(B)	1.0[c]: 1.1: 1.5: 0.4: 62	AFI	79
10	S1.1–1.5–0.2	1.0: 1.1: 1.5: 0.2: 62	AFI	72
11	S1.1–1.5–0.6	1.0: 1.1: 1.5: 0.6: 62	AFI	72
12	S1.1–1.5–124	1.0: 1.1: 1.5: 0.4: 124	AFI	44

[a] EU is the short form of eutectic mixture.
[b] aluminum hydroxyacetate.
[c] pseudo-boehmite. Unless otherwise specified, ferric ammonium citrate and aluminum isopropoxide are used as the iron source and aluminum source, respectively. Crystallization temperature and time: 180 °C, 1 h. Heating method: microwave irradiation.