Microporous and Mesoporous Materials 151 (2012) 56–63

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Facile synthesis of FeAlPO-5 molecular sieve in eutectic mixture via a microwave-assisted process

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ARTICLE INFO

Article history:
Received 19 July 2011
Received in revised form 25 October 2011
Accepted 10 November 2011
Available online 18 November 2011

Keywords:
Ionothermal synthesis
FeAlPO-5 molecular sieve
Microwave
Eutectic mixture
Mesoporous

ABSTRACT

FeAlPO-5 molecular sieve with AFI topology was ionothermally prepared under microwave irradiation in a three-component eutectic mixture and characterized by various techniques. N_2 adsorption/desorption measurements implied that the resultant samples exhibited a mesopore characteristic. Electron spin resonance (ESR) and diffuse reflectance UV–Visible spectra (DR UV–Vis) results revealed that various iron species coexisted on the mesoporous FeAlPO-5 molecular sieve. CHN elemental analysis, thermogravimetry–differential thermal analysis (TG–DTA) and the results of Fourier transform infrared spectra (FT-IR) suggested that tetraethylammonium bromide acted as the structure-directing agent in the synthetic process of FeAlPO-5 molecular sieve. In addition, the factors affecting the crystallization of FeAlPO-5 molecular sieve were investigated in detail. Contrary to the effect of the composition of the eutectic mixture, the types of iron and aluminum sources, as well as the addition of water, did not have major influences on the phase selectivity of the crystallization reaction. Relatively low P_2O_5/Al_2O_3 ratio, the addition of appropriate amount of HF, a longer time and higher temperature favored the crystallization of FeAlPO-5 molecular sieve.

1. Introduction

Iron-containing aluminophosphate molecular sieves have been broadly used as catalysts for various reactions due to their unique catalytic properties [1–4]. Normally these types of molecular sieves are prepared by hydrothermal or solvothermal methods in a sealed autoclave under autogenous pressure. Recently, Morris and co-workers reported pioneering work on the crystallization of zeolites in ionic liquids (ILs) with a technique termed “ionothermal synthesis” [5]. The peculiar properties of ILs endow the ionothermal synthesis many interesting features and potential advantages over the traditional synthetic methods of molecular sieves. For instance, because of the vanishingly low vapor pressure of ILs, synthesis can take place at ambient pressure, thus eliminating safety concerns associated with high hydrothermal pressure. In addition, the excellent microwave-absorbing property of ILs allows the ionothermal synthesis being carried out under microwave condition [6], leading to the rapid crystal growth rate and high product selectivity. Eutectic mixture is a related class of IL, which is usually composed of organic halide salts and hydrogen bonding donors. Advantages of eutectic mixture over ILs are their ease of preparation as pure states from easily available components and their relative nonreactivity with water. Therefore, eutectic mixture could be used in ionothermal synthesis as an alternative to ILs [7].

In our previous work, FeAlPO-16 molecular sieve with AST topology had been ionothermally synthesized by microwave irradiation in eutectic mixture comprising of succinic acid and choline chloride [8]. The highlight of the synthetic method reported by us may be well combining the advantages of eutectic mixture with that of microwave synthesis. Yet to date, there is little literature regarding the application FeAlPO-16 molecular sieve due to its possessing no real channels [9]. In this context, an effort to synthesize a more interesting framework was made by this method. Recent results reported by Tian and co-workers [10,11] revealed that the additions of amine or quaternary ammonium cation to ILs cannot only change the crystallization pathway, most importantly can improve the selectivity of the crystallization for ionothermal synthesis. Inspired by these results, we have reason to believe that this synthetic strategy created by them can be applied to eutectic mixture in the same way. Thus, in the current work, tetraethylammonium bromide as a very attractive template, which had been widely used to the synthesis of many molecular sieves, such as AlPO4-18, Beta, SAPO-34, SAPO-42 and ZSM-12 [12], was introduced to above mentioned eutectic mixture. Then, a novel three-component eutectic mixture including succinic acid, choline chloride and tetraethylammonium bromide was constructed and used to the synthesis of iron-containing aluminophosphate molecular sieves. A systematic study of the

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doi:10.1016/j.micromeso.2011.11.016

resultant products was carried out for their characterizations by powder X-ray diffraction (XRD), nitrogen adsorption/desorption, electron spin resonance (ESR), diffuse reflectance UV–Visible (DR UV–Vis) spectroscopy and scanning electron microscope (SEM). The structure-directing effect and the reaction conditions affecting the crystallization were also investigated in detail.

2. Experimental

2.1. Synthesis of samples

Synthesis of eutectic mixture solvent (denoted as EU): the as-bought succinic acid (denoted as SA), choline chloride (denoted as ChCl) and tetraethylammonium bromide (denoted as TEABr) were measured out in a molar ratio of 8:8:1 and ground in a mortar.

General synthesis procedure of FeAlPO-5: a round-bottom flask was successively charged with the eutectic mixture solvent, aluminum isopropoxide, phosphoric acid (85 wt.% in water), ferric citrate, hydrofluoric acid (40 wt.% in water) and deionized water if required. The round-bottom flask containing the final reaction mixture was placed in a microwave reaction system and heated to designated temperature at about 20 °C/min, then kept under ambient pressure for appropriate time. After the synthesis mixture had cooled to room temperature, the solid product was recovered by diluting the final mixture with distilled water and subsequent filtration. The resulting product was washed thoroughly with acetone and distilled water, and then dried in air to get the as-synthesized sample. The as-synthesized sample was calcined at 550 °C for 6 h to remove the template. Detailed synthesis conditions and the corresponding product phases were listed in Table 1.

2.2. Characterizations of samples

Powder X-ray diffraction (XRD) patterns of the synthesized materials were recorded on a Bruker D8 Advance diffractometer with Cu Ka radiation operated at 40 kV and 40 mA. 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 1.5 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 desorption branches by BJH method. Electron spin resonance (ESR) spectra were recorded at room temperature using a Bruker ER200D-SRC instrument. Diffuse reflectance UV–Vis spectra were measured with a spectrometer of Shimadzu UV-240, and $BaSO_4$ was an internal standard sample. Scanning electron microscope images were obtained from a SEM (JSM-6701F) instrument. CHN analysis was carried out on an Elementar Vario EL analyzer. Thermogravimetric (TG) and differential thermal analysis (DTA) (Netzsch, STA409) was performed in air at a heating rate of 10 °C/min. FT-IR spectra of the samples were recorded using a Thermo Electron Corporation Nicolet Nexus 670 FT-IR spectrometer in KBr media.

3. Results and discussion

3.1. Structure and morphology analysis

Fig. 1 illustrates the X-ray diffraction patterns of three typical as-synthesized samples (Table 1, A3, B3 and E3) and that of A3 calcined at 550 °C. These samples will be used in the following characterizations. As Fig. 1 displays, the peaks at $2\theta = 7.44°$, 12.90°, 14.96°, 19.80°, 20.94°, and 22.44°, corresponding to the diffractions of (1 0 0), (1 1 0), (2 0 0), (2 1 0), (0 0 2), and (2 1 1) of $AlPO_4$-5 [JCPDS: 41-0044] are clearly observed for the fresh and calcined samples, demonstrating that these samples are aluminophosphate molecular sieve with AFI topology. The characteristic XRD patterns exhibited by these materials match well with those reported in the literature [1–3]. By careful inspection of the XRD patterns one can see minor cristobalite is also detected in addition to AFI phase for the sample E3. Upon calcination a main change in peak position is observed for the sample A3 at the contribution of the 0 0 2 plane indicating a reduction of the *d* value in the *c* direction, which is possibly due to the removal of the template from the hexagonal channels [13]. The content of iron determined by ICP-AES is 0.45 wt.%, 1.32 wt.% and 0.40 wt.%, respectively for the as-synthesized A3, B3 and E3. These results clearly indicate that FeAlPO-5 molecular sieve has been successfully synthesized by ionothermal method. It should be noted that the content of the iron is so much different in the three samples. It is known that aluminum species preferentially bonds to phosphorus species to form the framework of aluminophosphate molecular sieve during the synthesis. For A3 and E3, it seems that the P_2O_5/Al_2O_3 ratios are so lower that no enough phosphorus atoms can be utilized to form a chemical bond with iron species, thus leading to lower incorporation amounts of iron species. On the other hand, the difference of the starting synthesis mixture in pH may also affect the incorporation amounts of iron species.

Table 1
Synthesis conditions and the corresponding products.

Entry	Al_2O_3:P_2O_5:F:Fe_2O_3:EU (molar ratio)	*T* (°C)	Time (min)	Product phases
A1	1.0:1.1:0:0.4:62	180	60	Amorphous
A2	1.0:1.1:0.5:0.4:62	180	60	AFI
A3	1.0:1.1:1.0:0.4:62	180	60	AFI
A4	1.0:1.1:2.0:0.4:62	180	60	AFI
B1	1.0:2.2:0:0.4:62	180	60	AFI + cristobalite
B2	1.0:2.2:0.5:0.4:62	180	60	AFI
B3	1.0:2.2:1.0:0.4:62	180	60	AFI
B4	1.0:2.2:2.0:0.4:62	180	60	AFI + berlinite
C1	1.0:4.0:0:0.4:62	180	60	Tridymite
C2	1.0:4.0:0.5:0.4:62	180	60	Berlinite
C3	1.0:4.0:1.0:0.4:62	180	60	AFI + unknown
C4	1.0:4.0:2.0:0.4:62	180	60	AFI + unknown + berlinite
D1	1.0[a]:1.1:1.0:0.4:62	180	60	AFI
D2	1.0[b]:1.1:1.0:0.4:62	180	60	AFI
E1	1.0:1.1:1.0:0.4[c]:62	180	60	Amorphous
E2	1.0:1.1:1.0:0.36[c]:62	180	60	AFI
E3	1.0:1.1:1.0:0.4[d]:62	180	60	AFI + cristobalite
E4	1.0:1.1:1.0:0.4[e]:62	180	60	AFI
E5	1.0:1.1:1.0:0.4[e]:62	190	60	AFI
F1	1.0:1.1:1.0:0.4:62	180	20	Amorphous
F2	1.0:1.1:1.0:0.4:62	180	40	AFI
G1	1.0:1.1:1.0:0.4:62	160	60	AFI + amorphous

[a] Pseudo-boehmite.
[b] Aluminum hydroxyacetate.
[c] Ferric nitrate.
[d] Ferric trichloride.
[e] Ferric ammonium citrate. Unless otherwise specified, aluminum isopropoxide and ferric citrate are used as the aluminum and iron sources, respectively.

The N_2 adsorption/desorption isotherms and their corresponding pore size distribution curves (PSDs) for the samples A3, B3 and E4 are shown in Fig. 2. The isotherms and PSDs of the other samples, such as A2, A4, C3, E2, and E3, were also measured for comparison, and given in Figs. S1–S5. Evidently, these samples exhibit typical adsorption curve of type IV plus type I [14], similar to those found in the mesoporous CrAPO-5 [15] and hierarchical SAPO-5 [16,17]. A steep increase in adsorbed volume occurs in