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Ionothermal syntheses and characterizations of cobalt-substituted extra-large pore aluminophosphate molecular sieves with -CLO topology

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ABSTRACT

Cobalt-substituted aluminophosphate molecular sieves with -CLO structure (denoted as CoDNL-1) have been synthesized in the ionic liquid 1-ethyl-3-methylimidazolium bromide with 1,6-hexanediamine as the cooperative structure-directing agent (co-SDA). The influence of various synthesis parameters (*e.g.* gel compositions and crystallization time) on the synthesis of CoDNL-1 has been investigated in detail. The products have been characterized by powder XRD, SEM, XRF, TG, N_2-adsorption, diffuse reflectance UV–Vis spectroscopy, ^{27}Al and ^{31}P MAS NMR spectroscopy and in situ XRD. Powder XRD, TG, chemical analysis and NMR indicate the incorporation of Co^{2+} ions into the -CLO framework. UV–Vis spectra reveal that Co^{2+} ions are present in tetrahedral sites of the -CLO framework. In situ XRD analyses show that CoDNL-1 possesses good thermal stability and the cobalt content in the framework influences the thermal stability of CoDNL-1.

1. Introduction

Crystalline molecular sieves, especially aluminosilicates and aluminophosphates, have been widely studied due to their wide applications in adsorption, ion-exchange and catalysis processes [1–3]. Since the discovery of VPI-5 aluminophosphate molecular sieve (VFI, 18-ring) in 1988 [4], a great deal of attention has been paid to the synthesis of open-framework materials with extra-large pores for their potential applications in chemical processes involving bulky molecules [5]. According to Brunner and Meier, open-framework structures with low framework density and extra-large pores should contain a large number of small three- and four-ring units [6]. On the basis of this suggestion, two synthetic routes toward the synthesis of extra-large pore materials have been developed. One is the use of fluoride ions, which have been found to direct and stabilize the formation of double four rings (D4Rs) [7], in the synthesis. The well-known example for this route is the synthesis of gallophosphate cloverite (-CLO, 20-ring) [8]. The other is the incorporation of heteroatoms into the T-site framework, such as Ge, which also has a directing effect toward the formation of small building units [5]. A number of germanosilicate zeolites with extra-large pores have been reported by Corma's group, such as ITQ-37 (30-ring) [9], ITQ-43 (28-ring) [10] and ITQ-44 (IRR, 18-ring) [11].

In 2004, Morris and co-workers first reported a novel method, ionothermal synthesis, for the preparation of aluminophosphate molecular sieves, using ionic liquids (ILs) or deep eutectic mixtures as both the solvent and the template [12]. Compared to water and organic solvents, ILs possess remarkable properties, such as negligible vapor pressure, high chemical and thermal stability, and recyclability, which make ionothermal synthesis safe and environmentally benign [13]. Since the pioneer work by Morris et al., a lot of work has been done on the ionothermal synthesis of molecular sieves. Many of them involve the use of water or organic amine in the synthesis. Research results revealed that reagent quantities of water can accelerate the crystallization kinetics, while additional organic amine can improve the phase selectivity of the reaction [14,15]. In addition, many novel porous materials have been ionothermally prepared due to the different chemistry of the ionothermal system compared to that of the hydrothermal and solvothermal systems [16–27]. Among them, some have extra-large pore frameworks, such as aluminophosphate SIZ-1 (16-ring) [12], cobalt borophosphate $(NH_4)_7Co_4(H_2O)[B_2P_4O_{15}$

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$(OH)_2]_2[H_2PO_4][HPO_4]$ (16-ring) [26], nickel phosphite JIS-3 (18-ring) [16], zinc phosphite NIS-3 (16-ring) [27] and aluminophosphate DNL-1 (20-ring) [25].

DNL-1 was prepared by using a co-templating ionothermal method, in which organic amine 1,6-hexanediamine (HDA) and ionic liquid 1-ethyl-3-methyl imidazolium bromide ([Emim]Br) acted as the cooperative structure-directing agents (co-SDAs) [25]. This material was then confirmed as an aluminophosphate analogue of the -CLO structure by using a combination of Rietveld refinement of powder X-ray diffraction data and NMR analysis. As a member of -CLO family, DNL-1 consists of two nonintersecting three-dimensional channel systems, one containing 8-ring openings and the other consisting of 20-ring openings with supercages (about 30 Å in diameter) at their intersections. Recent NMR research by Martineau et al. revealed that, in DNL-1, the HDA molecules are selectively in the *lta* cages, while the $Emim^+$ cations are found in both the *lta* cages and the supercages; the fluorine atoms are not only trapped in some of D4Rs but also covalently bonded to terminal Al or P atoms [28]. DNL-1 is thermally stable up to 950 °C in dry air and calcined DNL-1 shows high BET surface area and micropore volume [25]. These characteristics make DNL-1 of potential interest in catalytic applications that involve bulky molecules.

The synthesis of transition-metal-substituted aluminophosphate molecular sieves is of great interest due to the exceptional catalytic properties transition-metal ions can provide to these neutral frameworks [29]. Among the large variety of transition-metal-substituted aluminophosphates, cobalt-containing aluminophosphates have attracted much attention because of their promising applications in selective oxidation catalysis [30]. For example, CoAPO-18 exhibits remarkable catalysis activity and product selectivity in the oxidation of *n*-alkanes using molecular oxygen [31]. In this work, we present the synthesis of cobalt-substituted aluminophosphate molecular sieves with -CLO topology (designated as CoDNL-1) by using a co-templating ionothermal method. The different parameters that control the synthesis of CoDNL-1 have been studied. The incorporation of Co^{2+} ions into the -CLO framework has been revealed by powder XRD, TG, chemical analysis, NMR and UV–Vis spectra. The thermal stability of CoDNL-1 samples has been investigated with in-situ XRD.

2. Experimental

2.1. Synthesis

CoDNL-1 was synthesized according to the original procedures of DNL-1 with modifications [25]. A typical synthesis procedure was as follows: H_3PO_4 (85 wt% in H_2O), $Co(OAc)_2{\cdot}4H_2O$ and $Al[OCH(CH_3)_2]_3$ were first added into [Emim]Br with stirring at 90 °C in an oil bath for 30 min. Next, HF (40 wt% in H_2O) was introduced and the mixture was stirred for another 30 min. Finally, HDA was added and the mixture was stirred until it was homogeneous. The reaction mixture was sealed in a 100 ml Teflon-lined stainless steel autoclave and heated statically at 210 °C for appropriate time. The solid products were recovered by filtration, washed with water and ethanol, and dried at 110 °C overnight. The as-synthesized samples were calcined in air at 500 °C for 6 h to remove organic templates. Complete details of the synthesis conditions are summarized in Table 1.

2.2. Characterization

All samples were characterized by powder X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer, operating at 40 mA and 40 mkV, and using CuK_α radiation ($\lambda = 1.5418$ Å). The chemical composition of the samples was determined with a PANalytical MagiX X-ray fluorescence (XRF) spectrometer. The crystal morphology of the samples was studied by scanning electron microscopy (SEM) on a Hitachi S4800 field-emission scanning electron microspore operating at 20 kV. Textural properties of the calcined samples were determined by N_2 adsorption–desorption isotherms on a Micromeritics ASAP 2420 at 77 K. The diffuse reflectance UV–Vis spectra were obtained on a Hitachi U-3900H spectrophotometer equipped with an integrating sphere with $BaSO_4$ as

Table 1
Synthesis conditions and resulting products.

Sample	Gel compositions (molar ratio)							*t* (h)	*T* (°C)	Product
	Co	Al	P	HF	HDA	IL	H_2O[a]			
1	0	1	1.1	2.0	0.6	40	4.4	3	210	-CLO
2	0.05	1	1.1	2.0	0.6	40	4.6	3	210	-CLO
3	0.10	1	1.1	2.0	0.6	40	4.8	3	210	-CLO
4	0.15	1	1.1	2.0	0.6	40	5.0	3	210	CHA
5	0.20	1	1.1	2.0	0.6	40	5.2	3	210	CHA
6	0.10	1	1.1	2.0	0	40	4.8	3	210	AEL
7	0.10	1	1.1	2.0	0.2	40	4.8	3	210	AEL
8	0.10	1	1.1	2.0	0.4	40	4.8	3	210	-CLO
9	0.10	1	1.1	2.0	0.8	40	4.8	3	210	CHA
10	0.10	1	1.1	2.0	1.0	40	4.8	3	210	CHA
11	0.10	1	1.1	0	0.6	40	1.5	3	210	Amorphous
12	0.10	1	1.1	0.4	0.6	40	2.1	3	210	-CLO + CHA
13	0.10	1	1.1	0.8	0.6	40	2.8	3	210	-CLO + CHA
14	0.10	1	1.1	1.6	0.6	40	4.1	3	210	-CLO + CHA
15	0.10	1	1.1	2.4	0.6	40	5.5	3	210	-CLO
16	0.10	1	1.1	2.8	0.6	40	6.1	3	210	-CLO + CHA
17	0.10	1	1.1	3.2	0.6	40	6.8	3	210	–[b]
18	0.10	1	1.1	2.0	0.6	40	4.8	0	210	Amorphous
19	0.10	1	1.1	2.0	0.6	40	4.8	1	210	Amorphous
20	0.10	1	1.1	2.0	0.6	40	4.8	1.5	210	-CLO
21	0.10	1	1.1	2.0	0.6	40	4.8	2	210	-CLO
22	0.10	1	1.1	2.0	0.6	40	4.8	4	210	-CLO + CHA
23	0.10	1	1.1	2.0	0.6	40	4.8	6	210	-CLO + CHA
24	0.10	1	1.1	2.0	0.6	40	4.8	12	210	CHA

[a] All water in the reaction gel came from reagents and no extra water was added.
[b] No solid product was obtained.