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Synthesis and characterization of DNL-6, a new silicoaluminophosphate molecular sieve with the RHO framework

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ABSTRACT

A new silicoaluminophosphate molecular sieve with the RHO framework (designated as DNL-6, Dalian National Laboratory Number 6) has been hydrothermally synthesized for the first time with diethylamine (DEA) template in the presence of cetyltrimethylammonium bromide (CTAB). Influence factors, such as CTAB amount and silica content in the starting gel, crystallization time and temperature, were investigated. It was observed that DEA together with CTAB were necessary for the formation of pure RHO phase, which appeared in a narrow range of the starting gel compositions and synthesis conditions. Only DEA and water molecules were found in the as-synthesized DNL-6 without any existence of CTAB. All Si atoms incorporated into the framework with Si(4Al) environment at a high amount close to the theoretical maximum value. DNL-6 molecular sieve possessed high micropore surface area (777 m^2/g) and large micropore volume (0.36 cm^3/g) with good thermal and hydrothermal stability. Crystallization course was studied by monitoring solid products at different crystallization times with XRD, SEM, XRF, NMR and CHN elemental analysis. It is proposed that DNL-6 crystals were more likely formed directly from the crystallization of liquid phase rather than from the transformation of amorphous materials, and Si atoms directly incorporated into the DNL-6 framework from the very beginning of the crystallization via a SM2 mechanism.

1. Introduction

Molecular sieves have been widely used in many industrial fields as sorbents, catalysts and ion exchangers [1,2]. Increasing numbers of new framework types with compositional variability have been synthesized in recently years due to the impressive synthetic efforts [3], providing more chance for understanding of crystallization mechanisms and for practical application. However, rational design of novel materials with targeted properties (structure, composition, morphology, etc.) still remains a challenge, although some evident progress has been made by several research teams [4–7].

Union Carbide firstly reported aluminophosphate (AlPO) and silicoaluminophosphate (SAPO) molecular sieves in 1980s, which are formed by the self-assembling of tetrahedrally connected TO_4 (T = Si, Al, P, etc.) building units with the assistance of organic directing agents [8–11]. AlPO and SAPO molecular sieves contain many different framework types, in which some are analogous to certain known zeolites, but a large numbers have unique structures [12]. Since their discovery, some important industrial applications have been developed. For example, SAPO-11 was used as catalyst for hydroisomerization of long-chain paraffins [13] and SAPO-34 as catalyst for methanol to olefin (MTO) reaction [14].

Aluminosilicate zeolite RHO, firstly reported by Robson, is often synthesized in the presence of sodium and cesium cations [15]. The body-centered cubic symmetry structure of RHO is composed of α-cages linking through double 8-rings (D8R) with pore size of 3.6 × 3.6 Å. This structure would undergo a framework distortion with change of unit cell symmetry or even collapse upon extra framework cation exchange or dehydration [16–18]. Extensive pioneer works have shown that zeolite RHO owns excellent performance for selective synthesis of dimethylamine from methanol and ammonia [19,20]. However, the use of expensive cesium cations in the synthesis of RHO zeolite is a limitation on its application. Other RHO analogs, containing beryllophosphate [21], berylloarsenate [22], aluminogermanate [23], ECR-10 [20], LZ-214 [24], have also been synthesized with inorganic cations as structure directing agents. Me-AlPOs (Me = Co, Mg, Mn) RHO analogs were reported using organic amine as structure directing

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agent, but their framework structures were unstable upon the removal of organic templates [25].

In this paper, we report the synthesis of DNL-6, a new silicoaluminophosphate molecular sieve with RHO-type framework, by using DEA as the template in the presence of CTAB surfactant. Si incorporation and crystallization mechanism were discussed based on the investigation of the entire crystallization process. During the present synthesis research, our group found that DNL-6 could also be prepared through a phase-transition method from the SAPO-5 precursor [26].

2. Experimental

2.1. Synthesis

Typical hydrothermal synthesis procedure was as follows. Orthophosphoric acid (85 wt.%) and tetraethyl orthosilicate were mixed with a solution of aluminium isopropoxide and deionized water, and then an aqueous solution of cetyltrimethylammonium bromide (CTAB) was added with final addition of DEA template. Stirring was kept during all the above mixing procedure. The final gel mixture was transferred into a stainless-steel autoclave and heated up to 200 °C under rotation. Crystallization time was recorded once the temperature reached 200 °C. After certain time at the temperature for crystallization, the autoclave was cooled down and the solid product was recovered by filtration, washed three times with deionized water and further three times by ethanol, and dried at 110 °C overnight. Calcination was carried out at 600 °C for 4 h to remove organic species. The detailed gel compositions for the hydrothermal synthesis of DNL-6 are given in Table 1.

To investigate the crystallization mechanism, some experiments were performed with different crystallization times in separate batches from the same gel composition of 1.0DEA:1.0Al:0.8P:0.2Si:0.1CTAB:50H_2O.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm). Scanning electron microscopy (SEM) images were taken on a KYKY-AMRAY-1000B electron microscope at 25 kV. Chemical composition was determined with an X-ray fluorescence (XRF) spectrometer (Philips Magix-601). CHN elemental analysis was measured using VARIO EL III elemental analyzer (Germany Elementar Company). N_2 adsorption measurement was carried out on a Micromeritics 2010 analyzer at 77.35 K after the sample was degassed at 350 °C under vacuum. MAS NMR measurements were conducted on a Varian Infinity plus 400 WB spectrometer, where resonance frequencies were 79.41, 104.17, 161.83 and 100.5 MHz for ^{29}Si, ^{27}Al, ^{31}P and ^{13}C, respectively. Spinning rates of the samples at the magic angle were 4, 10, 6 and 8 kHz for ^{29}Si, ^{27}Al, ^{31}P and ^{13}C, respectively. Reference materials for the chemical shift (in ppm) determination were 2,2-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) for ^{29}Si and ^{13}C, 1.0 M $Al(H_2O)_6^{3+}$ for ^{27}Al and 85% H_3PO_4 for ^{31}P. Thermal analysis was carried out on a TA Q600 analyzer at a heating rate of 10 °C/min under an airflow rate of 100 ml/min.

Relative crystallinity of the samples was calculated by the formula: $I_{rel.}(\%) = (I_1 + I_2 + I_3)_{sample} \times 100/(I_1 + I_2 + I_3)_{standard}$, where I_n (n = 1, 2, 3) represents the intensities of the three strongest diffraction peaks on the XRD pattern. The sample crystallized at 200 °C for 24 h was chosen as a standard one.

3. Results and discussion

3.1. Synthesis

The detailed synthetic conditions of samples are shown in Table 1. In the case of no CTAB addition to the gel, it could be seen from Table 1 (C1) that only small amount of RHO was observed, coexisting with the main product of CHA phase. This is partly consistent with our previous research, in which CHA was the only product [27]. Addition of small amount of CTAB (C2, 0.05 mol) to the gel led to a product mainly in RHO phase. Increase of CTAB (C3, C4) gave a pure RHO phase. However, further increase of CTAB (C5, 0.2 mol) would cause the formation of an amorphous product. Pure RHO phase appeared only in a narrow CTAB range (0.1–0.15 mol). The above results indicate that DEA together with CTAB were necessary for the formation of RHO phase, which was also sensitive to the amount of CTAB in the starting gel.

Silica content effect was investigated by keeping CTAB at an optimized amount for the formation of pure RHO phase. It is evident that from S1, C3, S2 and S3 samples in Table 1, the change of silica contents in the gel caused different solid products, without pure RHO phase except for C3. Similar phenomena were observed when changing crystallization time and temperature. Longer crystallization time (T2, 48 h) led to a mixture of RHO and CHA. Decreasing crystallization temperature to 180 °C, RHO formed together with amorphous solids.

For most investigations in the syntheses, an interesting phenomenon is the coexistence of RHO and CHA phases. A reasonable explanation is that RHO and CHA have the same loop configuration of T-atoms in their frameworks, and similar coordination sequences from N1 to N4 [3].

3.2. Physicochemical characterization of DNL-6

The sample C3 in Table 1 was used for various physicochemical characterizations.

3.2.1. XRD, XRF and SEM

The XRD patterns of the samples are shown in Fig. 1. Peak positions of as-synthesized sample C3 were almost identical to those of the aluminosilicate RHO zeolite except the difference in the

Table 1
Gel compositions and resultant products of hydrothermal synthesis.

Sample	Al	P	Si	DEA	CTAB	H_2O	Time (h)	Product phase
C1	1	0.8	0.2	1	0	50	24	CHA + small RHO
C2	1	0.8	0.2	1	0.05	50	24	RHO + small CHA
C3	1	0.8	0.2	1	0.1	50	24	RHO
C4	1	0.8	0.2	1	0.15	50	24	RHO
C5	1	0.8	0.2	1	0.2	50	24	Amorphous
S1	1	0.8	0.0	1	0.1	50	24	Amorphous + minor RHO + minor CHA
S2	1	0.8	0.3	1	0.1	50	24	RHO + minor CHA
S3	1	0.8	0.4	1	0.1	50	24	CHA
T1[a]	1	0.8	0.2	1	0.1	50	24	RHO + small amorphous
T2	1	0.8	0.2	1	0.1	50	48	RHO + CHA

[a] Crystallization temperature was 180 °C.