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Aluminophosphates

Ionothermal Synthesis of an Aluminophosphate Molecular Sieve with 20-Ring Pore Openings**

Ying Wei, Zhijian Tian, Hermann Gies, Renshun Xu, Huaijun Ma, Renyan Pei, Weiping Zhang, Yunpeng Xu, Lei Wang, Keda Li, Bingchun Wang, Guodong Wen, and Liwu Lin*

Crystalline porous materials with large or extralarge pores continue to be of particular significance in both industry and academia for their potential applications in shape-selective catalysis and adsorption/separation.[1–3] Of these zeolitic materials, especially aluminosilicate- and aluminophosphate-based molecular sieves are of prime interest because of their high stability associated with their widespread use in many established process and emerging applications.[4] The materials VPI-5 (VFI framework type, 18-ring)[5] and UTD-1 (DON framework type, 14-ring)[6] were the first extra-large pore (pores constructed of more than 12 T atoms) aluminophosphate and aluminosilicate materials discovered. The oxide frameworks are built up by corner-sharing [AlO_4] and [PO_4] tetrahedra as well as [AlO_4] and [SiO_4] tetrahedra. In the search for materials with even larger pores, an anionic open-framework aluminophosphate JDF-20 (20-ring) was reported; however, it could not be classified as a zeolite because its framework (with an Al/P ratio of 5:6) is unstable upon removal of the occluded protonated templates by calcination.[7] Larger pore openings were also achieved using Ge or Ga as the framework T atom in a high amount, for example in ECR-34 (ETR framework type, 18-ring),[8] ITQ-33 (18-ring),[9] cloverite (-CLO framework type, 20-ring),[10] and ITQ-37 (30-ring).[11] In this context, the use of Ge or Ga as framework atoms as well as fluoride has been found to facilitate the formation of a double four-ring (D4R) unit.[12,13] This is in agreement with the prediction by Brunner and Meier that structures with extra-large pores should contain a large number of three- and four-membered rings.[14]

Ionothermal synthesis, in which ionic liquids act as both the solvent and template, is a novel method that has attracted great interest in the synthesis of zeolitic and other porous materials.[15–17] Besides the advantage of experimenting at ambient pressure, ionic liquids offer different chemistry and structural variety associated with the use of additional amines as structure-directing agents (SDA), and therefore open up new vistas for the synthesis of new porous materials.[15–20] Herein, we report the ionothermal synthesis of the first aluminophosphate molecular sieve with 20-ring pore openings, denoted as DNL-1 (Dalian National Laboratory Number 1). This molecular sieve was confirmed as a structural analogue to the gallophosphate molecular sieve cloverite by using a combination of Rietveld refinement of powder X-ray diffraction (PXRD) data and NMR analysis. Moreover, in comparison to cloverite, DNL-1, as-synthesized and calcined, exhibits excellent stability.

DNL-1 was synthesized in the ionic liquid 1-ethyl-3-methylimidazolate bromide ([emim]Br) with 1,6-hexanediamine (HDA) as the co-SDA. The detailed synthetic procedure is described in the Experimental Section. The as-synthesized DNL-1 material displays uniformly globular agglomerates of grainlike nanocrystals with a diameter of about 20 μm (see the Supporting Information). Analysis by energy dispersive X-ray spectroscopy (EDX) indicates the P/Al/F molar ratio of approximately 3:3:1. The inductively coupled plasma (ICP) analysis gives the content (wt %) of Al 16.50 and P 16.65. The elemental and thermogravimetric (TG) analyses show the content (wt %) of C 9.72, N 3.64, H 3.29, and a total weight loss of 34 %. Combined with the results of the structure refinement (see below), the chemical formula of DNL-1 was determined as $|(C_6N_2H_{18})_{104}(C_6N_2H_{11})_{80}(H_2O)_{910}|[Al_{768}P_{768}O_{2976}(OH)_{192}F_{288}]$.

Using the initial structure model from cloverite, the Rietveld refinement of as-synthesized DNL-1 was successfully performed in space group $Fm\bar{3}c$ with refined unit cell parameter $a = 51.363(1)$ Å, which is comparable to that of cloverite $a = 51.713$ Å, considering the smaller ionic radius of Al.[10] Similar results were observed in the all-silica and Ge-containing polymorph C of zeolite Beta.[21,22] Figure 1 shows the very good agreement between observed and calculated PXRD patterns, taking into account the limited signal to noise ratio, in particular for the data collected at a high angle which can be reflected from the expected R factor of 14.5 %. These results adequately confirm that DNL-1 is a pure aluminophosphate analogue of the -CLO structure. The skeletal model of the refined framework structure is shown in Figure 2. The framework of DNL-1 shows the general features of the -CLO structure: 1) two nonintersecting three-dimensional channel systems with 20-ring and 8-ring windows, respectively, 2) four terminal hydroxy groups (Al–

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[*] Y. Wei, Prof. Z. Tian, R. Xu, Dr. H. Ma, R. Pei, Prof. W. Zhang, Prof. Y. Xu, Dr. L. Wang, K. Li, Dr. B. Wang, G. Wen, Prof. L. Lin
State Key Laboratory of Catalysis
Dalian National Laboratory for Clean Energy
Dalian Institute of Chemical Physics
Chinese Academy of Sciences, Dalian 116023 (China)
Fax: (+86) 411-843-79151
E-mail: tianz@dicp.ac.cn

Y. Wei, R. Xu, R. Pei, K. Li, G. Wen
Graduate School of Chinese Academy of Sciences
Beijing 100049 (China)

Prof. H. Gies
Institute for Geology, Mineralogy and Geophysics
Ruhr University, 44780 Bochum (Germany)

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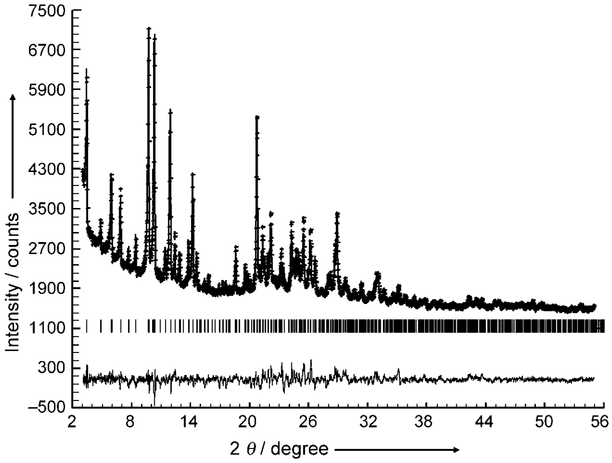

Figure 1. Observed (crosses) and calculated (lines) XRD patterns of as-synthesized DNL-1 as well as the difference profile (bottom).The short tick marks below the patterns give the positions of Bragg reflections.

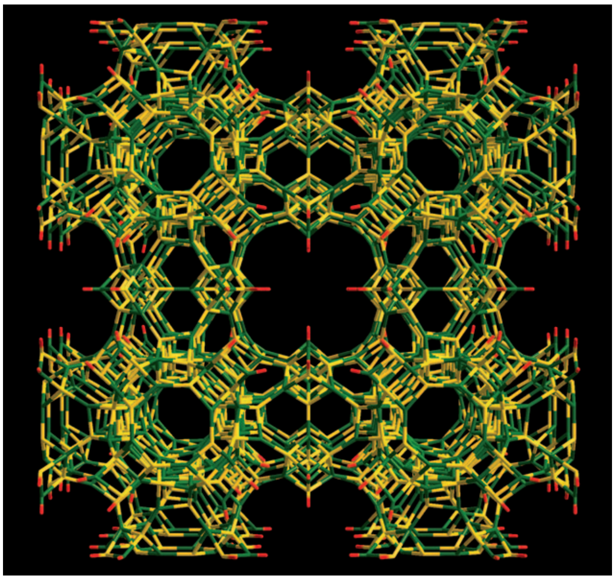

Figure 2. A [001] perspective view of the framework structure of DNL-1 obtained from the structure refinement. The bridging oxygen atoms in the framework and all hydrogen atoms have been omitted for clarity. Al yellow, P green, and O red.

Table 1: Comparison of relevant averaged bond lengths and angles between the refined DNL-1 and cloverite.[13]

	DNL-1	Cloverite
averaged bond length [Å]		
Al/Ga–O	1.74(3)	1.81
P–O	1.59(3)	1.52
averaged bond angle [°]		
T-O-T	141.9(1.3)	139.6
O-T-O	108.2(2.1)	108.9

OH and P–OH) extending into the 20-ring opening to give a cloverleaf shape, 3) the super cages at the intersection of the 20-ring channels, and 4) half of the D4R units not fully connected.[13] The details of the Rietveld refinement are given in the Experimental Section and the Supporting Information. The relevant averaged bond lengths and angles of the refined DNL-1 are compared with those of cloverite in Table 1.

The intense resonance at $\delta = 35.7$ ppm in the ^{27}Al magic-angle spinning (MAS) NMR spectrum and $\delta = -20.4$ ppm in the ^{31}P MAS NMR spectrum (Figure 3) correspond well to tetrahedrally coordinated Al and P atoms in the frameworks of aluminophosphate molecular sieves.[23] The resonance at $\delta = -11.0$ ppm in the ^{31}P MAS NMR spectrum demonstrates the existence of structural P–OH groups in the framework. This observation is confirmed by the ^{1}H→^{31}P cross polarization (CP)/MAS NMR (see the Supporting Information), and shows enhanced signal intensity at $\delta = -11.0$ ppm for the faster CP rates than the phosphorus resonances of the framework. The faster rate is the result of closer proximity of the phosphorus atoms to the CP source, that is, the acid protons of the P–OH group itself.[24] The ^{27}Al MAS NMR spectrum displays two more resonances at $\delta = 8.1$ and -4.3 ppm, which are assigned to five- and six-coordinated aluminum caused by the interaction with fluoride ions and water.[23,25] In the ^{19}F MAS NMR spectrum (see the Supporting Information), signals are observed at $\delta = -95.2$, -123.1, -142.8, and -172.7 ppm. The signal at $\delta = -95.2$ ppm, similar to that previously found in the LTA- and AST-type aluminophosphates, unambiguously demonstrates F$^-$ trapped in the D4R units of the structure.[25,26] The latter signals should be assigned to the terminal fluorine atoms (Al–F group), which have also been observed in the AST-type aluminophosphate synthesized with different templates.[27] After deconvolution of the spectrum, the intensity ratio of F(D4R)/F(Al–F) is close to 2:1, which corresponds well to the element analysis results assuming a fluoride ion in every D4R of DNL-1.

DNL-1 could not be obtained when the synthesis was carried out in the absence of HDA, though cloverite has been ionothermally prepared previously without addition of any amines.[28] From the ^{13}C CP/MAS NMR spectrum of the as-synthesized DNL-1 (see the Supporting Information), we can clearly see the partially resolved resonance of HDA centered at $\delta = 25.6$ ppm from the resonances corresponding to [emim]$^+$. The solution ^{13}C NMR spectrum of the DNL-1,

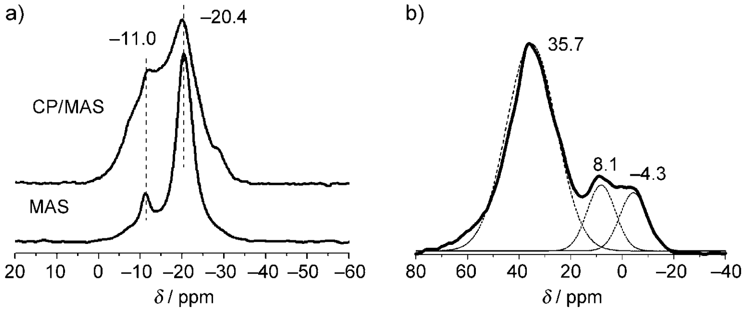

Figure 3. a) ^{31}P MAS NMR and ^{1}H→^{31}P CP/MAS NMR spectra; b) ^{27}Al MAS NMR spectra of as-synthesized DNL-1.

dissolved with concentrated HCl solution (see the Supporting Information), confirms that this signal should be assigned to the C_b and C_c carbon atoms of the protonated HDA, and that the resonance of C_a overlaps with the broad line of $[emim]^+$ at about $\delta = 36.7$ ppm. This observation reveals that both $[emim]^+$ and protonated HDA remains intact upon occlusion inside the -CLO structure. Thus, we consider that the protonated HDA is essential and acts as a co-SDA together with the ionic liquid cation in the crystallization process of DNL-1.[16,17] Moreover, it was found that the signal at $\delta = 25.6$ ppm disappeared after DNL-1 was calcined at 250 °C, while the other signals still remained even after calcination at 300 °C (see the Supporting Information). The N_2 isotherm of DNL-1 (see the Supporting Information) after calcination at 250 °C shows the Brunauer–Emmett–Teller (BET) surface area and micropore volume of 351 $m^2 g^{-1}$ and 0.12 $cm^3 g^{-1}$, respectively. These values indicate that the protonated HDA is located in the super cages with 20-ring openings, from where it can be easily removed.

To investigate the thermal stability of DNL-1, thermogravimetric/differential thermal analyzer (TG/DTA) and in situ XRD experiments (see the Supporting Information) were performed under atmospheric condition with the same heating rate of 5 °C min^{-1}. In the TG/DTA diagrams, the first weight loss of 12 % is observed between 30 °C and 200 °C with endothermic effect which can be attributed to the removal of physically adsorbed water. The remaining weight loss of 22 % takes place between 200 °C and 700 °C with two exothermic peaks at 380 °C and 530 °C. This weight loss corresponds to the decomposition and combustion of the organic templates accompanied with the elimination of the H_2O and HF in the framework. [29] In situ PXRD patterns show that distinct intensity changes occur accompanied by the loss of physically adsorbed water and the organics; however, no significant shift in lattice parameter and loss of crystallinity was observed until about 950 °C, at which temperature the dense phase $AlPO_4$ tridymite was formed. According to the literature,[10] the phase transformation of cloverite into $GaPO_4$ tridymite occurs at about 700 °C, thus reflecting the higher thermal stability of DNL-1. Calcined DNL-1 remains stable when stored in a desiccator at room temperature. Exposure of DNL-1, which was calcined at 850 °C, to 60 % humidity at room temperature led to gradual decrease of the crystallinity with increasing exposure time (see the Supporting Information). Noticeably, the diffraction peaks at at low 2θ angles still existed after exposure to humidity for 6 days, whereas detemplated cloverite was reported to suffer total collapse of the framework within several hours.[23] This result further indicates that DNL-1 is more stable than its analogue cloverite.

The -CLO framework has the lowest framework density among the approved zeolite framework types.[13] The true framework density of DNL-1 is 11.3 T atoms per 1000 Å³. The preliminary results of N_2 isotherm measurements of DNL-1 after calcination at 600 °C (see the Supporting Information) shows high BET surface area and micropore volume of 631 $m^2 g^{-1}$ and 0.20 $cm^3 g^{-1}$, respectively, with a high external surface area of 146 $m^2 g^{-1}$ owing to its small crystal size.

In conclusion, ionothermal synthesis is an alternative synthetic strategy for the exploration of crystalline materials with extralarge pores. This approach has the advantages of the ionic liquid's low interface tension, negligible autogenous pressure, and unique chemistry. We have shown the co-SDA ionothermal synthesis of the first aluminophosphate molecular sieve with the 20-ring pore opening, DNL-1. It is the structural analogue of cloverite as shown by Rietveld refinement of PXRD data and multinuclear NMR analysis of framework nuclei and SDA. DNL-1 shows excellent stability in comparison with cloverite and exhibits high BET surface area and micropore volume. These characteristics suggest that DNL-1 has great potential applications in separation, catalysis, and gas storage.

Experimental Section

Synthesis procedure of DNL-1: A glass beaker was charged with [emim]Br (52.8 g, 0.276 mol), H_3PO_4(0.79 g, 0.007 mol, 85 wt % in H_2O), $Al[OCH(CH_3)_2]_3$ (1.41 g, 0.007 mol), and HF (0.35 g, 0.007 mol, 40 wt % in H_2O). The reaction mixture was stirred electromagnetically at 100 °C in an oil bath for 1 h, before HDA (0.40 g, 0.004 mol) was added. After it had been stirred for 5 min, the final mixture with a gel composition $1\,Al_2O_3{:}1\,P_2O_5{:}80$ [emim]Br:2 HF:1 HDA was transferred and sealed into a PTFE-lined autoclave (volume 100 mL), and then heated in an oven at 210 °C for 2 h. The white solid products were filtered, washed thoroughly with distilled water and ethanol, and dried at 110 °C overnight.

Rietveld refinement: The Rietveld refinement was performed using the program FULLPROF, with a Thompson–Cox–Hastings profile function and a linear interpolation of background. Soft distance restraints were placed on the bonds between the aluminum and oxygen atoms 1.75(2) Å, the bonds between the phosphorus and oxygen atoms 1.52(2) Å, the distances between tetrahedral oxygen atoms 2.65(2) Å and the distances between neighboring T atoms 3.10(1) Å. Extra-framework scatterers identified from difference Fourier maps were considered to represent disordered SDA. All calculations for the structure refinement were carried out with the FULLPROF suite including FULLPROF 2 K and GFOUR.[30] The residuals of the refinement were $R_{exp} = 0.145$, $R_{wp} = 0.183$, $R_B = 0.080$, and $\chi^2 = 1.59$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421563.

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