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The Ionothermal Synthesis of Cobalt Aluminophosphate Zeolite Frameworks

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Crystalline porous materials such as zeolites are of interest in a number of areas of modern science,[1] particularly those associated with catalysis[2] and gas storage.[3] Recently, we have developed a new method, ionothermal synthesis, for preparing aluminophosphates based on the use of ionic liquids as both the solvent and the structure-directing agent (sometimes known as the template).[4] This new method has some interesting features and potential advantages over the traditional methods of molecular sieve synthesis. For example, most ionic liquids have vanishingly small vapor pressures, which means that no autogenous pressure is produced on heating and that ionothermal synthesis can take place at high temperature while keeping the pressure at ambient levels. In addition, altering the chemistry of the solvent system away from a molecular solvent (e.g., water) to an ionic liquid can also change the chemistry of the system, leading to the formation of novel types of frameworks.[4]

In this communication we report the synthesis of three zeolites, including one previously unknown framework structure, using the ionic liquid 1-methyl 3-ethyl imidazolium bromide (mp 83 °C) as both the solvent and template. The materials are all cobalt aluminophosphate solids (CoAlPOs)—an indication that the ionothermal synthesis method is suitable for the preparation of transition metal-functionalized frameworks that may be useful for applications such as catalysis or gas adsorption. CoAlPOs have been of particular interest over the years because of the redox and catalytic properties of the Co^{2+} ion. [5,6]

The synthetic method used in this study was similar to that we have reported previously for pure aluminophosphate materials,[4] except that a cobalt compound was added to the reaction mixtures to test for incorporation of cobalt as a tetrahedral ion in the zeolite frameworks.[7] By using this method we were able to isolate crystals of three different zeolitic framework materials (Figure 1), all of which contain cobalt (as indicated by their strong blue color and confirmed by EDX elemental analysis using a scanning electron microscope). The three materials are all different from those reported in our previous preparations of aluminophosphate frameworks,[4] indicating that the cobalt hydroxide added to the synthesis mixture may contribute an additional structure-directing effect on top of that supplied by the organic cation of the ionic liquid. We have designated the three CoAlPOs prepared in this way as SIZ-7 (**S**t. Andrews **I**onothermal **Z**eolite-7), SIZ-8, and SIZ-9.

SIZ-8 and SIZ-9 are isostructural with materials that have been prepared using traditional hydrothermal techniques,[8] and have the AEI and SOD zeolite frameworks, respectively. However, SIZ-7 is a novel framework structure,[9] which joins a family of related zeolites that includes the PHI, GIS, and MER structure types. This family can be described as consisting of the double-crankshaft chain illustrated in Figure 2.

In SIZ-7 these chains run parallel to the crystallographic *a*-axis in the structure and are connected to form a one-dimensional small-pore zeolite structure with windows into the pores delineated by rings containing eight tetrahedral atoms (known as 8-ring windows). The repeat unit in the *a*-direction is 10.2959 (4) Å and equals one repeat unit of the double crankshaft chain. These chains are linked via four rings in both the *b*- and *c*-directions to form the 8-ring windows. The relative orientation of neighboring chains (Figure 2) means that there are two types of 8-ring channels. The two different windows are of similar size (3.66 × 3.26 Å and 3.40 × 3.52 Å) but are different in shape (this is most clearly seen in Figure 1a). In the *b*-direction the same type of 8-ring channel is repeated, leading to a repeat unit in this direction of 14.3715 (5) Å, while in the *c*-direction the two types of channel alternate, leading to an approximate doubling of the unit cell dimension in this direction to 28.599 (1) Å. Figure 2 shows the four closely related zeolites, SIZ-7, MER, GIS, and PHI, and how the orientation of the chains (denoted by the red arrows) changes between the four structures. The structure of SIZ-7 consists of eight crystallographically independent tetrahedral atoms in the asymmetric unit. Four of these (T1−T4) are occupied by either Co or Al. The remaining four tetrahedral sites (P5−P8) are occupied by phosphorus.

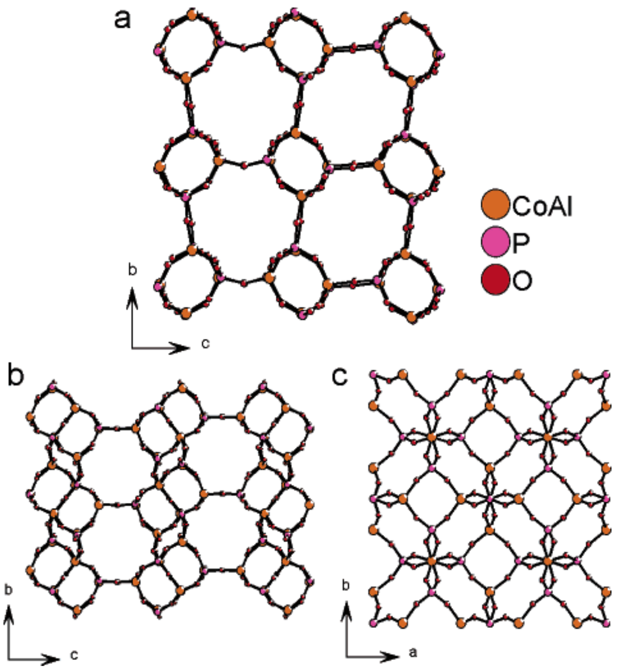

Figure 1. Projections of the three cobalt aluminophosphate zeolite frameworks (a) SIZ-7, (b) SIZ-8 (AEI), and (c) SIZ-9 (SOD).

Interestingly, the refined bond distances indicate that there is some preferential ordering of the cobalt ions onto the T1 site. As the Co−O (∼1.93 Å) and the Al−O (∼1.74 Å) bond distances differ considerably, an observed interatomic distance nearer to 1.93 Å for the Co/Al disordered T site indicates a site predominantly occupied by cobalt.[5] In the case of the T1 site (Figure 3) the T−O bond distances range from 1.857(4) to 1.892(4) Å, indicating that the T1 site is approximately 75% occupied by cobalt. In contrast, the observed interatomic distances around T2 (1.795(4)−1.833(4) Å), T3 (1.796(4)−1.893(4) Å), and T4 (1.767(4)−1.787(4) indicate

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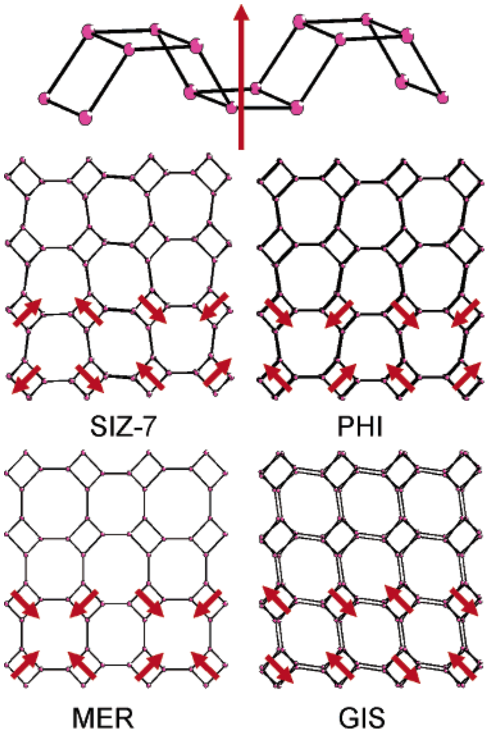

Figure 2. Double crankshaft chain present in SIZ-7, PHI, MER, and GIS zeolite frameworks. The crankshaft chains run into the plane of the paper and the red arrows indicate the relative orientations of the chains in the structures. For clarity only the tetrahedral nodes in the structures are shown (i.e. oxygen atoms are omitted).

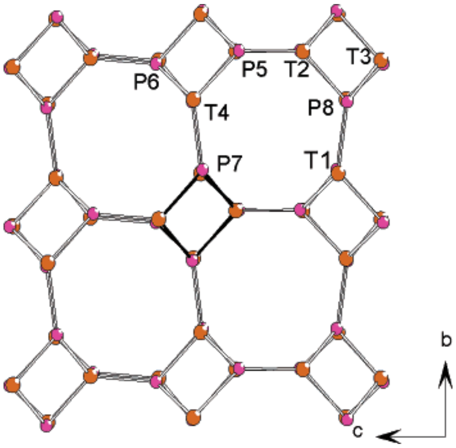

Figure 3. A view of SIZ-7 parallel to the *a* -axis showing the location of the eight crystallographically independent tetrahedral nodes in the structure. For clarity oxygen atoms are not shown. T1, T2, T3, and T4 are occupied with Co:Al ratios of ~75:25, 35:65, 35:65, and 15:85, respectively.

lower Co occupancies of ~35%, 35%, and 15% respectively. The average interatomic distance is often a much more reliable method for ascertaining relative occupancy than, for example, refining the occupancy factors;[5] thus in the final cycle of least-squares refinement the relative Co/Al occupancies were fixed at these levels.

In conclusion, the ionothermal synthesis method has been used to prepare a novel small-pore cobalt aluminophosphate zeolite framework. Such a material may be of interest for gas separation and storage applications. The same ionic liquid, 1-methyl 3-ethyl imidazolium bromide, can be used to make three aluminophosphate frameworks[4] and three different cobalt aluminophosphate structures (this work). This illustrates the rich potential of the method to produce both known and unprecedented frameworks. However, it is also clear that subtle changes in reaction conditions can alter the product selectivity markedly, which sometimes makes it quite difficult to prepare pure phase samples. For example, lowering the cobalt concentration in the original reaction mixture leads to the formation of the material SIZ-4,[4] although elemental analysis indicates that there is no cobalt incorporation to this phase. We are continuing to work on control of the product selectivity more precisely in ionothermal syntheses of this kind.

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Supporting Information Available: Crystallographic information (CIF) for SIZ-7. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Typical synthesis procedure: A Teflon-lined autoclave (volume 23 mL) was charged with 0.172 g of H_3PO_4 (85 wt % in H_2O, Aldrich), 0.107 g of $Al[OCH(CH_3)_2]_3$ (Aldrich), 0.079 g of $Co(OH)_2$ (Avocado), 4.00 g of ethylmethylimidazolium bromide (IL), and 0.015 g of HF (48 wt % in H_2O, Aldrich). Initial molar ratios for $Al[OCH(CH_3)_2]_3$:H_3PO_4:HF:IL:Co-$(OH)_2$:H_2O were 1:2.9:0.69:40:1.6:3.6. The stainless steel autoclave was heated to 170 °C for 3 days. After cooling to room temperature the product was suspended in distilled water, sonicated, filtered, and washed with acetone. The product was a blue solid and contained all three phases, SIZ-7, SIZ-8, and SIZ-9 as a physical mixture.

(8) (a) Unit Cell data for SIZ-8: Monoclinic space group C^2/c, a = 13.999(2) Å, b = 12.763(2) Å, c = 18.680(2) Å, β = 90.01(1)°; see Marchese, L.; Chen, J. S.; Thomas, J. M.; Coluccia, S.; Zecchina, A. *J. Phys. Chem.* **1994**, *98*, 13350 for structural details. (b) Unit cell data for SIZ-9: Cubic $Pm3m$, a = 8.9332(6) Å. See ref 5a for structural details.

(9) Crystal data for SIZ-7, $Co_{12.8}Al_{19.2}(PO_4)_{32}$: M_r = 4311.44, monoclinic space group C^2/c (No. 15), a = 10.2959(4) Å, b = 14.3715(5) Å, c = 28.599(1) Å, β = 91.094(1)°, V = 4231.0(3) Å^3, Z = 1, T = 150(2) K, ρ_{calc} = 1.649 g/cm^3, crystal size 0.05 mm × 0.05 mm × 0.04 mm, λ = 0.6910 Å using station 9.8 at the Synchrotron Radiation Source, Daresbury, UK. Refinement of 217 parameters against 6637 reflections (R_{int} = 0.0340, 5270 reflections with $I > 2(\sigma)$), led to $R1$ (observed data) = 0.060, wR_2 (all data) = 0.200 and S = 1.035. The organic template was disordered and could not be located. The diffuse electron density in the pores was therefore treated using the SQUEEZE routine in the program PLATON.

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