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AMINE TEMPLATED ZINC PHOSPHATES PHASES FOR MEMBRANE SEPARATIONS

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ABSTRACT

Our research is focused on developing inorganic molecular sieve membranes for light gas separations such as hydrogen recovery and natural gas purification, and organic molecular separations, such as chiral enantiomers. We focus on zinc phosphates because of the ease in crystallization of new phases and the wide range of pore sizes and shapes obtained. With our hybrid systems of zinc phosphate crystalline phases templated by amine molecules, we are interested in better understanding the association of the template molecules to the inorganic phase, and how the organic transfers its size, shape, and (in some cases) chirality to the bulk. Furthermore, the new porous phases can also be synthesized as thin films on metal oxide substrates. These films allow us to make membranes from our organic/inorganic hybrid systems, suitable for diffusion experiments. Characterization techniques for both the bulk phases and the thin films include powder X-ray diffraction, TGA, Scanning Electron Micrograph (SEM) and Electron Dispersive Spectrometry (EDS).

INTRODUCTION

Separation membranes is a technology area for which there exists opportunities for significant energy and cost savings. Examples of industrial needs for gas separation include hydrogen recovery, natural gas purification, and dehydration. In addition, examples of organic separations include molecular chiral purifications.

A membrane capable of separating H₂ from other gases at high temperatures could recover hydrogen from refinery waste streams, and facilitate catalytic dehydrogenation and the water gas shift ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) reaction. Natural gas purification requires separating CH₄ from mixtures with CO₂, H₂S, H₂O, and higher alkanes. A dehydrating membrane would remove water vapor from gas streams in which water is a byproduct or a contaminant, such as refrigeration systems.

A membrane capable of separating chiral molecules in both intermediate and final compounds are currently extremely important areas of research, especially for the chemical, pharmaceutical, agrochemicals, and biomedical industries.¹ These industries are looking for separations materials to greatly aid in the production of enantiomerically pure final products. The development of tunable, highly sensitive and selective molecular recognition materials for important chemical drug species will require enantioselective capabilities. The resultant separations materials are envisioned to either become

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enantioselective chromatography materials or be developed into membrane separations barriers.

The methods by which we synthesized porous inorganic frameworks in bulk powders (to be used for future separations studies when grown as films) included the use of organic templating molecules, whose size, shape and in some cases chirality, would be transferred to the framework. The resultant products contain "designed" pores tuned for the separations required. Zinc phosphates (ZnPOs) were chosen to study because they generally have pore diameters that are smaller than those of zeolites; in particular, the range of pore sizes currently available is ideal for dehydration and hydrogen recovery. ZnPO phases are also stable at higher temperatures (up to 700 °C) than those generally tolerated by typical alkali zeolites.^{1,2} Furthermore, our past experiences with nonaluminosilicate molecular sieves³⁻⁵, led us to study the zinc phosphate system.

We have also focused on enantioselective separations materials by undertaking a study to design chiral inorganic zinc phosphate molecular sieves. We have employed the knowledge and successes of recent work with chiral tetrahedral framework topologies that have been recently synthesized.⁶⁻⁸ Furthermore, chiral organometallic templates have been used to synthesize zeolitic and layered frameworks.⁹⁻¹¹ We have explored the transfer of size, shape and chirality of *d*-glucosamine to the crystalline zinc phosphate system.

EXPERIMENTS

Synthesis:

Methylamine Zinc Phosphate: Clear single crystals of this phase were grown by preparing a stirred mixture of 2.30g H₃PO₄ and 5.60g H₂O, to which was added a stirred mixture of 0.81g ZnO and 7.23g CH₃NH₂. The entire reaction mixture was placed in a capped Teflon bottle and cooked at 70°C for 14 days. The product was recovered by vacuum filtration, washed with deionized water, and dried in air.

A thin film of this phase was synthesized in the following manner. A calcined ZnO pellet was soaked in 50% zinc acetate (Zn(CH₃CO₂)₂) solution for 1 hour. The pellet was then transferred to a reaction mixture containing the following solution: 14.46g CH₃NH₂, 4.60g H₃PO₄ and 11.20g H₂O. The reaction proceeded for 4 hours at room temperature. The resultant film was removed from the solution, washed with deionized water, and dried in air.

***d*-glucosamine Zinc Phosphate:** The phase space explored for this work is defined by the ratios of zinc, phosphorus and hydroxide/template. The reactions are performed at room temperature, with reaction times of 3, 6 and 24 hours. The starting materials are 4M H₃PO₄, 25% wt. tetramethyl ammonium hydroxide (TMAOH) in water, *d*-glucosamine hydrochloride (C₁₂H₂₂N₂O₅•HCl; DGA) and 2M Zn(NO₃)₂.

Typical synthesis parameters for the **hexagonal phase** were as follows: 1.179g of 4M H₃PO₄, 3.6435g TMAOH, and 1.08g DGA are mixed in a capped Teflon bottle. To the clear solution is added 1.94g 2M Zn(NO₃)₂. The thixotropic mixture was shaken until milky and allowed to stand at room temperature. The phase precipitated out of a gel-like

solution in 24 hours. The product was then recovered by vacuum filtration, washed repeatedly with de-ionized water, and allowed to dry in air.

Characterization:

Single crystal X-ray data were collected on a Siemens P4 automated diffractometer (graphite monochromated Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$) at room temperature. Data were collected using the $\omega/2\theta$ scan mode to a maximum 2θ of 65° . Absorption was monitored by ψ scans and corrected for at the data reduction stage. The structures were solved by direct methods using SHELXS86. **Powder X-ray** diffraction data were collected at room-temperature on a Siemens Model D500 automated diffractometer, with θ - 2θ sample geometry and Cu K α radiation, between $2\theta = 5$ and 60° , step size 0.05° . Data presented were collected on "as synthesized" materials. **Transmission Electron Microscopy (TEM)** was performed on a JEOL 1200EX at 120 keV. Images were collected using a Gatan 694 retractable multiscan CCD camera. **Scanning Electron Microscopy (SEM)** was performed JEOL model JSM-T300 coupled with an IXRF Systems, Inc IRIDIUM data acquisition and analysis system. Images were acquired using an accelerating voltage of 15-25 kV and EDS 10-30 kV. **^{31}P Cross-polarization magic angle spinning (CP/MAS)** and Bloch-decay MAS NMR data were acquired at 121.4Mhz on a Varian Unity Plus Spectrometer using a 7mm supersonic probe manufactured by Doty Scientific. Typical experimental parameters were 6.0kHz spinning speed, $6\mu\text{s}$ rf-pulse lengths ($\pi/2$ -pulse for both ^{31}P and ^1H), and pre-pulse delays of 30s for CP/MAS experiments and between 120s and 600s for Bloch-decay experiments. ^1H decoupling was performed during all experiments.

RESULTS

Microporous. The **methylamine zinc phosphate** phase, $(\text{CH}_3\text{NH}_3)_3\text{Zn}_4\text{O}(\text{PO}_4)_3$ consists of a type of three-dimensional, microporous framework, enclosing guest methylamine cations and water molecules. One zinc atom (tetrahedral), one phosphorus atom (tetrahedral) and two oxygen atoms make up the framework asymmetric unit of the structure, with a configuration of $[\text{Zn}_4\text{O}(\text{PO}_4)_3]^{3-}$, which is charge balanced by the organic cations. This framework is comprised of tetrahedral OZn_4 clusters at the corners, edges and face centers of the unit cell. These clusters are linked via phosphate groups into the Zn/P/O framework configuration, which results in large, roughly spherical cavities, interlinked by a three-dimensional network of tilted 8-ring channels, propagating in the orthogonal [100], [010] and [001] directions. Unlike in the analog alkali metal templated phases, the organic cations of this phase are very densely packed in the cages, with probably N-H---O/framework H-bonds forming. (This presently has not been confirmed by diffraction due to large scattering effects). Therefore, in the as-synthesized state of the phase, no porosity is possible. However, calcination at 350°C in O_2 for 2 hours results in a partially detemplated phase (as determined by elemental analysis and powder

X-ray diffraction). Ongoing work is focused on structure refinement and permeation studies of this material.

Figure 1: [001] projection of a layer of the $(\text{CH}_3\text{NH}_3)_3\text{Zn}_4\text{O}(\text{PO}_4)_3$ structure, showing the connectivity into the 8-ring windows (methylamine cations are not shown).

We have successfully synthesized the pre-calcined methylamine zinc phosphate phase as a thin film (as determined by SEM, EDS and XRD) with the method described above. However, defect sites are evident from characterization studies. Refinement in reaction parameters (such as reaction time, reactant concentrations, and substrate pre-treatment) is ongoing.

Mesoporous. Within the strict phase reaction limitations, we synthesized a mesoporous phase, with a hexagonal crystal lattice. Using powder X-ray diffraction, identifiable peaks for the mesoporous, phase are d (in Å) = 31.223, 24.966, 9.982.

An investigation of the phase space indicates there is a very narrow range of reactants that provide for the synthesis of the mesoporous phase. We observed a transition in phase growth which is dependent on time of reaction; an evolution of phase growth began with an interim layered templated-zinc phosphate phase (observed at 3 hours) with a primary d spacing of 33 (± 1) Å. This layered phase disappears with an additional few hours of reaction time. After 24 hours of reaction, the mesoporous phase was observed, with identifiable d spacings of 35 and 25 (± 1) Å. When the reaction was allowed to continue until 48 hours, Hopeite (a condensed mineral analog) was the only crystallographic phase present.

The X-ray data is reinforced by TEM data. The coherent spacings were all approximately 32 Å, the pore sizes are consistent and the pores are distinct. Measurements of the repeat distance of the pores to be approximately 36 Å. This corresponds to $2d_{100}/\sqrt{3}$ of the (100) peak (assignment of 31.2 Å powder X-ray diffraction peak to the (100)). There is a degree of shorter range ordering to the pores, however, there is a lesser degree of long range coherent crystalline pore ordering. Much like some water:co-solvent silica/surfactant disordered mesophases (d-H),^{12,13} the liquid crystalline packing of the d -glucosamine molecules may have a disordered arrangement of cylindrical 1-d pores (quasi-hexagonal) that are intersecting disordered unimodal channels. Both systems exhibit similar long range disorder of the hexagonal packed pores in TEM images and only two diffraction peaks in powder X-ray diffraction.

³¹P MAS NMR data indicate a crystalline framework for the mesoporous phase. The three peaks (8.0, 4.5 and 2.5 ppm chemical shifts) are all consistent with tetrahedral monophosphate species with varying degrees of distortion of the tetrahedral unit. The resonances are assigned as follows: the peaks at 8.0 and 4.5 ppm correspond to an impurity phase, consisting of Hopeite (4.5ppm) and an unidentified related phase (8.0ppm), and the peak at 2.5 ppm attributed to the framework of the mesoporous phase. The narrow peak widths (HWHM = 0.75 ppm) suggest, at most, a very small degree of

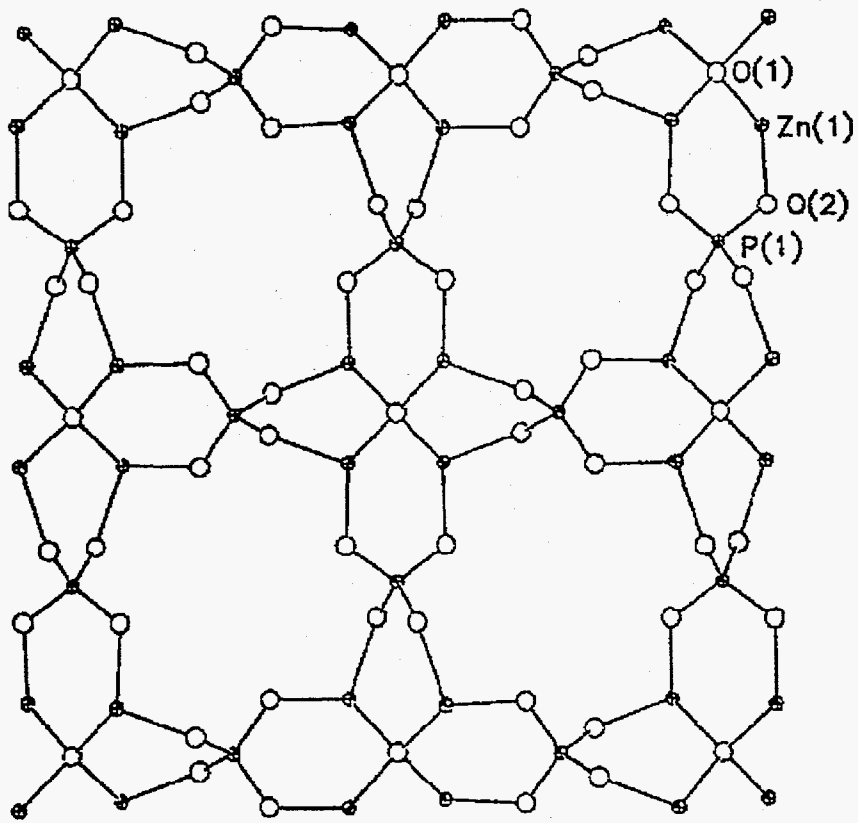


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variation in the geometry of the phosphate tetrahedra within the framework and thus show no evidence for the formation of an amorphous phosphate phase. Instead, data shows that the walls of this zinc phosphate mesoporous phase have an ordered arrangement of its tetrahedral atoms. Cross polarization and relaxation studies suggest that the mesoporous and Hopeite phases are phase separated on the nanometer scale or greater. The chemical shift for the mesoporous phase was found to be close to that of the ^{31}P MAS NMR data for crystalline ZnPO-X molecular sieves (5.8ppm).¹⁴ The data strongly suggests the walls of this zinc phosphate mesoporous phase have an ordered arrangement of its tetrahedral atoms.

Characterization results show that the zinc phosphate mesopore we describe is successfully templated by the chiral *d*-glucosamine hydrochloride. Powder X-ray diffraction data showed a hexagonally packed mesoporous phase, with short range coherent order. The ^{31}P MAS NMR data indicated that the walls of the phase are crystalline and similar in local structure to Zn/P zeolite-analogs. The single unidirectional pore size and shape of this mesopore also substantiates chirality in the framework, in a fashion similar to the earlier reported chiral polymorph of Zeolite B and of Co/P, -ABW, and -HEX phases.^{7,9} With those reported materials, the crystallographic screw axis (which describes the chirality of the tetrahedral framework atoms) is shown to run in the direction of the channel system of the largest pore opening. Furthermore, by using one enantiomer of the chiral template in the reactions, we have ensured that structure direction will be enantiomerically pure.

Figure 2: TEM of chirally templated zinc phosphate mesoporous phase. The white spots are 31.2 Å pores, the walls are zinc phosphate. The template was removed under mild vacuum with time. A 20 nm bar is shown for scale.

CONCLUSIONS

The focus of this research is to synthesis novel porous inorganic materials in bulk, characterize each phase so as to determine the role of the templating organic molecules incorporated, and then synthesize them as films. The result of this research not only produces separation membranes under mild conditions, but also further develops our understanding in structure directing templates.

The amine-based organic molecules used in the syntheses described above are similar in size, yet were incorporated into completely differently pored inorganic framework systems. The methylamine zinc phosphate is a microporous framework with an approximate pore opening of 3.4Å. This pore size is considered very useful for light gas separations (e.g. He and H₂), and has been shown effective in films of the analog CsZn₂OPO₄ framework.^{2,15} These charge-balancing cations, acting much like the alkali metal cations in the analogs, are packed into the pores, resulting in a non-permeable porous material; this phase, as-synthesized would not be useful as a separations membrane. However, because partial calcination is possible, the resultant pores may produced enhanced selectivity through a small effective pore size.

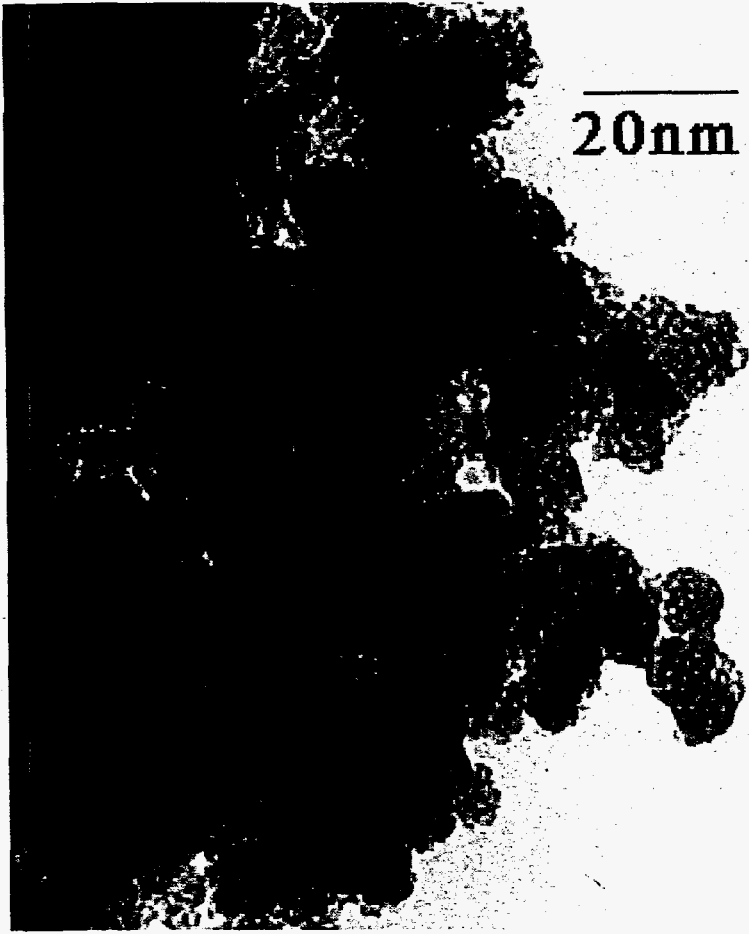


Figure 2 Nano JF

In the case of the chiral d-glucosamine zinc phosphate, the amine template is not acting as a single molecule, but is cooperating with the other molecules to form a much larger effective template molecule that is large enough to fill the mesopore. The DGA is approximately 9 Å in diameter, however, it is templating a 31.2 Å pore. Two possible explanations are that a few DGA molecules "cooperate" in a type of planar conformation through hydrogen bonding, or all the DGA molecules arrange to form a large liquid crystalline cholesteric mesophase.¹⁶ Work is continuing to successfully synthesize this phase as a thin film, that can be used in the separations of large chiral molecules.

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