

Synthesis of Organically Templated Nanoporous Tin(II/IV) Phosphate for Radionuclide and Metal Sequestration

Dawn M. Wellman,* Shas V. Mattigod, Kent E. Parker, Steve M. Heald, Chongmin Wang, and Glen E. Fryxell

Pacific Northwest National Laboratory, Richland, Washington 99352

Received November 10, 2005

Nanoporous tin(II/IV) phosphate materials, with spherical morphology, have been synthesized using cetyltrimethylammonium chloride $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Cl}]$ as the surfactant. The structure of the material is stable at 500 °C; however, partial oxidation of the material occurs with redox conversion of Sn^{2+} to Sn^{4+} , resulting in a mixed $\text{Sn}^{\text{II}}/\text{Sn}^{\text{IV}}$ material. Preliminary batch contact studies were conducted to assess the effectiveness of nanoporous tin phosphate, NP-SnPO, in sequestering redox-sensitive metals and radionuclides, technetium(VII), neptunium(V), thorium(IV), and a toxic metal, chromium(VI), from aqueous matrixes. Results indicate that tin(II) phosphate removed >95% of all contaminants investigated from solution.

Nanoporous materials offer an efficient way of selectively sequestering many types of metals and radionuclides in a very small volume. The high surface area of a nanoporous structure enhances mass transfer in sequestration applications and enables ions to be highly concentrated in a very small volume of material. Operations related to nuclear energy and weapons production have produced significant quantities of radioactive waste over the last half century. The waste is targeted to be processed and buried in a deep geological repository (e.g., Yucca Mountain in Nevada). The current proposal is to include “getter materials” with this waste in order to sequester any radionuclides that might leach from the wasteforms. Of particular interest in this regard are the long-lived actinide species (e.g., Pu, Am, Np, etc.) and the anions (e.g., pertechnetate, iodide, etc.). Getter materials must be able to survive long-term exposure to elevated temperatures (>150 °C) and moderately high radiation fluxes. The frailty of organic components toward radiolytic degradation precludes their use for either structure or function in the final getter material.

Over the past decade, metal phosphates have been extensively studied because of their potential use in catalysis, ion exchange, and phase separation.^{1,2} Since the first open-framework tin phosphates were prepared nearly 15 years ago,

there has been interest in the structural flexibility of tin phosphates crystallizing in one-dimensional, three-dimensional, or layered structures.^{3–12} Open-framework tin phosphates have been prepared by direct precipitation¹⁰ and by incorporation of organic amines into the crystal lattice.^{3–9,11,12} Surfactant-templated, open-framework tin phosphates have been reported using structure-directing amine compounds including ethylenediamine,^{4,7,12} 1,6-diaminohexane,⁵ 1,2-diaminopropane,⁶ 1,8-diaminooctane,⁵ and 1,4-diaminobutane.⁶ Only recently, however, has a nanoporous tin(IV) phosphate been reported, and to date, this is the only known report of a nanoporous tin phosphate.¹³ The cationic quaternary ammonium salt $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$ was used as the surfactant. The use of cetyltrimethylammonium bromide

- (1) Polarz, S.; Smarsly, B. Nanoporous Materials. *J. Nanosci. Nanotechnol.* **2002**, 2 (6), 581.
- (2) Cheetham, A. K.; Ferey, G.; Loiseau, T. Open-Framework Inorganic Materials. *Angew. Chem., Int. Ed.* **1999**, 38, 3268.
- (3) Natarajan, S. Synthesis and Structure of a New Open-Framework Tin(II) Phosphate, $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$, Possessing One-Dimensional Channels. *J. Solid State Chem.* **1999**, 148, 50.
- (4) Natarajan, S.; Attfield, M. P.; Cheetham, A. K. $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_4]_{0.5}^{2+}[\text{Sn}_4\text{P}_3\text{O}_{12}]^-$: An open-framework tin(II) phosphate. *Angew. Chem., Int. Ed. Engl.* **1997**, 36 (9), 978.
- (5) Natarajan, S.; Ayyappan, S.; Cheetham, A. K.; Rao, C. N. R. Novel open-framework tin(II) phosphate materials containing Sn–O–Sn linkages and three-coordinated oxygens. *Chem. Mater.* **1998**, 10, 1627.
- (6) Natarajan, S.; Cheetham, A. K. Synthesis and structure of an open-framework tin phosphate, $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_4]_{0.5}^{2+}[\text{Sn}_4\text{P}_3\text{O}_{12}]^-$, containing intersecting channels. *Chem. Commun.* **1997**, 1089.
- (7) Natarajan, S.; Cheetham, A. K. First example of a tin(II) oxy-phosphate with an open-framework structure: synthesis and structure of $[\text{NH}_4]^+[(\text{Sn}_3\text{O})_2(\text{PO}_4)_3]^-$. *J. Solid State Chem.* **1997**, 134, 207.
- (8) Ayyappan, S.; Bu, X.; Cheetham, A. K.; Rao, C. N. R. Synthesis and Structural Characterization of a Chiral Open-Framework Tin(II) Phosphate, $[\text{CN}_3\text{H}_6][\text{Sn}_4\text{P}_3\text{O}_{12}]$ (GUAN–SnPO). *Chem. Mater.* **1998**, 10, 3308.
- (9) Ayyappan, S.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **2000**, 152, 207.
- (10) Bontchev, R. P.; Moore, R. C. A series of open-framework tin(II) phosphates: $\text{A}[\text{Sn}_4(\text{PO}_4)_3]$ (A = Na, K, NH_4). *Solid State Sci.* **2004**, 6, 867.
- (11) Serre, C.; Auroux, A.; Gervasini, A.; Hervieu, M.; Ferey, G. Hexagonal and Cubic Thermally Stable Mesoporous Tin(IV) Phosphates with Acidic and Catalytic Properties. *Angew. Chem., Int. Ed.* **2002**, 41, 1594.
- (12) Serre, C.; Ferey, G. Synthesis and structure determination from powder data of the first organically templated tin(IV) phosphate: MIL-76 or $\text{Sn}_3^{\text{IV}}\text{O}_2(\text{H}_2\text{O})(\text{HPO}_4)_4\{\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{NH}_2\}_{2.5}\{\text{H}_2\text{O}\}_2$. *Chem. Commun.* **2003**, 1818.
- (13) Mal, N. K.; Ichikawa, S.; Fujiwara, M. Synthesis of a novel mesoporous tin phosphate, SnPO_4 . *Chem. Commun.* **2002**, 112.

* To whom correspondence should be addressed. E-mail: dawn.wellman@pnl.gov. Tel: (509) 375-6936. Fax: (509) 375-2017.

as the surfactant resulted in a surface area of 230 m²/g and pore sizes of 35–38 Å. Although the pore size was reduced from 39 to 35 Å, the structure was stable following calcination.

The goal of this study was to produce a similarly stable, mesoporous solid using tin(II) as the starting material to produce a material capable of sequestering redox-sensitive species such as pertechnetate, neptunium, chromium, iodide, etc. The large pores afforded with quaternary ammonium surfactants and the high surface area of a nanoporous structure are valuable features for enhanced mass transfer in sequestration applications. This Communication summarizes efforts to make a nanoporous tin(II) phosphate phase.

The synthesis method consists of preparing 200 mL of 6.87 mM cetyltrimethylammonium chloride [CH₃(CH₂)₁₅N-(CH₃)₃Cl] in deionized water. The solution is acidified with 0.626 mL of concentrated phosphoric acid. A concentrated solution of 15.22 g of stannous chloride was dissolved in 100 mL of hydrochloric acid. A total of 2.5 mL of a SnCl₂/HCl solution was added with stirring at room temperature to the acidified surfactant. The solution was stirred for 30 min at room temperature and was placed in an oven at 65 °C for 48–72 h. The synthetic material was collected via vacuum filtration using a 0.45-μm filter, washed with deionized water, and dried under ambient conditions. Chemical analysis of the synthetic material indicates that the structure is composed of Sn/P/O with a ratio of 1:1:5.

Calcination of the as-synthesized material at 500 °C produced a material with a surface area of 262 m²/g. The X-ray diffraction (XRD) patterns of the surfactant SnPO₄ and calcined SnPO₄ are shown in Figure 1. The *d* spacing of the 100 plane in surfactant SnPO₄ is 5.01 nm, whereas after calcination, it was reduced to 4.62 nm. Subjecting the nanoporous SnPO₄ (NP-SnPO) to high temperatures during calcination has little impact on the pore size.

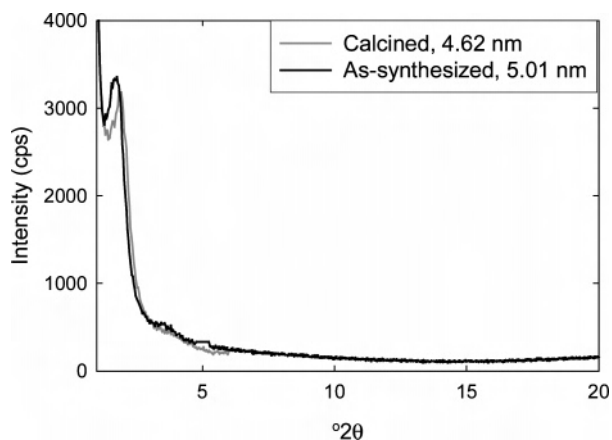


Figure 1. XRD pattern for surfactant SnPO₄ and calcined SnPO₄.

Selected-area electron diffraction analysis of a typical tin phosphate (NP-SnPO1) illustrates a completely amorphous structure (Figure 2a). Analyses with high-resolution transmission electron microscopy revealed a spherical particle morphology approximately 150 nm across, with uniform pore distribution narrowly distributed around 2 nm (Figure 2b). It was also observed that directly precipitated NP-SnPO

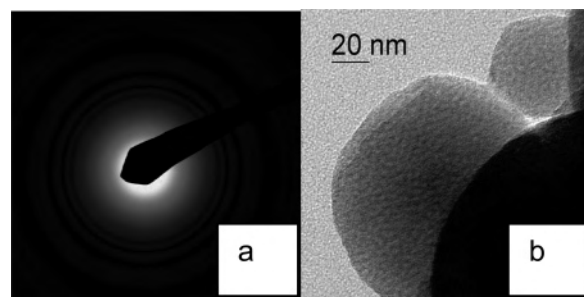


Figure 2. (a) Selected-area electron diffraction pattern indicating amorphous structure. (b) Nanoporous tin(II) phosphate with uniform pore distribution narrowly distributed around 2 nm.

Table 1. Affinity of NP-SnPO for Technetium(VII), Neptunium(V), Thorium(IV), and Chromium(VI)

sorbate	test matrix	<i>K_d</i> (mL/g)
Tc(VII)	0.002 M NaHCO ₃	>9.0 × 10 ⁴
Np(V)	0.002 M NaHCO ₃	>1.1 × 10 ⁵
Th(IV)	deionized H ₂ O	>2.2 × 10 ⁴
Cr(VI)	0.002 M NaHCO ₃	>5.6 × 10 ⁴
Cr(VI)	groundwater + 0.02 M Na ₂ SO ₄	>4.4 × 10 ⁴

materials, in addition to being thermally stable (500 °C), are chemically stable over the entire pH range (pH = 0–14); therefore, Sn will not leach into water during remediation operations.

Preliminary batch contact studies have been conducted to assess the effectiveness of NP-SnPO in sequestering redox-sensitive metals and radionuclides, technetium(VII), neptunium(V), thorium(IV), and a toxic metal, chromium(VI), from aqueous matrixes (Table 1). Equilibrium was achieved in less than 1 h at a solution-to-solids ratio of 100; therefore, a batch contact time of 2 h was used to ensure that these values represent true equilibrium conditions. Under these conditions, the nanoporous, calcined tin(II) phosphate removed >95% of all contaminants investigated from solution. Distribution coefficients, *K_d*, are defined as a mass-weighted partition coefficient. *K_d* values were typically >10 000 in groundwater for the nanoporous tin(II) phosphate, whereas *K_d* values for nonporous tin(II) phosphate were ~100. At a solution-to-solids ratio of 100, a *K_d* value of 10 000 indicates that at equilibrium there was 100 times as much contaminant in the nanoporous metal phosphate phase as there was remaining in the supernatant solution.

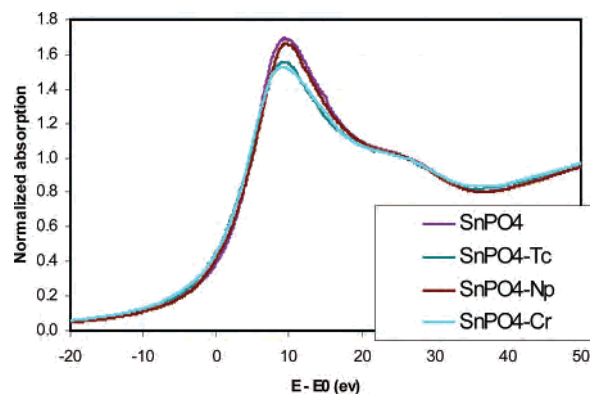


Figure 3. EXAFS spectra of NP-SnPO collected after batch sequestration tests with technetium(VII), neptunium(V), and chromium(VI). Data clearly illustrate the oxidation of NP-SnPO with concurrent reduction of the target metal contaminant.

COMMUNICATION

Data obtained via X-ray absorption near-edge spectra/extended X-ray absorption fine structure (XANES/EXAFS) clearly illustrate that the sequestration of technetium(VII), neptunium(V), and chromium(VI) with NP-SnPO occurs through redox-coupled reactions, with the target metals being reduced to their least-soluble valence states, namely, technetium(IV), neptunium(IV), and chromium(III), with oxidation of Sn in NP-SnPO (Figure 3). Although lacking spectroscopic data, we surmise that thorium(IV) adsorption on NP-SnPO is due to Lewis acid–base interaction with PO₄ groups.

These nanoporous tin(II) phosphates exhibited significant promise as sorbent materials for anionic and redox-sensitive

metals and actinides. The detailed kinetic studies of these materials will be published in due course.

Acknowledgment. This research was supported by the U.S. Department of Energy (DOE), Office of Civilian Radioactive Waste. This work was performed at Pacific Northwest National Laboratory, which is operated for the DOE by Battelle Memorial Institute under Contract DE AC05-76RLO 1830.

IC051949V