Supporting Information

Nanolayered Tin Phosphate: A Remarkably Selective Cs Ion Sieve for Acidic Waste Solutions

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Materials:

Monosodium dihydrogen phosphate (NaH₂PO₄, 99% Sigma-Aldrich), tin chloride (SnCl₄, 98% Alfa), sodium hydroxide, (NaOH, 98.8%, J.T.Baker), Cesium chloride (CsCl, 99.9%, Alfa) and hydrochloric acid (HCl, w/w 34%-37%, BDH Chemicals) were purchased and used as-received.

Synthesis of nanolayered 15Å SnP-H⁺ phase

Since Yamanaka and Tanaka (Ref. 21, main text) previously showed that the presence of Na ions in the phosphate solutions plays an important role in the formation of γ -ZrP phase, we used similar starting Na phosphate sources to see whether we can crystallize γ -SnP. However, instead of crystallizing the γ -SnP phase we crystallized a 15Å SnP-H⁺ phase. Table S1 shows the different pH values under which the microwave-hydrothermal reactions were carried out using the following method (Table S1):

Stannic chloride solution (5 mL, 1M SnCl₄ in 1M HCl) was added drop-wise into a solution of NaH_2PO_4 (20 mL, 3M) while stirring. The pH of the suspension was then adjusted with concentrated HC1 or NaOH. The suspensions adjusted to different pH values were then treated under the M-H conditions at 195°C/2h to investigate the role of pH.

The microwave-hydrothermal reactions were carried out in Teflon vessels using a microwave digestion system, MARS-5, from CEM Corporation. The MARS-5 apparatus was operated under controlled temperature conditions. This system uses 2.45 GHz frequency and has a maximum power of 1200 W. The power of this unit can be controlled from 0 to 100 % and the system can be operated to a maximum pressure of 350 psi and 240°C, and both these parameters can be controlled by a computer. The temperature inside the vessels was measured by an optical probe using a phosphor as a sensor in a sapphire thermowell. For comparison with the microwave-assisted reactions, conventional-hydrothermal experiments were conducted at 195°C using Parr vessels (Parr Instrument Co., Moline, Illinois).

After the M-H treatment, the various samples were washed four times with 1M HC1 to replace the alkali ions with protons and three times with deionized water or two times with ethanol before X-ray diffraction (XRD) analysis for phase identification. Powder XRD results showed that when Na⁺ ions are present in solution, a 15Å phase was crystallized under all pH conditions below pH 6. The 15Å phase was washed with 1M HC1 and was found to be stable only under acidic conditions. The acid washing was given to exchange the interlayer alkali cations, if any, with protons (Ref. 21, main text).

Synthetic Na₂Ti₂SiO₇·2H₂O (CST) phase

The Na₂Ti₂SiO₇ (CST) used in this study for comparison with the 15Å SnP-H⁺ phase was supplied by UOP Company (Tonawanda, NY). The above commercial product was characterized by powder X-ray diffraction and found to be phase pure.

Synthesis of α-SnP, Sn(HPO₄)₂·H₂O

The α -SnP, Sn(HPO₄)₂·H₂O was synthesized by using 5mL of 1M SnCl₄ in 1M HCl and 10mLof 6M H₃PO₄ under M-H conditions at 194°C for 2 hours. After the M-H treatment, the sample was washed four times with 1M HCl as above for 15Å SnP-H⁺ phase. The synthetic product was characterized by powder X-ray diffraction and found to be phase pure.

Synthesis of α-ZrP, Zr(HPO₄)₂·H₂O

The α -ZrP, Zr(HPO₄)₂·H₂O was synthesized by using Zr oxychloride (5 mL, 1 mol 1⁻¹) and Na₂HPO₄ solution (50 mL, 2 mol kg⁻¹) after adjusting the pH to 0.2 with conc. HCl under M-H conditions at 194°C for 2 hours. After the M-H treatment, the sample was washed four times with 1M HCl as above for the 15Å SnP-H⁺ phase. The synthetic product was characterized by powder X-ray diffraction and found to be phase pure.

Synthesis of γ-ZrP, Zr(HPO₄)₂·2H₂O

The γ -ZrP, Zr(HPO₄)₂·2H₂O was synthesized by using 50mL of 5M NaH₂PO₄·H₂O and 11.36mL of 2.20M ZrOCl₂ by C-H treatment in Teflon vessels using Parr reactors at 190°C for 1 week. After the C-H treatment, the sample was washed four times with 1M HC1 as above for the 15Å SnP-H⁺ phase. The synthetic product was characterized by powder X-ray diffraction and found to be phase pure.

Instrumental techniques for analyses

Powder XRD analysis was carried out using a PANalytical Empryean X-Ray Diffractometer with CuKα radiation. Synchrotron XRD plot was obtained with Beamline HRPD (High resolution powder diffraction) of the Pohang Light Source, Korea using 1.46390 wave length of X-rays. Particle size and shape were determined by scanning electron microscopy (SEM) using FEI Nova NanoSEM 630 FESEM. High resolution transmission electron microscopy (TEM) was done on a JEOL JEM-2010F microscope operated at 200kV.

Fourier transform infrared spectroscopy (FTIR) analyses were performed using a Bruker Vertex V70 Spectrometer (Bruker Optics Billerica MA). DSC-TGA data were obtained from a TA Instruments Q600 (SDT) analyzer.

Chemical analysis of the 15Å SnP-H⁺ phase was done by dissolving in HF followed by neutralization with boric acid. Analyses of Sn and P were done by inductively coupled plasma emission spectrometry using a Perkin-Elmer Optima 5300 ICP.

Cesium analyses were done using the Perkin Elmer AAnalyst 800 using Standard Methods 3111B, Direct Air-Acetylene Flame method. Detection limit of Cs by this technique is 0.01mg/L.

Selective Cs⁺ removal or uptake study

Selective cesium exchange isotherm was constructed using different CsCl solutions of 0.0125, 0.025, 0.05, 0.1, 0.15 and 0.2mM in 1M HCl. The H⁺ : Cs⁺ milliequivalent ratios of the above solutions are 80000, 40000, 20000, 10000, 6667 and 5000, respectively. A 25mg sample was equilibrated with 25 mL each of all the above solutions by shaking for 24 hours. Other exchangers such as α -SnP, α -ZrP, γ -ZrP and Na₂Ti₂SiO₇ were also tested for Cs⁺ uptake by equilibrating 0.0002M CsCl in 1M HCl and compared with the 15Å SnP-H⁺ phase by

equilibrating as above. Kinetics of Cs⁺ removal was determined for the 15Å SnP-H⁺ phase by equilibrating with 0.2mM CsCl in 1M HCl for 1, 2, 4 and 8 days. Cs⁺ removal was also determined for the 15Å SnP-H⁺ phase and Na₂Ti₂SiO₇ by equilibrating with 0.2mM CsCl in 1M or 2M or 3M HCl for 1day to determine the effect of acid concentration on Cs⁺ removal. Fixation of Cs⁺ by the 15Å SnP-H⁺ phase and Na₂Ti₂SiO₇ was determined by re-exchanging the Cs⁺ in 1M HCl after equilibration for 24 hours. The samples used in determining fixation of Cs⁺ were previously used for Cs⁺ removal from 1M HCl. All the Cs⁺ removal/exchange experiments were conducted in triplicates. After equilibration the solid and solution phases were separated by centrifugation and the solutions were analyzed for Cs⁺ by atomic absorption method as described above.



Figure S1. Powder XRD pattern of the 15Å SnP-H⁺ phase synthesized at pH = 0 under microwave-hydrothermal conditions at 195°C/2h.



Figure S2. DTA-TGA curves of the 15Å SnP-H⁺ phase synthesized at pH=0 by microwavehydrothermal process at 195°C /2 hours showing 14.4% loss of interlayer water.



Figure S3. Infrared Spectroscopic analyses of (a) 15Å SnP phase and (b) 7.6Å α -SnP phase, both synthesized by microwave-hydrothermal process at 195°C/2 hours.



Figure S4. Scanning electron micrographs of 15Å SnP phase synthesized at pH=0 by microwave-hydrothermal process at 195°C/2 hours at low (a) and high (b) magnifications.



Figure S5. Transmission electron micrograph of 15Å SnP-H⁺ phase synthesized by microwave-hydrothermal process at $195^{\circ}C/2$ hours



Figure S6. Schematic ball and stick model of 15Å SnP-H⁺ phase.

Sample number	Temperature, °C	Time of Treatment (hour)	рН	d-values (Å)
1	195	2	0	15.1, 8.4, 7.4, 6.1, 5.6, 3.2, 3.0
2	195	2	1	14.9, 8.4, 7.4, 6.0, 5.5, 3.8, 3.3, 3.0
3	195	2	2	15.1, 8.4, 7.3, 3.0
4	195	2	3	15.2, 8.6 7.4, 5.7, 3.3, 3.0
5	195	2	4	15.6, 8.5, 7.3, 3.0
6	195	2	5	15.5, 3.0
7	195	2	6	No noticeable peaks

Table S1. Syntheses of the 15Å SnP-H⁺ by microwave hydrothermal treatment under different pH conditions using Method I.

* 15Å SnP-H+ phases were prepared using 5mL of 1M SnCl₄ in 1M HCl and 20mL of 3M NaH₂PO₄. * Conc. HCl was used for adjustment to pH=0 and 1.

* 10M NaOH was used to adjust to pH=2, 3, 4, 5 and 6.

Sample	$K_{d} (mL/g)^{*}$		
Name			
15Å SnP-H ⁺ phase	1527±72		
$Na_2Ti_2SiO_7(CST)$	1241 ± 31		
α -SnP, Sn(HPO ₄) ₂ ·H ₂ O	3 ± 5		
α -ZrP, Zr(HPO ₄) ₂ ·H ₂ O	-38 ± 148		
γ -ZrP, Zr(HPO ₄) ₂ ·2H ₂ O	-5 ± 64		

Table S2: Comparative uptake of Cs by novel 15Å SnP-H⁺ phase with well-known cation exchangers from 1M HCl (initially 0.2mM Cs in 25 mL of 1 M HCl using 0.025 g sample).

 K_d is defined as the ratio of the amount of Cs exchanged per g of exchanger to the amount of remaining (unexchanged) Cs per milliliter of solution.

Table S3: Theoretical cation exchange capacities (CECs) of different exchangers tested in this study.

Cation exchanger	Theoretical CEC* (meq/100g)		
15Å SnP-H ⁺ phase	548		
$Na_2Ti_2SiO_7 \cdot 2H_2O$	629		
α -SnP, Sn(HPO ₄) ₂ ·H ₂ O	608		
α -ZrP, Zr(HPO ₄) ₂ ·H ₂ O	664		
γ -ZrP, Zr(HPO ₄) ₂ ·2H ₂ O	627		

*Based on their chemical formula