Supporting information

Mechanochemistry-based Synthesis of Highly Crystalline γ-Zirconium Phosphate for Selective Ion Exchange

Yu Cheng,[‡] *Xiao Dong (Tony) Wang,*[§] *Stephan Jaenicke,*[‡] *Gaik-Khuan Chuah**[,‡]

[‡]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

[§]Bruker Singapore, 11 Biopolis Way, #10-10, Helios, Singapore 138667

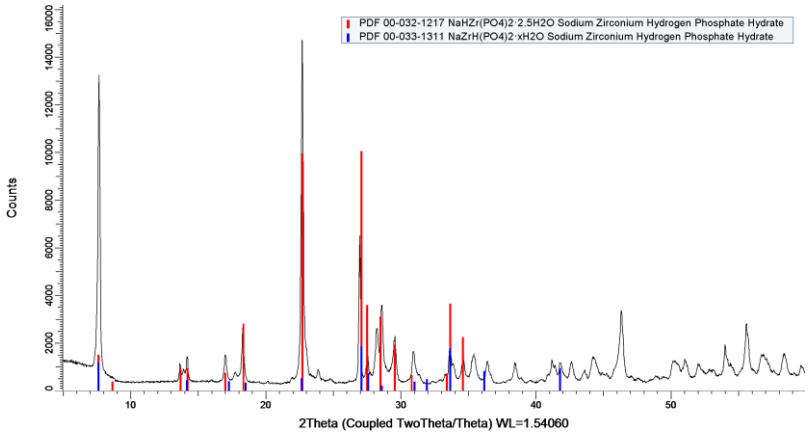

Figure S1. XRD pattern of sodium zirconium hydrogen phosphate synthesized with $ZrOCl_2 \cdot 8H_2O$: *4*$NaH_2PO_4 \cdot H_2O$: *0.3*NaF at 120 °C for 24 h. Peaks fitted for $NaHZr(PO_4)_2 \cdot 2.5H_2O$ and $NaZrH(PO_4)_2 \cdot xH_2O$.

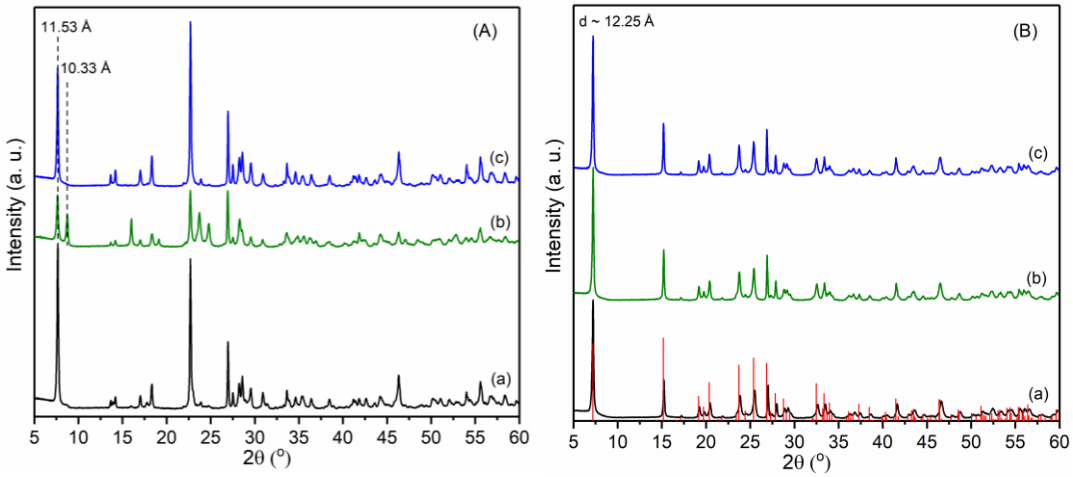

Figure S2. XRD patterns of (A) sodium zirconium hydrogen phosphate synthesized with $ZrOCl_2 \cdot 8H_2O$: *5*$NaH_2PO_4 \cdot H_2O$: *0.3*NaF after heating at 120 °C for 24 h, (a-c) from different batches and (B) after treatment in 0.5 M HCl. Red lines indicate peak positions for $Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ (ICDD 04-011-1172).

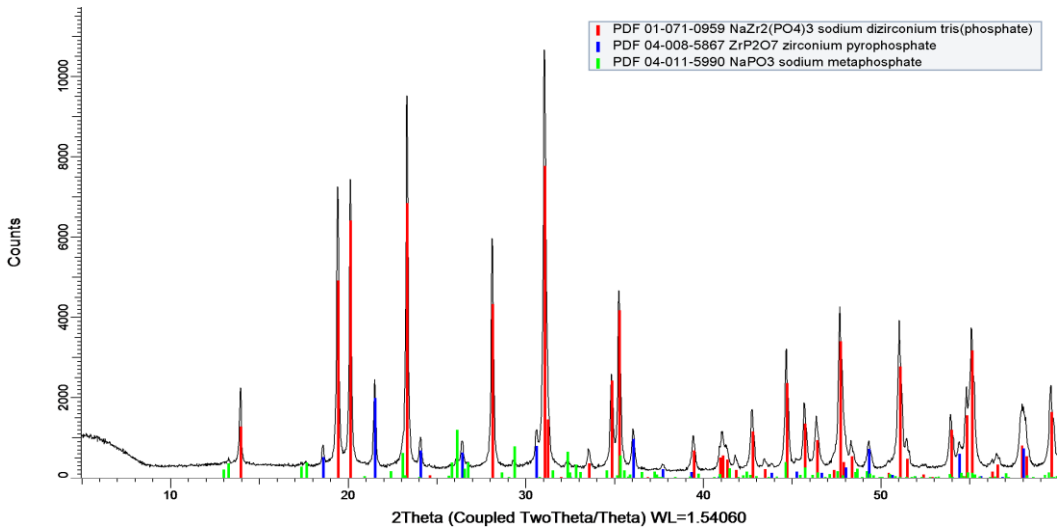

Figure S3. XRD of sodium zirconium phosphate after calcination at 500 °C for 5 h. Peaks fitted for $NaZr_2(PO_4)_3$ (ICDD 01-071-0959), ZrP_2O_7 (04-008-5867) and $NaPO_3$ (04-011-5990).

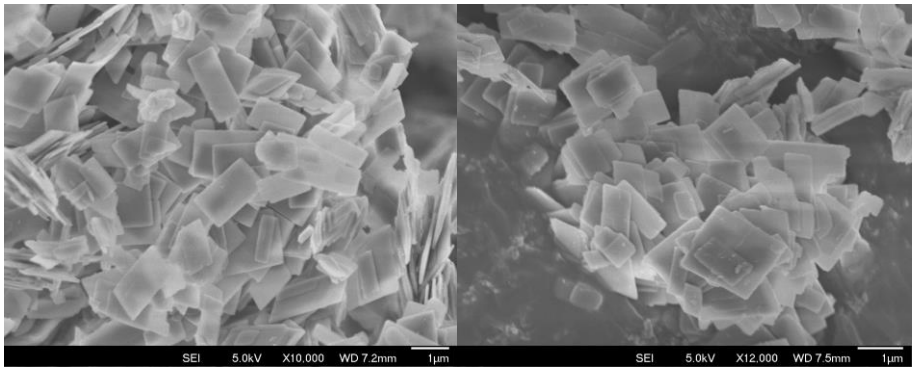

Figure S4. SEM images of γ-ZrP synthesized with NaH_2PO_4/Zr molar ratio of 5.

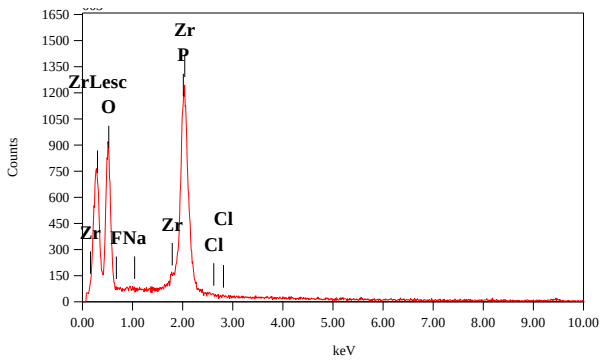

Figure S5. EDS spectrum of γ-ZrP formed after treatment with 0.5 M HCl solution.

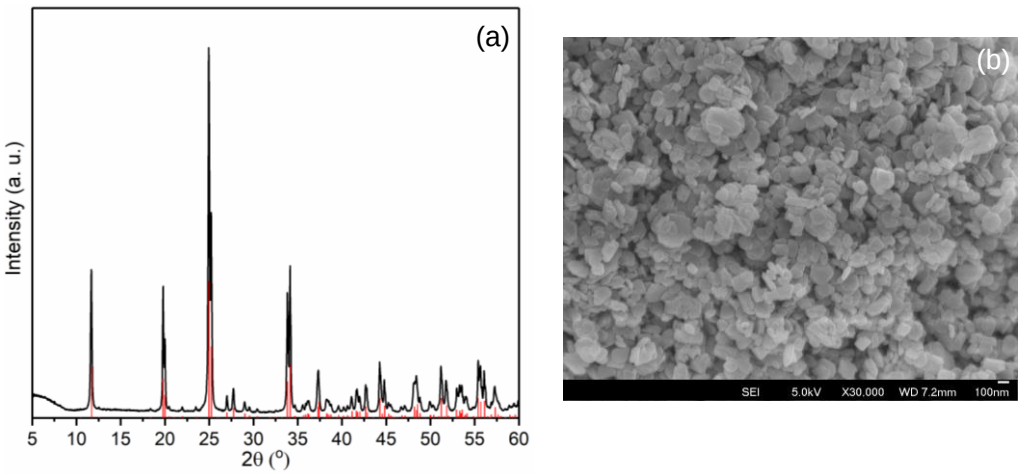

Figure S6. (a) XRD pattern and (b) SEM image of α-ZrP used in this study. Red lines indicate peak positions for α-$Zr(HPO_4)_2 \cdot H_2O$ (ICDD 04-010-6268).

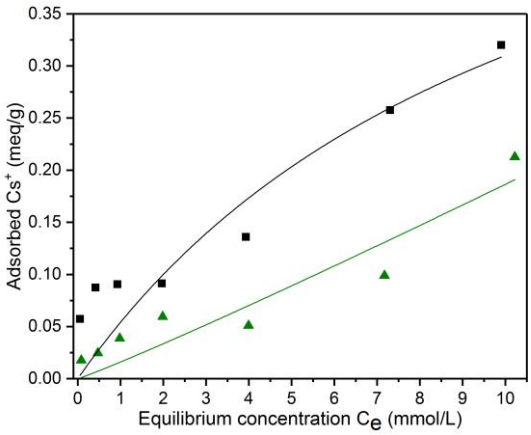

Figure S7. Adsorption isotherms of Cs^+ on α-ZrP (■) in aqueous CsCl solutions (pH=5.5), (▲) in the presence of 0.05 M $CaCl_2$ (pH=5.1).

Table S1: Ionic and hydrated radii of cations studied.[46]

Cations	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
Ionic radius (Å)	0.95	1.33	1.69	0.65	0.99	1.13
Hydrated radius (Å)	3.58	3.31	3.29	4.28	4.12	4.12