

Electronic Supplementary Information

Phosphonate-functionalized large pore 3-D cubic mesoporous (KIT-6) hybrid as highly efficient actinide extracting agent

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Experimental Section

Synthesis of ordered mesoporous SBA-15/KIT-6 silica materials. High quality mesoporous KIT-6 silica material was obtained in large quantities following the method reported by Kleitz *et al.* [F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136; F. Kleitz, F. Bérubé, R. Guillet-Nicolas, C.-M. Yang and M. Thommes, *J. Phys. Chem. C*, 2010, **114**, 9344]. Briefly, 9.0 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀, Sigma-Aldrich) was dissolved in 325 g of distilled water and 17.40 g HCl (37 %) under vigorous stirring. After complete dissolution, 9.0 g of *n*-butanol (BuOH, Aldrich, 99%) was added. The mixture was left under stirring at 35°C for 1 h, after which 19.35 g of tetraethoxysilane (TEOS, Acros, 99 %) were added at once to the homogeneous clear solution. The molar composition of the starting reaction mixture is TEOS/P123/HCl/H₂O/BuOH = 1/0.017/1.83/195/1.31. This mixture was left under stirring at 35 °C for 24 h, followed by an aging step at 80 °C for 48 h under static conditions. The resulting solid products were then filtered and dried for 48 h at 100 °C. For comparison purpose, 2-D hexagonal SBA-15 was synthesized following the method proposed by Choi *et al.* [M. Choi, W. Heo, F. Kleitz and R. Ryoo, *Chem. Commun.*, 2003, 1340]. This synthesis of SBA-15 is briefed as follows: 13.9 g of Pluronic P123 was dissolved in 252 g of distilled water and 7.7 g HCl

(37%). After complete dissolution, 25.0 g of TEOS was added at once. The mixture was left under stirring at 35 °C for 24 h, followed by hydrothermal treatment at 100 °C for 48 h under static conditions. In both cases, for template removal, the as-synthesized silica powders were first shortly slurried in an ethanol-HCl mixture and subsequently calcined at 550 °C for 2 hours.

Grafting of 2-diethylphosphatoethyl) triethoxysilane on mesoporous KIT-6 and SBA-15 silicas. For surface modification of both supports, 1 g of the given activated mesoporous silica (treated overnight at 150 °C under vacuum) was dispersed in 50 mL of dry toluene. Then, 6 mmol of (2-diethylphosphatoethyl) triethoxysilane (DPTS, Gelest, 98%) was added at once to the dispersion in toluene under nitrogen atmosphere at room temperature. The resulting mixture was left under further stirring for 24 h under reflux conditions. After cooling to room temperature, the suspended solid product was filtered, washed thoroughly with 20 mL of toluene and ethanol three times, and then dried at 70 °C overnight in air.

Characterization

N₂ adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2010 analyzer. Before the sorption measurements, the samples were outgassed for 6 h at 80 °C. Specific surface area, S_{BET} , were determined using the BET equation in the range $0.05 \leq P/P_0 \leq 0.20$ and the total pore volume was measured at $P/P_0 = 0.95$. Pore size distributions were calculated using non-local density functional theory (NLDFT) methods applying the cylindrical pore model. TG-DTA measurements were performed using a Netzsch STA 449C thermogravimetric analyzer, under air flow of 20 mL/min with a heating rate of 10 °C/min. FTIR-ATR spectra were recorded using a Nicolet Magna FTIR spectrometer with a narrow band MCT detector and a diamond ATR Golden-Gate accessory (Specac Ltd., London). The spectra were obtained from 128 scans with a resolution of 4 cm⁻¹. Solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DRX300 MHz NMR spectrometer. ²⁹Si MAS NMR spectrum was measured at 59.60 MHz using 7 mm rotors spinning at 4 kHz. ³¹P spectra were measured at 121.4 MHz using 4 mm rotors spinning at 8 kHz. The 75.4 MHz ¹³C CP-MAS spectra were obtained using a 7 mm rotor spinning at 4 kHz. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) for ²⁹Si and ¹³C and

relative to phosphoric acid for ^{31}P . Low angle X-ray diffraction (XRD) measurements were conducted on a Siemens D5000 X-ray diffractometer using Cu radiation. Transmission electron microscopy (TEM) was performed using a JEOL JEM1230 at an accelerating voltage of 80kV with a LaB6 filament. X-ray photoelectron spectroscopy (XPS) measurements were performed with a KRATOS Axis-Ultra instrument (UK) using a monochromatic $\text{K}\alpha$ Al X-ray source at 300W. Survey spectra used for determining the elemental composition were collected at a pass energy of 160 eV with a step size of 1 eV.

Batch extraction experiments

Solutions of U(VI) and Th(IV) in HNO_3 were prepared from radioactive standards from NIST. The U/TEVA resins were purchased from Eichrom, USA (Lisle, IL). Competition studies were performed with a mixture of $1\ \mu\text{g L}^{-1}$ of U(VI), Th(IV) and a multi-element solution (Multi-element solution 2A, SPEX, Metuchen, USA) consisting in the following cations: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn. The solution/solid ratio was fixed to 200 (V/m). All extraction experiments except the extraction of U(VI) with the commercial resin (1.8 M HNO_3) were performed at pH=4. Samples were stirred in an orbital shaker for 30 min. Subsequently, the supernatant was filtered through a $0.2\ \mu\text{m}$ syringe filter. The initial and final concentrations of the actinides in solutions were determined by ICP-MS measurements and distribution coefficients (K_d) were calculated by the following formula [D. T. Pierce and J. X. Zhao, *Trace Analysis with Nanomaterials*, 2010. Germany: Wiley-VCH (p.191)]:

$$K_d (\text{mL/g}) = \frac{(C_i - C_f)}{C_f} \times \frac{V_{\text{solution}} (\text{mL})}{m_{\text{solid}} (\text{g})}$$

where C_i and C_f are the initial and final concentration. Batch experiments were done in triplicates.

Adsorption kinetics study of U(VI) on KIT-6-P was performed under similar conditions as the batch extractions. The studied contact times were set for 1, 2, 3, 5, 10 and 30 min, in duplicates.

Table S1 Physicochemical parameters of parent and functionalized silica samples derived from N₂ physisorption, thermogravimetric analysis and XPS.

Samples	Surface area S_{BET} (m ² /g)	Pore size NLDFT _{ads} (nm)	Pore size NLDFT _{des} (nm)	Total pore volume (cm ³ /g)	Weight loss (%)	P/Si (at%)
KIT-6	1128	7.3	7.9	1.18	-	-
KIT-6-P	846	6.8	7.0	0.93	9.4	3.99
SBA-15	1038	8.5	9.1	1.46	-	-
SBA-15-P	653	8.2	8.5	0.91	8.6	5.07

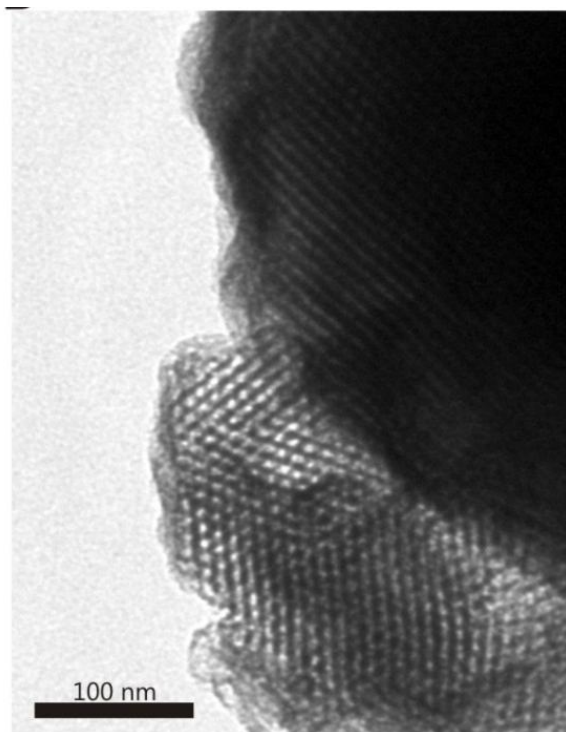


Fig. S1 Representative TEM image of the reference 2-D hexagonal SBA-15-P hybrid.

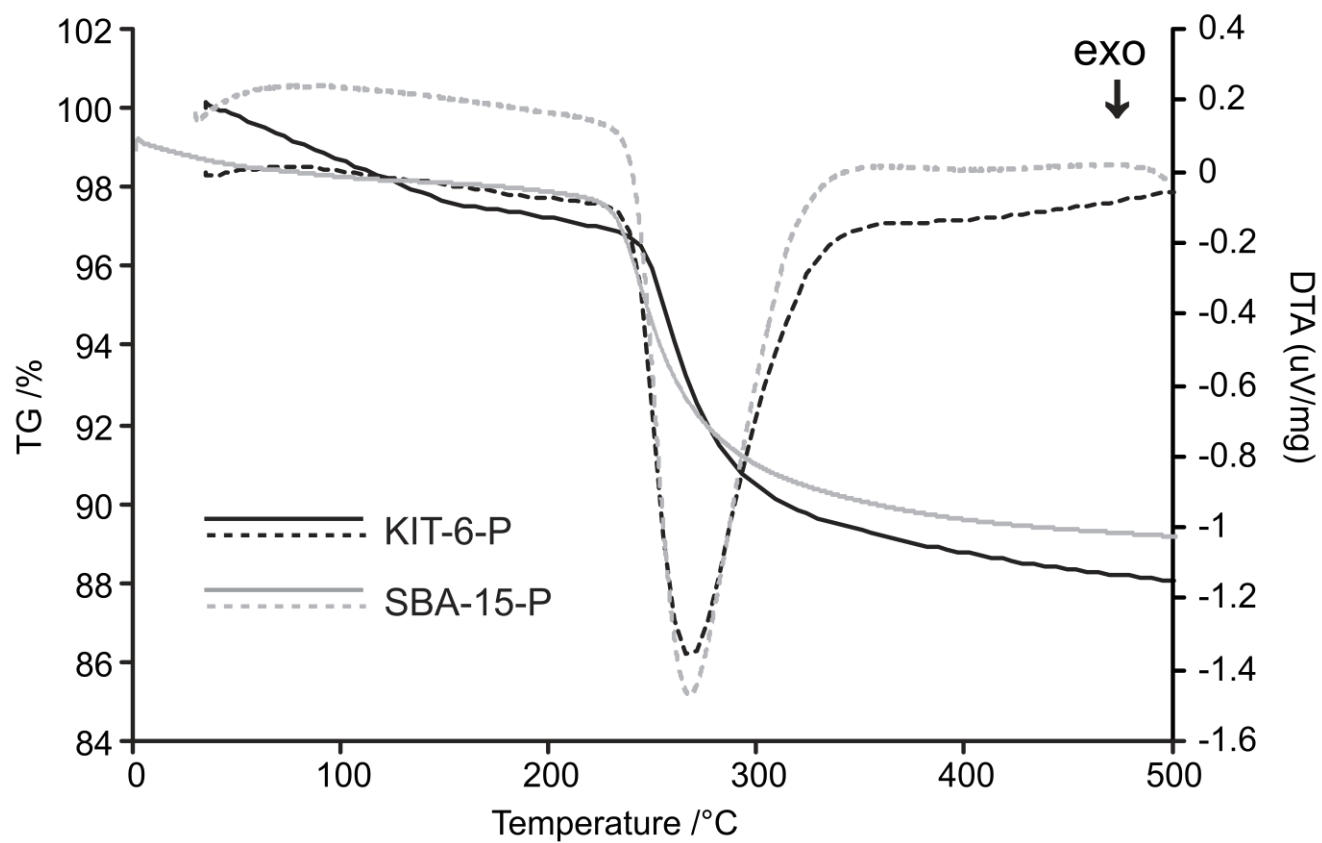


Fig. S2 TG-DTA curves of KIT-6-P and SBA-15-P measured under air flow, as indicated.

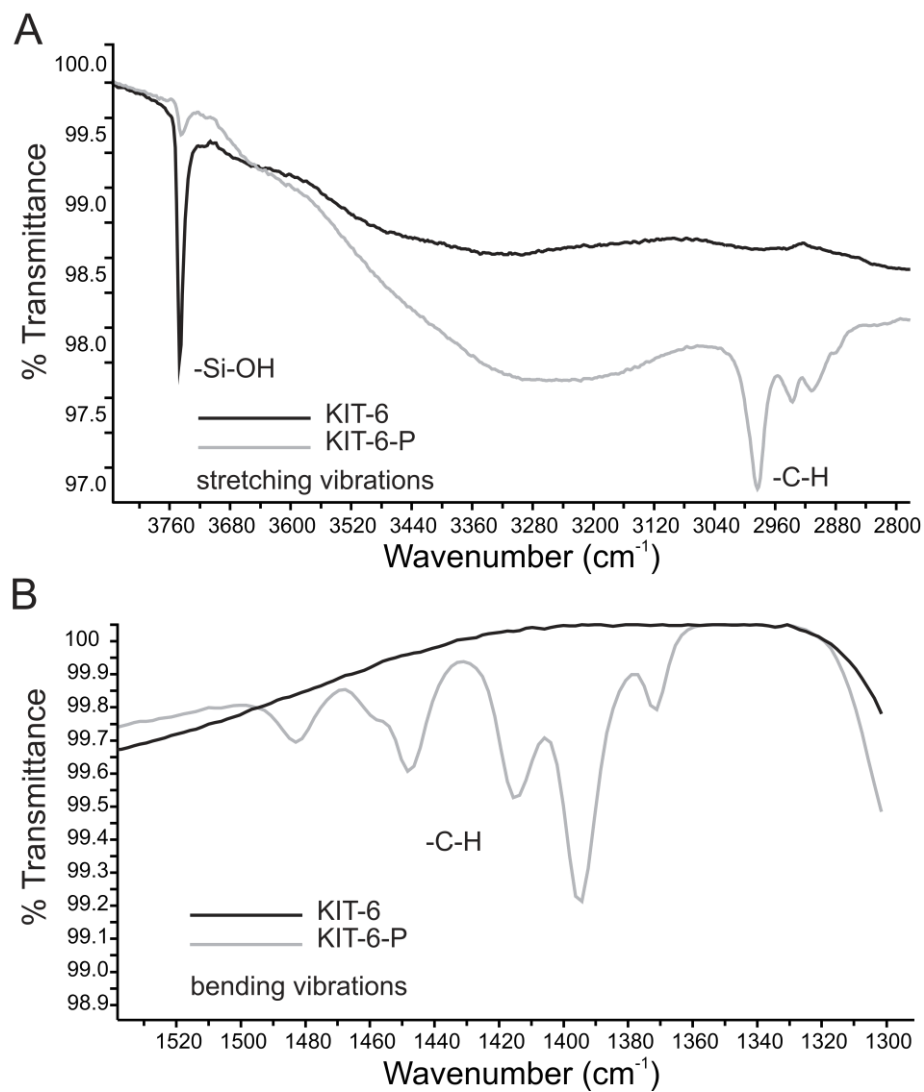


Fig. S3 FTIR spectra of KIT-6 and KIT-6-P, as indicated.

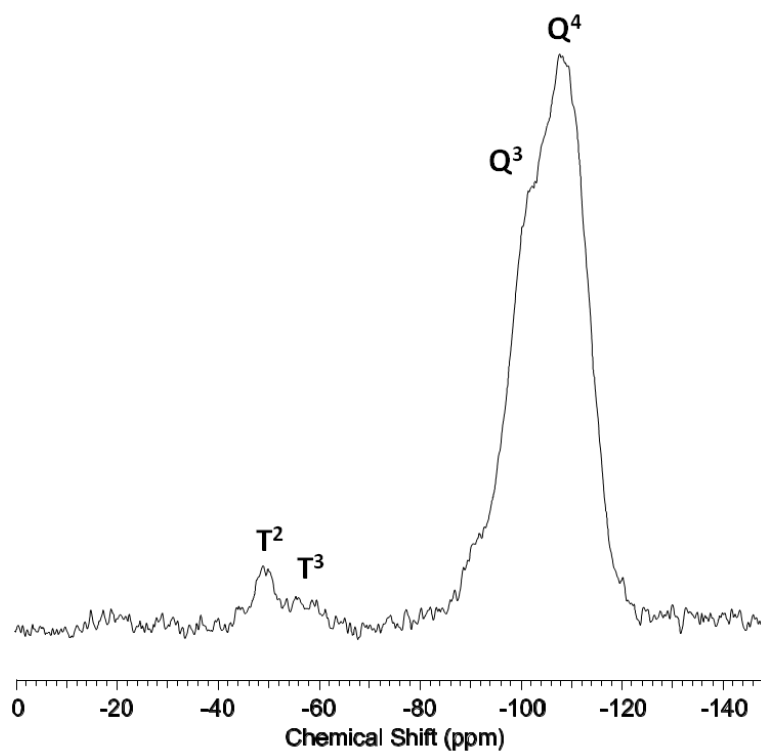


Fig. S4 Solid state ^{29}Si MAS NMR spectrum of KIT-6-P.

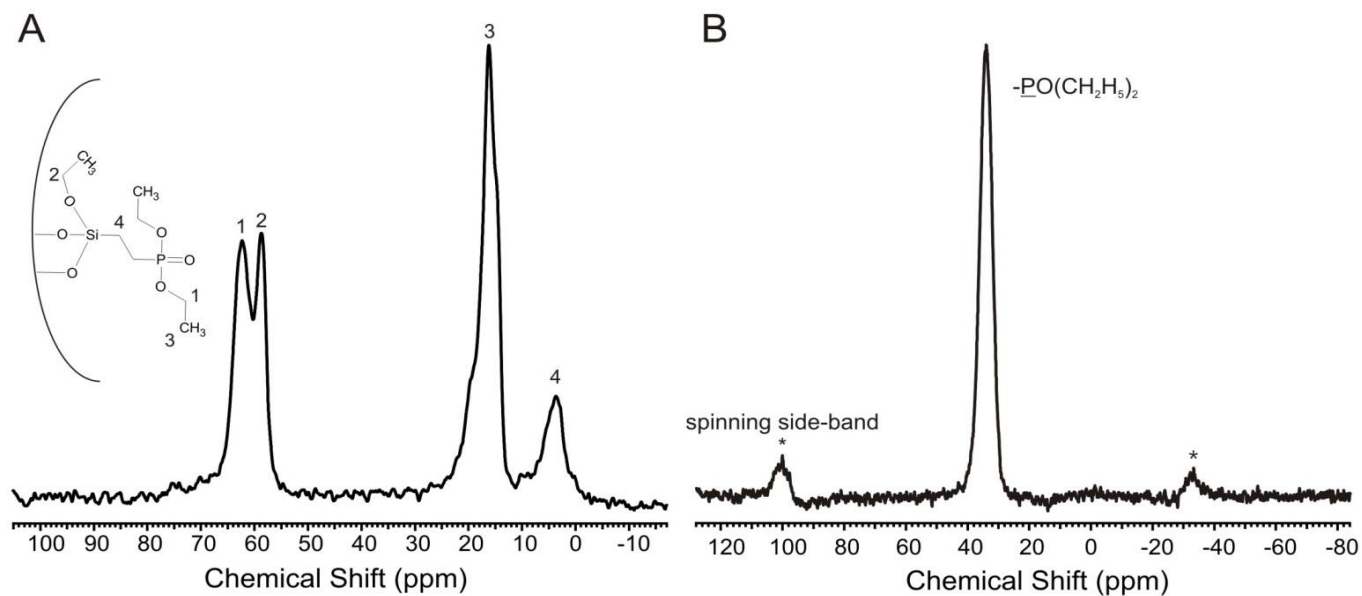


Figure S5 Solid state ^{13}C CP/MAS A) and ^{31}P MAS NMR B) spectra of SBA-15-P.