Supporting Information

Nonaqueous Template-Assisted Synthesis of Mesoporous Nanocrystalline Silicon Orthophosphate

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Experimental

General procedures

All manipulations were performed under dry N2 using Schlenk techniques or in an M. Braun dry box with both H2O and O2 levels below 1 ppm. Xerogels were not exposed to atmosphere during any phase of handling. Si(OAc)4 was prepared according to the literature.1 SiCl4 (Merck, 99 %) and acetic acid anhydride (Riedel de Haën, 98 %) were distilled prior to use. Tris(trimethylsilyl)phosphate (TTP) was prepared from H3PO4 and Me3SiCl and vacuum-distilled. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Sigma Aldrich, Pluronic P123) was dried overnight in vacuo at 60 ºC and dissolved in toluene. Toluene was freshly distilled from Na/benzophenone under N2. α-Methylstyrene for the catalytic test reactions was dried over Na/benzophenone and distilled under N2.

Characterization methods

The IR spectra (4000–400 cm−1) were recorded on a Bruker Tensor T27 spectrometer. Samples were prepared as KBr pellets. N2 adsorption–desorption experiments were performed at 77 K using a Quantachrome Autosorb-1MP porosimeter. Surface areas (SA) and total pore volumes (Vtot at p/p0 = 0.98) were determined by volumetric technique.2,3 Prior to the measurements, the samples were degassed at 25 ºC for at least 24 h until the outgas rate was less than 0.4 Pa min−1. The adsorption–desorption isotherms were measured for each sample at least three times. The specific surface area was determined by the multipoint BET method with at least five data points with relative pressures between 0.05 and 0.30. Thermal analysis (TG/DSC) was measured on a Netzsch STA 449C Jupiter apparatus from 25–1000 ºC under flowing air (70 cm³ min−1) with a heating rate of 5 K min−1. Samples for elemental analyses of Si and P were melted with Na2O2 in a sealed metal container (0.1 cm³ of ethylene glycol was

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added to initiate the combustion). The melt was then dissolved in ca 150 cm$^3$ of distilled water in a plastic beaker in an ultrasonic bath and then diluted to 250 cm$^3$. All manipulations of these samples were performed excluding contact with glass in order to avoid the contamination with external SiO$_2$. The Si and P contents were analyzed on an ICP OE spectrometer iCAP 6500 Duo (Thermo, generator 27.12 MHz, amplitude 1.15 kW, plasma gas flow 12 dm$^3$ min$^{-1}$) using emission lines 213.618 nm and 214.914 for P and 212.412 and 251.611 nm for Si. Solid-state $^1$H MAS, $^{31}$P MAS, $^{29}$Si and $^{13}$C CPMAS NMR spectra were acquired on a Bruker 700 MHz NMR spectrometer. Inside a dry box, samples were loaded into 5 mm zirconia rotors and stoppered with teflon plugs. Magic angle spinning rates were 5 kHz for $^{29}$Si and $^{13}$C CPMAS and 10 kHz for $^1$H and $^{31}$P MAS spectra. Chemical shifts were referenced externally to $^1$H $\delta$ [adamantane]: 1.87 ppm, $^{31}$P $\delta$ [H$_3$PO$_4$ (85%)]: 0.0 ppm; $^{29}$Si $\delta$ [(Me$_3$Si)$_8$Si$_8$O$_{20}$]: 11.72 ppm; $^{13}$C $\delta$ [adamantane]: 38.68 ppm. GC-MS spectra were obtained on a Thermo Scientific Trace GC Ultra–TSQ Quantum XLS mass spectrometer. TS-SQC column (15 m, 0.25 mm, 0.25 $\mu$m) was heated with following program: 50 °C (0 min), 5 °C min$^{-1}$ up to 80 °C, 15 °C min$^{-1}$ up to 120 °C, 35 °C min$^{-1}$ up to 200 °C (0.5 min). Split mode, injector, interface, and detector temperatures were set to 200 °C. Column pressure was 31.5 kPa and ionization energy 70 eV. A Rigaku diffractometer SmartLab operating in Bragg-Brentano geometry with a CuK$_{\alpha}$ radiation and equipped with a linear detector D-Tex was used for the XRD data acquisition at ambient temperature. Crystallite size was estimated from the halfwidth of diffractions by mathematical fit of diffractogram using Debye-Scherrer equation. Natural halfwidth of diffraction lines was measured on a silicon standard. Quantitative analyses of amorphous phases were performed by Rietveld refinement of diffractograms of samples which consisted of 20 wt% of CaF$_2$ and 80 wt% of silicophosphate. SAXS data were collected using a Rigaku BioSAXS-1000 instrument. A Lyra3 Tescan microscope was used for the SEM analysis of the samples. Transmission electron microscopy (TEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB$_6$ cathode, point resolution 1.7 Å) with an Energy Dispersive X-ray (EDX) detector attached.

Scheme 1S: α-Methylstyrene dimerization to its dimers.
Figure 1S: $^{29}$Si CPMAS NMR spectra of samples SiP, SiP-P, and SiP-P-500 and MAS NMR spectrum of SiP-P-500.

Figure 2S: $^{13}$C CPMAS NMR spectra of samples SiP and SiP-P. * marks spinning sidebands.
Figure 3S: SAXS profiles of samples SiP-P and SiP-P-500.

Figure 4S: SEM image of nonporous SiP sample after calcination at 500 °C.
References