

Electronic Supplementary Information

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Experimental Section

Synthesis of triblock N₃-PO₃-N₃ SDA

N,N,N',N'-tetramethyl-1,6-hexanediamine (0.3 mol) and 1-bromohexane (0.03 mol) were dissolved in toluene/acetonitrile (300 mL, 1:1 vol/vol) and heated at 70 °C for 1 day. After cooling to room temperature, the mixture was dried by rotary evaporation and the solid was then repeatedly washed with diethyl ether and finally dried at 80 °C in vacuum to obtain compound **1** (C₆H₁₃-N⁺(CH₃)₂-C₆H₁₂-N(CH₃)₂(Br⁻)). Compound **1** (0.02 mol) was then reacted with 1,6-dibromohexane (0.2 mol) in toluene/acetonitrile (200 mL, 1:1 vol/vol) and heated at 70 °C for 1 day. After cooling to room temperature, the mixture was dried by rotary evaporation and compound **2** (C₆H₁₃-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₆H₁₂Br(2Br⁻)) was obtained by extraction using diethyl ether and was dried at 70 °C in vacuum. Poly(propylene glycol) bis(2-aminopropyl ether) (NH₂-(PO)₃-NH₂, 0.003 mol) was mixed with formic acid (0.02 mol) and formaldehyde (0.045 mol) in ice bath, and the mixture was then heated at 80 °C for 12 h. After cooling to room temperature, 6 N HCl (0.45 mL) was added and the mixture was dried by rotary evaporation. The mixture was added with water (30 mL) and then extracted with diethyl ether (30 mL) three times. The resulting organic phase was mixed with anhydrous MgSO₄, filtered, and finally the solvent was removed by rotary evaporation to get compound **3** ((CH₃)₂N-(PO)₃-N(CH₃)₂). To obtain the final product, compound **2** (0.0022 mol) and compound **3** (0.001 mol) were mixed in toluene/acetonitrile (100 mL, 1:1 vol/vol) and heated at 80 °C for 3 days, and N₃-PO₃-N₃ (bromide form) was extracted by diethyl ether and finally dried at 70 °C in vacuum. The bromide ions were replaced with hydroxide (OH⁻) ions by repeated ion exchange using the anion-exchange resin (Amberlite, IRN-78).

Synthesis of hierarchical silicalite-1 octahedrons and bulk silicalite-1

In a typical synthesis of hierarchical silicalite-1 octahedrons, N₃-PO₃-N₃ (0.27 mmol) was added to aqueous solution (9.6 mL) containing calculated amounts of NaOH and H₂SO₄ and the mixture was stirred to become homogeneous. Tetraethylorthosilicate (TEOS, 0.013 mol) was then added under vigorous stir, resulting in a mixture with molar composition of 50 SiO₂ : 1 N₃-PO₃-N₃ : 12 Na₂O : 9 H₂SO₄ : 2000 H₂O. The mixture was transferred to an autoclave and was heated at 150 °C for 2 days. The solid product was filtered and dried at 90 °C. The as-synthesized sample of silicalite-1 octahedrons was either calcined at 540 °C for 6 h or stirred in aqueous solution of H₂SO₄ (45 wt%) at 95 °C for 1 day to remove completely or partially the SDA molecules. After the treatment, the acid-treated sample was filtered, repeatedly washed by water and acetone, and finally dried at 70 °C in air. The bulk silicalite-1 was synthesized at 150 °C for 5 days by following the procedure reported by Heitmann et al. using TEOS as a silica source (*J. Catal.* **1999**, *186*, 12-19).

Materials characterizations

PXRD patterns were obtained on a Bruker D8 Advance diffractometer using Cu K α radiation. SEM images were taken on a field emission JEOL JSM-7000F microscope operating at 10 kV. HRTEM images were taken from crushed samples on a FEI Tecnai G2 F20 field-emission electron microscope operated at 200 keV. N $_2$ physisorption isotherms were measured at 77 K using a Quantachrome Autosorb-1-MP instrument. The isotherms were analyzed by NLDFT method to evaluate pore sizes using the kernel of NLDFT equilibrium capillary condensation isotherms of N $_2$ at 77 K on silica (adsorption branch, assuming cylindrical pore geometry). BET surface areas were calculated from adsorption branches in the relative pressure range of 0.05–0.20. Total pore volumes were evaluated at a relative pressure of 0.95. FT-IR spectra were obtained on a Thermo-Nicolet 6700 IR spectrometer with Harrick DRIFT accessories. For evacuating water, all samples were in-situ heated to 400 °C for 12 h in vacuum. ^{29}Si MAS NMR spectra were measured on a Bruker Avance III 400 MHz NMR spectrometer using 4 mm MAS probe probes at a spinning rate of 6.5 kHz. Thermogravimetry analysis (TGA) data were obtained using a Linseis STA PT1600 device.

Catalytic test

The vapor-phase Beckmann rearrangements of CHO and COO were carried out in a glass fixed-bed reactor with 10 mm inner diameter. A catalyst (0.1 g) was packed in the reactor and activated at 623 K for 3 h under N $_2$ flow before the reaction started. The reactant was dissolved in ethanol in 1: 9 weight ratio, carried into the reactor by a N $_2$ gas stream (30 mL min $^{-1}$) with a controlled feed rate. The reaction temperature was 623 K, and weight hourly space velocity was 1.5 g $_{\text{oxime}}$ g $_{\text{catal}}^{-1}$ h $^{-1}$. The products were collected at time intervals and analyzed by a gas chromatograph. In order to examine the reusability of the acid-treated silicalite-1 octahedrons, a new batch of sample was prepared, applied for the reaction for 50 h, regenerated by heating at 400 °C in air flow for 2 h, and was then used for the next cycle of catalytic test. The conditions for catalyst regeneration were determined based on the thermogravimetric analysis showing that the used silicalite-1 octahedrons contained ~8 wt% of coke that could be completely burned off in air at 400 °C.

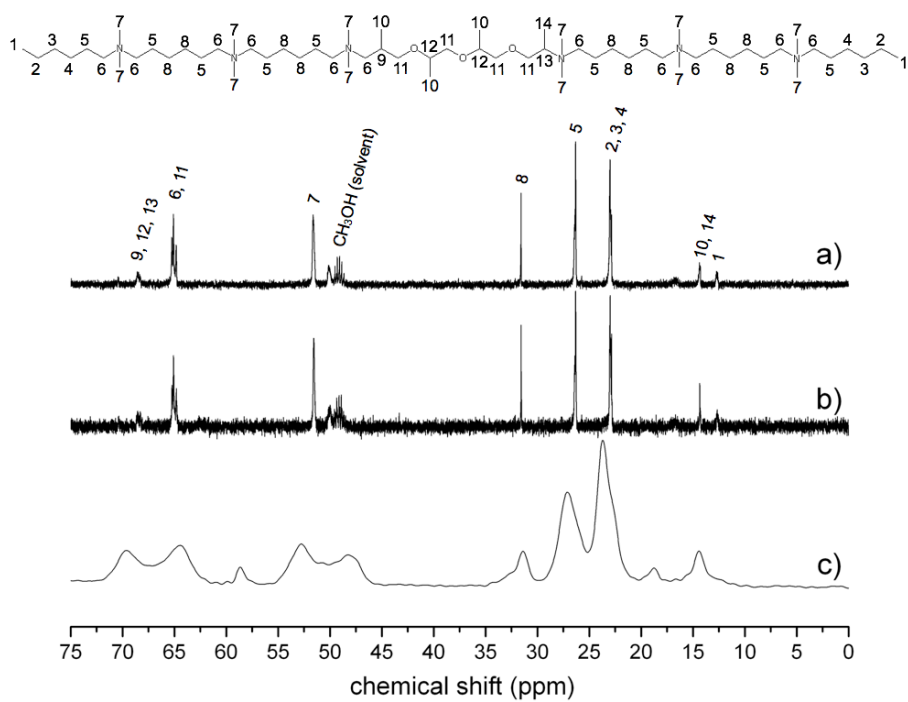


Fig. S1 (a and b) ^{13}C NMR spectra of $\text{N}_3\text{-PO}_3\text{-N}_3$ before (a) and after (b) heating at 150°C for 2 days. (c) Solid-state ^{13}C CP/MAS NMR spectrum of the as-synthesized silicalite-1 octahedrons.

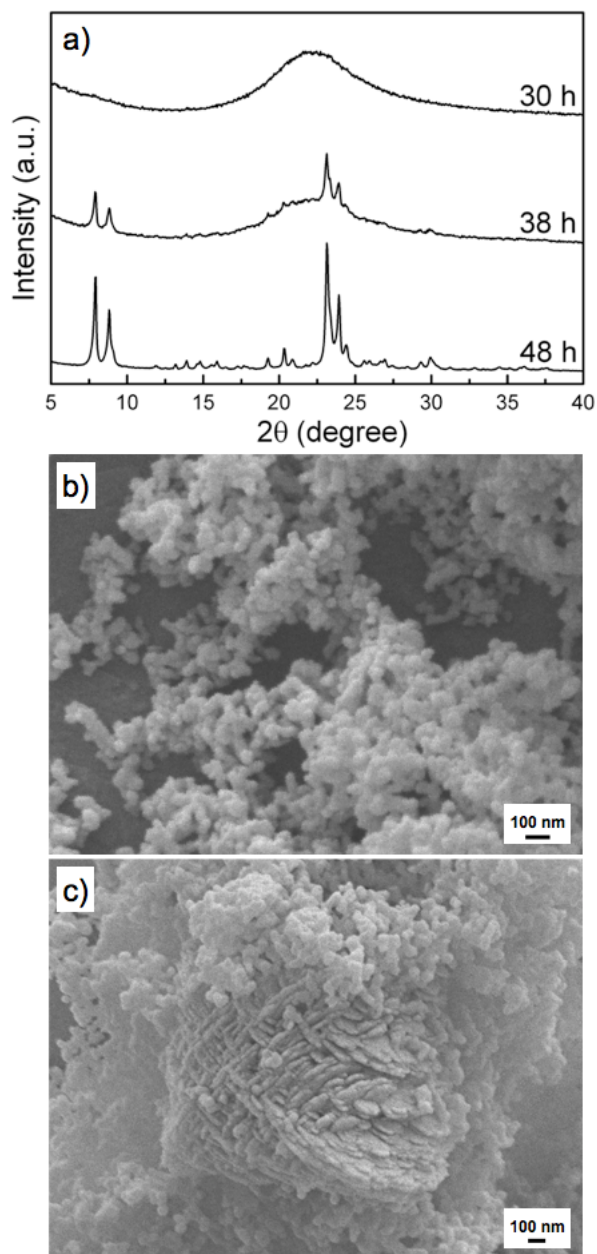


Fig. S2 (a) PXR D patterns of the products collected at hydrothermal time of 30 h, 38 h and 48 h. (b and c) SEM images of the products collected at 30 h (b) and 38 h (c).

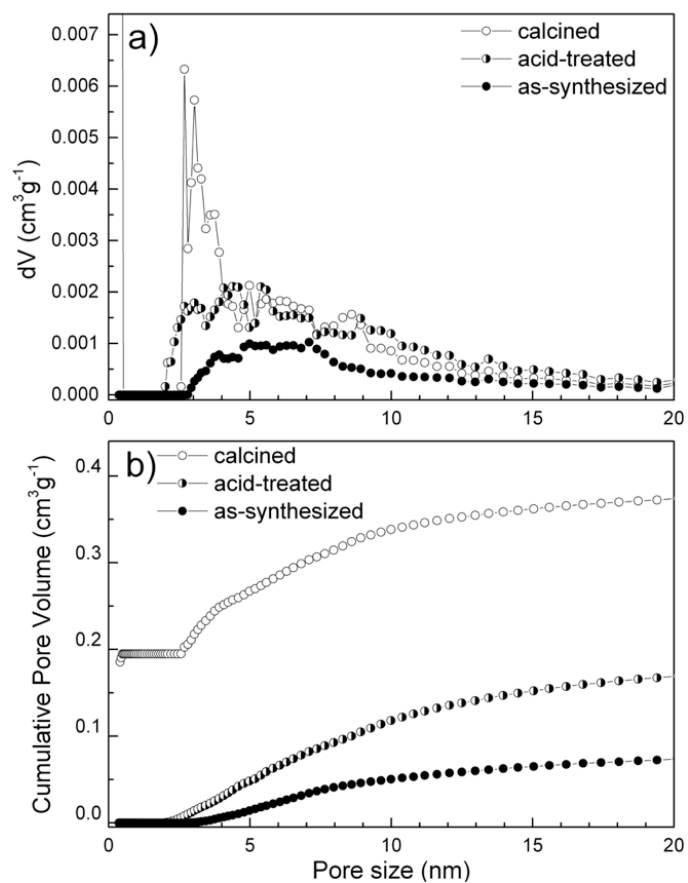


Fig. S3 Pore size distributions (a) and plots of accumulated pore volume versus pore size (b) of as-synthesized, acid-treated and calcined samples of hierarchical silicalite-1 octahedrons derived from nitrogen physisorption isotherms by NLDFT.

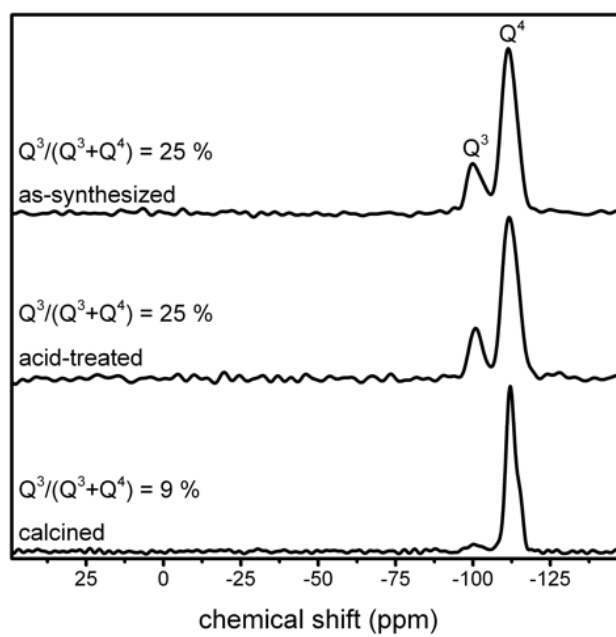


Fig. S4 ^{29}Si MAS NMR spectra of as-synthesized, acid-treated and calcined samples of hierarchical silicalite-1 octahedrons.

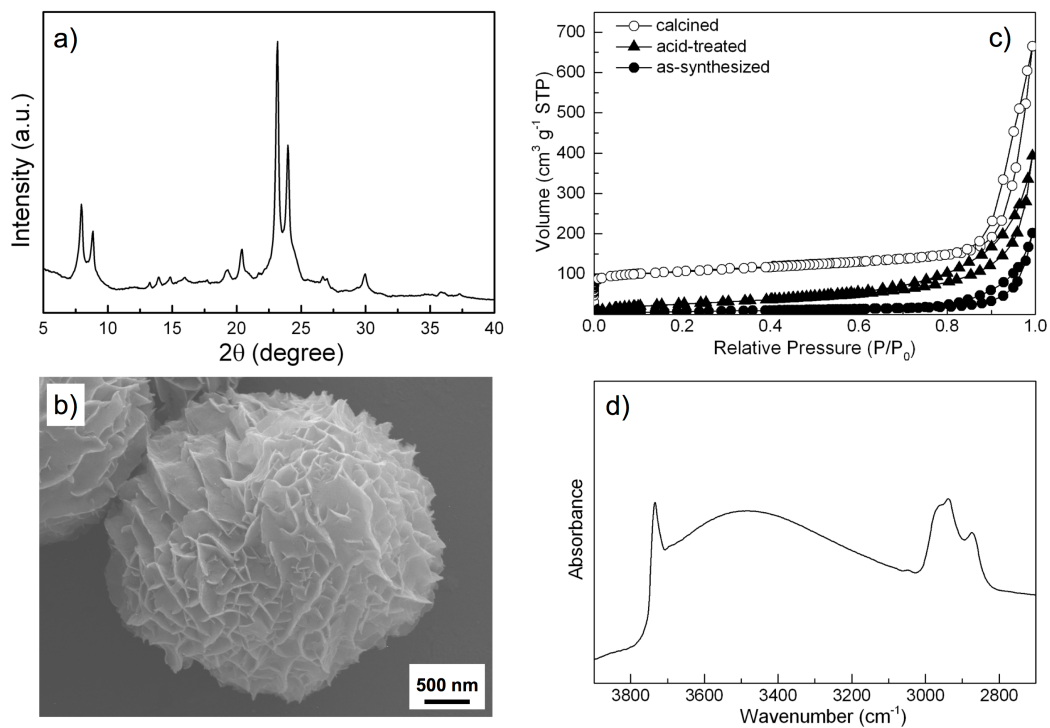


Fig. S5 (a) PXRD pattern, (b) SEM image, (c) nitrogen physisorption isotherms of as-synthesized, acid-treated and calcined samples and (d) FT-IR spectrum of acid-treated sample of the silicalite-1 material synthesized by using $\text{N}_3\text{-PO}_{33}\text{-N}_3$.

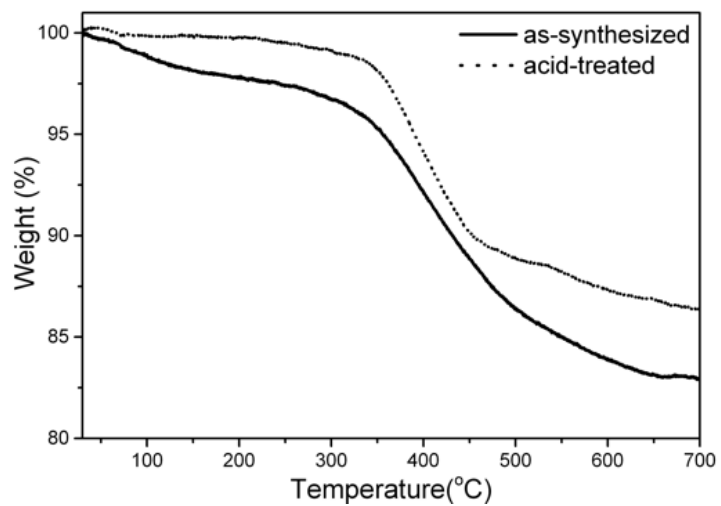


Fig. S6 TGA curves of as-synthesized and acid-treated samples of hierarchical silicalite-1 octahedrons.

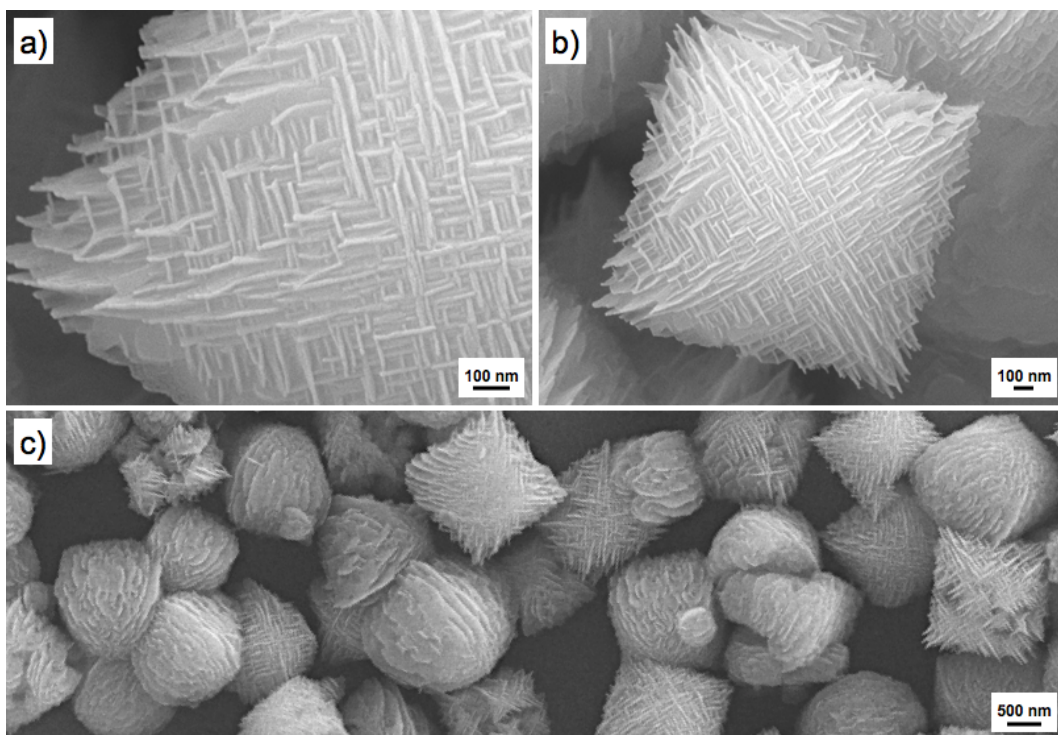


Figure S7 SEM images of calcined octahedrons.

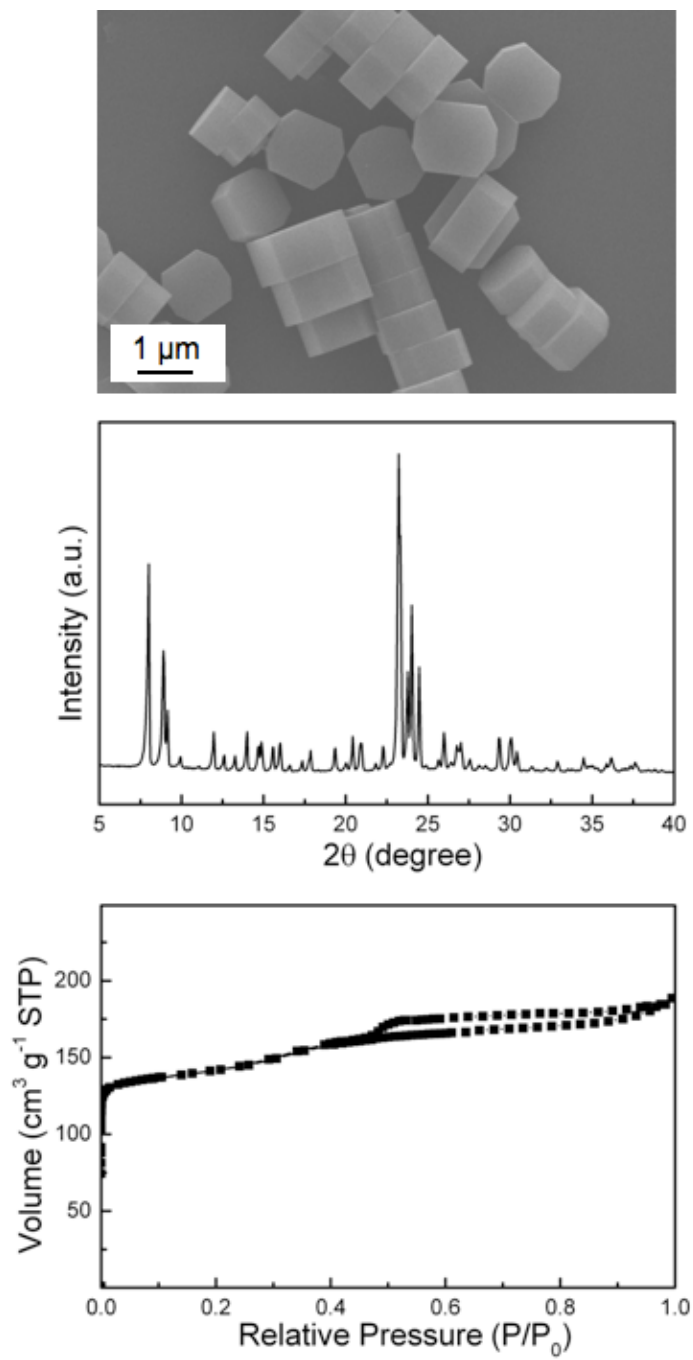


Fig. S8 SEM image, XRD and N_2 physisorption isotherm of bulk silicalite-1.

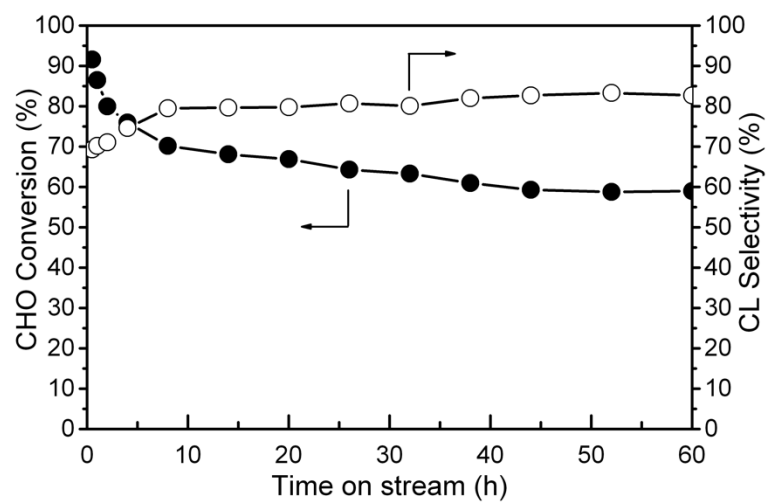


Fig. S9 Changes in CHO conversion (solid symbols) and CL selectivity (open symbols) with on-stream time for the Beckmann rearrangement of CHO over the acid-treated silicalite-1 material synthesized by using $N_3-PO_{33}-N_3$.

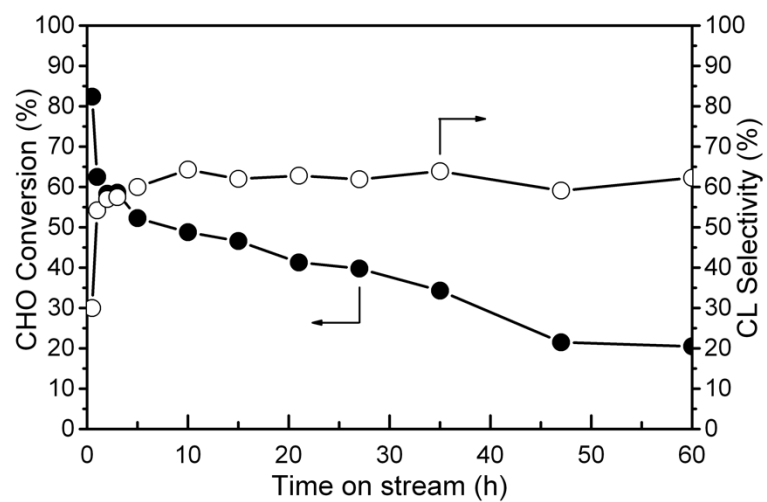


Fig. S10 Changes in CHO conversion (solid symbols) and CL selectivity (open symbols) with on-stream time for the Beckmann rearrangement of CHO over the solvent-extracted MCM-41.

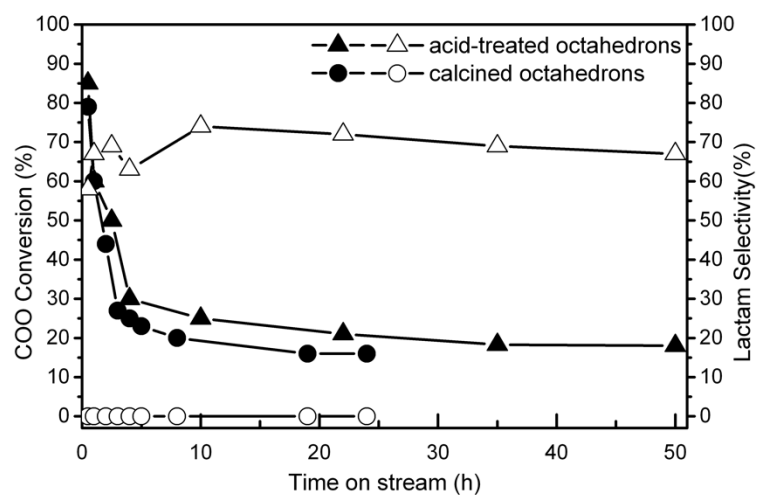


Fig. S11 Changes in COO conversion (solid symbols) and the selectivity to corresponding lactam (open symbols) for acid-treated and calcined silicalite-1 octahedrons.

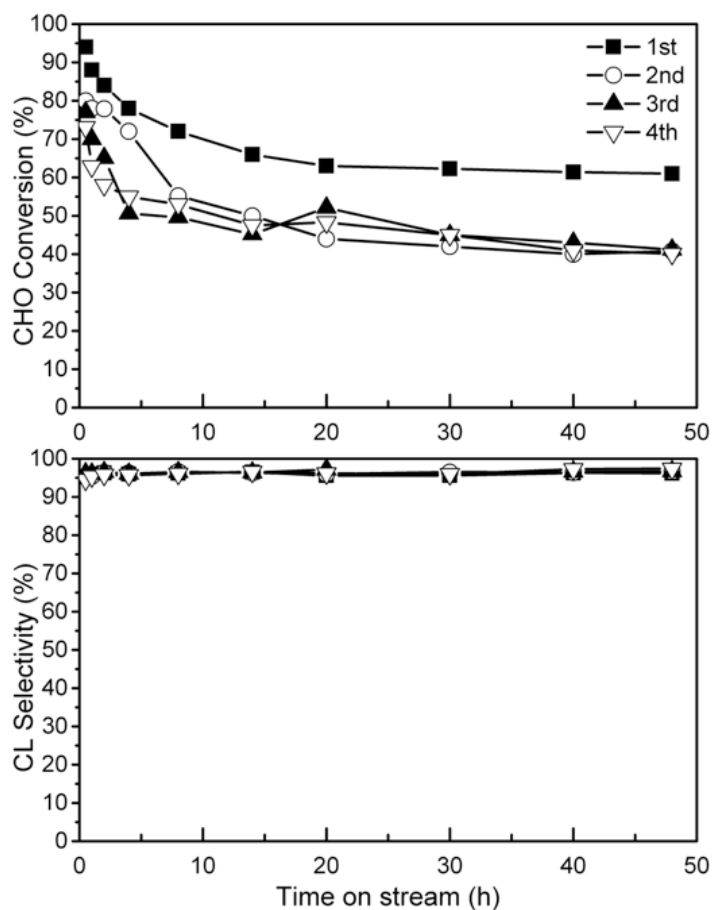


Fig. S12 Changes in CHO conversion (top) and CL selectivity (bottom) with on-stream time for the Beckmann rearrangement over acid-treated (first cycle) and regenerated (second to fourth cycles) silicalite-1 octahedrons.

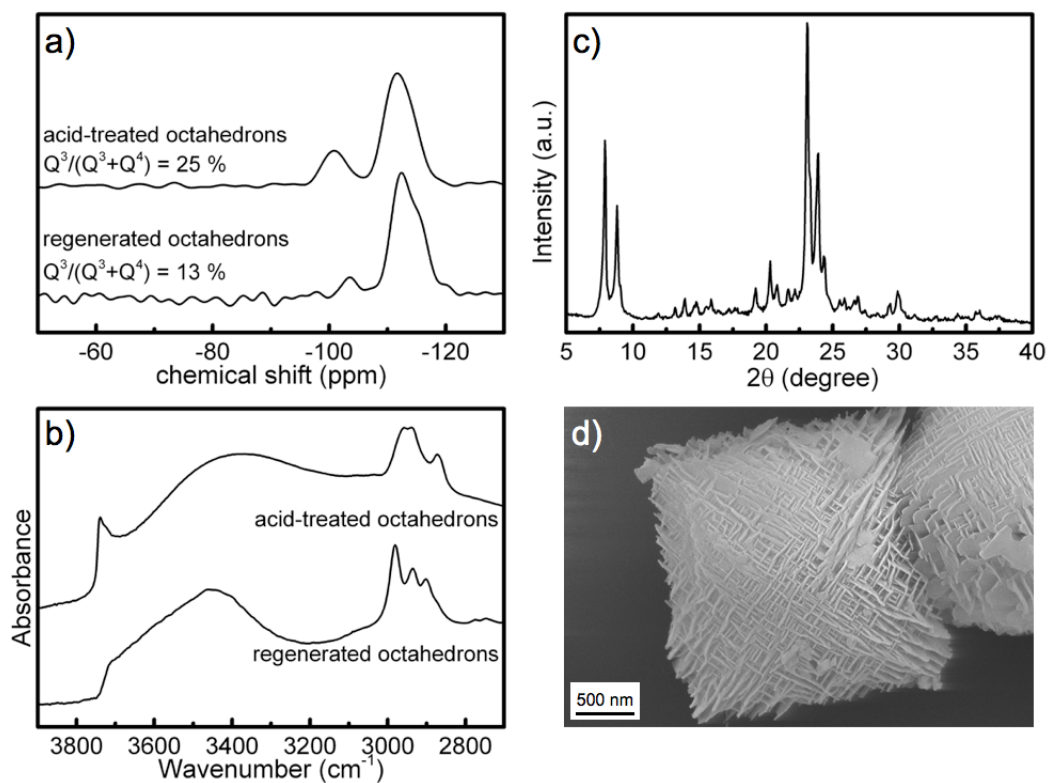


Fig. S13 Comparison of ^{29}Si MAS NMR (a) and FT-IR (b) spectra of the acid-treated and regenerated silicalite-1 octahedrons. PXRD (c) and SEM image (d) of the regenerated silicalite-1 octahedrons.