

**Synthesis of All-silica Hollow Zeolites by Selective Demetallation**

*Teng Li, Frank Krumeich, Jeroen A. van Bokhoven\**

**Supporting Information**

## 1. Experimental Sections and Characterizations

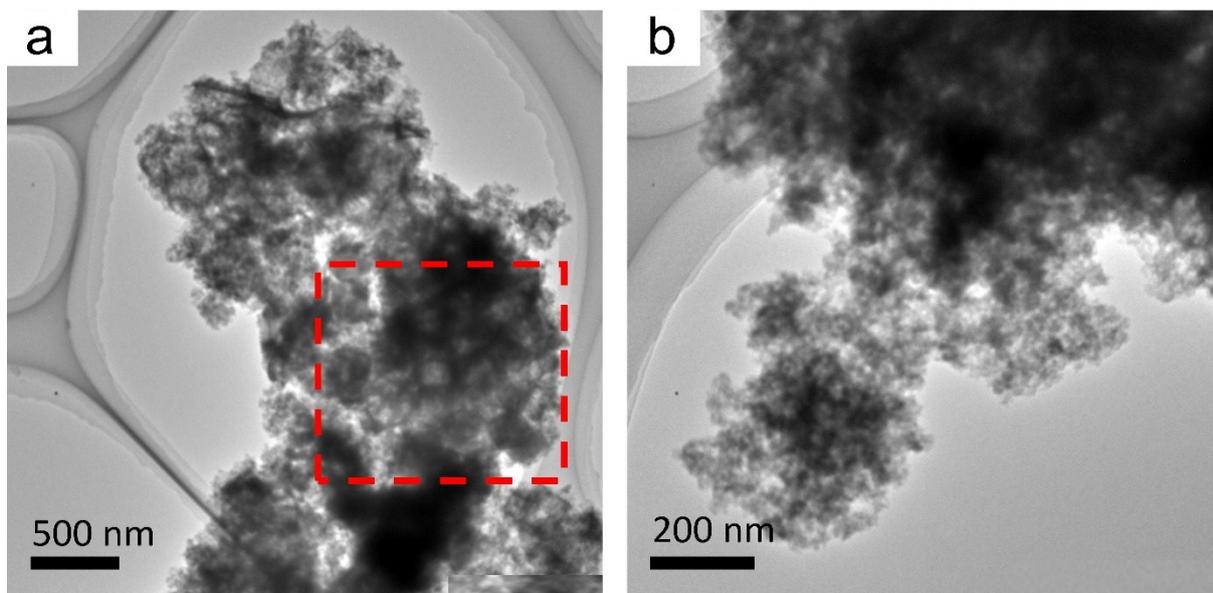
### 1.1 Synthesis and post-synthesis

The defect-rich silicalite-1, i.e. S1, and the defect-poor silicalite-1, i.e. S2, were synthesized according to previous report.<sup>1</sup> Both of them were calcined for 10 h at 550 °C to remove the template completely. Base leaching with sodium aluminate solution (35 mL/g zeolite) was carried out at different concentrations at 60 °C and stirring at 500 rpm for 4 h. The reaction was subsequently quenched in an ice/water bath, and the resulting solid product was separated by centrifugation for 15 min at 15,000 rpm, washed three times and dried overnight at 100 °C. Acid was (35 mL/g zeolite) was carried out at 0.3 M hydrochloric acid solution at 60 °C and stirring at 500 rpm for 4 h. The collecting of samples are the same as above.

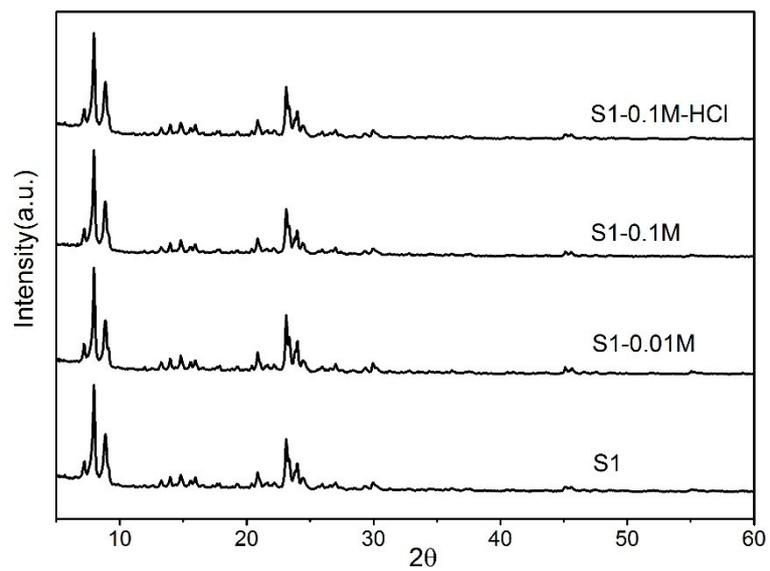
### 1.2 Characterization

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert PRO MPD diffractometer with Cu K $\alpha$  radiation at room temperature. Nitrogen physisorption isotherms were measured with a Micromeritics Tristar instrument at 77 K. Zeolite samples were degassed at 300 °C under vacuum for four hours prior to physisorption measurements. The surface area was derived using the BET model. The external surface area and micropore volume were derived from constructed t-plots. Finally, the total pore volume was determined from a single point measured at  $p/p_0 = 0.96$ . Elemental analysis was measured with a Varian SpectraAA 220FS atomic absorption spectrometer (AAS). Prior to measuring, samples were digested in a 2:3 solution of HF (40%) and HNO<sub>3</sub> (2.5 M) and diluted with distilled water to the required volume. Fourier-transform infrared spectra were collected on a Bio-Rad FTS 3000 instrument. The samples were pressed to self-supporting wafers, placed in the IR cell, and annealed at 400 °C for 2 h in a vacuum. After cooling to 40 °C, spectra were collected by averaging 512 scans. Solid-state <sup>27</sup>Al MAS NMR were performed on a Bruker 400 UltraShield spectrometer operating at a resonance frequency of 104.29 MHz. The rotor was spun at 10 kHz and the spectra were recorded with a 4 mm MAS probe, with 3,000 scans averaged for each spectrum. All spectra were normalized to the sample weight. Chemical shifts were referenced to (NH<sub>4</sub>)Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O for

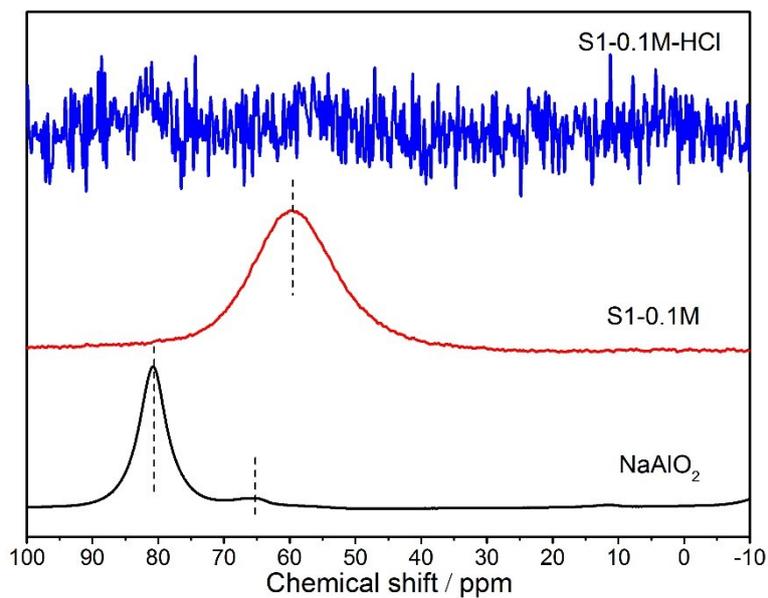
aluminum. Transmission electron microscopy (TEM) images were obtained with FEI Tecnai F30 (FEG) operated at 300 kV. Scanning electron microscopy (SEM) images were obtained with a Zeiss Gemini 1530 instrument operated at 1 kV. High-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) measurements were carried out with a Hitachi HD-2700CS microscope operated at 200 kV.



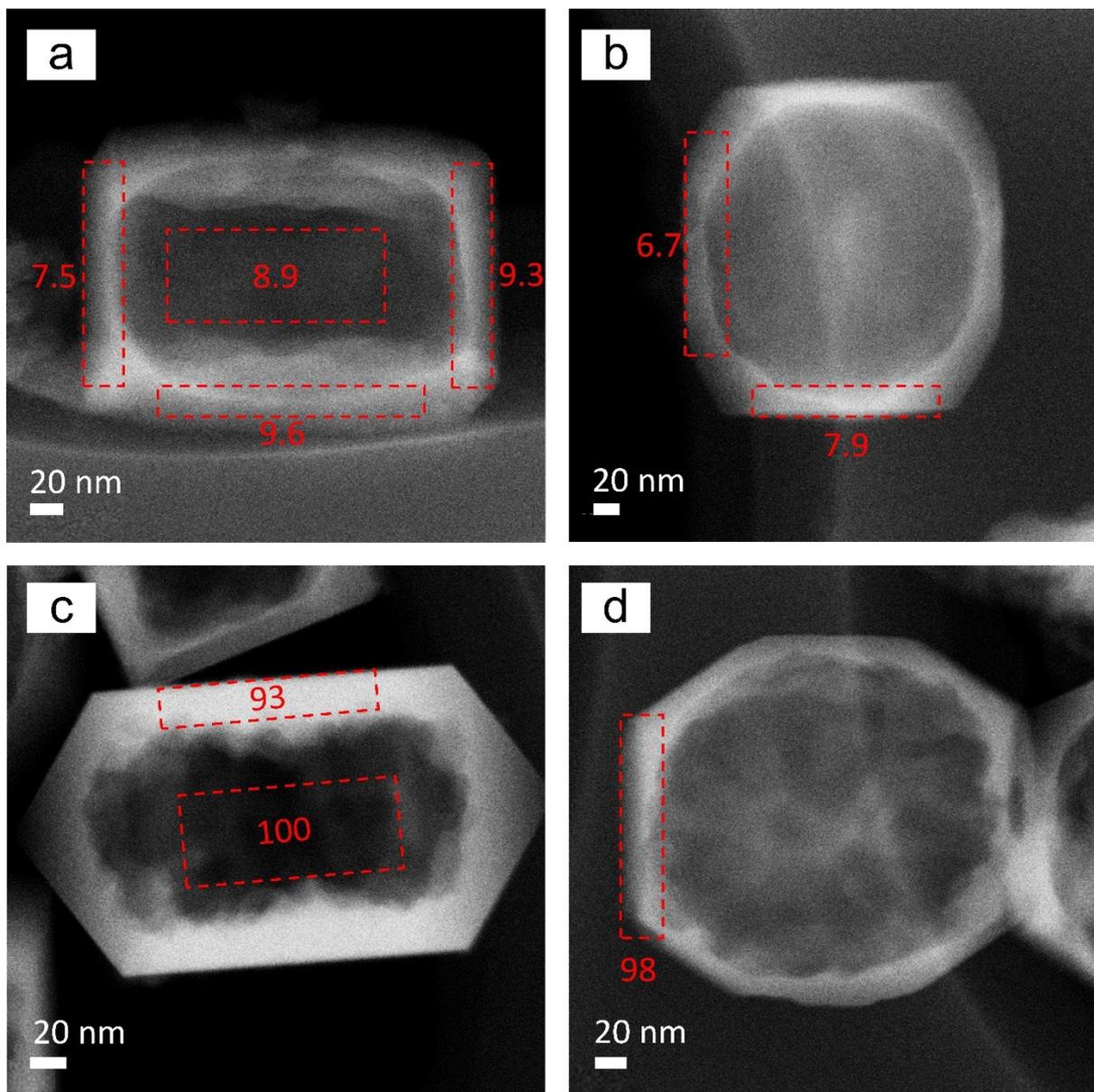
**Fig. S1** TEM images of (a, b) the base leached hollow crystals S1-0.5M. The red rectangle indicates the damaged hollow crystals.



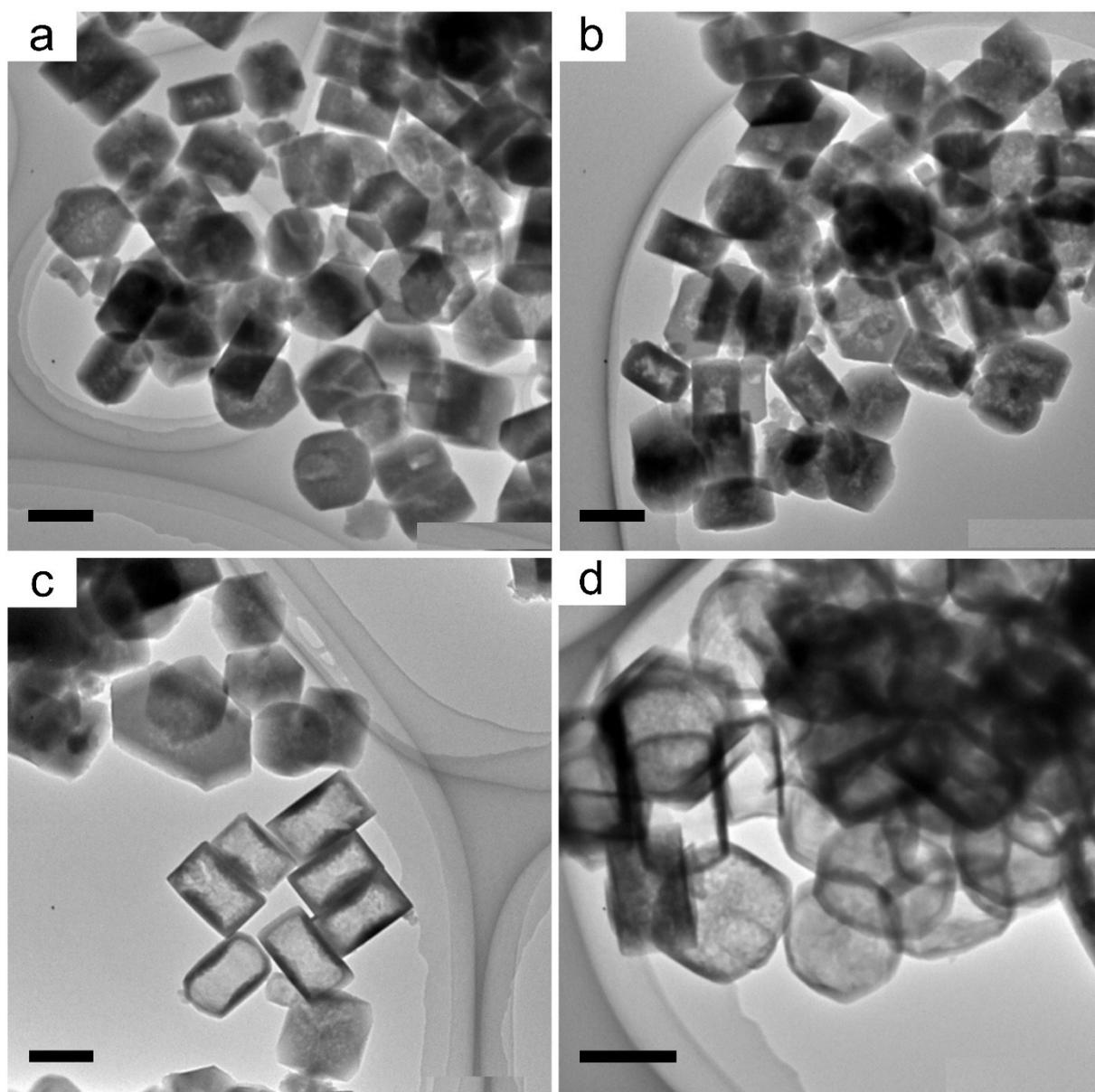
**Fig. S2** XRD patterns of the samples.



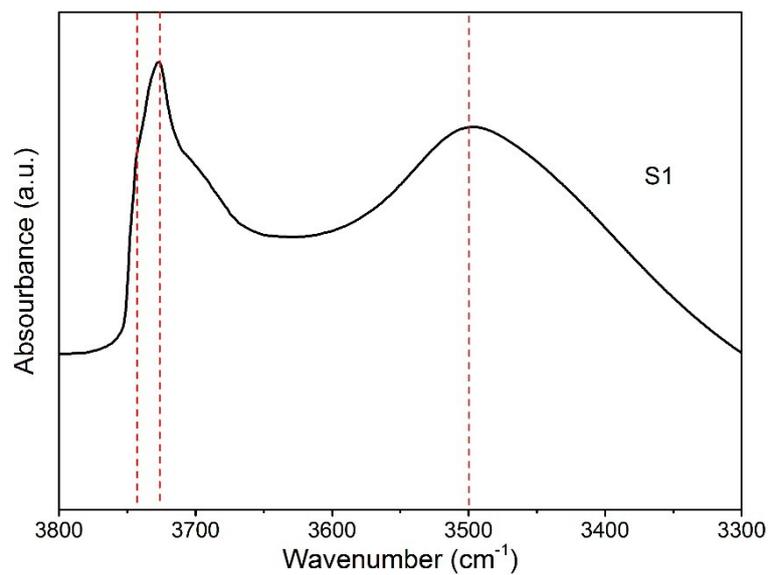
**Fig. S3**  $^{27}\text{Al}$  MAS NMR spectra of the samples. All the samples were strictly measured with the same accumulated number of scans, and the amplitude for the spectrum of S1-0.1M-HCl was magnified deliberately in case any resonance related to aluminum escape detection.



**Fig. S4** Energy-dispersive X-ray spectroscopy (EDX) of (a, b) S1-0.1M and (c, d) S1-0.1M-HCl. Si/Al ratios are indicated close to the analyzed area. The Si/Al ratios in (c, d) is close to background (Si/Al is around 100).



**Fig. S5** TEM images of the leached crystals with different leaching time, (a) 15 minutes, (b) 30 minutes, (c) 1 hour and (d) 2 hours. Scare bars are 200 nm.



**Fig. S6** IR spectrum of S1.

## REFERENCES

- 1 T. Li, F. Krumeich, J. Ihli, Z. Ma, T. Ishikawa, A. B. Pinar and J. A. van Bokhoven, *Chem. Commun.*, 2019, 55, 482-485.