# **Supporting information**

Heavy Atom Labeling Enables Silanol Defect Visualization in Silicalite-1 Crystals

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# **3. REFERENCES**

#### 1. Experimental Sections and Characterizations

#### 1.1 Chemicals

Tetrapropylammonium hydroxide (TPAOH) was purchased from Acros (25 wt% in water), tetraethyl orthosilicate (TEOS) and 3-amino-1-propanol (99.0 wt%) from Aldrich ( $\geq$  99.0 wt%), sodium hydroxide from Merck (ACS reag. Ph Eur), and hydrogen tetrachloroaurate (III) trihydrate from ABCR-Chemicals (99.99%, metal base). Chemicals were used as obtained.

#### **1.2** Synthesis and post-synthesis

The defect-rich silicalite-1, i.e. S1, was synthesized according to the description given in Dai et al.<sup>1</sup> For the defect-poor silicalite-1, i.e. S2, which has monoclinic phase, the synthesis was synthesized according to Fodor without adding aluminum source.<sup>2</sup> Both of them were calcined for 10 h at 550 °C to remove the template completely. Base leaching with NaOH solution (35 mL/g zeolite) was carried out at different concentrations (0.1 M and 0.2 M) at 80 °C and stirring at 500 rpm for 10 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.

#### **1.3 Heavy atom labeling**

Silanol defects in silicalite-1 zeolites were marked using a two-step process consisting of linker grafting and succeeding heavy atom adsorption. Grafting of the organic linker (3-amino-1-propanol) onto present silanol defects was carried out as described in.<sup>3</sup> Briefly, silicalite-1 was pretreated at 250 °C for one day and then mixed with 3-amino-1-propanol. The reaction took place at 110 °C for two days under nitrogen flow with agitation. Then the solid sample was separated and degassed at room temperature. After complete drying, the sample was treated in vacuum at 150 °C for one day. Gold adsorption was achieved by immersing the functionalized

zeolites in a 10<sup>-3</sup> M HAuCl<sub>4</sub> solution for one day. The heavy atom labeled zeolites were retrieved by centrifuge, washed more than five times and dried at room temperature without disturbing.

#### 1.4 Characterization

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert PRO MPD diffractometer with Cu Ka radiation at room temperature. To compare the crystallinity change, we used the single silicon crystal as the internal standard. The mass ratio between zeolite sample and silicon crystal is fixed. The gold loading was measured with a Varian SpectrAA 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. Thermal gravimetric analysis was performed with the thermogravimetric analyzer from TGA/SDTA851e, Mettler-Toledo. The sample was heated to 750 °C in air at 20 °C/min heating rate. 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. As to the functionalized sample, the pre-treatment in the IR cell was operated at room temperature in case of losing organic moiety. Solid-state <sup>29</sup>Si magic angle spinning nuclear magnetic resonance measurements were performed on a Bruker 400 UltraShield spectrometer at a resonance frequency of 79.51 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. For single pulse experiments, a 4.7 µs pulse ( $\theta = 90^{\circ}$ ) was used with a relaxation delay of 10 s. <sup>1</sup>H-<sup>29</sup>Si cross polarization magic angle spinning (CP MAS) NMR spectra were taken with 30° pulses (4.7 µs needed for 90° was divided by 3), 4 ms contact time and 5 s relaxation delay. 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/po = 0.96. 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. The possible occurrence of excessive metal agglomeration during TEM characterization could be excluded since the continual electron exposure of the gold clusters did not induce the particle size increase within a reasonable measuring time. Also, after optimizing beam conditions on one particle, the electron beam was moved to a neighboring particle quickly to check.

#### 1.5 Calculation of organic loading

#### **1.5.1** Total organic loading

The weight percentage of organic moieties ( $-CH_2CH_2CH_2NH_2$ , MW = 58) in the heave atom labeled silicalite-1 zeolites is 4.75 wt % according to TGA. Assuming the weight of zeolite is one gram, then total organic loading can be calculated as follows:

$$0.0475 \times 1 \div 58 = 0.82 \ mmol/g$$

#### **1.5.2** Surface organic loading

Small crystals have a larger external surface areas compared to their large counterparts. Based on the crystal size of S1 crystals (between 200 and 300 nm) obtained from electron microscopy, we adopted a simple model, i.e. a cube with 200 nm dimension, to estimate the surface organic loading. The density of calcined pure-silica MFI was 1.78 g/cm<sup>3</sup>, and we assumed an external

surface silanol density of 4 Si-OH/nm.<sup>4, 5</sup> Also, we assumed the weight of zeolite is one gram. The areas of external surface for a cube:

$$200 \times 200 \times 6 = 240,000 \text{ nm}^2$$

The number of cubes:

$$1 \div 1.78 \times 10^{21} \div 200^3 = 7 \times 10^{13}$$

Assume the external surface are fully grafted, then surface organic loading should be equal to the silanol groups on the external surface, which can be calculated as following (Avogadro constant =  $6.022 \times 10^{23}$ ):

 $2.4 \times 10^5 \times 7 \times 10^{13} \times 4 \div (6.022 \times 10^{23}) = 0.11 \, mmol/g$ 

# 2. Supplementary Fig.s and Table



Fig. S1 TEM image of S1 crystals etched in 0.2 M NaOH.



**Fig. S2** (a) XRD spectra, (b) IR spectra, (c) <sup>29</sup>Si MAS NMR spectra of S1 crystals and leached crystals. The crystallinity change was calculated by using silicon single crystal as the internal standard method. The above characterization results suggest an efficient elimination of silanol groups after base leaching.



**Fig. S3** (a) Thermal gravimetric analysis (TGA), (b) <sup>29</sup>Si MAS NMR spectra, (c) <sup>29</sup>Si CP MAS NMR spectra of S1 and functionalized S1. Functionalized S1 stands for the defect-rich silicalite-1 after reaction with 3-amino-1-propanol. The above characterization results suggest an efficient graft of organic linker on the accessible silanol defects.



Fig. S4 <sup>13</sup>C CP MAS NMR of functionalized S1.



Fig. S5 XRD spectra of functionalized S1 and defect-labeled S1.



**Fig. S6** (a) Secondary electron STEM, (b-e) HAADF-STEM images of defect-labeled S1 with a lower concentration of HAuCl<sub>4</sub> solution (10<sup>-4</sup> M) and (f) EDX result of red area of a crystal in (e). The existence of gold was proved by EDX and element analysis (AAS, 0.09 wt %). However, no gold atoms can be observed from STEM.



**Fig. S7** TEM and SEM images of (a, d) S2 (b, e) the crystals leached in 0.1 M NaOH (c, f) the crystals leached in 0.2 M NaOH.



**Fig. S8** (a) XRD pattern of the S2 in 22.0~26.0° 2 $\theta$  range, (b) IR spectra and (c) <sup>29</sup>Si MAS NMR spectra of S2 and leached crystals, (d) Deconvolution of <sup>29</sup>Si MAS NMR spectrum of S2. In (a), the two peaks within the red dashed line indicates a monoclinic phase.<sup>6</sup>

	$\mathbf{S}_{\text{BET}}^{\mathbf{b}}$	S <sub>ext</sub> <sup>c</sup>	$V_{tot}{}^d$	$V_{micr}^{c}$
Sample	$[m^2 g^{-1}]$	$[m^2 g^{-1}]$	$[cm^3 g^{-1}]$	$[cm^3 g^{-1}]$
S1	420	131	0.27	0.13
Functionalized S1	169	25	0.10	0.07

Table S1 Parameters obtained from N<sub>2</sub> physisorption isotherms

<sup>a</sup> Determined by AAS. <sup>b</sup> Derived from the BET model. <sup>c</sup> Derived from the t-plot method.

<sup>d</sup> Derived from single point at  $p/p_0 = 0.96$ .

Peak (ppm)	Area (%)	Ratio <sub>expriment</sub>	Ratio <sub>theory</sub>	T-site
109.4	4.66	1.12	1	21
111.4	9.17	2.20	2	5,10
112.2	10.94	2.62	3	9,22,13
112.8	18.24	4.37	4.5	19,7,18,4,3
113.5	30.87	7.40	7.5	3,2,20,24,17,1,12,15
114.0	8.76	2.10	2	23,11
114.5	4.45	1.07	1	6
115.4	8.14	2.10	2	14,16
116.4	4.17	1.00	1	8

 Table S2
 The attribution of T-sites for S2 based on <sup>29</sup>Si MAS NMR

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