Supporting Information

Spectroscopic signature of Lewis acidic framework and extra-framework Sn sites in Beta zeolites

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1. Sample preparation

Sn-containing Beta zeolites were prepared through a two-step post-synthesis procedure, which consisted of the dealumination of parent H-Beta and then introduction of Sn species into the dealuminated [Si]Beta. Briefly, commercial Beta zeolite with nominal nSi/nAl ratio of 13.5 (Sinopec Co.) was stirred in a 13 $molL^{-1}$ nitric acid aqueous solution (20 $mLg_{zeolite}^{-1}$) at 373 K overnight to obtain a dealuminated Beta ([Si]Beta). The powder was filtered, washed thoroughly with deionized water, and dried at 353 K overnight. Before the incorporation of Sn, the sample was pre-treated at 473 K overnight under vacuum to remove physisorbed water. Afterwards, 1.0 g of the solid powder was finely ground with appropriate amount of $(CH_3)_2SnCl_2$ in the glovebox to achieve an intimate mixture with the Sn weight contents of 5% and 10%, respectively. The solid mixture was put into a tubular reactor, then sealed and heated to 823 K for 6 h (heating rate at 5 K/min) under vacuum. After that, it was calcined under flowing air at 823 K for 6 h to derive the final product, denoted as X%Sn-Beta-I where X indicates the weight contents of Sn metal.

2. Sample Characterization

X-ray diffraction (XRD) patterns of the samples under study were performed on a Rigaku SmartLab powder diffractometer utilizing Cu-Kα radiation (λ = 1.5418 Å) with a scanning rate of 4°/min in the range of 2θ = 5-50°.

The surface areas and pore volumes of the dehydrated samples were analyzed according to nitrogen adsorption on a Quantachrome iQ-MP gas adsorption analyzer at 77 K. Before the nitrogen adsorption, samples were dehydrated at 573 K for 6 h. The total surface area was calculated via the Brunauer Emmett Teller (BET) equation, while the micropore size distribution was determined utilizing the t-plot method.

Samples for electron microscopy analysis were prepared by drying a drop of sample-containing alcohol suspension on carbon-coated copper grids. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and high angle annular dark filed (HAADF) images were acquired on a FEI Talos electron microscope.

Mapping of the elemental distribution of zeolite crystals was conducted under HAADF-STEM (scanning transmission electron microscopy) mode using a FEI built-in energy dispersive spectrum (EDS) software.

The exact Sn weight contents of the Sn-containing zeolites were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Series X7, Thermo Electron Corporation).

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of samples were measured on a Bruker Tensor 27 spectrometer with 128 scans at a resolution of 2 cm^{-1}. A self-supporting pellet made of sample material was placed in the reaction chamber and pretreated in flowing dry air at 673 K for 1 h. The spectra were recorded in dry air against KBr as background.

Diffuse reflectance ultraviolet-visible (UV-vis) spectra of the dehydrated Sn-containing Beta samples were measured in the range of 200~600 nm with a PerkinElmer Lambda 750 UV-VIS-NIR spectrophotometer. The nature of Sn species in the Sn-containing Beta zeolites during the hydration and dehydration process was *in situ* monitored by UV-vis spectroscopy. UV-vis spectra were recorded via an AvaSpec-2048 Fiber Optic spectrometer using an AvaLight-DH-S deuterium light source by Avantes and a glass fiber reflection probe HPSUV1000A by Oxford Electronics. Before the hydration, the glass fiber reflection probe was placed in the fixed-bed reactor on the top of the catalyst with a gap of ca. 1.0 mm. Reference UV-vis spectra of dehydrated $BaSO_4$ were recorded firstly, and then the Sn-containing zeolites were filled and dehydrated at 673K for 1h. After cooling to the room temperature, the initial UV-vis spectra of the dehydrated sample was recorded, thereafter, water was pumped in at 0.2 mL/h, and the in situ UV-vis spectra was recorded simultaneously. After 15 min, water was stopped, and the hydrated samples was heated up to 473K with a heating ratio of 10 K/min for dehydration. *In situ* UV-vis spectra were recorded in the diffuse reflection mode and over a spectral range of 200~500 nm.

X-ray photoelectron spectra (XPS) of the fresh and spent catalysts were recorded on a Thermo Scientific ESCALAB 250Xi spectrometer using a monochromatic Al-Kα X-ray source (hν = 1486.6 eV) as the excitation source. High-resolution spectra were recorded by using an aperture slot of 300×700 microns. The binding energies (±0.1 eV) were determined with respect to the position of the C 1s peak at 284.8 eV.

The solid-state NMR measurements were performed on a Bruker Avance III spectrometer at resonance frequencies of 400.1, 100.6, 161.9, and 149.5 MHz for ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn nuclei, respectively. The ^{1}H, ^{13}C and ^{119}Sn MAS NMR spectra were recorded with a sample spinning rate of 8 kHz, while the ^{31}P MAS NMR spectra were obtained with 10 kHz. ^{1}H, ^{31}P, and ^{119}Sn MAS NMR spectra were obtained upon single-pulse excitation with pulse durations of 2.6

(π/2), 4.0 (π/2) and 2.0 (π/4) μs, repetition times of 20, 30 and 20 s and the number of scans of 80, 360 and 25000, respectively. ^{13}C CPMAS NMR spectra were recorded applying cross polarization (CP), contact pulse of 4 ms, repetition time of 4 s and number of scans of 3000. All of the ^{1}H, ^{13}C and ^{31}P MAS NMR studies were performed using dehydrated samples, which were treated at 723 K in vacuum (below 10^{-2} Pa) for 12 h. Thereafter, the probe molecules, i.e., acetone-2-^{13}C, TMPO and NH_3, were loaded for further measurements. For the adsorption of acetone-2-^{13}C (99.5 % ^{13}C-enriched, Sigma-Aldrich) on the dehydrated materials, the sample tubes were connected with a vacuum line and the probe molecules were adsorbed at 40 mbar within 10 minutes. Subsequently, the acetone-2-^{13}C-loaded samples were evacuated ($p < 10^{-2}$ mbar) at 295 K for 10 minutes to remove weakly physisorbed acetone-2-^{13}C. Loading of the dehydrated catalysts with TMPO (Alfa Aesar) was performed inside a glove box, purged with dry nitrogen gas, by mixing ca. 50 mg of the dehydrated samples with ca. 2.5 mg TMPO inside a rotor, which was subsequently sealed with an O-ring-containing Marcor-Cap. In a further step, the TMPO-loaded samples inside the sealed rotors were heated at 533 K for 2 h for reaching a homogeneous distribution of the probe molecules on the sample material. The ammonia loading of the dehydrated samples was done on a vacuum line by adsorption of 100 mbar ammonia (Griesinger) at 298 K for 10 minutes, followed by an evacuation ($p < 10^{-2}$ mbar) at 453 K for 2 h for removing weakly physisorbed ammonia. Quantitative ^{1}H MAS NMR measurements were performed by using zeolite 35H,65Na-Y (decationization degree of 35%) as an external intensity standard. ^{1}H MAS NMR difference spectra of the unloaded and ammonia-loaded samples under study were utilized for the signal separation and the determination of the relative signal intensities. For the calculation of the number of NH_3 coordinated at Lewis acid sites, the integral intensities of the corresponding ^{1}H MAS NMR signals were divided by 3. ^{119}Sn MAS-NMR spectra of Sn-containing Beta zeolites were recorded on both hydrated and dehydrated samples. The dehydrated samples used for the ^{119}Sn MAS NMR studies were dehydrated at 723 K in vacuum (below 10^{-2} Pa) for 12 h.

3. Results

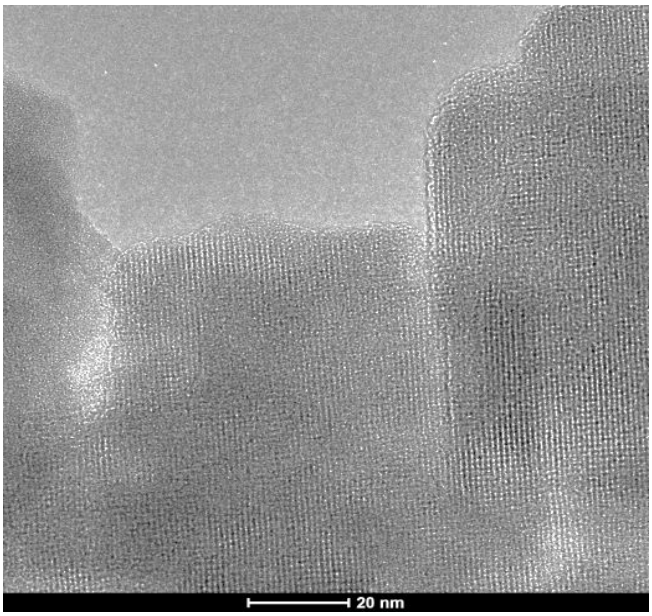

Figure S1. HRTEM image of 5%Sn-Beta-I

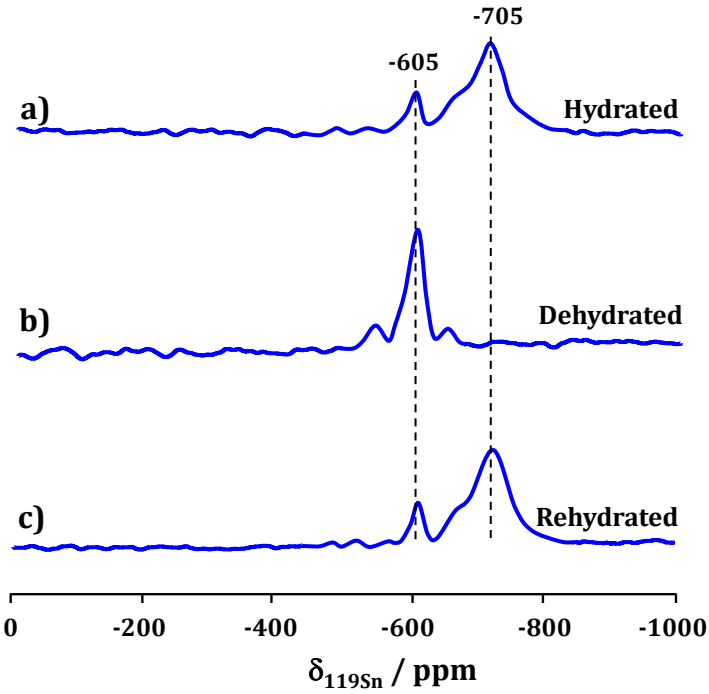

Figure S2. ^{119}Sn MAS NMR spectra of 5% Sn-Beta-II samples after different treatments, (a) hydrated, (b) dehydrated under vacuum, (c) rehydrated after step (b).

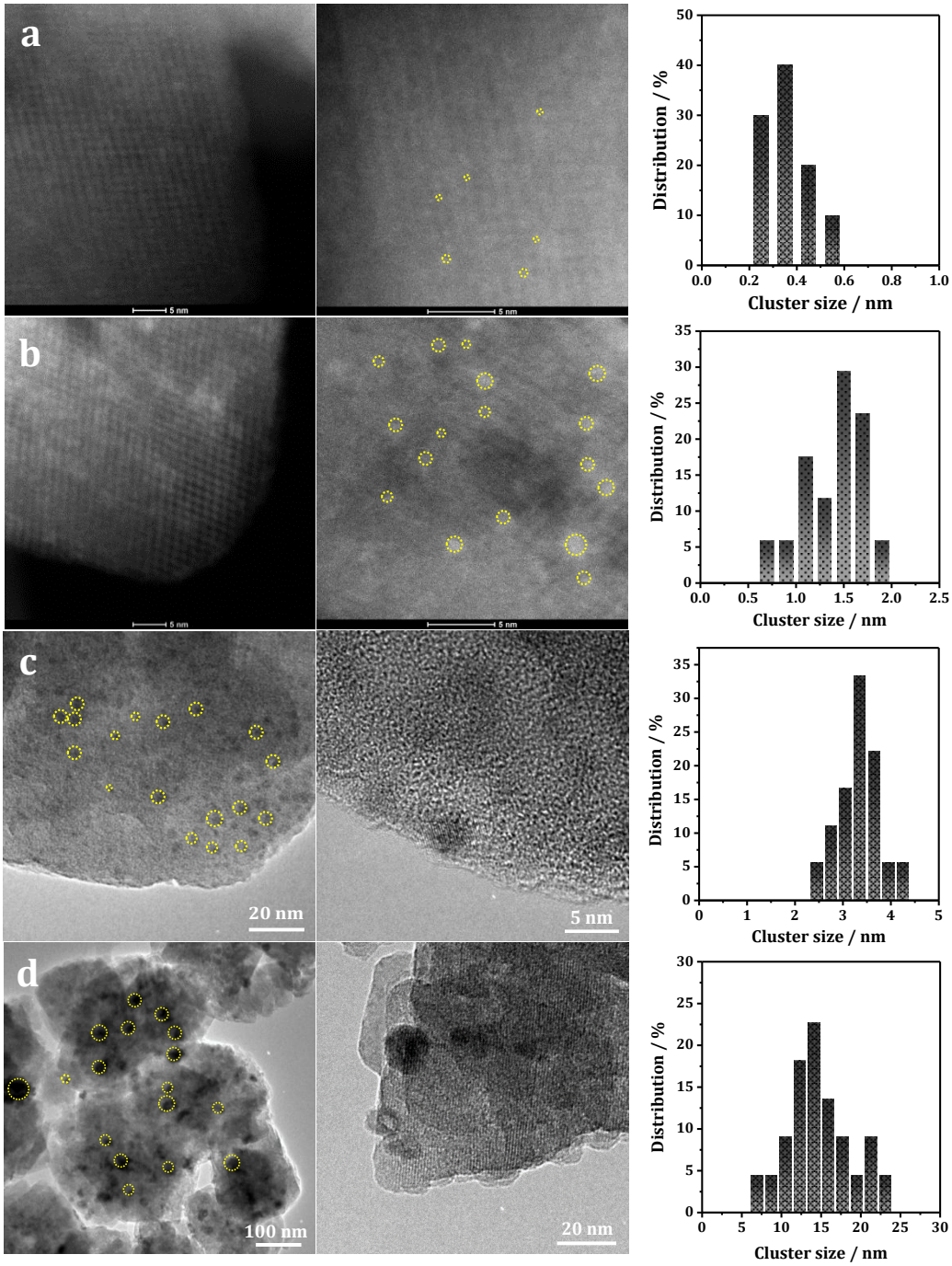

Figure S3. High-resolution HAADF-STEM images of 5%Sn-Beta-I (a) and 5%Sn-Beta-II (b) and TEM images of 5%Sn-Beta-III (c) and 5%SnO_2/[Si]Beta (d) samples, and the corresponding size distribution of SnO_2 clusters.

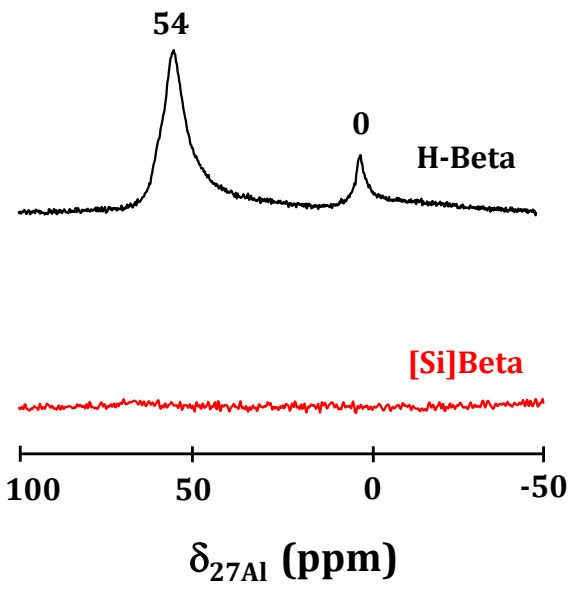

Figure S4. ^{27}Al MAS NMR spectra of H-Beta and [Si]Beta.

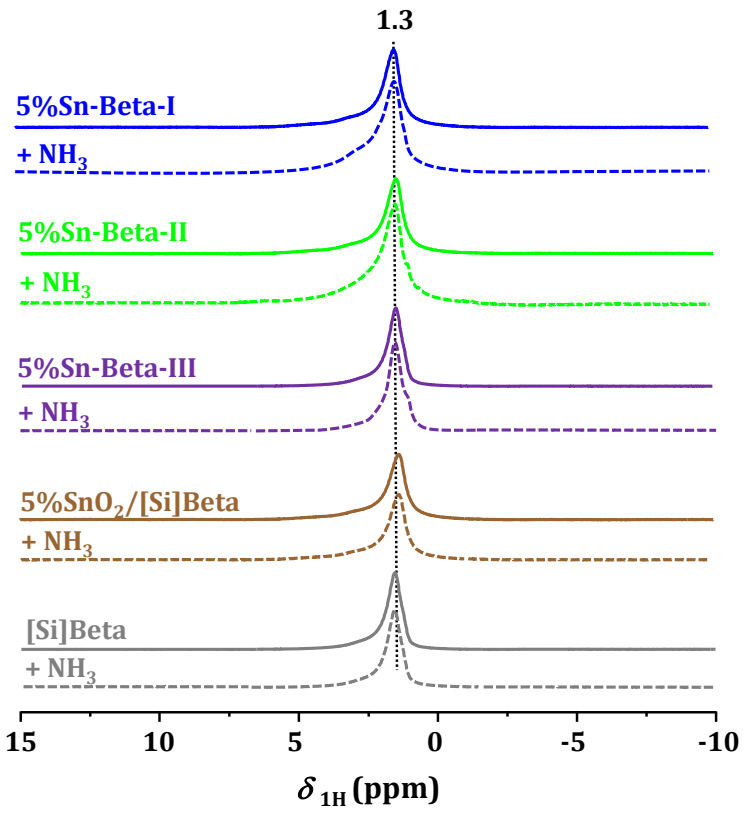

Figure S5. ^{1}H MAS NMR spectra of dehydrated 5%Sn-Beta-I, 5%Sn-Beta-II, 5%Sn-Beta-II, 5%SnO_2/[Si]Beta and [Si]Beta recorded before and after adsorption of ammonia.

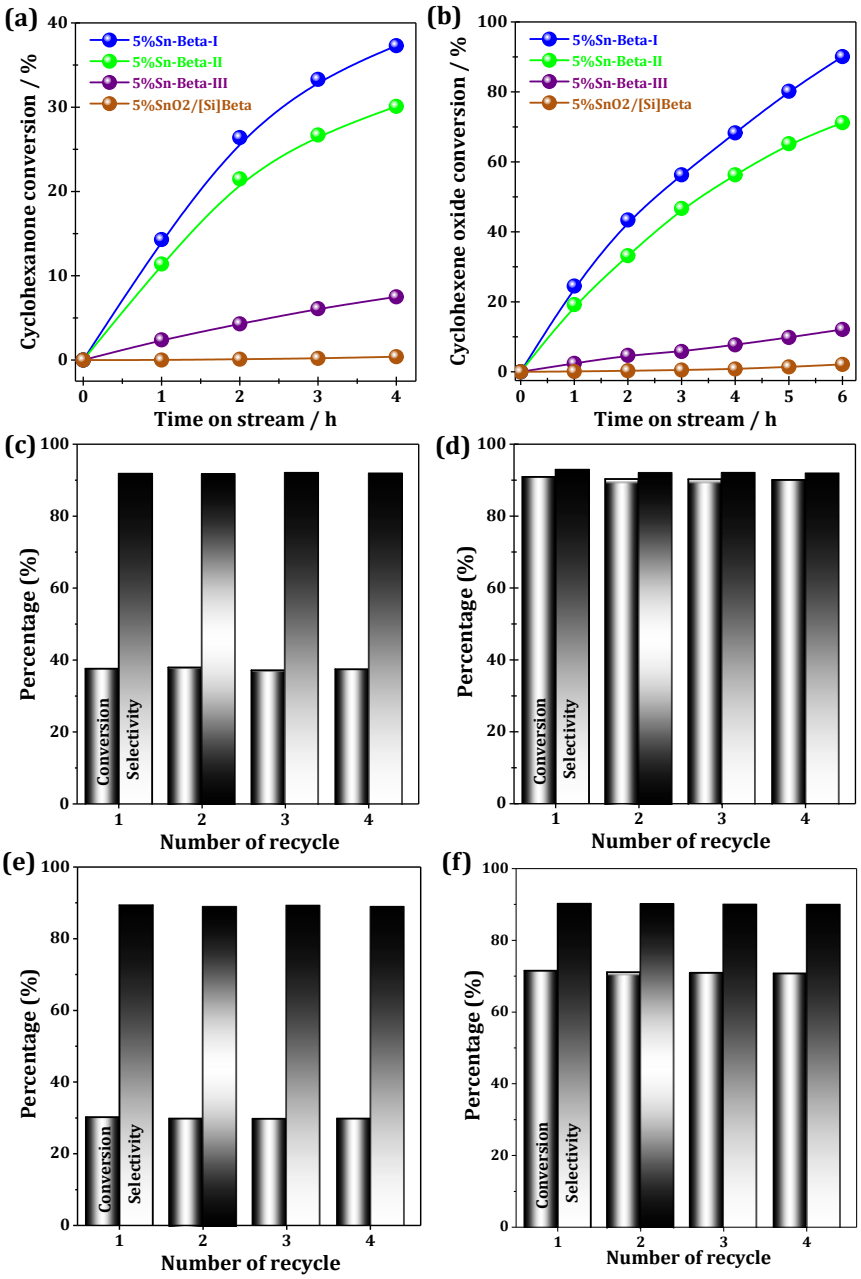

Figure S6. Kinetic plots of Baeyer–Villiger oxidation of cyclohexanone (a) and cyclohexene oxide hydration (b) catalyzed by different zeolite catalysts. Baeyer–Villiger oxidation reaction conditions: 0.33 mol/L cyclohexanone in 1,4-dioxane, H_2O_2/ketone=1.0, 5 mL 1,4-dioxane, 20 mg catalyst, temperature = 363K; Cyclohexene oxide hydration reaction conditions: 10 mmol cyclohexene oxide, 20 mmol H_2O, 0.1 g catalyst, temperature = 313 K. Recycling test for Baeyer–Villiger oxidation of cyclohexanone catalyzed by 5%Sn-Beta-I (c-d) and 5%Sn-Beta-II (e-f)(conditions, as described above, TOS=4 h and 6h, respectively).