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# **Electronic Supplementary Information (ESI)**

for

## Structural reconstruction: a milestone in hydrothermal synthesis of

# highly active Sn-Beta zeolite

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### **Experimental section**

#### **Material preparation**

*Preparation of siliceous Beta sample*. The siliceous Beta sample, denoted as Beta-DA, was prepared by acid-assisted dealuminaton of commercially available H-Beta aluminosilicate (Si/Al = ca. 11, Shanghai Xinnian Petrochemical Additives Co., Ltd). First, the parent H-Beta was calcined in air at 873 K for 6 h, and then it was refluxed in HNO<sub>3</sub> solution (65 wt %) at a solid-to-liquid ratio of 1 g : 50 mL for 8 h, resulting a siliceous zeolite with a Si/Al ratio over 1900. The acid-treated product was washed repeatedly with deionized water until the pH value of the filtrate reached around 7. Finally, the dried product, denoted as Beta-DA, was employed as the silica source for synthesizing following Sn-Beta zeolite.

*Synthesis of Sn-Beta via structural reconstruction*. As illustrated in Scheme 1, Sn-Beta zeolite was hydrothermally synthesized via structural reconstruction by employing the Beta-DA sample as a silica source. In a typical synthesis, Beta-DA powder and SnCl<sub>4</sub>@5H<sub>2</sub>O were added into tetraethylammonium hydroxide (TEAOH) (25 wt %) aqueous solution under stirring at 343 K for approximate 30 min, resulting in a gel composition of 1.0 SiO<sub>2</sub>: *x* SnCl<sub>4</sub> : 0.5 TEAOH :7.5 H<sub>2</sub>O, where *x* represents the Sn/Si ratio in the synthetic gel. Subsequently, the gel was transferred into a Teflon-lined autoclave and pre-heated at 413 K for 45 min statically. After quenching down to ambient temperature with water, the mixture was denoted as Sn-Beta-Re-*x*P and then ammonium fluoride (NH<sub>4</sub>F) was blended with the mixture. The final molar composition of the mixture was SiO<sub>2</sub> : *x* SnO<sub>2</sub> : 0.5 TEAOH : 7.5 H<sub>2</sub>O : 0.5 NH<sub>4</sub>F. The mixture was further

treated at 413 K for a certain time under static conditions. The as-made product was then recovered by filtration, dried at 353 K overnight, and calcined at the temperature of 873 K for 6 h. Finally, the calcined Sn-Beta zeolite is denoted as Sn-Beta-Re-*n*, where *n* indicates the Si/Sn ratio in the synthetic gel. Additionally, Sn-free siliceous Beta, designated as Beta-Re, was hydrothermally synthesized via structural reconstruction without adding Sn source in the synthetic gel. Subsequently, Sn-impregnated SnO<sub>2</sub>/Beta-Re sample with a Sn content of 6 wt % was also prepared following the procedure reported in the literature.<sup>1</sup>

Synthesis of Sn-Beta by conventional fluoride method. For the control experiment, Sn-Beta-F-y, where y represents the Si/Sn in the synthetic gel, was also prepared in our laboratory according to well-established procedures reported in the literature.<sup>2</sup> Note that Sn-Beta-F was synthesized utilizing ammonium fluoride as the fluorine source. Typically, SnCl<sub>4</sub>**@** 5H<sub>2</sub>O was added into TEAOH (25 wt %) and tetraethoxysilane (TEOS) aqueous solution under stirring at 343 K for approximate 30 min, resulting in a gel composition of 1.0 SiO<sub>2</sub>: *m* SnCl<sub>4</sub> : 0.5 TEAOH :7.5 H<sub>2</sub>O, where *m* indicates the Sn/Si ratio in the synthetic gel. The gel was denoted as Sn-Beta-F-*m*P and then NH<sub>4</sub>F was mixed with the gel. The final molar composition of the mixture was SiO<sub>2</sub> : *m* SnCl<sub>4</sub> : 0.5 TEAOH : 7.5 H<sub>2</sub>O : 0.5 NH<sub>4</sub>F. The mixture was treated at 413 K for a certain time under static conditions. After crystallization, the as-synthesized catalyst was washed three times with deionized water, dried at 353 K for 10 h, and then calcined at the temperature of 823 K for 6 h.

Synthesis of Sn-Beta by post-synthesis approaches. Additionally, Sn-Beta zeolites were

also post-synthesized by solid-gas isomorphous substitution with  $SnCl_4$  vapor<sup>3</sup> or solidstate ion-exchange with  $SnCl_4 \mathbf{0} 5H_2O^4$  following well-established procedures. The samples prepared by  $SnCl_4$  vapor and ion-exchange were denoted as Sn-Beta-GPS-*c* and Sn-Beta-SSIE-*d*, respectively, where *c* and *d* indicate the Si/Sn ratio in the products. Experimental details of the synthesis procedures have been described elsewhere.<sup>3,4</sup>

## Characterizations

The X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV X-ray diffractometer with Cu-Ka radiation ( $\lambda$ =1.5405 Å) at 35 kV and 25 mA. UV-Raman spectra were collected with an excitation line at 244 nm and with a spectral resolution of 2 cm<sup>-1</sup> on UV Raman spectrograph utilizing a Jobin-Yvon T6400 triple-stage spectrograph. Transmission electron microscopy (TEM) images were taken on an FEI G2F30 and those of scanning electron microscopy (SEM) were collected on a Hitachi S-4800 microscopy. The N<sub>2</sub> adsorption isotherms were measured on a BELSORP-MAX instrument equipped with a precise sensor for low-pressure measurement at 77 K after activating the samples at 573 K at least for 5 h under vacuum conditions. The Si, Al, and Sn contents were determined using inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. UV-visible (UV-vis) diffuse reflectance spectra were carried out on a Shimadzu UV-2700 spectrophotometer utilizing barium sulfate as the reference after the zeolite materials were dehydrated at 673 K. FT-IR spectra of pyridine and acetonitrile-d3 adsorption were carried out on a Nicolet Nexus 670 FT-IR spectrometer with a spectral resolution of 2 cm<sup>-1</sup> in absorbance mode. After the zeolite material was compressed into a self-supported wafer, the wafer was then set in a quartz cell and sealed with CaF2 windows. The cell was connected to a vacuum system. After the sample was dehydrated at 723 K for 2 h to remove any water in the material, FT-IR spectra in the hydroxyl stretching vibration region were measured at room temperature. Subsequently, the pyridine and acetonitrile-d3 adsorptions were realized by exposing the wafer to the corresponding vapors at room temperature for 1 h. The FT-IR spectra of adsorbed pyridine were collected for 1 h as the desorption temperature was increased from 323 to 523 K. The adsorbed acetonitrile-d3 was desorbed successively from 303 to 423 K for 3 min and the spectra were recorded simultaneously. X-ray photoelectron spectroscopic (XPS) analyses were performed on a Kratos Axis Ultra spectrometer (Kratos Analytical, UK) equipped with a monochromatized aluminum X-ray source. The <sup>29</sup>Si solid-state MAS NMR spectra were performed on a VARIAN VNMRS-400WB spectrometer using [(CH<sub>3</sub>)<sub>3</sub>SiO]<sub>8</sub>SiO<sub>12</sub> as the chemical shift reference at a frequency of 79.43 MHz, a spinning rate of 3 kHz, a recycling delay of 60 s. The thermogravimetric (TG) analysis was measured on a METTLER TOLEDO TGA/SDTA851<sup>e</sup> apparatus from 298 to 1073 K with a temperature gradient of 10 K min  $^{-1}$  in  $N_2$  atmosphere.

## **Catalytic reactions**

The catalytic performance was evaluated in a 25mL flask linked to a water condenser under appropriate stirring. In the conversion of 2-adamantanone, 2-adamantanone (2 mmol), hydrogen peroxide (4 mmol, 30 wt %) or tert-butyl hydroperoxide (TBHP) (4 mmol, 5.5 M in decane), chlorobenzene (10 mL), benzonitrile (0.5 g, as a GC internal standard), and catalyst (50 mg) were stirred in the flask at 363 K for a certain time. For the isomerization-esterification reaction of DHA, DHA (2 mmol), ethanol (4 g), and decane (0.5 g, as a GC internal standard) were first dissolved in the vessel at 318 K for 45 min. Then the catalyst was added into the solution at room temperature and the reaction mixture was heated at 363 K for 10 min. In the Meerwein-Ponndorf-Verley reaction of cyclohexanone with isopropanol, the flask was charged with cyclohexanone (1 mmol), isopropanol (60 mmol), chlorobenzene (0.5 g, as a GC internal standard), and catalyst (75 mg) at 358 K for 2 h. For all reactions, the catalyst was removed from the reaction system by centrifugation, and the reaction mixture was analyzed using a gas chromatograph (Shimadzu GC-14B, FID detector) equipped with a 30 m DB-1 capillary column to obtain the conversion and selectivity. The products were identified using a GC-MS (Agilent-6890GC/5973MS).

# **Results and discussion**

Sample	Time <sup><i>a</i></sup>	Yield <sup><math>b</math></sup> (%) -	Si/Sn ratio		V <sub>micro</sub> <sup>d</sup>	$SSA^e(m^2 g^{-1})$	
			Gel	Product <sup>c</sup>	$(cm^3 g^{-1})$	$\mathbf{S}_{\text{BET}}$	$S^{d}_{ext}$
Sn-Beta-Re-30	1 h	95.2	30	33	0.19	641	225
Sn-Beta-Re-60	1 h	94.1	60	62	0.19	650	218
Sn-Beta-Re-90	1 h	94.6	90	93	0.19	660	213
Sn-Beta-Re-150	1 h	95.9	150	152	0.20	669	209
Sn-Beta-F-150	14 d	92.8	150	155	0.20	552	118

Table S1 Textural properties of various Sn-containing Beta samples.

<sup>*a*</sup> The time required for full crystallization of Sn-Beta zeolite.

<sup>b</sup> Yield = amount of calcined product/amount of initial added Beta-DA.

<sup>*c*</sup> Determined by ICP analysis.

<sup>*d*</sup> Calculated with *t*-plot method.

<sup>e</sup> Specific surface area (SSA), determined by N<sub>2</sub> adsorption at 77 K.

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No.	Catalyst	Si/Sn <sup>b</sup>	Conv. <sup><i>c</i></sup> (%)	Lactone sel. (%)	$TOF^d$ (h <sup>-1</sup> )	$\frac{\text{STY}^e}{(h^{-1})}$					
1	blank	-	0	-	0	0					
2	Beta-Re	$\infty$	0	-	0	0					
3	SnO <sub>2</sub> /Beta-Re	30	0.3	91.1	0.4	0.04					
4	Sn-Beta-Re-150	152	26.9	99.5	195	3.6					
5	Sn-Beta-Re-60	62	49.7	99.3	147	6.7					
6	Sn-Beta-Re-30	33	61.6	99.6	98	8.3					
7	Sn-Beta-F-150	153	16.6	99.1	123	2.2					
8	Sn-Beta-GPS-36	36	48.6	99.5	84	6.4					
9	Sn-Beta-SSIE-30	30	47.3	99.3	73	6.2					

**Table S2** Catalytic activity of various catalysts for Baeyer-Villiger oxidation of 2-adamantanone with hydrogen peroxide. $^{a}$ 

<sup>a</sup> Reaction conditions: cat, 50 mg; 2-adamantanone, 2 mmol; H<sub>2</sub>O<sub>2</sub> (30 wt %), 4 mmol;
chlorobenzene, 10 mL; temp., 363 K; time, 0.5 h.

<sup>*b*</sup> Molar ratio determined by ICP.

<sup>*c*</sup> Conv. = moles of 2-adamantanone converted/initial moles of 2-adamantanone  $\times$  100%.

<sup>*d*</sup> Turnover frequency (TOF), moles of lactone produced hourly per mole of Sn active sites in catalysts.

<sup>e</sup> Space-time-yield (STY), grams of lactone produced hourly per gram of catalysts.



Fig. S1 <sup>29</sup>Si MAS NMR spectra of highly dealuminated sample of Beta-DA (a) and Sn-Beta-Re-30 samples crystallized for 0 min (b), 20 min (c), 40 min (d), 60 min (e), and 1 d (f). Other crystallization conditions:  $SnO_2/SiO_2 = 0.033$ ; TEAOH/SiO\_2 = 0.5;  $NH_4F/SiO_2 = 0.5$ ;  $H_2O/SiO_2 = 7.5$ ; temp., 413 K.

The band at around -101.8 ppm, assigned to  $(SiO)_3Si(OH)$  groups  $(Q^3)$ ,<sup>3</sup> was obviously observed for pristine Beta-DA, resulting from an extensive removal of Al ions from the framework of Beta aluminosilicate. Once Beta-DA was subjected to structural reconstruction-assisted hydrothermal synthesis of Sn-Beta-Re in the presence of alkaline SDA of TEAOH at elevated temperature (413 K), the band intensities of the  $(SiO)_4Si$ groups  $(Q^4)$  (from -105 to -120 ppm)<sup>3</sup> sharply decreased at initial stage in comparison to that of the parent Beta-DA, implying that the long-range order of crystalline structure lost completely. Subsequently, the Q<sup>4</sup> groups became more and more obvious with prolonging the crystallization time, whereas the Q<sup>3</sup> groups were nearly not noticed in final products. This was indicative of a rapid recovery of the \*BEA structure with a high hydrophobicity even within 1 h (Fig. S1e).



**Fig. S2** Scanning electron micrographs of Beta-DA (a) and Sn-Beta-Re-30 samples crystallized for 0 min (b), 20 min d (c), 40 min (d), 60 min (e), and 1 d (f). Other crystallization conditions: see Fig. S1.

After pre-treatment of the Beta-DA sample in the presence of TEAOH at 413 K, the original nanocrystals of 60-80 nm in size became amorphous phase completely (Fig. S2b), indicating a great structural degradation. When the subsequent crystallization time was prolonged to 20 min, many nanoparticles appeared with the co-existence of amorphous gels in the whole region. At 40 min, the amorphous platelet phase disappeared completely and the nanosized crystals became dominant at the expanse of amorphous phase. After the crystallization for 60 min at 413 K, irregular nanoparticles with a size of 30-50 nm formed (Fig. S2e) and the crystal morphology didn't change when the hydrothermal treatment time was further extended to 1 d, suggesting the Sn-Beta-Re-30 sample was crystallized fully within 1 h at 413 K.



Fig. S3 Time-dependent crystallinity curve of Sn-Beta-Re-30 sample. The product crystallinity was quantified from the XRD patterns in Fig. 1. Other crystallization conditions: see Fig. S1.

The crystallization took place following a S-type curve, which is typical in the zeolite hydrothermal synthesis.<sup>5</sup> Additionally, The induction period for the zeolite crystallization was quite short (ca. 10 min) and the crystallization time (1 h) decreased by a factor of 336 in comparison to conventional fluride method (presented in Table S1, 14 d).



Fig. S4 Transmission electron microscope images of Sn-Beta-Re-30 sample.

The TEM images showed that Sn-Beta-Re-30 were composed of the nanosized crystals of 30–50 nm, in agreement with the SEM results (Fig. S2). The TEM images clearly revealed the presence of lattice fringes (Fig. S4b), again proving the Sn-Beta-Re-30 zeolite was highly crystalline.



Fig. S5 XRD patterns of Sn-Beta-Re zeolites at Si/Sn of 150 (a), 90 (b), 60 (c), 30 (d), and 20 (e). Other crystallization conditions: TEAOH/SiO<sub>2</sub> = 0.5; NH<sub>4</sub>F/SiO<sub>2</sub> = 0.5;  $H_2O/SiO_2 = 7.5$ ; temp., 413 K; time, 1 h.

Highly crystalline Sn-Beta-Re zeolites were hydrothermally synthesized successfully at Si/Sn molar ratios of 30–200, whereas the Sn-Beta-Re zeolites couldn't be crystallized or fully crystallized when the Sn contents in the synthetic gels were high as Si/Sn  $\leq$  20, probably due to the retarding effects of large Sn ions on the crystallization.<sup>6</sup> However, Sn-Beta-Re was readily crystallized at Si/Sn of 30, which corresponded to an extremely high Sn content if comparing the limitation of Si/Sn ratio of 100 achieved by conventional synthesis (Sn-Beta-F)<sup>2</sup> or Si/Sn ratio of 63 obtained by interzeolite transformation.<sup>6</sup>



Fig. S6 UV Raman spectra of calcined Sn-Beta-Re-30P (a) and Sn-Beta-F-30P (b).

The Raman spectrum of calcined Sn-Beta-Re-30P sample prepared via structural reconstruction obviously exhibited the primary structural units of Beta zeolite (Fig. S6a), including five-membered rings (321 and 348 cm<sup>-1</sup>), six-membered rings (405 cm<sup>-1</sup>), and four-membered rings (469 cm<sup>-1</sup>),<sup>6</sup> which would intensively facilitate nucleation and growth for Sn-Beta-Re zeolite. However, the primary structural units of Beta zeolite were not observed in Raman spectrum for Sn-Beta-F-30P prepared by conventional fluoride approach (Fig. S6b). This unique character for Sn-Beta-Re-30P sample leads to the well crystallization even at extremely high Sn contents in the synthetic gels (Si/Sn = 30).



**Fig. S7** Scanning electron micrograph images of conventional Sn-Beta-F-150 (a), Sn-Beta-GPS-36 (b), and Sn-Beta-SSIE-30 (c) zeolites.

Sn-Beta-F-150 zeolite synthesized via conventional approach possessed the crystal size of more than 1 µm and the particle sizes of post-synthesized Sn-Beta-GPS-36 and Sn-Beta-SSIE-30 ranged from 60 to 80 nm.



Fig. S8 Thermogravimetric curves for Sn-Beta-Re-30 (a), Sn-Beta-F-150 (b), Sn-Beta-GPS-36 (c), and Sn-Beta-SSIE-30 (d) after saturated with water vapor over aqueous  $NH_4Cl$  solution overnight in a desiccator.

Thermogravimetric analysis was performed to assess the hydrophilicity/hydrophobicity of these materials. Before 673 K, the weight loss, resulting from physical adsorbed water,<sup>6</sup> of Sn-Beta-Re-30, Sn-Beta-F-150, Sn-Beta-GPS-36, and Sn-Beta-SSIE-30 was 3.3 wt %, 3.9 wt %, 11.3 wt %, and 11.4 wt %, respectively. When the temperature was ranged from 673–1073 K, Sn-Beta-GPS-36 and Sn-Beta-SSIE-30 showed much more weight loss than Sn-Beta-Re-30 and Sn-Beta-F-150, identifying that more hydroxyl condensation appeared in Sn-Beta-GPS-36 and Sn-Beta-SSIE-30. These results indicated that these materials possessed the hydrophobicity in the sequence of Sn-Beta-Re-30 > Sn-Beta-F-150 > Sn-Beta-GPS-36 ≈ Sn-Beta-SSIE-30.



**Fig. S9** (A) XPS and (B) UV–vis spectra of dehydrated Sn-Beta-Re samples synthesized at Si/Sn ratio of 30 (a), 90 (b), and 150 (b).

As shown in Fig. S9A, the signal peaks at 486.0 and 494.4 eV, derived from the  $3d_{5/2}$ and  $3d_{3/2}$  photoelectrons of octahedral Sn species,<sup>6</sup> were not observed in the XPS spectra. This result indicates the presence of extra-framework octahedrally coordinated Sn species in the zeolites could be ruled out. Two signal bands at around 487.7 and 496.2 eV, which are ascribed to  $3d_{5/2}$  and  $3d_{3/2}$  photoelectrons of tetrahedrally coordinated framework Sn species,<sup>7</sup> were obviously observed for all samples, indicating that the Sn species in Sn-Beta-Re samples were tetrahedrally coordinated in the framework. Fig. S9B shows the UV-visible diffuse reflectance spectra of Sn-Beta-Re samples with different Sn contents. An intense band at around 208 nm was clearly observed in all three spectra, suggesting that most of the Sn ions existed in the terms of tetrahedrally coordinated state.<sup>6</sup> What's more, as the Sn content in the Sn-Beta-Re samples increased, the intensity of the band at around 208 nm also increased. The results of UV-visible were quite consistent with that from the XPS spectra.



**Fig. S10** <sup>119</sup>Sn MAS NMR spectra of SnO<sub>2</sub> (a), hydrated Sn-Beta-Re-30 (b), dehydrated Sn-Beta-Re-30 (c). Spinning side bands are indicated by asterisks.

As shown in the following Fig. S10, only a sharp resonance at -605 ppm was observed for the bulk  $SnO_2$ , which is attributed to octahedrally coordinated tin species.<sup>7</sup> Since the same resonance was not observed in the spectrum of Sn-Beta-Re-30, the presence of octahedrally coordinated Sn ions in this zeolite could be ruled out. The hydrated sample showed a broad signal centered at -745 ppm, which was reported to be characteristic of the Sn<sup>4+</sup> species with adsorbed water. After dehydration, a broad peak at around -450 ppm, assigned to the tetrahedral Sn<sup>4+</sup> in the Beta framework,<sup>3</sup> was clearly observed.



Fig. S11 SEM image (a) and corresponding Si (b), O (c), and Sn (d) elemental maps of Sn-Beta-Re-30.

*Si, O, and Sn elements were distributed uniformly within the crystals of Sn-Beta-Re-30 zeolite and no phenomenon of oxide particles aggregation appeared.* 



**Fig. S12** (A) FT-IR spectra of Sn-Beta-Re-30 after pyridine adsorption at 298 K for 1 h and desorption at 323 K (a), 373 K (b), 423 K (c), and 523 K (d) for 1 h, respectively. (B) FT-IR spectra of Sn-Beta-Re with Si/Sn ratio of 30 (a), 60 (b), 90 (c), and 150 (d) after pyridine adsorption at 298 K for 1 h and desorption at 523 K for 1 h.

The Lewis acidity of the Sn-Beta-Re zeolites was characterized by the pyridine adsorption FT-IR spectra as illustrated in Fig. S12. In the case of Sn-Beta-Re-30, the bands at 1445 and 1596 cm<sup>-1</sup>, attributed to hydrogen-bonded pyridine molecules,<sup>3,6</sup> vanished completely after evacuation at 523 K, indicative of weakly interacted pyridine molecules. On the other hand, the bands around 1451, 1490, and 1611 cm<sup>-1</sup>, associated with Lewis acid sites,<sup>6</sup> became obvious after the desorption at 423 K. Noted that the band at around 1540 cm<sup>-1</sup> was absent in the spectra of Sn-Beta-Re-30 zeolite, indication of free of Brönsted acid sites. Therefore, the Sn-Beta-Re samples were characterized by Lewis acidity, supporting the fact that the Sn ions were tetrahedrally incorporated into the Beta zeolite framework. What's more, the Lewis acidity increased gradually with the increase of Sn contents in the Sn-Beta-Re zeolites in the Si/Sn ratio range of 30–150.



**Fig. S13** (A) FT-IR spectra of Sn-Beta-Re-30 after CD<sub>3</sub>CN adsorption at 298 K for 1 h and desorption at 303 K (a), 313 K (b), 323 K (c), 373 K (d), and 423 K (e) for 3 min, respectively. (B) FT-IR spectra of Sn-Beta-Re with Si/Sn ratio of 30 (a), 60 (b), 90 (c), and 150 (d) after CD<sub>3</sub>CN adsorption at 298 K for 1 h and desorption at 313 K for 3 min.

FT-IR study of acetonitrile-d3 adsorption is a widely available method for detecting the presence of framework  $Sn^{4+}$  ions in Sn-containing zeolites.<sup>8</sup> As shown in Fig. S13, the appearance of bands at 2316 and 2308 cm<sup>-1</sup>, which are related to open and closed Sn sites in the Sn-substituted framework,<sup>6,8</sup> indicated that the Sn-Beta-Re zeolite possessed partially hydrolyzed Sn sites and framework-integrated Sn sites, Moreover, the gradual increase in the contents of both open and closed Sn sites was observed with the Sn contents increasing, and the ratio of open to closed Sn contents remained ca. 0.4, in line with Sn-Beta zeolite synthesized by conventional approach.<sup>9</sup>



**Fig. S14** Dependence of initial reaction rate for lactone production on the Sn content in Sn-Beta-Re (a), Sn-Beta-SSIE (b), Sn-Beta-GPS (c), and Sn-Beta-F (d) for the Baeyer-Villiger oxidation of 2-adamantanone. Reaction conditions: cat, 50 mg; 2-adamantanone, 2 mmol;  $H_2O_2$  (30 wt %), 4 mmol; chlorobenzene, 10 mL; temp., 363 K.

As shown in Fig. S14, with the Sn loading increasing, the initial reaction rate for lactone production increased linearly, further evidencing that isolated framework Sn species are responsible for the catalytic performances. Post-synthesized Sn-Beta-GPS and Sn-Beta-SSIE with poor hydrophobicity and nanosized particles (60–80 nm) demonstrated slightly higher initial reaction rate than hydrothermally synthesized Sn-Beta-F with excellent hydrophobicity and large crystal size (more than 1  $\mu$ m) probably because the diffusion issue may dominate this reaction, in line with the literature reported previously.<sup>3</sup> It is important to point out that the range of initial reaction rate for Sn-Beta-F was narrow owning to limited Sn contents. The initial reaction rate for Sn-Beta-Re was beyond that for Sn-Beta-F, Sn-Beta-GPS, and Sn-Beta-SSIE, resulting from its outstanging hydrophobicity and nanosized crystals (30–50 nm).



Fig. S15 XRD patterns of fresh catalyst (a), fourth run (b), b after calcination (c) for Sncontaining Beta catalysts.

Obviously, the zeolitic structure, attributed to \*BEA topology, remained intact after fourth run in the Baeyer-Villiger oxidation of 2-adamantanone with aqueous  $H_2O_2$ .



**Fig. S16** UV–vis spectra of dehydrated Sn-Beta-Re-30 (A), Sn-Beta-F-150 (B), Sn-Beta-GPS-36 (C) samples. Used catalysts indicate the calcinated Sn-containing samples after fourth run in the Baeyer-Villiger oxidation of 2-adamantanone.

A sharp absorbance band at about 208 nm, assigned to four-fold coordination Sn species,<sup>6,7</sup> was clearly observed for all fresh Sn-Beta zeolites. After fourth run, Sn-Beta-Re-30 and Sn-Beta-F-150 showed nearly unaltered Sn coordination state. Conversely, a clear increase of extra-framework Sn species (250–300 nm) was observed for post-synthesized Sn-Beta-GPS-36 and Sn-Beta-SSIE-30 (Fig. S16C and D).



**(B)** 



**Fig. S17** (A) Reaction pathways for isomerization–esterification reaction of dihydroxyacetone to ethyl lactate and diethyl acetal of pyruvic aldehyde. (B) Catalytic performances of isomerization–esterification reaction of dihydroxyacetone in ethanol over various Sn-Beta zeolites. Space-time-yield (STY), grams of desired products produced hourly per gram of catalysts. Reaction conditions: cat, 50 mg; DHA, 2 mmol; ethanol, 4 mL; temp., 363 K; time, 10 min.

(A)



**Fig. S18** (A) Reaction pathway for the Meerwein–Ponndorf–Verley (MPV) reaction in isopropanol with cyclohexanone. (B) Catalytic performances of the MPV reaction over various Sn-Beta zeolites. Space-time-yield (STY), grams of desired products produced hourly per gram of catalysts. Reaction conditions: cat, 75 mg; cyclohexanone, 1 mmol; isopropanol, 60 mmol; temp., 358 K; time, 2 h.

As can be seen from Fig. S17 and S18, Sn-Beta-Re catalysts, especially Sn-Beta-Re-30 with unpredictably high framework Sn contents, possessed significant higher catalytic

performances in terms of yield and space-time-yield in comparison to conventional Sn-Beta-F-150, further proving that the Sn-Beta-Re zeolites hydrothermally synthesized via structural reconstruction are productive and reliable Lewis catalysts.

# References

- 1 N. K. Mal, V. Ramaswamy, S. Ganapathy and A. V. Ramaswamy, *Appl. Catal. A: Gen.*, 1995, **125**, 233.
- 2 A. Corma, L. T. Nemeth, M. Renz and S. Valencia, Nature, 2001, 412, 423.
- 3 P. Li, G. Liu, H. Wu, Y. Liu, J. Jiang and P. Wu, J. Phys. Chem. C, 2011, 115, 3663.
- 4 C. Hammond, S. Conrad and I. Hermans, Angew. Chem. Int. Ed., 2012, 51, 11736.
- 5 F.-S. Xiao, L. Wang, C. Yin, K. Lin, Y. Di, J. Li, R. Xu, D. S. Su, R. Schlögl, T. Yokoi and T. Tatsumi, *Angew. Chem. Int. Ed.*, 2006, **45**, 3090.
- 6 Z. Zhu, H. Xu, J. Jiang, Y. Guan and P. Wu, J. Catal., 2017, 352, 1.
- 7 B. Tang, W. Dai, G. Wu, N. Guan, L. Li and M. Hunger, ACS Catal., 2014, 4, 2801.
- 8 C. Hammond, D. Padovan, A. Al-Nayili, P. P. Wells, E. K. Gibson and N. Dimitratos, *ChemCatChem.*, 2015, 7, 3322.
- 9 J. W. Harris, M. J. Cordon, J. R. Di Iorio, J. C. Vega-Vila, F. H. Ribeiro, R. Gounder, J. *Catal.*, 2016, **335**,141.