

## Supporting Information

### **Self-Pillared, Single-Unit-Cell Sn-MFI Zeolite Nanosheets and Their Use for Glucose and Lactose Isomerization**

*Limin Ren, Qiang Guo, Prashant Kumar, Marat Orazov, Dandan Xu, Saeed M. Alhassan, K. Andre Mkhoyan, Mark E. Davis, and Michael Tsapatsis\**

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### *Experimental Section*

#### Materials

The catalysts used in this study are summarized in Table S1.

Table S1. List and synthesis mixture composition of Sn-containing materials prepared. The Si/Sn ratio as determined by ICP-OES is shown in the parentheses.

Material	Synthesis mixture composition
Sn-SPP(186)	1.0SiO <sub>2</sub> :0.3TBPOH:10H <sub>2</sub> O:4.0EtOH:0.01SnO <sub>2</sub>
Sn-SPP(75)	1.0SiO <sub>2</sub> :0.3TBPOH:10H <sub>2</sub> O:4.0EtOH:0.02SnO <sub>2</sub>
<sup>119</sup> Sn-SPP(223)	1.0SiO <sub>2</sub> :0.3TBPOH:10H <sub>2</sub> O:4.0EtOH:0.01SnO <sub>2</sub>
Sn-BEA(125)	1.0SiO <sub>2</sub> :0.54TEAOH:10.6H <sub>2</sub> O:0.54HF:0.008SnO <sub>2</sub>
Sn-MCM-41(80)	1.0SiO <sub>2</sub> :0.16CTAB:0.35TPAOH:25H <sub>2</sub> O:0.01SnO <sub>2</sub>

Three self-pillared pentasil (SPP) Sn-containing catalysts were used in this study. Two of them have similar Si/Sn ratio of approximately 200, with one (Sn-SPP(186)) prepared with regular tin(IV) chloride and the other (Sn-SPP(223)) prepared with <sup>119</sup>tin enriched tin(II) chloride. The third material (Sn-SPP(75)) has a Si/Sn ratio of 75.

**Sn-SPP(186)** and **<sup>119</sup>Sn-SPP(223)** were synthesized as follows: 0.129 g of tin(IV) chloride pentahydrate (98 %, Sigma-Aldrich) or 0.0684 g of <sup>119</sup>Sn enriched tin(II) chloride (Cambridge Isotopes, 82 % enrichment) was dissolved into 7.35 g of tetra(n-butyl)phosphonium hydroxide

(TBPOH 40 wt%, TCI America) followed by the addition of 7.5 g tetraethyl orthosilicate (TEOS, 98 %, Sigma-Aldrich). After hydrolysis, 3.2 g of deionized water was added to the mixture. The mixture was stirred overnight, and a clear sol was obtained. The composition of the final tin silicate sol is:  $1.0\text{SiO}_2:0.03\text{TBPOH}:4.0\text{EtOH}:30\text{H}_2\text{O}:0.01\text{SnO}_2$ . The sol was sealed in a Teflon-lined stainless steel autoclave and heated for 5 days in a pre-heated static oven operating at 388 K.

**Sn-SPP(75)** was synthesized from a starting tin silicate sol with a molar ratio of  $1.0\text{SiO}_2:0.03\text{TBPOH}:4.0\text{EtOH}:30\text{H}_2\text{O}:0.02\text{SnO}_2$  prepared via the same procedure as that of the Sn-SPP(186) except that 0.258 g of tin(IV) chloride pentahydrate (98 %, Sigma-Aldrich) was added. The sol was sealed in a Teflon-lined stainless steel autoclave and heated for 21 days in a pre-heated static oven operating at 388 K.

All the solid products were centrifuged, washed with distilled water and then dried at 343 K overnight. All the samples were calcined at 823 K for 6 h in air under static conditions. The calcined samples were washed with water, dried at 343 K overnight and calcined at 823 K for 6 h in air under static conditions and this process was repeated to ensure removal of  $\text{P}_2\text{O}_5$ .

**Sn-MCM-41** was synthesized by modifying the method described in the literature:<sup>24</sup> First, 1.46 g of hexadecyltrimethylammoniumbromide (CTAB, >99 %, Amresco) was dissolved in 5.43 g of water by heating in an oil bath at 323 K for 10 min. Then, 3.95 g of tetrapropylammonium hydroxide solution (TPAOH, 40 wt%, SACHEM) was added to the clear solution. After stirring for 1 h, 0.088 g of tin(IV) chloride pentahydrate (98 %, Sigma-Aldrich) and 5.01 g of colloidal silica solution (30 wt%, Sigma-Aldrich, LUDOX® HS-30) were added with stirring. A gel with chemical composition  $1.0\text{SiO}_2:0.16\text{CTAB}:0.35\text{TPAOH}:25\text{H}_2\text{O}:0.01\text{SnO}_2$  was obtained. The gel was sealed in Teflon-lined stainless steel autoclaves and heated at 388 K for 48 h. The product was separated and fully washed by filtration followed by drying at 343 K overnight, then calcined at 823 K for 6 h in air under static conditions. It is noted as **Sn-MCM-41(80)** with 80 indicating the Si/Sn ratio determined by ICP.

**Sn-BEA** zeolite was prepared according to the literature procedure:<sup>24-26</sup> First, 30.612 g of TEOS (98 %, Sigma-Aldrich) was mixed with 33 g of TPAOH solution (35 wt%, SACHEM) and stirred for 1 h. A clear solution of 0.412 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (98 %, Sigma-Aldrich) in 2.75 g of water was added

into the above mixture and stirred overnight to fully evaporate the ethanol. Then 3.143 g of hydrofluoric acid (HF 48-51 wt% in H<sub>2</sub>O, Sigma-Aldrich) was added under stirring followed by adding a seed suspension of dealuminated zeolite Beta (0.36 g dealuminated zeolite Beta seeds in 1.75 g H<sub>2</sub>O). After manually mixing for 5 min, the final gel with a chemical composition 1.0SiO<sub>2</sub>:0.54TEAOH:10.6H<sub>2</sub>O:0.54HF:0.008SnO<sub>2</sub> was transferred to autoclaves and hydrothermally treated in a rotation oven at 413 K for 21 days. The product was separated and fully washed by filtration followed by drying at 343 K overnight. After calcination at 873 K in static air for 6 h, the final product was obtained and noted as **Sn-BEA(125)**, with 125 indicating the Si/Sn ratio determined by ICP.

**ICP:** Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) methodology was used for elemental analysis. Samples were analyzed on a Thermo Scientific iCAP 6500 duo optical emission spectrometer (serial no. 20083410) fitted with a simultaneous charge induction detector. For each sample, standard and blank, the data were replicated 3 times to determine a mean and standard deviation for each selected elemental wavelength.

**XRD:** X-ray diffraction patterns were recorded on a Bruker D8 Advance with a Cu source and theta-theta diffractometer equipped with a Lynx-eye position sensitive detector.

**Argon adsorption:** Argon adsorption was performed using a commercially available automatic manometric sorption analyzer at 87 K (Quantachrome Instruments AutosorbIQ MP).

**NMR:** A Bruker DSX-500 spectrometer and 4 mm Bruker MAS probe were employed to record <sup>119</sup>Sn (186.4 MHz) NMR spectrum. Around 55 mg sample was packed into a 4 mm zirconia rotor, and underwent vacuum dehydration at 573 K for 4 h. <sup>119</sup>Sn chemical shift was referenced to externally standards of tetramethyltin. A spin echo sequence under MAS condition was used to collect <sup>119</sup>Sn signal using rf pulses of 3 microseconds for 90 and 6 microseconds for 180 degree. The recycle delay time for <sup>119</sup>Sn MAS NMR was 10.0 seconds.

**FTIR:** Deuterated acetonitrile dosing and desorption experiments were performed using a Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer with a Hg-Cd-Te (MCT) detector. Self-supporting wafers (10-20 mg/cm<sup>2</sup>) were pressed and sealed in a heatable quartz

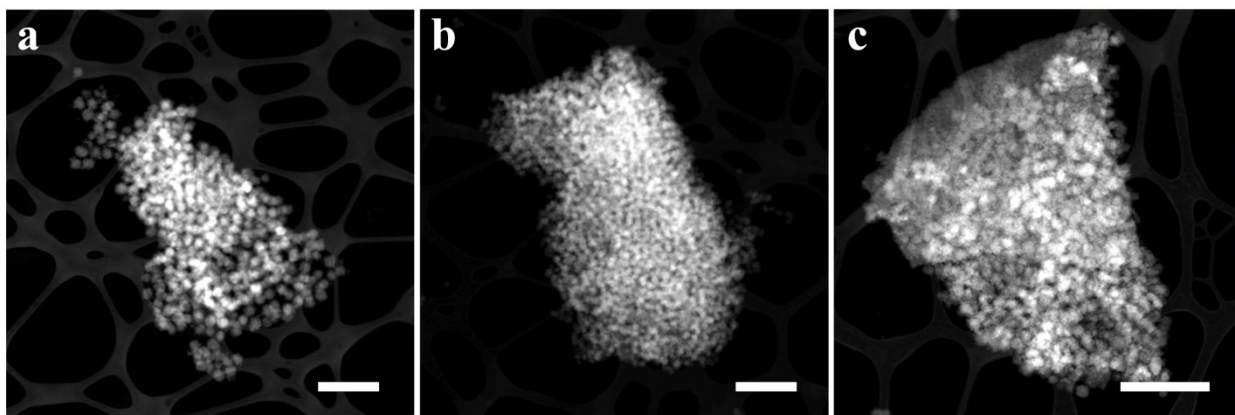
vacuum cell with removable KBr windows. The cell was purged with air ( $1\text{ cm}^3/\text{s}$ , Air Liquide, breathing grade) while heating to 773 K ( $1\text{ K/min}$ ), where it was held for 2 h, followed by evacuation at 773 K for  $>2\text{ h}$  ( $<0.01\text{ Pa}$  dynamic vacuum; oil diffusion pump), and cooling to 308 K under dynamic vacuum. At this point, a baseline spectrum was recorded.  $\text{CD}_3\text{CN}$  (Sigma-Aldrich, 99.8 % D-atoms) was purified by three freeze (77 K), pump, thaw cycles, then dosed to the sample at 308 K until the Lewis acid sites were saturated. The cell was evacuated down to 13.3 Pa, and the first spectrum in each desorption series was recorded. Then, the cell was evacuated under dynamic vacuum while maintaining the sample at 308 K. Concurrently, a series of representative FTIR spectra was recorded. The corresponding baseline spectrum was subtracted from each collected spectrum.

**UV/Vis Spectrophotometry:** UV/Vis spectra were recorded using Evolution 201/220 UV/Visible Spectrophotometers (Thermo Scientific) equipped with a diffuse reflectance cell.

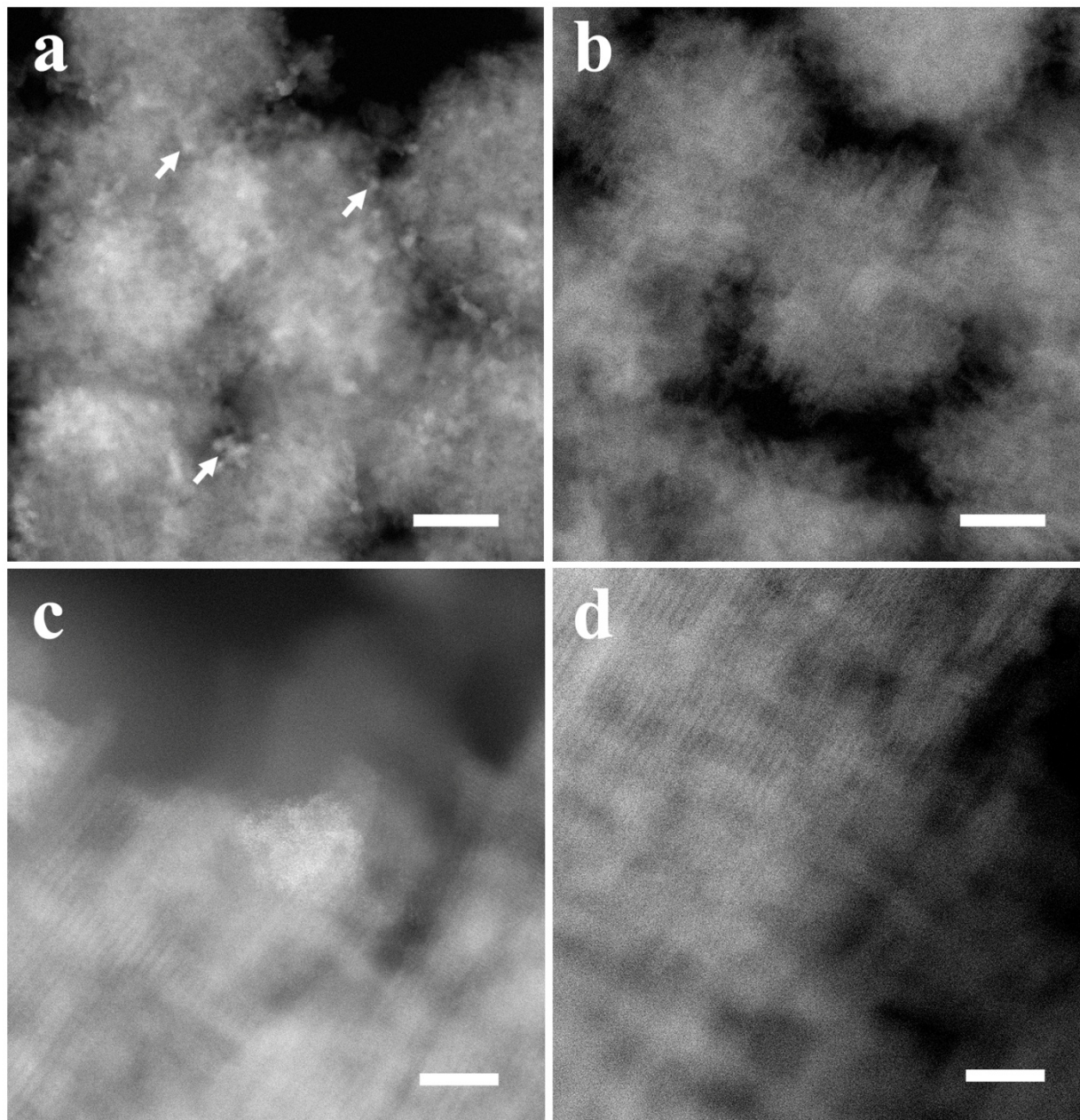
**TEM:** Samples for high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were prepared by grinding the powder with a quartz mortar and pestle in isopropanol. This suspension was allowed to settle for 10 min. Then, a thin film of the supernatant was applied onto a copper grid coated with holey carbon film supported with a uniform ultrathin carbon film (Ted Pella Inc.). HAADF-STEM images and STEM-EDX maps were acquired in an aberration-corrected FEI Titan 60-300 (S)TEM, equipped with an analytical Super-Twin pole piece and FEI SuperX EDX detector, operating at 300 kV and having a STEM incident probe convergence angle of  $19.3\text{ mrad}$  with  $30\text{ pA}$  current, and  $58.5\text{ mrad}$  HAADF detector inner angle. EDX spectrum maps were acquired using the Bruker Esprit software at an electron dose rate of approximately  $1.9\text{ e}^-/\text{nm}^2/\text{s}$ . All scans used an  $18\text{ }\mu\text{sec}$  pixel dwell time with probe step size of 20 nm, 15 nm and 10 nm for samples with Si/Sn atomic ratio as 100, 183 and 223 respectively. Elemental maps of the Si  $\text{K}\alpha$ , O  $\text{K}\alpha$  and Sn  $\text{L}\alpha$  peaks were generated after  $8\times 8$  binning of the raw data from Esprit software.

**Catalytic reactions:** Reactions with D-glucose (Sigma–Aldrich,  $\geq 99.5\%$ ) and  $\alpha$ -lactose monohydrate (Sigma–Aldrich,  $>99\%$ ) were carried out in stirred 20-mL thick-walled glass reactors (VWR) sealed with crimp tops (PTFE/silicone septum, VWR). In a typical reaction with

glucose, 0.05 g of glucose, 4.95 g of ethanol (1 wt% glucose in ethanol solution) and 0.042 g of Sn containing catalyst were added into the reactor and sealed. The reactor was placed in a temperature-controlled oil bath at 363 K for a certain period of time denoted as reaction time in Figure 4a. After quenching the reactor in an ice bath, 6.45 g of deionized water was added to hydrolyze the ethylated sugars at 363 K for 24 h. The fructose yields plotted in Figure 4a are those obtained after the reaction time and the 24h hydrolysis. Reactions with lactose were carried out in methanol (0.5 wt% lactose in methanol solution) at a 1:25 Sn/lactose molar ratio in stirred 20-mL thick-walled glass reactors with temperature control provided by an oil bath at 363 K. All the reactants and products were analyzed by high performance liquid chromatography (HPLC) using a refractive index detector with a Bio-Rad Aminex HPX87C (300 x 7.8 mm) column (Phenomenex). The mobile phase was ultrapure water (pH=7) and the column temperature was 353 K. Figure S4 gives examples of HPLC traces from representative experiments.

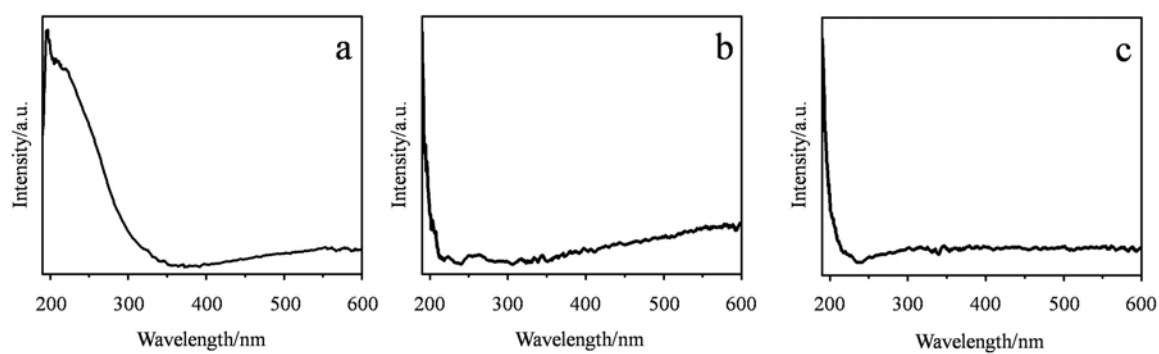


**Figure S1.** HAADF-STEM images of aggregate of particles analyzed using EDX mapping in Figure 2 a-c. Scale bar is 1  $\mu\text{m}$ .

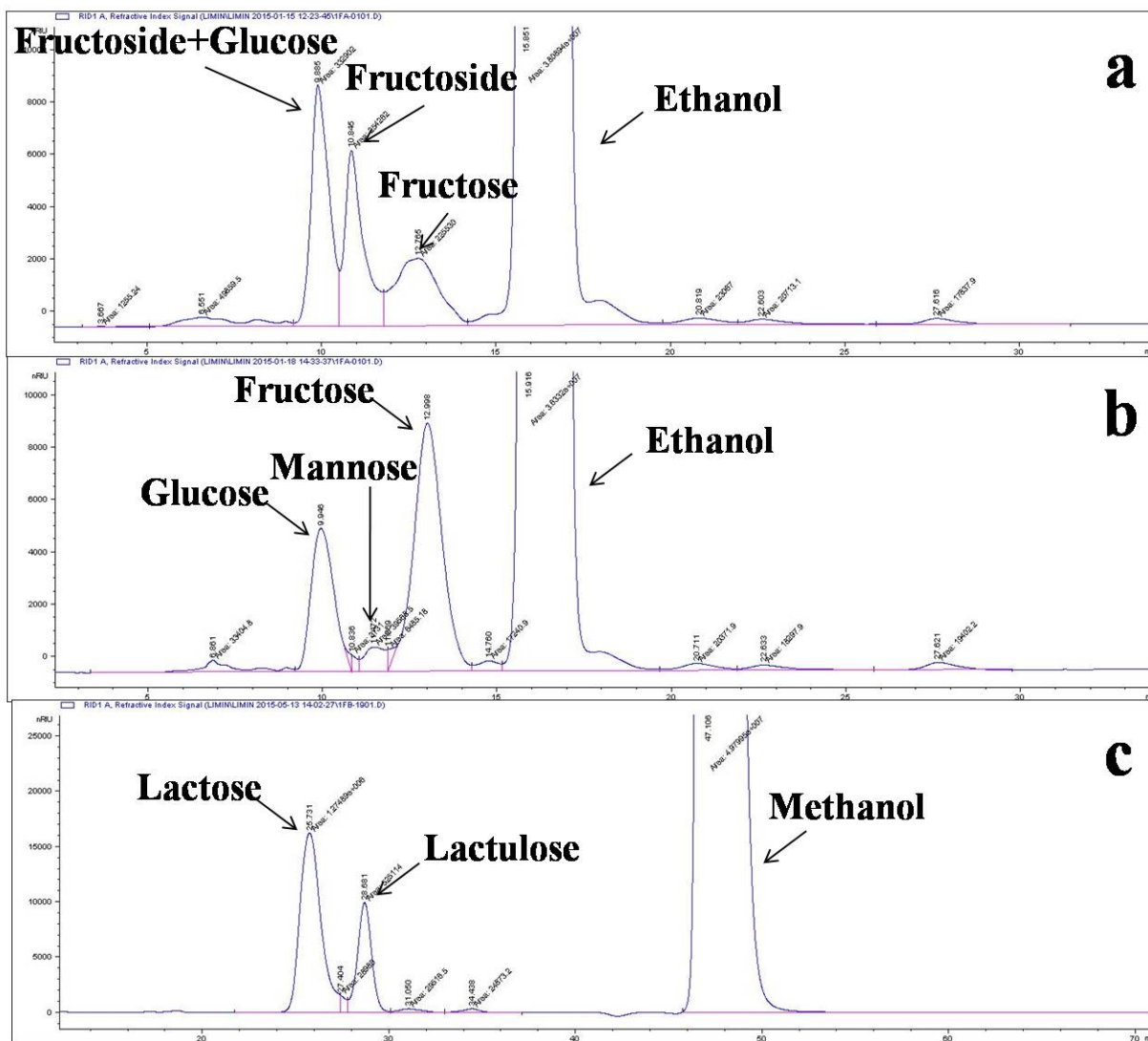


**Figure S2.** HAADF-STEM images showing particles in (a), (c) Sn-SPP(75) and in (b), (d) Sn-SPP(186). Bright circular clusters of Sn atoms over the SPP framework are visible only in particles of Sn-SPP(75). Scale bar is 50 nm in (a) and (b), and 5 nm in (c) and (d).





**Figure S3.** UV/Vis spectra of (a) Sn-SPP(75), (b) Sn-SPP(186) and (c)  $^{119}\text{Sn}$ -SPP(223).



**Figure S4.** Representative HPLC traces for Glucose ((a): after 24h reaction time in ethanol but before water addition and hydrolysis; (b): after water addition and 24h hydrolysis) and Lactose isomerization (c) over Sn-SPP(186) at 24 h.

Table S2. Isomerization of GLU (glucose) to FRU (fructose) over different catalysts.

Catalyst	Conv.	FRU Yield	FRU Selec.	Reaction conditions <sup>#</sup>	Ref.
Sn-BEA	55 %	32 %	58 %	10 wt% GLU in water, 383 K, 30 min, GLU/Sn=50	24
Sn-BEA	41 %	32 %	78 %	10 wt% GLU in water, 383 K, 120 min, GLU/Sn=926	27
Hierarchical MFI	37 %	27 %	73 %	3 wt% GLU in water, 353 K, 120 min, GLU/Sn=71	18
USY	72 %	55 %	76 %	3 wt% GLU in Methanol, 393 K, 60min, GLU/Al=3.9 Water*	23
Al-BEA	70 %	40 %	57 %	3 wt% GLU in Methanol, 393 K, 60min, GLU/Al=7.5 Water*	23
USY	52 % <sup>†</sup>	32 % <sup>†</sup>	62 %	3 wt% GLU in Ethanol, 393 K, 60 min, GLU/Al=3.9 Water*	23
Sn-SPP(186)	88 %	64.8 %	74 %	1 wt% GLU in Ethanol, 363 K, 30 h, GLU/Sn=74 Water*	This work
Sn-SPP(186)	78 %	56.1	72 %	1 wt% GLU in n-Propanol, 363 K, 24 h, GLU/Sn=74 Water*	This work
<sup>119</sup> Sn-SPP(223)	88 %	66.5 %	76 %	1 wt% GLU in Ethanol, 363 K, 24 h, GLU/Sn=89 Water*	This work
Sn-SPP(75)	71 %	57 %	80 %	1 wt% GLU in Ethanol, 363 K, 24 h, GLU/Sn=30 Water*	This work

<sup>†</sup> Stated values read from the figures in the corresponding references.

<sup>#</sup> For the cited references, this column lists the reaction conditions that give highest fructose yield in each reference.

\*Reactions were conducted in alcohol and water in consecutive reactions. Hydrolysis times were 24h at 363 K in this work and 1 h at 393 K in Ref 23.

Table S3. Isomerization of LAC (lactose) to LACTU (lactulose) over different catalysts.

<b>Catalyst</b>	<b>Conv.</b>	<b>LACTU Yield</b>	<b>LACTU Selec.</b>	<b>Reaction conditions<sup>#</sup></b>	<b>Ref.</b>
Sn-BEA	24 %	18 %	76 %	1 wt% LAC in water, 373 K, 90 min, LAC/Sn=20	28
Sn-BEA(125)	6 %	6 %	100 %	0.5 wt% LAC in methanol, 363 K, 24 h, LAC/Sn=25	This work
Hierarchical MFI	32 % <sup>†</sup>	24 %	75 %	3 wt% LAC in water, 353 K, 120 min, LAC/Sn=37	18
Sn-MCM-41(80)	48 %	31 %	65 %	0.5 wt% LAC in methanol, 363 K, 24 h, LAC/Sn=25	This work
Sn-SPP(186)	31 %	30 %	97 %	0.5 wt% LAC in methanol, 363 K, 24 h, LAC/Sn=25	This work

<sup>†</sup> Stated values read from the figures in the corresponding references.

<sup>#</sup> For the cited references, this column lists the reaction conditions that give highest lactulose yield in each reference.