

Supplementary Information

Rapid Synthesis of Sn-Beta for the Isomerization of Cellulosic Sugars

Chun-Chih Chang,[†] Zhuopeng Wang,[†] Paul Dornath, Hong Je Cho and Wei Fan*

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA;

[†] These authors contribute equally to this work.

* Corresponding author: wfan@ecs.umass.edu

Synthesis and Characterization

Preparation of seed solution

0.1 g of sodium hydroxide ($\geq 98\%$, Aldrich) were dissolved in 11.83 g of tetraethylammonium hydroxide solution (TEAOH, 35%, Alfa Aesar), followed by dropwise adding 17.85 g of Ludox HS-30 colloidal silica (30%, Aldrich). After dissolving LUDOX HS-30 at room temperature, 0.365 g of aluminum isopropoxide (Aldrich) were added into the solution. The composition of the solution was 25 SiO₂: 0.25 Al₂O₃: 9 TEAOH: 0.35 Na₂O: 331 H₂O. The mixture was aged for 1 day at room temperature and filtered with a 200 nm syringe filter to obtain a clear solution. The clear solution was charged into a Teflon-lined stainless steel autoclave, and heated at 120 °C for 3 days in a preheated oven. The formed zeolite nanocrystals were collected by centrifugation and repeatedly washed by deionized water until the pH is around 9. Finally, the aluminosilicate zeolite beta nanocrystals were re-dispersed into deionized water without

drying. The crystal concentration in the suspension was 0.192 g/mL. Dealumination of the crystals was achieved by treating 2.5 mL of the suspension with 25 mL of concentrated nitric acid (69%, Fisher) in a Teflon-lined stainless steel autoclave at 80 °C for 24 h. The dealuminated zeolite beta was collected by centrifugation and thoroughly washed by deionized water until the supernatant approached a neutral pH. The obtained products were then re-dispersed into deionized water by sonication without drying. The final crystal concentration in the suspension was 0.145 g/mL.

Synthesis of Sn-Beta

In a typical run, 6.98 g of tetraethylorthosilicate (TEOS, Alfa Aesar, 98%) were added into 7.67 g of tetraethylammonium hydroxide solution (TEAOH, Alfa Aesar, 35%), and stirred at room temperature until it became a homogeneous solution (about 1 h to 1.5 h). Then, 0.1 g of tin chloride (Alfa Aesar) were dissolved in 0.64 g of deionized water. These two solutions were mixed together, and stirred in a hood until the ethanol generated from the hydrolysis of TEOS was completely evaporated. The final weight loss was 7.99 g (6.04 g of ethanol and 1.95 g of water). Then, 0.74 g of hydrofluoric acid (Alfa Aesar, 48%) were added into the solution with stirring. Finally, 0.579 mL of dealuminated zeolite beta seed solution (0.145 g/mL) were added into the solution (4.1wt% with respect to the silica content), and homogenized with a plastic spatula. The composition of the final gel was SiO₂: 0.54 TEAOH: 0.54 HF: 0.008 SnO₂: 7.5 H₂O. The obtained gel was then loaded into a Teflon-lined stainless steel autoclave, and heated at 140 °C with a rotation of 2 rpm for various times. The product was filtered and thoroughly washed by deionized water, and dried in a 100 °C oven overnight. The

obtained solid was calcined with a ramping rate of 1 °C/min to 550 °C for 12 h to remove the organic structure directing agent and fluoride ions.

Synthesis of siliceous zeolite beta

Siliceous zeolite beta was prepared by seeded growth method using the seed solution prepared with the method described above. The synthesis gel for the seeded growth was prepared according to the literature method¹. First, 1.04 g of hydrofluoric acid were added into 10.52 g of 35% TEAOH solution. Then, 3 g of fumed silica (CAB-O-SIL M-5, Cabot) were slowly added into the solution and mixed with stirring. The composition of the gel was SiO₂: 0.5TEAOH: 0.5HF: 7H₂O. Finally, 0.331 mL dealuminated zeolite beta seed solution (0.145 g/mL) was added into the gel (1.6 wt% with respect to silica content in synthesis gel), and homogenized by stirring with a plastic spatula. The resulting gel was charged into a Teflon-lined stainless steel autoclave and reacted at 140 °C for various times. The product was centrifuged, washed by deionized water, and dried in a 70 °C oven. The yield was calculated based on the silica amount in the initial gel and the weight of crystals after the removal of the organic structure directing agent (1 °C/min, 550 °C for 12 h). Siliceous zeolite beta was also made without adding the seed solution into the synthesis gel.

Characterizations

The crystalline phase of the Sn-Beta was examined by using an XRD diffractometer (X'pert Pro, PANalytical) operated at an acceleration voltage of 45 kV and a current of 40 mA. The morphology of the product was investigated by using a scanning electron

microscope (Magellan 400, FEI) with Pt coating. The nitrogen adsorption-desorption isotherm was collected on an automated gas sorption analyzer (Autosorb iQ, Quantachrome) after degassed at 200 °C under vacuum. Chemical analysis of the sample was performed on an inductively coupled plasma-optical emission spectrometer (iCap 6500 dual view, Thermo Scientific). The FT-IR spectrum was collected on an FT-IR spectrometer (Equinox 55, Bruker) in absorbance mode at a spectral resolution of 2 cm⁻¹ with the Praying Mantis™ High Temperature Reaction Chamber (Harrick). The sample was heated at 823K for 1 h. The pyridine adsorption was carried out by exposing the pretreated sample to a pyridine vapor at 393 K for 30 min and followed by He flow for 1 h to remove weakly adsorbed and residue species in the chamber. The adsorbed pyridine was desorbed successively at different temperatures (423 K, 523 K, 623 K and 723 K) for 1h. All the spectra were collected at 393 K.

Catalytic Tests

All the chemicals (xylose, glucose, dihydroxyacetone dimer and methanol) used in the reactions were purchased from Sigma-Aldrich.

Isomerization of glucose

A glucose isomerization reaction was used to test the catalytic activity of the synthesized Sn-Beta catalyst. The reaction was performed according to the work of Moliner *et al.*² Sn-Beta was added at a 1:50 Sn: glucose molar ratio to a 10wt% glucose solution in a 3 mL thick-walled glass reactor. The reaction vial was placed in a temperature-controlled aluminum heating block set to 90°C with 500 rpm stirring. After reaction for various

times, the glass reactors were quenched in ice for 15 min, dried, and weighed before opening to make sure no leaking during the reaction.

Isomerization of xylose

The isomerization of xylose was performed according to the work of Choudhary *et al.*³ Sn-Beta was added at a 1:70 Sn: glucose molar ratio to a 10wt% xylose solution in a 3 mL thick-walled glass reactor. The reaction vial was placed in a temperature-controlled aluminum heating block set to 100 °C with 500 rpm stirring. After reaction for various times, the glass reactors were quenched in ice for 15 min, dried, and weighed before opening to make sure no leaking during the reaction.

Conversion of dihydroxyacetone (DHA) to methyl lactate (ML)

Conversion of dihydroxyacetone (DHA) to methyl lactate (ML) in methanol was performed according to the work of Taarning *et al.*⁴ In a typical experiment, 1.25 mmol of DHA, 4 g methanol and 80 mg Sn-Beta were added to a 3 mL thick-walled glass reactor. The reactor was placed in temperature-controlled aluminum heating block set to 70 °C with 500 rpm stirring. After reaction for various times, the glass reactors were quenched in ice for 15 min, dried, and weighed before opening to make sure no leaking during the reaction.

Sample analyses

For the reactions with pentose and hexose, sample analyses were performed using liquid chromatography (Shimadzu LC-20AT). Sugars were detected with a RI detector

(RID-10A), and other products were detected with a UV–Vis detector (SPD-20AV) at wavelengths of 210 and 254 nm. The HPLC column used was a BIO-RAD HPX-87H sugar column. The mobile phase was 0.005 M H₂SO₄ flowing at a rate of 0.6 mL/min. The column oven was set to 30 °C. The column can efficiently separate the isomers of C₆ sugar, such as glucose, fructose and mannose, but shows poor separation for xylulose (10.118 min) and lyxose (10.175 min). It was found that the response factors of xylulose and lyxose on the RI detector are similar (difference is less than 20%). The combined yield of xylulose and lyxose were, thus, calculated from the peak with a retention time from 10.1 min to 10.2 min.

DHA and ML were detected on an Agilent 6890 gas chromatography equipped with an FID-detector and a Restek RTX-VMS capillary column (30.0 m/0.25 mm id/1.4 µm film thickness). A helium flow rate of 6.0 mL/min pressurized at 1.498 bar was used. The oven temperature program is as follows: the initial temperature is 50 °C (hold 2 min) and then heated to 240 °C (ramp 20 °C/min, hold 20 min).

Conversion and yield are defined as follows:

$$\text{Conversion}_{\text{glucose}} = (\text{moles}_{\text{glucose reacted}})/(\text{moles}_{\text{glucose initial}})$$

$$\text{Conversion}_{\text{DHA}} = (\text{moles}_{\text{DHA reacted}})/(\text{moles}_{\text{DHA initial}})$$

$$\text{Conversion}_{\text{xylose}} = (\text{moles}_{\text{xylose reacted}})/(\text{moles}_{\text{xylose initial}})$$

$$\text{Yield}_{\text{glucose}} = (\text{moles}_{\text{glucose}})/(\text{moles}_{\text{glucose initial}})$$

$$\text{Yield}_{\text{fructose}} = (\text{moles}_{\text{fructose produced}})/(\text{moles}_{\text{glucose initial}})$$

$$\text{Yield}_{\text{mannose}} = (\text{moles}_{\text{mannose produced}})/(\text{moles}_{\text{glucose initial}})$$

$$\text{Yield}_{\text{xylulose+lyxose}} = (\text{moles}_{\text{xylulose+lyxose produced}})/(\text{moles}_{\text{xylose initial}})$$

$$\text{Yield}_{\text{ML}} = (\text{moles}_{\text{ML produced}}) / (\text{moles}_{\text{DHA initial}})$$

Table S1 Textual analysis and elemental analysis of Sn-Beta.

	Micropore volume^a (cc/g)	Micropore volume^b (cc/g)	External surface area²_{b (m²/g)}	BET surface area²_{c (m²/g)}	Total pore volume^d (cc/g)	Si/Sn^e
Sn-Beta	0.188	0.176	131	488	0.32	126

^a From t-plot method;

^b From α_s -plot method;

^c Calculated from P/P_0 range of 0.05-0.25 using BET equation;

^d Calculated from amount adsorbed at $P/P_0=0.975$;

^e ICP-OES.

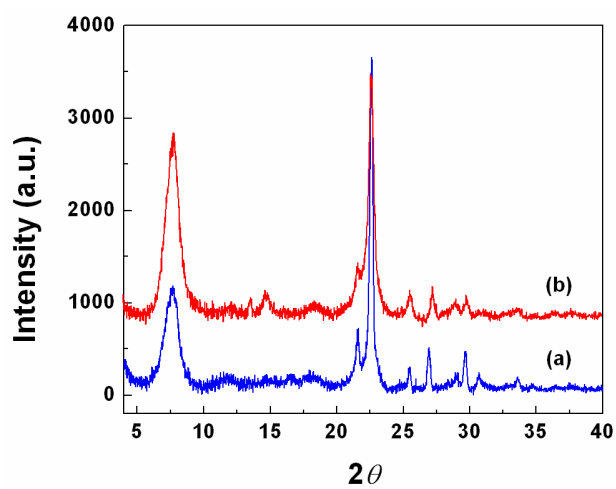


Fig. S1 XRD patterns of zeolite beta seeds before (a) and after (b) dealumination. XRD pattern (b) is shifted up 800 a.u. for an illustrative reason.

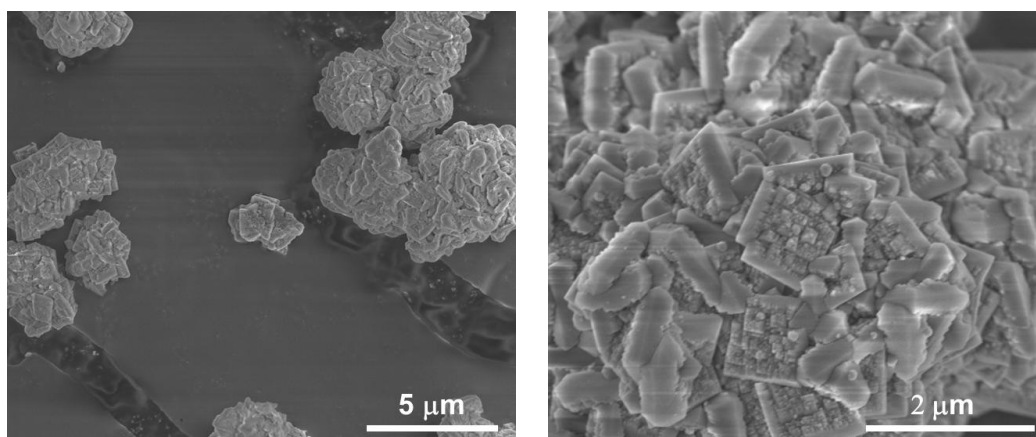


Fig. S2 SEM images of the synthesized Sn-Beta.

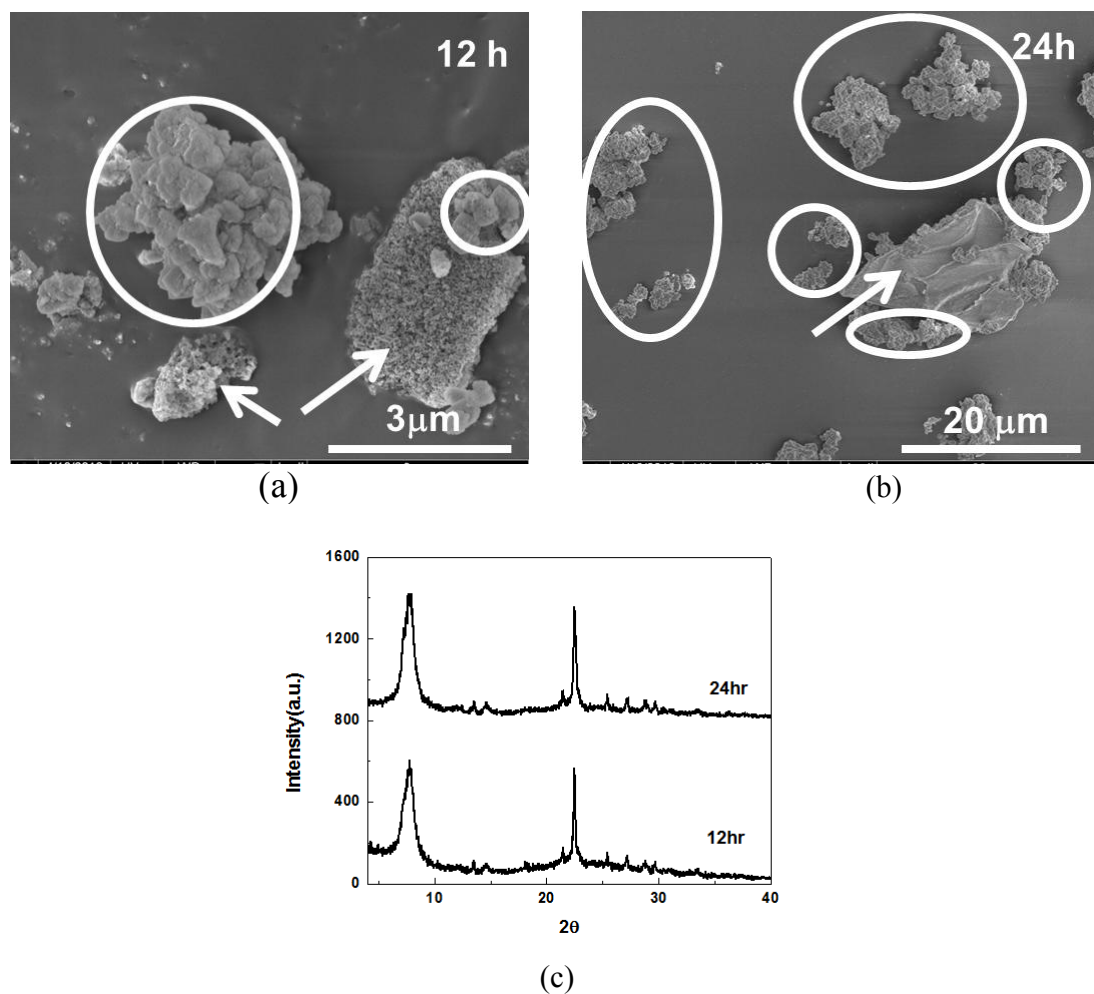


Fig. S3 SEM images of the products obtained after 12 h (a) and 24 h (b) hydrothermal treatment (arrows indicate the amorphous phase and circles point out the crystals) and the corresponding XRD patterns (c).

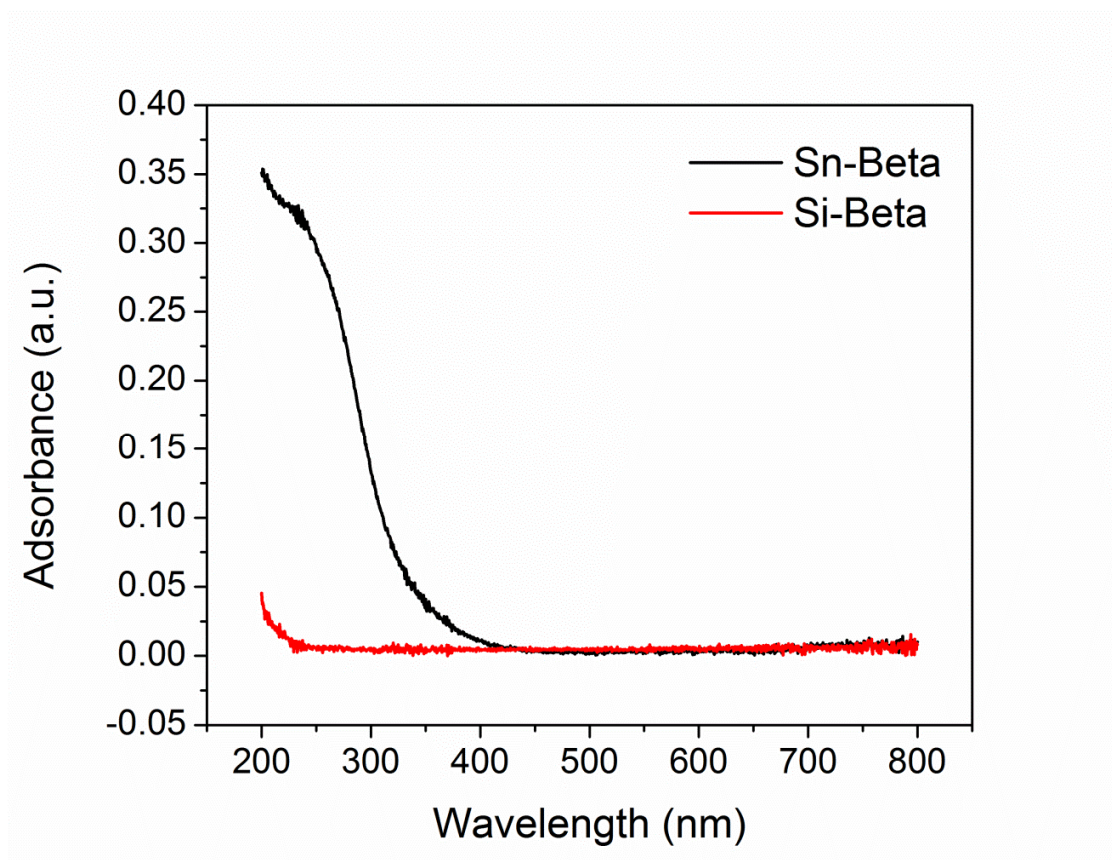


Fig. S4 UV-Vis diffuse reflectance spectrum of synthesized Sn-Beta and siliceous Beta

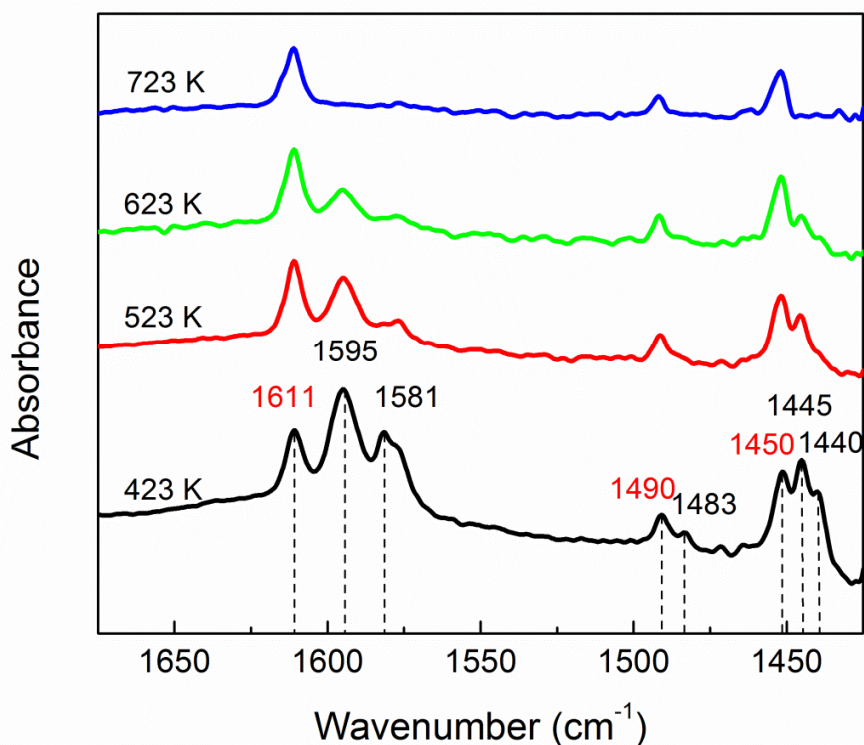


Fig. S5 IR spectra of Sn-Beta after pyridine adsorption at 393 K for 30 min and desorption at 423 (a), 523 (b), 623 (c), and 723 K (d) for 1 h, respectively. The bands (1611, 1490 and 1450 cm⁻¹) associated to Lewis acidity are marked in red.

The IR spectra of adsorbed pyridine in the range of pyridine ring-stretching modes on the Sn-Beta were measured after desorption at different temperatures. The vibrations of stretching modes of hydrogen-bonded (hb) and physically (ph) adsorbed pyridine were observed at 1595 cm⁻¹ (hb, mode 8a), 1581 cm⁻¹ (hb, ph, mode 8b), 1483 cm⁻¹ (ph, mode 19b) 1445 cm⁻¹ (hb, mode 19b) and 1440 cm⁻¹ (ph, mode 19b), respectively^{5, 6}. The physically adsorbed pyridine (bands at 1483 cm⁻¹ and 1440 cm⁻¹) completely diminished after the desorption at 523 K. Hydrogen-bonded pyridine at 1595 cm⁻¹ and 1445 cm⁻¹ contributed by the hydroxyl groups (from the defects and external surface of the catalyst) decreased in intensity with increasing the desorption temperature. Absorbance at 1550 cm⁻¹ associated with strong Brønsted acid sites was not observed in the sample. In addition to the hydrogen-bonded and physically adsorbed pyridine, the two distinct bands at 1611 cm⁻¹ and 1490 cm⁻¹ and a shoulder one at 1450 cm⁻¹ were observed in all spectra. The bands are associated with the different vibration modes of the pyridine-rings adsorbed on the Sn species within zeolite beta, clearly indicating the presence of Lewis acidity in the sample⁷⁻⁹. The three bands were remained even after desorption at 723 K showing the Lewis acid sites are resistant against the relatively high temperature.

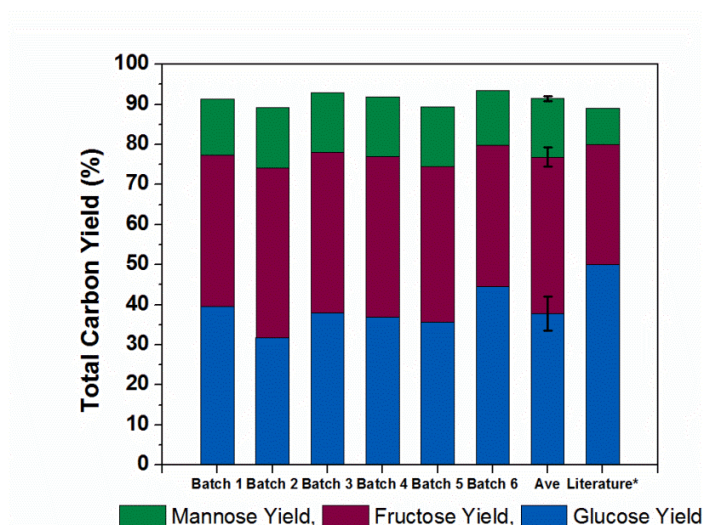
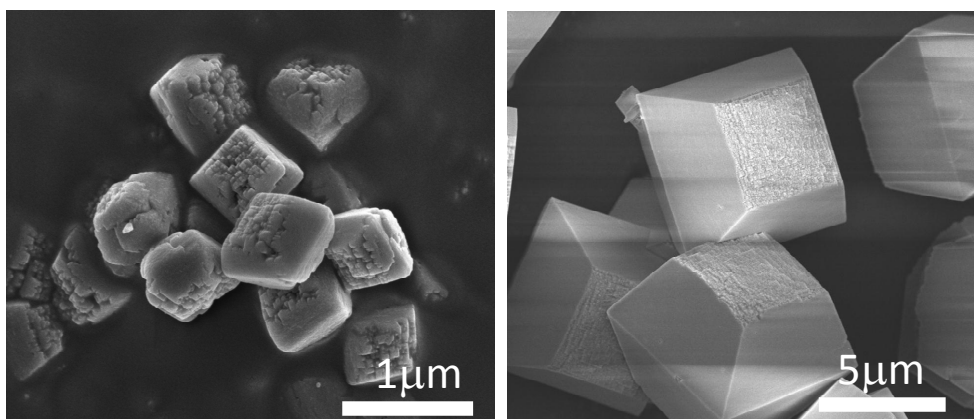


Fig. S6 Product distribution for the isomerization of glucose using the Sn-Beta synthesized from different batches. Reaction conditions: initial glucose concentration of 10wt%, glucose to tin molar ratio of 50:1, 100 mg Sn-Beta, 90 °C. *Literature data is from the work of Moliner *et al.*¹



(a)

(b)

Fig. S7 SEM images of the siliceous zeolite beta synthesized with (a) and without (b) using a seed solution. Siliceous zeolite beta can be synthesized in 50 h at 140 °C by adding a suspension containing well-crystalline zeolite seeds into the synthesis gel. The crystallization time of siliceous zeolite beta without using the seed solution is 307 h at 140 °C.

References:

1. O. Larlus and V. P. Valtchev, *Chem. Mater.*, 2005, **17**, 881-886.
2. M. Moliner, Y. Roman-Leshkov and M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 6164-6168.
3. V. Choudhary, A. B. Pinar, S. I. Sandler, D. G. Vlachos and R. F. Lobo, *ACS Catal.*, 2011, **1**, 1724-1728.
4. E. Taarning, S. Saravanamurugan, M. S. Holm, J. M. Xiong, R. M. West and C. H. Christensen, *ChemSusChem*, 2009, **2**, 625-627.
5. R. Buzzoni, S. Bordiga, G. Ricchiardi, C. Lamberti, A. Zecchina and G. Bellussi, *Langmuir*, 1996, **12**, 930-940.
6. C. Paze, S. Bordiga, C. Lamberti, M. Salvalaggio, A. Zecchina and G. Bellussi, *J. Phys. Chem. B*, 1997, **101**, 4740-4751.
7. F. Bonino, A. Damin, S. Bordiga, C. Lamberti and A. Zecchina, *Langmuir*, 2003, **19**, 2155-2161.
8. C. Ngamcharussrivichai, P. Wu and T. Tatsumi, *J. Catal.*, 2005, **235**, 139-149.
9. P. Li, G. Q. Liu, H. H. Wu, Y. M. Liu, J. G. Jiang and P. Wu, *J. Phys. Chem. C*, 2011, **115**, 3663-3670.