Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

of

Fluoride-free synthesis of Sn-BEA catalyst by dry gel conversion

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Synthesis of Sn-BEA-F

In a typical synthesis, 10.47 g of tetraethylorthosilicate (TEOS, Alfa Aesar) was added into 11.51 g of tetraethylammonium hydroxide solution (TEAOH, Alfa Aesar or SACHEM SDA 440, 35 wt%), and stirred at room temperature until it became a homogeneous solution. Then, 0.15 g of tin chloride hydrate ($SnCl_4 \bullet xH_2O$, 34.4 wt% Sn, Alfa Aesar) dissolved in 0.96 g of deionized water was added. The solution was stirred in a hood until ethanol generated from the hydrolysis of TEOS was completely evaporated. The final weight loss was 11.67 g (9.06 g of ethanol and 2.61 g of water). Then, 0.560 mL of dealuminated zeolite beta seed solution (0.224 g mL^{-1}) was added into the solution (4.1 wt% with respect to the silica content) and mixed by a plastic spatula. Finally, 0.971 mL of hydrofluoric acid (Alfa Aesar, 48 wt%) was added and homogenized by using a plastic spatula. The composition of the final gel was SiO_2: 0.54TEAOH: 0.54HF: $0.008SnO_2$: $7.5H_2O$. The obtained precursor was then loaded into a Teflon-lined stainless steel autoclave. The autoclave was heated at 140 °C with a rotation of 2 rpm for 4 day. The product was filtered and thoroughly washed by 1 L deionized water, and dried in a 100 °C oven overnight. The as-made solid was calcined in ~250 mL min^{-1} of humid air (24 Torr water vapor) with a ramping rate of 1 °C min^{-1} to 550 °C for 12 h to remove the organic structure directing agent and fluoride ions. The Si/Sn ratio of the final product was 126 as determined by ICP-MS measurement.

Synthesis of SnO_2/Si-BEA

Preparation of extraframework SnO_2 species on siliceous zeolite BEA framework was carried out according to Bermejo-Deval *et al.*[11] The procedure is the same as preparation of Sn-BEA-F, except for that SnO_2 (-325 mesh, Aldrich) was added as Sn source. The Si/Sn ratio was designed to be 125.

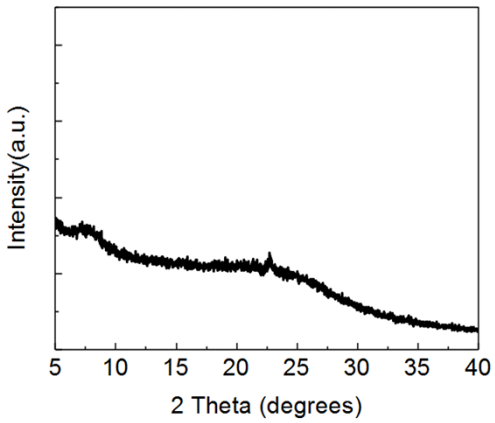

Fig. S1 XRD pattern of sample obtained without addition of alkali ions after 5 days of DGC at 140 °C. Only very weak reflections can be observed. They could originate from the seed crystals added in the gel.

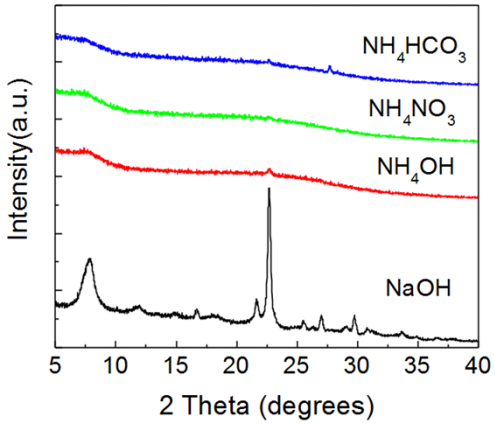

Fig. S2 XRD pattern of sample synthesized with ammonium hydrogen carbonate, ammonium nitrate, ammonium hydroxide and sodium hydroxide (Na_2O/SiO_2 or $(NH_4)_2O/SiO_2$ ratio is 0.096) after 5 days of DGC at 140 °C. Only very weak reflections can be observed except for sodium hydroxide case, and they could originate from the seed crystals added in the gel. The data clearly indicate that the alkali ions are essential for the synthesis from dry gel conversion.

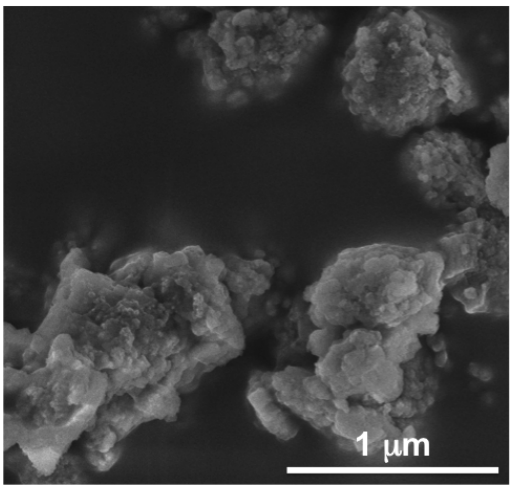

Fig. S3 Representative SEM image for Sn-BEA-IE.

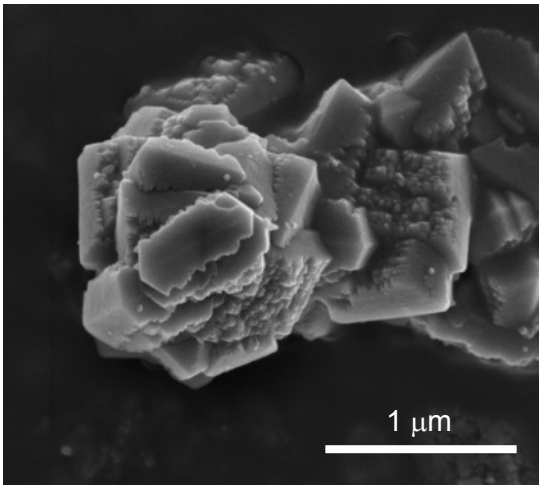

Fig. S4 Representative SEM image for Sn-BEA-F.

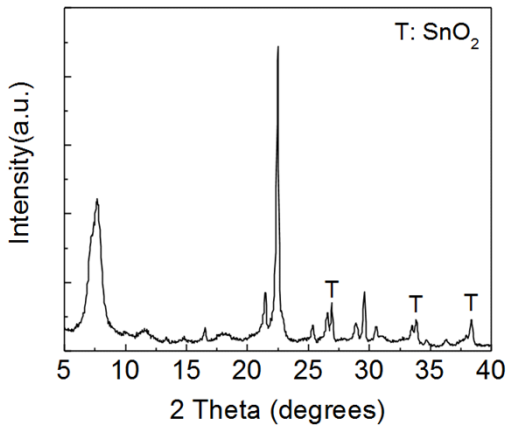

Fig. S5 XRD pattern of SnO_2/Si-BEA (Si/Sn=125) sample. The XRD shows that the sample has zeolite BEA topology and reflections from SnO_2.

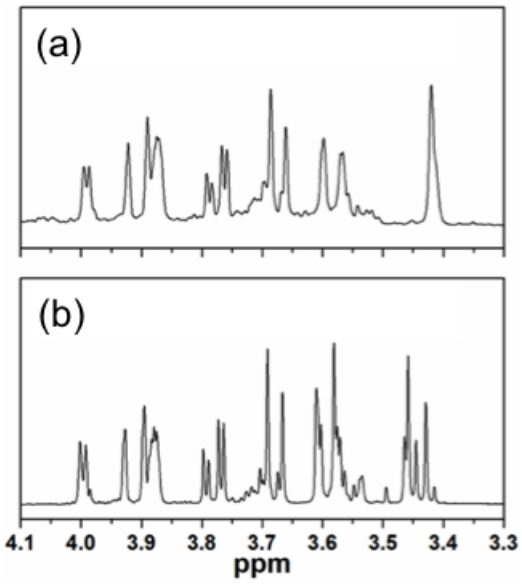

Fig. S6 ^{1}H-NMR spectrum of (a) fructose after isomerization reaction of deuterium substituted glucose over Sn-BEA-IE and (b) unlabeled fructose. Reaction conditions are the same as described in the manuscript, except for longer reaction time (2 h). The separation was achieved by running the reaction mixture on HPLC (LC-20, Shimadzu) with a Biorad HPX-87C column (Ca^{2+}-type), operated at 80 °C. Water was used as mobile phase at a flow rate of 0.6 mL min^{-1}. Fructose portion was collected by a fraction collector (FRC-10, Shimadzu). The solution containing fructose was then heated in a 70 °C oven to evaporate the solvent. The obtained solids were re-dissolved in D_2O prior to ^{1}H-NMR measurement (AVANCE 400, Bruker).

Table S1 Product distribution of PA over Sn-BEA catalysts (conditions: refer to main text)

Reaction time 15 min	Si/Sn	PA (%)	LA (%)	TOF (min^{-1})
Sn-BEA-IE	102	81.2	18.3	1.20
Sn-BEA-F	126	79.8	18.9	1.52

Table S2 Product distribution of glucose over Sn-BEA catalysts (conditions: refer to main text)

Reaction time 15 min	Si/Sn	Glucose (%)	Mannose+Fructose (%)	TOF (min^{-1})
Sn-BEA-IE	102	90.8	9.1	0.25
Sn-BEA-F	126	66.3	34.7	0.99

References

1 R. Bermejo-Deval, R. Gounder and M. E. Davis, *ACS Catal.*, 2012, **2**, 2705-2713.