Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Facile and Benign Conversion of Sucrose to Fructose Using Zeolites With Balanced Brønsted and Lewis Acidity

Shunmugavel Saravanamurugan,[a,b] Irene Tosi,[a] Kristoffer H. Rasmussen,[a,1] Rasmus E. Jensen,[a,1] Esben Taarning,[c] Sebastian Meier,[a]* and Anders Riisager[a]*

[a]Dr. S. Saravanamurugan, I. Tosi, K.H. Rasmussen, R.E. Jensen, Dr. S. Meier, Prof. A. Riisager, Technical University of Denmark, Department of Chemistry, Kemitorvet, 2800-Kgs. Lyngby, Denmark.

[b]Dr. S. Saravanamurugan, Center of Innovative and Applied Bioprocessing (CIAB), Mohali 160 071, Punjab, India.

[c]Dr. E. Taarning, Haldor Topsøe A/S, Haldor Topsøes Allé 1, 2800-Kgs. Lyngby, Denmark.

*e-mail: semei@kemi.dtu.dk or ar@kemi.dtu.dk

Catalyst characterization

X-Ray Powder Diffraction (XRPD)

H-USY (6) and (30), H-Beta (12.5) and Sn-DeAl-Beta zeolites were analyzed by powder X-ray diffraction using a Huber G670 imaging-plate Guinier powder diffraction camera using CuKα radiation at a wavelength of 0.15406. The X-ray diffractograms of the samples were recorded in the 2θ range of 3 to 80º at a rate of 1.5 º/min and the results are shown in Figures S1 and S2 below.

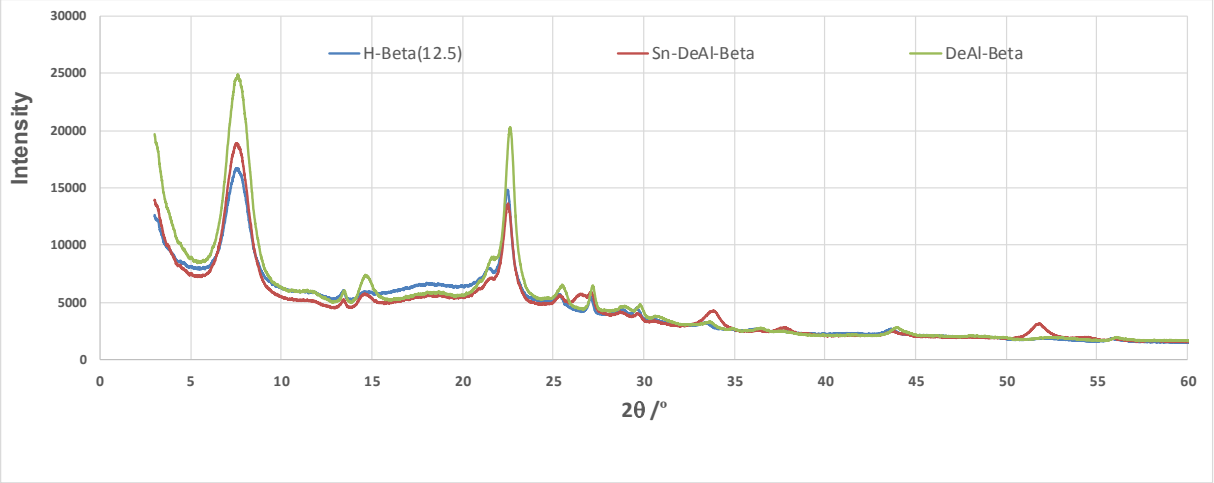

Figure S1. The powder XRD patterns of H-Beta (12.5) and modified H-Beta zeolites.

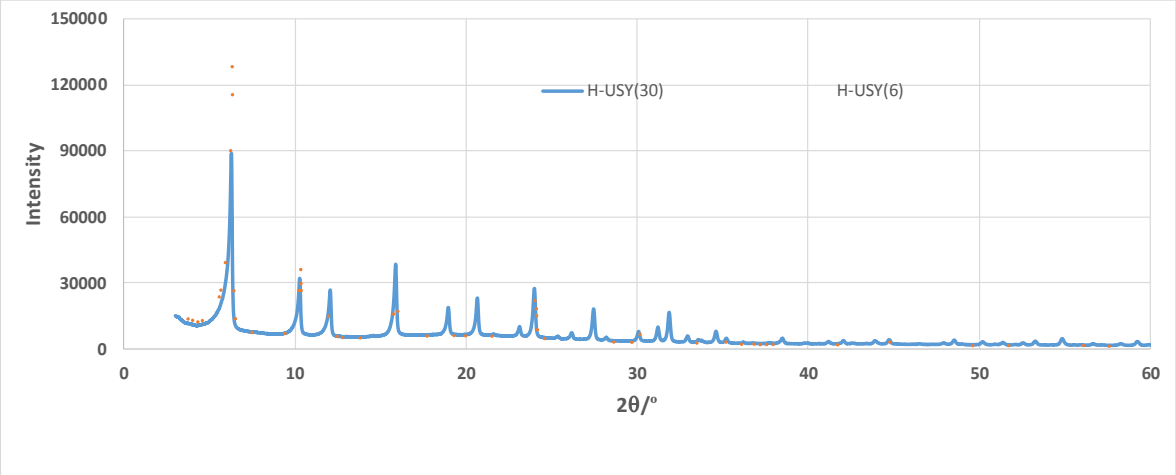

Figure S2. The powder XRD patterns of USY zeolites.

Ammonia-Temperature Programmed Desorption (NH_3-TPD)

The weak/medium/strong acid sites present in Beta, modified Beta and USY zeolites were measured by NH_3-TPD using an AutoChem II 2920 Chemisorption Analyzer from Micromeritics. About 100 mg sample was placed in U-tubes made up of quartz and treated at 500 °C for 1 h under helium (99.999%, AGA) with a flow rate of 50 mL/min, then cooled down to 100 °C. Ammonia (1% in He, AGA) with a flow rate of 50 mL/min was then passed through to the sample holder for 2 h. In order to remove any physisorbed ammonia, the samples were flushed with He (50 mL/min) prior to the measurement. Ammonia desorption was carried out and measured every second from 100 to 500 °C at a ramp of 10 °C/min, and the number of available acid sites was calculated based on the area under the desorption curve. The amounts of weak/medium (acid type 1) (desorption approx. between 100-270 °C) and strong acid sites (acid type 2) (desorption approx. between 270-500 °C) were calculated from the desorption area under the curve (Figure S3).

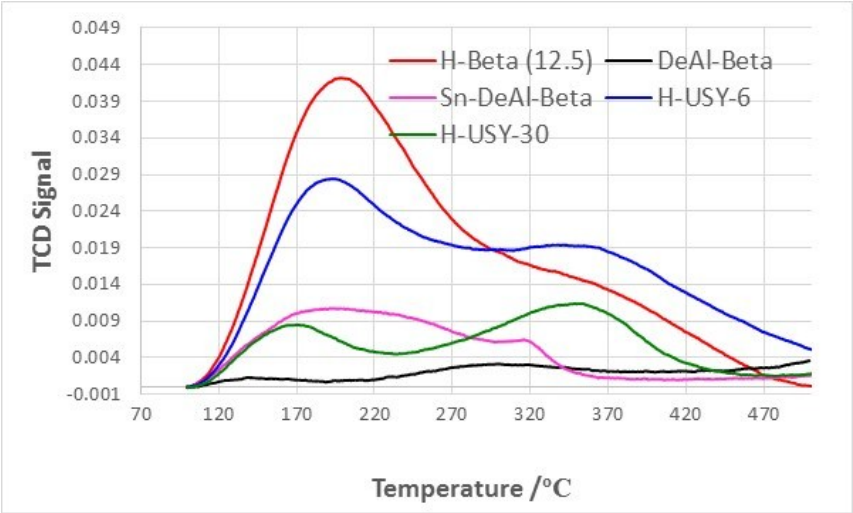

Figure S3. NH_3-TPD profiles of Beta and USY zeolites

Nitrogen-sorption measurement

Brunauer-Emmet-Teller (BET) surface area and pore volume were analyzed by nitrogen adsorption and desorption measurements using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer system at liquid nitrogen temperature. The sample was degassed at 300 °C overnight prior to the measurement, except for the acid-dealuminated Beta zeolite (DeAl-Beta) that was degassed at 90 °C.

Physicochemical properties of the zeolites described herein are compiled in Table S1 below.

Table S1. Physicochemical properties and composition of USY and Beta zeolites

Catalyst	Acid sites type 1 (100-270 °C) (µmol/g)	Acid sites type 2 (270-500 °C) (µmol/g)	Total acid sites (µmol/g)	BET area (m^2/g)	Pore volume (cm^3/g)	Si/Al[1]
H-USY (6)	488	539	1027	708	0.2436	6.5
H-USY(30)	140	226	366	792	0.2504	29.7
H-Beta(12.5)	693	395	1088	579	0.1631	12.5
DeAl-Beta[2]	28	91	119	526	0.1492	145
Sn-DeAl-Beta[3]	196	95	291	506	0.1767	144[4]
Amberlyst-36[5]	-	-	>5400	33	0.2	

[1]Determined using Panalytical Epsilon-3 X-ray Fluorescence Spectrometer.
[2]Nitric acid dealuminated H-Beta(12.5).
[3]Nitric acid dealuminated H-Beta(12.5) and washed with distilled water.
[4]Si/Sn ratio of 15.6.
[5]from Sigma-Aldrich

Catalyst reuse sequence

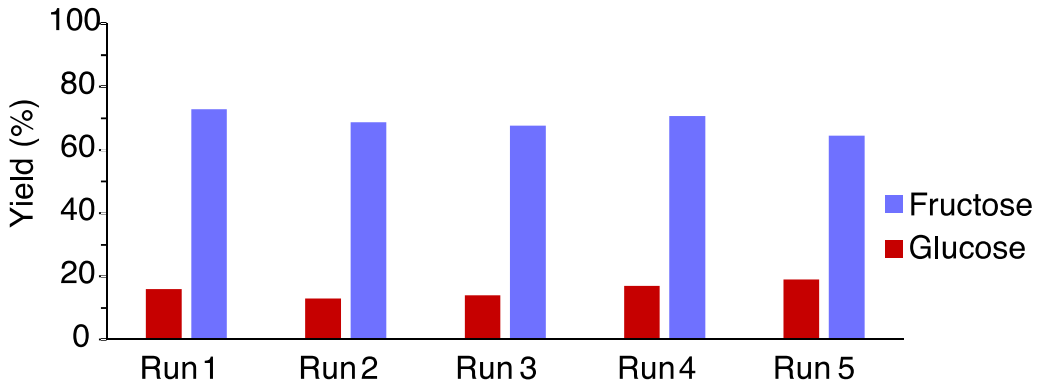

Figure S4. Catalyst reusability for H-USY (6). Reusability was assessed at elevated temperature (120 ºC) relative to optimized conditions.

SEM pictures of catalysts

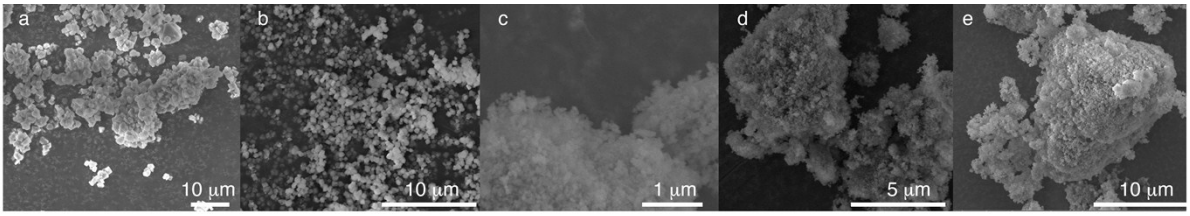

Figure S5. Scanning Electron Microscope images recorded on a FEI Quanta 200 ESEM FEG instrument of a) H-USY (6), b) Sn-DeAl-Beta (12.5), c) H-Beta (12.5), d) DeAl-Beta (Nitric acid dealuminated) and e) DeAl-Beta (steamed).

Conversion to rare functional tautomers

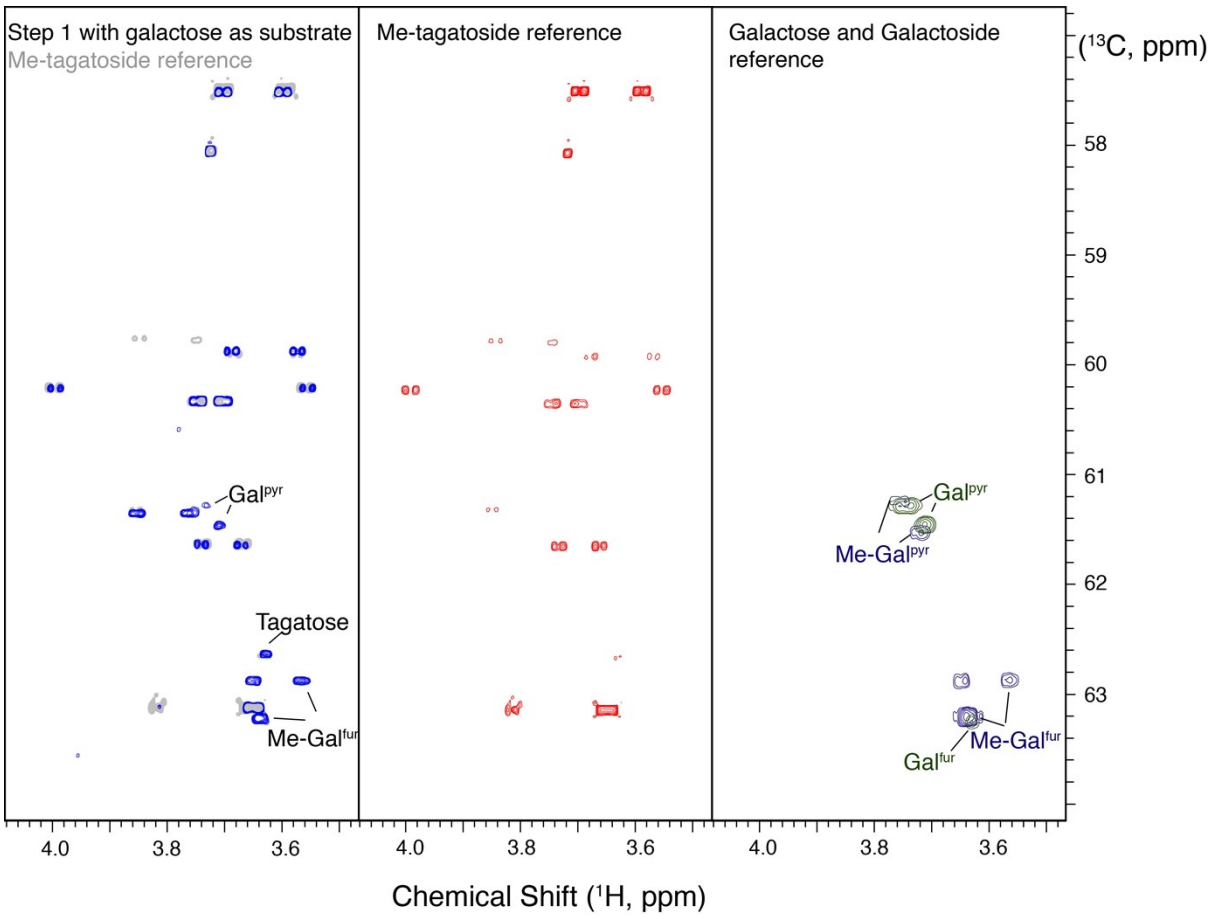

Figure S6. ^{1}H-^{13}C HSQC NMR spectra of a reaction mixture obtained by subjecting galactose to Sn-DeAl-Beta catalysed reaction at 100 °C (4 g methanol, 75 mg of catalyst and 125 mg galactose) for 2 hours. The reaction yields 61% methyl-tagatoside, 2% tagatose, 5% galactose and 23% methyl-galactoside. Reference spectra for methyl-tagatoside (middle and grey outline in the left panel), galactose and methyl-galactoside are shown.