Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Mechanism and Stereoselectivity of Zeolite-catalysed Sugar Isomerization in Alcohols

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Experimental Details

Chemicals

Glucose, fructose and methanol were obtained from Sigma-Aldrich (Andover, MO, USA). [2-^{2}H]-glucose and [1-*pro*-S-^{2}H] fructose were obtained from Omicron Chemicals (South Bend, IN, USA). The ammonium forms of USY (6) and USY (30) were purchased from Zeolyst International (Conshohocken, PA, USA), and calcined at 550 °C for 6 hours to get the corresponding H-zeolites. Sn-DeAl-Beta was prepared as previously described [1]: Briefly, the acidic form of Beta (12.5) zeolite was dealuminated at 100 °C for 16 hours with 13 M HNO_3 (20 ml/g of zeolite). The resultant dealuminated Beta zeolite (DeAl-Beta) was filtered off, washed with de-ionised water until the pH of the filtrate was neutral, and dried at 120 °C overnight. The dried DeAl-Beta was thoroughly grinded with 0.4369 g of $SnCl_4{\cdot}5H_2O$ (98%, Sigma-Aldrich) per gram catalyst for 15 min and calcined at 550 °C for 6 hours (ramp of 2.3°C/min) in order to get Sn incorporated DeAl-Beta (Sn-DeAl-Beta).

Catalyst characterization

X-Ray Powder Diffraction (XRPD)

The powder X-ray diffraction analyses for Beta and USY zeolite samples were performed on a Guber G670 using CuKα radiation at a wavelength of 0.15406. The diffractograms were recorded for the all samples in the 2θ range of 3 to 100º at the rate of 1.5 º/min. The obtained diffractograms are shown in Figure S1 and S2.

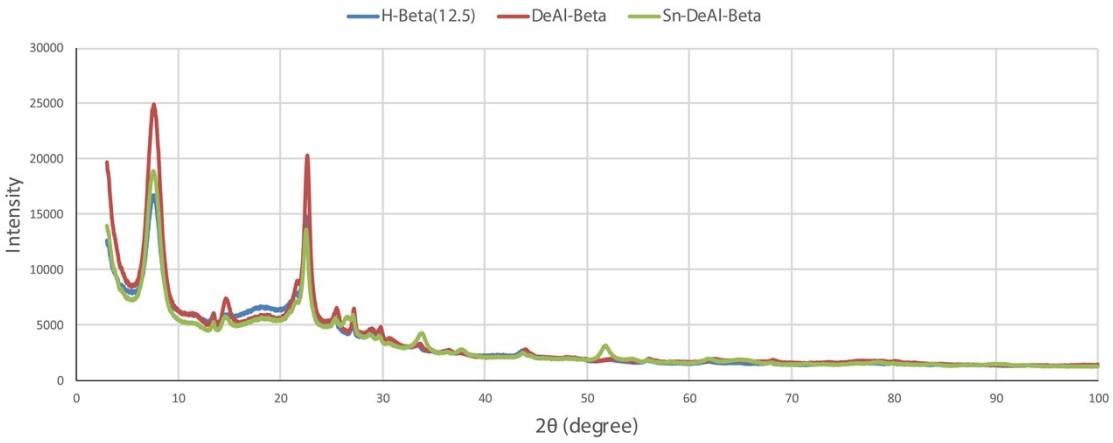


Figure S1. The powder XRD patterns of H-beta (12.5) and modified H-beta zeolites.

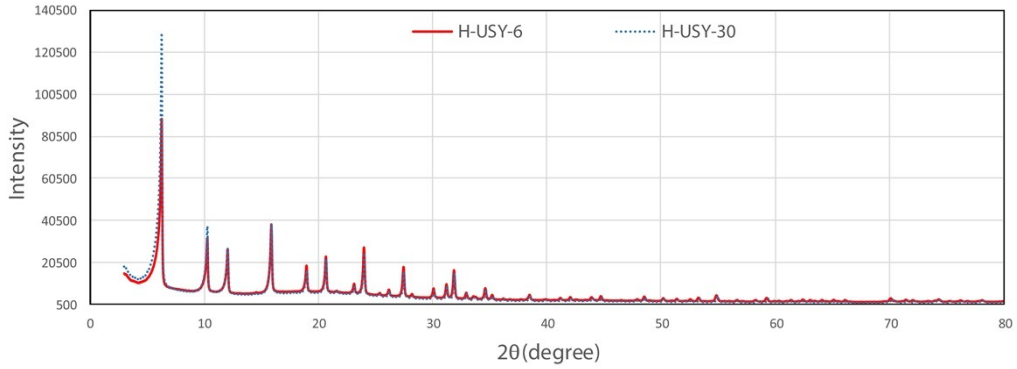


Figure S2. The powder XRD patterns of USY zeolites.

NH_3-Temperature Programmed Desorption (TPD)

The amount of available acid sites on Beta and USY zeolites were measured by NH_3-TPD using an AutoChem II 2920 from Micromeritics. Approximately 100 mg sample was placed in a quartz U-tube reactor and degassed at 500 °C for 1 hour under flow of helium (50 mL/min), and cooled down to 100 °C. Ammonia (50 mL/min) was then passed through to the sample holder at 100 °C for 2 hours. The sample was flushed with He (50 mL/min) prior to ammonia desorption in order to remove any physisorbed NH_3. Ammonia desorption was performed and measured every second from 100 to 500 °C at a ramp of 10 °C/min, and the number of acid sites calculated as the area under the desorption curve. The amount of medium (desorption approx. between 100-270 °C) and strong acid sites (desorption approx. between 270-500 °C) were calculated from the desorption area under the curve.

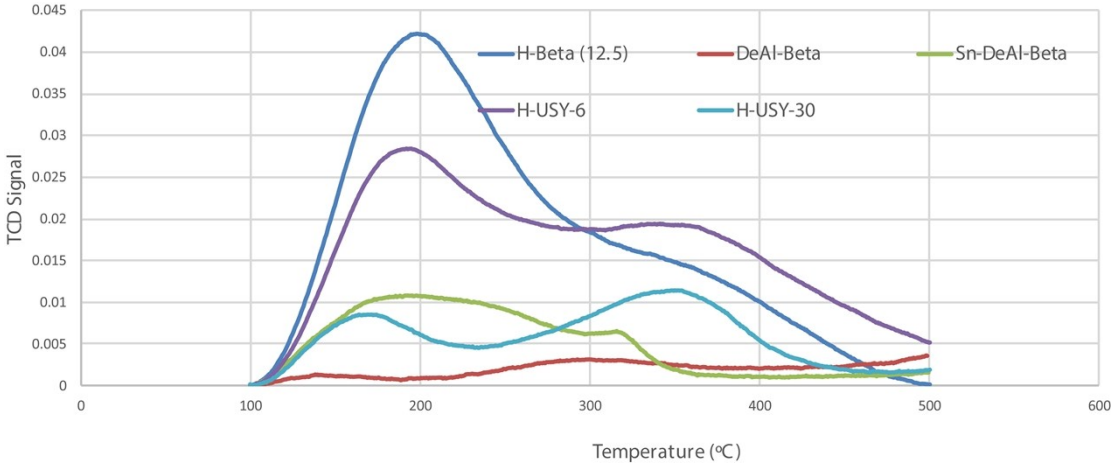


Figure S3. NH_3-TPD profiles of Beta and USY zeolites

N_2-Sorption measurement

Brunauer-Emmet-Teller (BET) surface areas and pore volumes were analysed by nitrogen adsorption and desorption measurements using a Micromeritics ASAP 2020 at liquid nitrogen temperature. The samples were degassed at 300°C overnight prior to the measurement, except for the acid-dealuminated Beta zeolite (DeAl-Beta) that was degassed at 90°C.

Table S1. Physico-chemical properties of USY and Beta zeolites.

Catalyst	Si/Al ratio	BET area (m^2/g)	Pore volume (cm^3/g)	Acid sites type 1 (100-270 °C) (µmol/g)	Acid sites type 2 (270-500 °C) (µmol/g)	Total acid sites (µmol/g)
H-USY	6	708	0.2436	488	539	1027
H-USY	30	792	0.2504	140	226	366
H-Beta	12.5	579	0.1631	693	395	1088
DeAl-Beta	-	526	0.1492	28	91	119
SnDeAl-Beta	12.5	492	0.1446	196	95	291

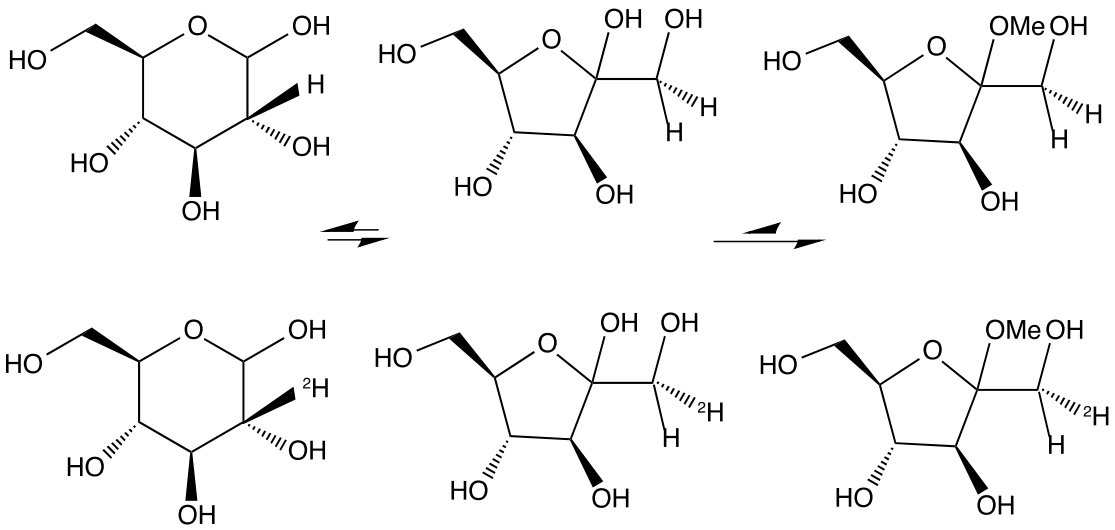
Catalytic experiments

Experiments using [2-^{2}H]-glucose were run in Ace pressure tubes with a capacity of 15 ml. Reaction mixtures containing 125 mg of glucose, 75 mg of the respective catalyst and 4 g of methanol were placed in the tubes and immersed in an oil bath preheated to the reaction temperature of 120 °C. Samples were reacted for 1 hour under stirring (700 rpm). Afterwards, the tubes were cooled with water and the catalysts filtered off. The recovered filtrates were evaporated to remove methanol and the residues were re-dissolved in identical amounts of MeOH-d_4 and subjected to ^{1}H-^{13}C HSQC NMR analysis. After establishing the stereoselectivity of the hydride shift in protonated methanol, reactions using $AlCl_3$. $6H_2O$, H-USY (30) and Sn-Beta were carried out in deuterated methanol using [2-^{2}H]-glucose and the reaction setup described above, prior to HSQC NMR analysis. Determinations of kinetic isotope effects were conducted in a reaction mixture containing equimolar amounts of protonated glucose and [2-^{2}H]-glucose. Samples were withdrawn from the reaction mixture after 0.5, 1, 2 and 24 hours, respectively.

NMR spectroscopy

HSQC NMR analysis was conducted on a Bruker (Fällanden, Switzerland) Avance II 800 MHz spectrometer equipped with an Oxford (UK) Magnet and a TCI z-gradient cryoprobe at 298 K. HSQC spectra were recorded by sampling 1024 and 256 complex data points in the ^{1}H and ^{13}C dimensions, corresponding to acquisition times of 160 and 43 milliseconds, respectively. No deuterium decoupling was applied to facilitate unambiguous identification of deuterated species as described in the main text. Analytes were identified by comparison of sufficiently resolved ^{1}H-^{13}C HSQC spectra to corresponding HSQC spectra of glucose, mannose and fructose reference standards and their methyl-glycoside variants formed upon gentle heating in the presence of 0.1% H_2SO_4 inside 5 mm NMR tubes.

All NMR spectra were acquired, processed with extensive zero filling in both dimensions, and integrated in Bruker Topspin 2.1. Kinetic isotope effects were obtained through fits of reaction progress curves conducted in ProFit 6.2.9 (QuantumSoft, Uetikon, Switzerland).



Scheme S1. Schematic overview of the concurrent use of protonated (top) and [2-^{2}H] (bottom) glucose for determining the kinetic H/D isotope effect on isomerisation to fructosides in single samples using high-resolution HSQCs that resolve different resultant fructose isotopomers.

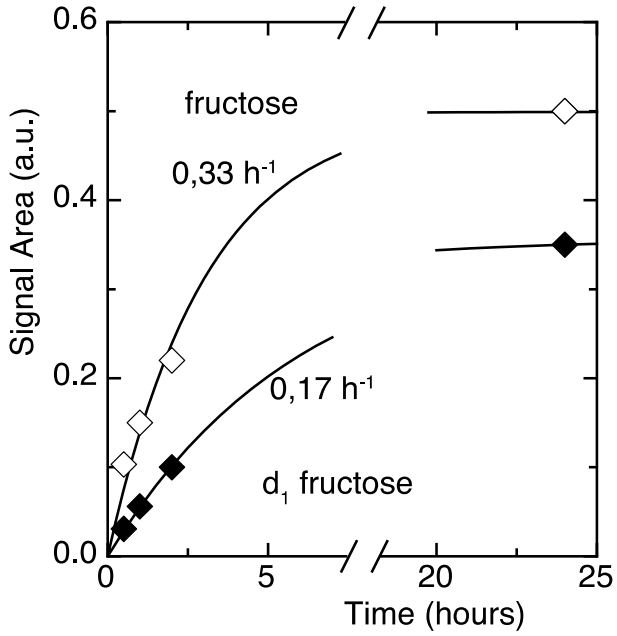


Figure S4. Kinetic profiles for the determination of the kinetic isotope effect in the isomerisation of natural abundance glucose and [2-^{2}H] glucose in methanol at 120°C using Sn-DeAl-Beta. The lower rate using Sn-DeAl-Beta as compared to H-USY (6) (main text Figure 3) is consistent with the 2.5-fold lower number of acid sites of type 1 (Table S1). Assuming that the acid sites of type 1 form the majority of Lewis acid sites responsible for isomerization, the site-normalised acitivity would be 49% higher in Sn-DeAl-Beta than in H-USY (6).

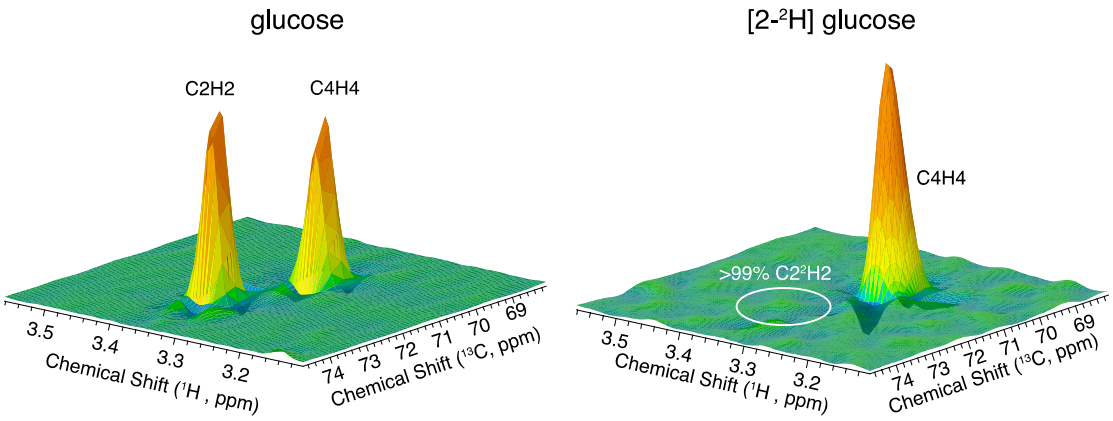


Figure S5. HSQC spectral regions of C2H2 and C4H4 in glucose and [2-^{2}H] glucose (see Scheme S1 above, bottom panel), showing – upon integration – a degree of deuteration >99% for [2-^{2}H] glucose. This high degree of deuteration at the C2 position, which in consequence does not yield a CH signal in the HSQC displayed to the right, underlines that the almost 5% fructose that are fully protonated at C1 result from protonation by the solvent rather than hydride transfer from a C2-protonated glucose impurity.

References

1. C. Hammond, S. Conrod and I. Hermans, Angew. Chem. Int. Ed., 2012, **51**, 11736.