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Facile and benign conversion of sucrose to fructose using zeolites with balanced Brønsted and Lewis acidity†

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

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Sucrose is by far the industrially most abundant simple carbohydrate with a production volume of more than 160 million metric tons from sugar cane and sugar beet per year. Many promising pathways towards bio-based organic compounds use, however, fructose as the pathway substrate. Hence, a chemocatalytic approach to convert sucrose into fructose would provide a means to channel sucrose into pathways for sugar valorization. Here, we show that a variety of heterogeneous zeolite catalysts with balanced Brønsted and Lewis acidity enable a simple route for the conversion of sucrose to more than 80% fructosides or fructose at 100 °C. The catalysts can encompass aluminium or tin Lewis acidic sites in various zeolite frameworks. The reaction proceeds in volatile alcohol solvents and broadly enables the channelling of sucrose into processes that use fructose as the pathway substrate.

Introduction

Carbohydrates constitute the predominant fraction of annually renewable biomass, mostly in the form of structural polysaccharides, storage polysaccharides or simple carbohydrates.[1] Among the simple carbohydrates, the disaccharide sucrose (α-D-glucopyranosyl-(1→2)-β-D-fructofuranoside) refined from sugar beet or sugar cane has particular relevance, reaching global production volumes of more than 160 million metric tons per year, orders of magnitude higher than worldwide glucose and fructose production.[1,2]

While its use as a chemical feedstock has remained limited, sucrose as the most abundant simple carbohydrate is poised to play a role as a substrate for the production of organic compounds from renewable biomass.[3,4] So far, fructose has played a central role as the entry point for molecular pathways leading to bio-based chemicals and fuels due to the higher reactivity of fructose relative to glucose.[5] These pathways often involve dehydration of the furanose form or dehydration and retro-aldol reactions of the open-chain form to products such as 5-hydroxymethylfurfural (HMF), levulinic acid, lactic acid or unsaturated α-hydroxy esters.[4–7] Both furanose and acyclic forms are orders of magnitude more highly populated in fructose solutions than in glucose solutions. Accordingly, chemocatalytic glucose-to-fructose isomerization procedures have been devised using Lewis acidic zeolite catalysts that also exhibit activity in carbohydrate dehydration and cleavage.[4,8,9] These Lewis acidic zeolite catalysts exhibit strongly improved stability in short-chain alcohols such as methanol, if compared to water.[9] In addition, the use of alcohols in glucose-to-fructose isomerization has been proven beneficial due to the fast sequestration of the formed fructose as fructosides.[10,11] Hence, the use of methanol in glucose-to-fructose isomerization permits the formation of fructosides in amounts near 60% from glucose, higher than the equilibrium distribution of 42% fructose (50% glucose, 8% other sugars, especially mannose) attainable in water.[11,12] Glucose-to-fructose isomerization has been shown to proceed by a stereoselective 1,2-hydride shift in the acyclic form in methanol when aluminium- and tin-containing zeolite catalysts were used.[10] This reaction mechanistically resembles the enzymatic glucose-to-fructose isomerization by xylose isomerase.

Sucrose is a non-reducing carbohydrate that does not lend itself directly to biomass conversion reactions occurring in the open-chain form. Accordingly, sucrose has been considered stable in isomerization reactions using Lewis acidic zeolites under mild reaction conditions (near 100 °C) in water.[13] Sucrose is, however, easily hydrolysed by Brønsted acids, but the instability of fructose under usual process conditions employing homogeneous Brønsted acids for biomass hydrolysis poses a potential problem for fructose production by such

[a] Department of Chemistry, Technical University of Denmark, Kemitorvet, 2800-Kgs. Lyngby, Denmark. E-mail: semei@kemi.dtu.dk, ar@kemi.dtu.dk
[b] Center of Innovative and Applied Bioprocessing (CIAB), Mohali 140 306, Punjab, India
[c] Haldor Topsøe A/S, Haldor Topsøes Allé 1, 2800-Kgs. Lyngby, Denmark

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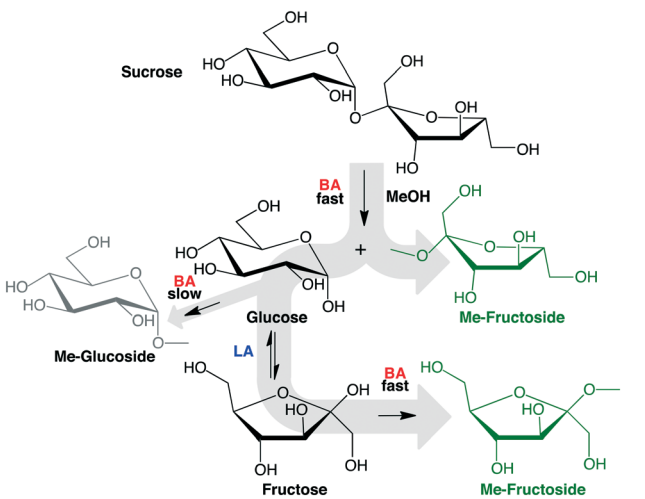
‡ These authors contributed equally.

processes. In contrast, this instability of fructose has permitted sucrose to be used as a substrate for the conversion by Lewis acid-containing materials to downstream products of fructose such as furanics, levulinic acid, lactic acid or unsaturated α-hydroxy esters at higher temperatures (near 160 °C).[4,14–16]

In the current study, we hypothesised that Al-zeolites with balanced Brønsted and weak Lewis acidic sites would be well-suited catalysts for the efficient conversion of sucrose to fructose. Sufficient Brønsted acidity should permit solvolysis of sucrose to methyl-fructoside and glucose in methanol. In the presence of weak Lewis acidic sites, isomerization of the formed glucose to fructose and its sequestration as fructosides should ensue without significant fructose degradation at moderate temperature in the absence of strong Lewis acidic sites (Scheme 1). The α-Glc(1→2)β-Fru glycosidic bond is notoriously labile as compared to other glycosidic bonds abundant in biomass. Thus, this glycosidic bond in sucrose has been reported to hydrolyze more than an order of magnitude faster than the α-Glc(1→3)Fru glycosidic bond in turanose and the α-Glc(1→5)Fru glycosidic bond in leucrose at temperatures below 180 °C.[17] Glycosidic bonds between two glucose units are even less easily hydrolysed than those in turanose and leucrose.[17] The susceptibility of sucrose to hydrolysis was shown in the presence of various dealuminated zeolites in their protonated forms[15,18] or of mesoporous aluminas of the TUD-1 structure.[14]

Here, we show that a simple process using a commercial aluminium-containing zeolite H-USY (6) in a two-step procedure fulfils this scenario. The two steps encompass (1) sucrose solvolysis and fructoside formation to levels exceeding 80% at 100 °C in methanol, followed by (2) quantitative hydrolysis of the fructosides in water at 100 °C using the same catalyst, yielding >80% fructose from sucrose (Fig. 1). The process avoids significant formation of mannose, sorbose and other carbohydrates reported for different process conditions employing zeolite-catalysed catalysis[19,20] and operates in volatile solvents. Thus, the process described in Fig. 1 can provide a facile entry point for sucrose into processes converting fructose to organic compounds.



Scheme 1 Schematic overview over the rationale behind the conversion of sucrose to fructose using heterogeneous catalysts with balanced Brønsted (BA) and Lewis acidity (LA). Brønsted acidity sequesters the fructose unit of sucrose as a fructoside, while sufficient Lewis acidity will isomerize the liberated glucose to fructose that is rapidly sequestered as a fructoside again. In the presence of sufficient Lewis acidity, glucoside formation is only a side reaction due to the slower formation of glucosides than that of fructosides.

Experimental

Materials

Sucrose (99.5%), methanol (99.8%, anhydrous), methanol-d_4 (99.8%), nitric acid (≥65%), tin(IV) chloride pentahydrate (98%) and Amberlyst 36 were obtained from Sigma-Aldrich. The ammonium forms of zeolites Beta (Si/Al ratio of 12.5), USY (Si/Al ratio of 6) and USY (Si/Al ratio of 30) were obtained from Zeolyst International. Commercial zeolites were calcined prior to use at 550 °C for 6 h to convert them into their H-forms. USY catalysts were used in these forms as H-USY (6) and H-USY (30). Beta zeolites were additionally modified by dealumination and by post-synthetic incorporation of tin atoms into a dealuminated Beta zeolite (Sn-DeAl-Beta).

Catalyst preparation

Sn-DeAl-Beta and DeAl-Beta zeolites were prepared following previously described procedures.[21] 1 g of H-Beta (Si/Al = 12.5, verified experimentally) was refluxed in 25 mL of nitric acid (13 M) at 100 °C overnight under magnetic stirring. The mixture was then cooled and filtered, and the DeAl-Beta was washed with distilled water until the filtrate reached neutral pH before finally drying at 120 °C overnight (resulting in a zeolite with a Si/Al ratio above 140). For the preparation of Sn-DeAl-Beta, Sn was incorporated by solid-state ion-exchange (SSIE). To this end, 1 g of DeAl-Beta zeolite was ground with 437 mg of tin(IV) chloride pentahydrate for 15 min and calcined at 550 °C for 6 h. Experimental determination yielded a Si/Sn ratio of 15.6 and a Si/Al ratio above 140 for this catalyst (see Table S1†). Thermally dealuminated H-Beta (DeAl-Beta-

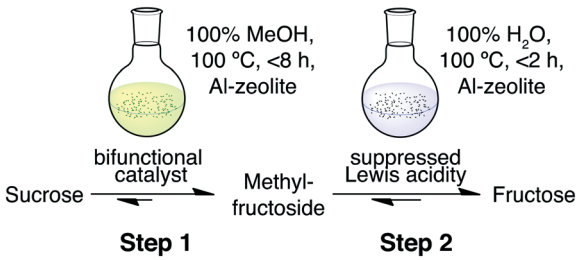


Fig. 1 Two-step conversion of sucrose to fructose under mild conditions (100 °C). Subsequent fructoside formation and hydrolysis can be achieved with the same catalyst, if (1) sufficient Brønsted and Lewis acidic sites are present and (2) the activity isomerizing glucose and fructose is suppressed by the presence of water in step 2 to allow full recovery of fructosides as fructose.

750) was obtained by treating the H-Beta (12.5) at 750 °C for 6 h in static air.

General procedure for catalytic experiments

Catalytic experiments were carried out in 15 mL Ace pressure tubes. In a typical reaction, 125 mg of sucrose, 75 mg of catalyst and 4 g of methanol were kept under magnetic stirring at 100 °C for up to 8 h. After this first step, the tubes were cooled in water, and a sample was collected and analysed after filtration of the heterogeneous catalyst. In the second step, 4 g of water was added and the mixture was reacted at 100 °C for up to 4 h. Optimal results were obtained by evaporating the methanol after the first step. Samples at different times were analysed by ^{1}H–^{13}C HSQC NMR.

NMR spectroscopy

^{1}H–^{13}C HSQC spectra of reaction mixtures were recorded on Bruker Avance III 600 and Bruker Avance III 800 MHz spectrometers at 25 °C, after addition of methanol-d_4 (10% (v/v)) for deuterium locking. The 600 MHz instrument was equipped with a BBO smart probe, while the 800 MHz instrument was equipped with a TCI CryoProbe. The ^{1}H–^{13}C HSQC spectra had a carrier offset of 62 ppm and a spectral width in the ^{13}C dimension of 30 ppm. The spectra acquired using the 600 MHz instrument were recorded as data matrices of 1024 × 256 complex data points sampling the NMR signal for 213 and 56 ms in the ^{1}H and ^{13}C dimensions, respectively. The spectra obtained using the 800 MHz instrument were recorded as data matrices of 1024 × 256 complex points sampling the NMR signal for 142 and 33 ms in the ^{1}H and ^{13}C dimensions, respectively. Bi-level ^{13}C decoupling was applied to avoid decoupling artefacts due to the strong methanol signal in the HSQC spectra. The HSQC spectra had sufficient resolution to baseline separate carbohydrates of interest. All spectra were processed after extensive zero filling in both dimensions using a shifted squared sine-bell apodisation function and integrated in Topspin 3.5. Areas of sucrose signal decay shown in Fig. 2 were fitted to exponential decays using pro Fit 6.2.9 (Quantumsoft, Zurich, Switzerland) to derive the pseudo-first-order rate constants of sucrose methanolysis.

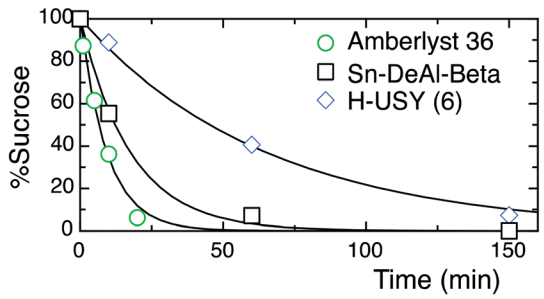


Fig. 2 Kinetics of sucrose methanolysis catalysed by various heterogeneous catalysts at 100 °C (4 g methanol, 75 mg catalyst and 125 mg sucrose).

Results and discussion

Sucrose solvolysis in methanol by heterogeneous catalysts

Efficient sucrose solvolysis by short-chain alcohols is the entry point to the reaction sequence depicted in Scheme 1. Hence, we evaluated the viability of heterogeneous catalysts in catalysing this first step of sucrose utilization under conditions that avoid further degradation of the liberated fructose and fructosides to downstream chemicals. Reactions catalysed by the Brønsted acidic resin Amberlyst 36 (a sulfonic acid ion-exchange resin developed for heterogeneous catalysis) and various zeolites, a popular group of mineral catalysts with nano-sized pores and tunable acid properties, were monitored at 100 °C. The reaction mixtures were analysed *ex situ* by NMR spectroscopy on the non-purified mixtures in protonated methanol in order to obtain unbiased high-resolution assays of the substrate and product signals, without the need to account for protocol-dependent calibration, retention, identification or recovery. ^{1}H–^{13}C HSQC spectra were adequately tailored to provide high resolution for the identification and quantification of carbohydrates and glycosides and to avoid spectral interference from the protonated alcohol background. Reference standards were used to validate identical responses of sucrose, glucose and fructose in HSQC spectroscopy due to the similar scalar couplings and NMR relaxation properties of their primary alcohol groups, used for quantification.[22]

Resultant data for the solvolysis of sucrose in methanol using 75 mg of Brønsted acidic and mixed Lewis/Brønsted acidic catalysts are shown in Fig. 2. Reaction curves are reasonably well approximated by pseudo-first-order kinetics with the H^{+}, methanol and catalyst concentrations constant during the reaction and the catalyst active sites not saturated by sucrose. The Amberlyst 36 resin hydrolyses sucrose with a rate constant of 0.10 min^{-1}. An equivalent amount of a high-defect Sn-Beta zeolite that was prepared *via* post-synthetic incorporation of tin atoms into a dealuminated Beta zeolite (Sn-DeAl-Beta) led to only slightly lower methanolysis of sucrose with a rate constant of 0.06 min^{-1}. A commercial aluminium-containing H-USY catalyst with a Si/Al molar ratio of 6 (H-USY (6)) led to slower methanolysis at 100 °C with a rate of 0.02 min^{-1} when using the same mass of catalyst. All of these catalysts thus provide sufficient Brønsted acidity to warrant near-complete methanolysis of 125 mg sucrose in 4 g methanol within 150 minutes at 100 °C (Fig. 2) using 75 mg catalyst.

Interplay of Lewis and Brønsted acidity in sucrose conversion to fructosides

Reaction progress curves were subsequently derived by integration of product signals with a focus on glucose, glucosides, fructose and fructosides. ^{1}H–^{13}C HSQC spectra as recorded herein on high-field (800 MHz) NMR instrumentation resolve all anomeric aldose and ketose forms (α/β anomers and pyranose/furanose forms) as well as their corresponding glycosides. In addition, NMR instrumentation

with a cryogenically cooled detection probe was used to warrant sufficient signal-to-noise ratios for reliable quantification even of minor reaction products. The resultant reaction progress curves are shown in Fig. 3 for the conversion of sucrose in methanol by Amberlyst 36, Sn-DeAl-Beta and H-USY (6).

The strongly Brønsted acidic Amberlyst 36 catalyst liberates methyl-fructoside and glucose as the principal products upon methanolysis of sucrose, as expected. Glucose is subsequently converted to methyl-glucoside, while no isomerization occurs in the absence of Lewis acidity. Methyl fructoside formation experiences a maximum as degradation products such as derivatives of levulinic acid appear, while methyl-glucosides are considerably more stable than their fructose counterparts (Fig. 3, top).

The interplay of Lewis and Brønsted acidic sites in the conversion of sucrose to fructosides was tracked using bifunctional Sn- and Al-containing zeolites. The post-synthetic Sn-DeAl-Beta catalyst exhibited rapid formation of methyl-fructosides with yields above 80% (Fig. 3, middle and Table 1). In contrast to the Amberlyst 36-catalysed reaction, where glucose accumulates prior to the slow conversion to methyl-glucosides, glucose only accumulates to lower levels using Sn-Beta. Here, a competing faster isomerization reaction to fructose occurs prior to the sequestration also of fructose derived from the glucopyranosyl unit of sucrose as fructosides. Fructose only accumulates to a minor degree, and its kinetic profile parallels that of glucose formation, as free fructose derives from glucose isomerization (Scheme 1). Also for the Sn-DeAl-Beta zeolite, fructoside formation exhibits a maximum before further degradation sets in, even at only 100 °C. By-products include α-hydroxy acids such as methyl lactate,[4] *trans*-2,5,6-trihydroxy-3-hexenoic acid methyl ester and 3-deoxy-γ-lactones,[6] reaching quantities of 1–3% within 5 h of reaction.

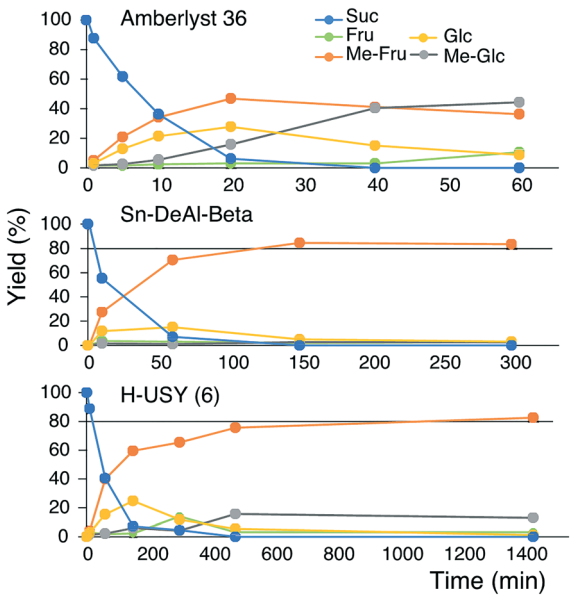


Fig. 3 Reaction progress curves for conversion as well as monosaccharide and glycoside formation by a Brønsted acid resin, a Sn-DeAl-Beta zeolite containing defects from the dealumination procedure and an Al-containing H-USY (6) zeolite at 100 °C (4 g methanol, 75 mg catalyst and 125 mg sucrose).

Table 1 Sucrose conversion to monosaccharides after step 1 using Sn-DeAl-Beta[a]

Time (min)	Conv. (%)	Fru (%)	Me-Fru (%)	Glc (%)	Me-Glc (%)
60	92.9	3.0	70.6	15.0	1.1
150	99.9	2.1	84.7	5.0	2.7
300	>99.9	2.8	83.7	3.1	2.7

[a] Reaction conditions: 4 g methanol, 75 mg Sn-DeAl-Beta, 125 mg sucrose, 100 °C. Minor carbon losses resulting in deviation of the sum from 100% are due to the formation of retro-aldol and dehydration products alongside mannoside and sorboside formation.

The kinetics of methyl-fructoside formation with aluminium-containing H-USY (6) resembles the kinetics for post-synthetic Sn-DeAl-Beta, albeit with slower overall reaction progress (Fig. 3, bottom). Like for Sn-DeAl-Beta, methyl-fructosides can be obtained with a yield of more than 80% on a monomer basis at similar conversion. This finding is consistent with the formation of approximately 60% methyl-fructoside from glucose in previous studies using H-USY (6).[11,12] The fructose moiety of sucrose can be expected to convert quantitatively into methyl-fructoside, while 60% of the liberated glucose then isomerizes to fructose and get stabilised as methyl-fructosides.

Suitability of various zeolites for sucrose conversion to fructoside

The formation of fructosides at a yield of above 75% on a monomer basis from sucrose is a feature that is found for a variety of zeolites containing Lewis and Brønsted acidic sites, including H-Beta and Beta zeolites that are partly dealuminated (thermally modified DeAl-Beta (750)) (Fig. 4). Such rapid formation of methyl-fructosides in high yield from sucrose, fructose and glucose by Lewis acid-containing zeolites at moderate temperatures hints at a general, central role of fructoside formation and hydrolysis in carbohydrate conversion by zeolites in alcohols. Accumulation of fructosides beyond a fraction expected for free equilibration of glucose, fructose and mannose is the consequence of more rapid fructoside formation as compared to glucoside and mannoside formation. Mannosides account for only ~1% of the reaction products formed from sucrose, again as a consequence of rapid fructose sequestration, prior to back-isomerization to glucose and mannose.[20] Minor mannoside formation is consistent with previous findings for alkali-free Sn-Beta used for isomerization in methanol under similar conditions. Likewise, sorbosides account for less than 2% of the reaction products due to minor isomerization of glucose to sorbose.[19]

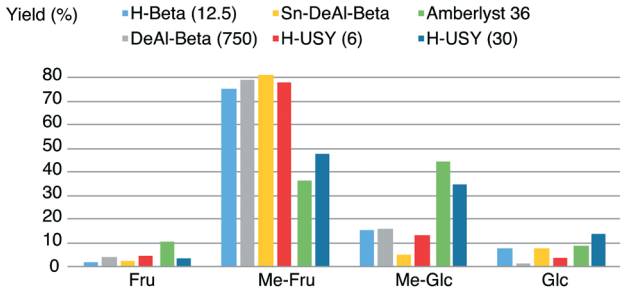


Fig. 4 Yields of the monosaccharides fructose, methyl-fructoside, glucose and methyl-glucoside after conversion of sucrose in step 1 using various catalysts at 100 °C (4 g methanol, 75 mg of catalyst and 125 mg sucrose). Yields are given after 8 h of reaction, except for Amberlyst 36 where yields are given after 1 h as further degradation ensues.

Formation of fructosides in high yield from sucrose in methanol at 100 °C is not observed for catalysts with insufficient Lewis acidity, as exemplified by the H-USY (30) and Amberlyst catalysts. Instead, these catalysts led to the accumulation of higher levels of methyl-glucoside (Fig. 4). The finding of insufficient Lewis acidity in H-USY (30) for efficient glucose isomerization is consistent with findings in previous assays using the glucose substrate, and with NH_3-TPD measurements yielding only 347 μmol total acid sites per gram catalyst as compared to 835 μmol total acid sites per gram H-USY (6).[23]

Fructose formation in a two-step reaction

Fructose can be quantitatively recovered from fructosides by hydrolysis in water. This reaction can be directly performed on the reaction mixture in step 1 including the catalyst in step 1 upon addition of water or preferably by evaporation of the alcohol and hydrolysis in pure water. An undesired equilibration between fructose, glucose and mannose upon fructoside hydrolysis requires that the catalyst acting in the hydrolysis does not catalyse sugar isomerization in aqueous solution, or only at rates that are much slower than rates of glycoside hydrolysis. In aluminium-containing zeolites, Lewis acidity is masked in aqueous solutions in contrast to Sn-Beta.[10,12,23,24] Sn-Beta retains its ability to catalyse hydride shifts and thus isomerization between the C1 and C2 positions of glucose/mannose and fructose, respectively, in aqueous solution.[24] As a consequence, Sn-DeAl-Beta exhibits an optimum time for fructose formation in step 2, subsequent to which fructose yields drop due to Lewis acid-catalysed isomerization in water. In contrast, fructose formation catalyzed by H-USY (6) in sequential two-step isomerization of sucrose to fructosides in alcohol and hydrolysis in aqueous solution yields stable product mixtures (Fig. 5). For both Sn-DeAl-Beta and H-USY (6), maximum fructose yields on the order of 80% can be obtained due to quantitative fructoside hydrolysis in step 2 (Fig. 5).

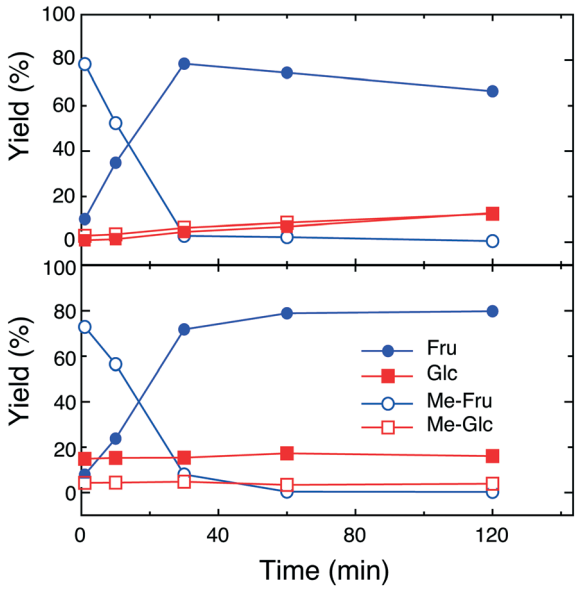


Fig. 5 Reaction progress in step 2, after exchanging the methanol solvent to 100% water, using Sn-DeAl-Beta (top) or H-USY (6) (bottom) as catalysts at 100 °C (4 g methanol, 75 mg catalyst and 125 mg sucrose).

Fructoside formation in methanol (step 1, Fig. 3) and the subsequent hydrolysis to fructose using Sn-DeAl-Beta and H-USY (6) (step 2, Fig. 5) were visualised and quantified using the ^{1}H–^{13}C HSQC NMR spectra as displayed in Fig. 6. Reactions were carried out by allowing methanolysis and

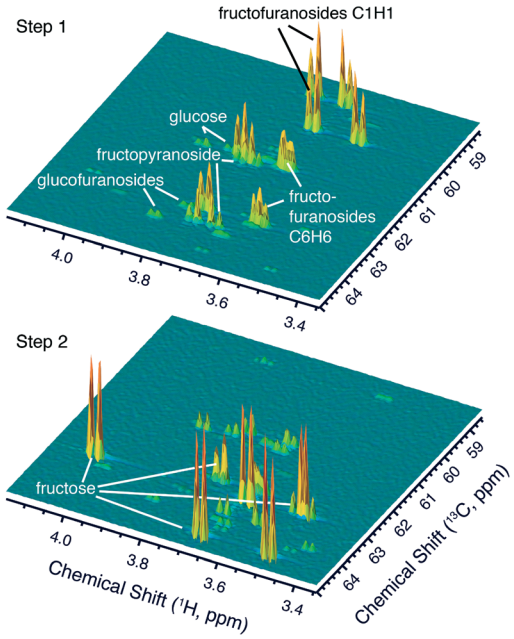


Fig. 6 ^{1}H–^{13}C NMR spectral region of primary alcohol signals (C1 in aldohexoses, C1 and C6 in ketohexoses) after subjecting sucrose to H-USY (6)-catalysed reaction steps 1 yielding predominantly fructoside isomers (top) and 2 yielding predominantly fructose (bottom) at 100 °C (4 g methanol, 75 mg catalyst and 125 mg sucrose). Fructosides were quantitatively hydrolysed in step 2 after 4 h.

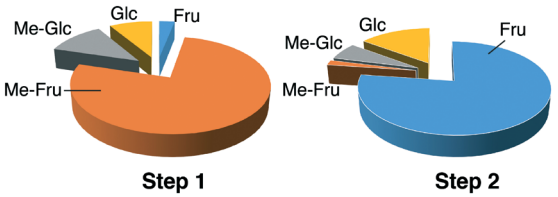


Fig. 7 NMR quantification of the fructose, fructoside, glucose and glucoside content in the samples shown in Fig. 6, obtained by subjecting sucrose to an H-USY (6)-catalysed reaction at 100 °C (4 g methanol, 75 mg catalyst and 125 mg sucrose).

isomerization for 8 h at 100 °C in methanol, followed by hydrolysis at 100 °C using the same catalyst. Resultant spectra show the predominant formation of fructosides, primarily fructofuranosides, with glucose and glucofuranosides as the main by-products. The prevalence of furanosides shows that glycoside formation occurs under kinetic reaction control at 100 °C on a short timescale as expected.[11]

Hydrolysis in step 2 quantitatively eliminates fructoside signals due to the quantitative conversion of these fructosides to fructose. In contrast, glucofuranosides are not quantitatively hydrolysed to glucose at 100 °C. This finding is consistent with the higher stability of acetals formed by glucose than of fructosides, as observed for instance in the slower hydrolysis of glycosidic bonds to the anomeric carbon of glucose in disaccharides and the faster hydrolysis of glycosidic bonds to the anomeric carbon of fructose.[17] The resulting distribution of glucose and fructose as well as their methyl acetals is displayed for a representative reaction in Fig. 7 (using data from the experiments displayed in Fig. 6). Quantification of the NMR signals gives a final yield of above 78% fructose, 1% fructoside, 16% glucose and 4% glucoside after step 2 using a reaction mixture obtained after step 1 with 3% fructose, 78% fructoside, 4% glucose and 15% glucoside.

Catalyst reusability was assessed for H-USY (6) in the reaction sequence with standard amounts of the reactant and catalyst but at elevated temperature (120 °C). No significant change in terms of fructose yield was observed during reuse and the fructose yield remained around 70% in five consecutive reaction runs under these harsher conditions. Each cycle of use consisted of filtration of the catalyst, extensive washing with water and drying at 140 °C overnight. Results for catalyst reuse are shown in the ESI† (Fig. S4), indicating that the system is suitable for reuse, consistent with previous results for H-USY (6) reuse in a two-step process in methanol/water.[12] We finally note that the designed catalysts with balanced Brønsted or Lewis acidity in a broader perspective hold promise for applications in the conversion of abundant substrates to rare tautomers. This prospect was exemplified by converting galactose *ad hoc* to more than 62% tagatoside and tagatose within 2 hours at 100 °C (Fig. S6†). Tagatose is a sweetener with low calorie content and low effects on the blood glucose level; it is rare in nature.

Conclusions

We report a simple and robust two-step process with zeolites that converts the abundant disaccharide sucrose to the less abundant monosaccharide fructose with a yield around 80%. This reaction approach is important as sucrose is highly abundant and cheap, while fructose is the entry point for many biomass-conversion pathways under recent scrutiny. Direct quantitative tracking of reaction products by high-resolution NMR spectroscopy shows that at 100 °C, sucrose is converted to methyl-fructoside and glucose, followed by isomerization of glucose to fructose and more rapid trapping of fructose as fructosides than that of glucose as glucosides. Kinetic profiles indicate that both Sn- and Al-containing zeolites can produce fructosides in yields significantly above 80% in step 1, while quantitative hydrolysis of fructosides is achieved in step 2 when operated in pure water. The process can be performed under mild conditions, which leads to negligible degradation of fructosides to furanics or other by-products. Fructosides are considerably easier to make in step 1 and hydrolyze in step 2 than glucosides. As a consequence, fructosides are likely general early intermediates in the conversion of glucose and saccharides containing glucose units using zeolites in short-chain alcohols.

Acknowledgements

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Notes and references

1 F. W. Lichtenthaler, *Acc. Chem. Res.*, 2002, **35**, 728.
2 *Sugar: World Markets and Trade, United States Department of Agriculture*, https://apps.fas.usda.gov/psdonline/circulars/sugar.pdf (accessed March 2017).
3 S. Frenzel, S. Peters, T. Rose and M. Kunz, in *Sustainable Solutions for Modern Economies*, The Royal Society of Chemistry, 2009, pp. 264–299; Y. Qu, L. Li, Q. Wei, C. Huang, P. Oleskowicz-Popiel and J. Xu, *Sci. Rep.*, 2016, **6**, 26067.
4 M. S. Holm, S. Saravanamurugan and E. Taarning, *Science*, 2010, **328**, 602.
5 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754; H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597; B. M. Kabyemela, T. Adschiri, R. M. Malaluan and K. Arai, *Ind. Eng. Chem. Res.*, 1999, **38**, 2888.

6 S. Tolborg, S. Meier, I. Sadaba, S. G. Elliot, S. K. Kristensen, S. Saravanamurugan, A. Riisager, P. Fristrup, T. Skrydstrup and E. Taarning, *Green Chem.*, 2016, **18**, 3360.
7 S. G. Elliot, C. Andersen, S. Tolborg, S. Meier, I. Sadaba, A. E. Daugaard and E. Taarning, *RSC Adv.*, 2017, **7**, 985.
8 M. Moliner, Y. Roman-Leshkov and M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 6164.
9 S. Saravanamurugan and A. Riisager, *ChemCatChem*, 2013, **5**, 1754.
10 S. Saravanamurugan, A. Riisager, E. Taarning and S. Meier, *Chem. Commun.*, 2016, **52**, 12773.
11 S. Saravanamurugan, A. Riisager, E. Taarning and S. Meier, *ChemCatChem*, 2016, **8**, 3107.
12 S. Saravanamurugan, M. Paniagua, J. A. Melero and A. Riisager, *J. Am. Chem. Soc.*, 2013, **135**, 5246.
13 R. Gounder and M. E. Davis, *J. Catal.*, 2013, **308**, 176.
14 S. Lima, M. M. Antunes, A. Fernandes, M. Pillinger, M. F. Ribeiro and A. A. Valente, *Molecules*, 2010, **15**, 3863.
15 C. Moreau, R. Durand, C. Pourcheron and S. Razigade, *Ind. Crops Prod.*, 1994, **3**, 85.
16 S. Tolborg, S. Meier, S. Saravanamurugan, P. Fristrup, E. Taarning and I. Sadaba, *ChemSusChem*, 2016, **9**, 3054.
17 T. Oomori, S. H. Khajavi, Y. Kimura, S. Adachi and R. Matsuno, *Biochem. Eng. J.*, 2004, **18**, 143.
18 C. Buttersack and D. Laketic, *J. Mol. Catal.*, 1994, **94**, L283; C. Moreau, R. Durand, F. Aliès, M. Cotillon, T. Frutz and M.-A. Théoleyre, *Ind. Crops Prod.*, 2000, **11**, 237.
19 R. Gounder and M. E. Davis, *ACS Catal.*, 2013, **3**, 1469.
20 R. Bermejo-Deval, M. Orazov, R. Gounder, S.-J. Hwang and M. E. Davis, *ACS Catal.*, 2014, **4**, 2288.
21 C. Hammond, S. Conrad and I. Hermans, *Angew. Chem., Int. Ed.*, 2012, **51**, 11736.
22 M. Bojstrup, B. O. Petersen, S. R. Beeren, O. Hindsgaul and S. Meier, *Anal. Chem.*, 2013, **85**, 8802; B. O. Petersen, O. Hindsgaul and S. Meier, *Analyst*, 2014, **139**, 401.
23 R. M. West, M. S. Holm, S. Saravanamurugan, J. Xiong, Z. Beversdorf, E. Taarning and C. H. Christensen, *J. Catal.*, 2010, **269**, 122.
24 Y. Román-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis, *Angew. Chem., Int. Ed.*, 2010, **49**, 8954.

