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Review

Sn-Beta Catalyzed Transformations of Sugars—Advances in Catalyst and Applications

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Abstract: Beta zeolite modified with Sn in the framework (Sn-Beta) was synthesized and introduced as a heterogeneous catalyst for Baeyer–Villiger oxidations about twenty years ago. Since then, both syntheses strategies, characterization and understanding as well as applications with the material have developed significantly. Remarkably, Sn-Beta zeolite has been discovered to exhibit unprecedented high catalytic efficiency for the transformation of glucose to fructose (i.e., aldoses to ketoses) and lactic acid derivatives in both aqueous and alcoholic media, which has inspired an extensive interest to develop more facile and scalable syntheses routes and applications for sugars transformations. This review survey the progress made on both syntheses approaches of Sn-Beta and applications of the material within catalyzed transformations of sugar, including bottom-up and top-down syntheses and catalyzed isomerization, dehydration, and fragmentation of sugars.

Keywords: Sn-Beta zeolite; bottom-up/top-down syntheses; sugars transformations; isomerization; dehydration; fragmentation; furan and lactate derivatives



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1. Introduction

An ambition towards accomplishing carbon recycling and CO₂ neutrality drives the utilization of fossil fuel-based energy towards replacement with green sustainable technologies. However, existing infrastructures still require hydrocarbon compounds to produce a wide range of products and materials [1]. Lignocellulosic biomass is an abundant carbon-neutral resource which is frequently considered renewable base for the syntheses of sustainable chemicals, polymers, and fuels [2,3]. Sugars and derived polymers, such as glucose, xylose, sucrose and cellulose, are major constituents of lignocellulose (60–75 wt.%), which can be converted into 5-hydroxymethylfurfural (HMF), furfural (FF), levulinic acid, and other value-added chemicals through benign catalytic processes [4–7].

Zeolites (aluminum silicates) have unique material properties such as, e.g., open crystal frame structures, pore configuration, and high surface area [8]. These properties facilitate the adsorption and transportation of reactants in catalytic transformations, and especially Lewis acidic derived materials (often referred as zeotype materials) provide excellent performance as heterogeneous catalysts in many sugar transformation reactions [9,10]. In particular, the Davis group was the first to report in 2010 that framework Lewis acidic Sn sites in Sn-Beta exhibit high activity for glucose isomerization to fructose in aqueous media [11]. Concurrently, Taarning and coworkers further discovered that Sn-Beta facilitated be conversion of sugars to lactic acid derivatives with high efficiency [12].

In general, the methods for synthesizing Sn-Beta zeolite and the understanding of the material have made great progress in the past twenty years, which also has resulted in several new catalytic applications [13–18]. This review surveys such developments in syntheses strategies of Sn-Beta zeolite, including both bottom-up and top-down approaches

(Figure 1). In the timeline of developments, the introduction of fluoride-mediated synthesis of Sn-Beta was a milestone, and the Sn-Beta catalyzed glucose to fructose and lactate derivatives sparked renewed interest in its synthesis and applications. At the same time, nuclear magnetic resonance (NMR) spectroscopy has presented a powerful tool to provide useful information on Sn-Beta catalysis and reveal catalytically active sites and reaction mechanisms in the conversion of carbohydrates [19]. As a solid Lewis acid zeolite, the acidic properties of Sn-Beta have been well-described by the Román-Leshkov group [20,21]. On the other hand, the sugar transformations are essential for the development of biomass valorization, and recent advanced in Sn-Beta catalyzed isomerization, dehydration, and fragmentation of sugars are therefore also summarized in this review.

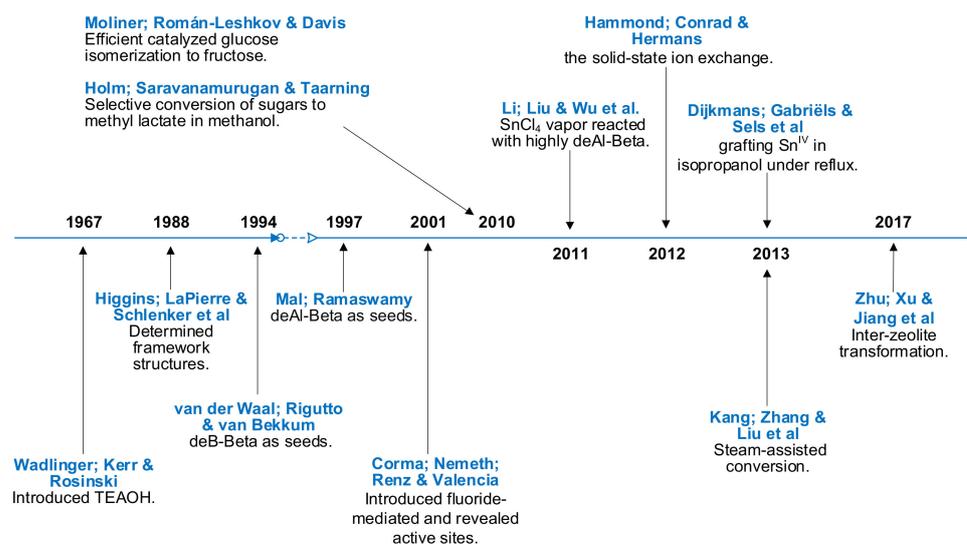


Figure 1. Developments in the synthesis strategies of Sn-Beta zeolite. Left to right: 1967 Ref. [22]; 1988 Ref. [23]; 1994 Ref. [24]; 1997 Ref. [25]; 2001 Ref. [26]; 2010 Refs. [11,12]; 2011 Ref. [27]; 2012 Ref. [28]; 2013 Ref. [29] (bottom); 2013 Ref. [30] (top); 2017 Ref. [31].

2. Syntheses of Beta Zeolite

The synthesis of unmodified high-silica Beta zeolite (Al-Beta) was firstly reported in 1967 by Wadlinger et al. from Mobil Oil Corp [22] using tetraethylammonium cations as template under hydrothermal treatment for 3 to 60 days. However, the structure of the zeolite remained unclear for a long time, and only in 1988 was the three-dimensional 12-ring framework structure determined by Higgins et al. [23] using a combination of model building, distance-least-squares refinement, and powder pattern simulation. Subsequently, van der Waal et al. [24] demonstrated in 1994 that gel seeds of boron-containing Beta (demetalized by acid treatment) could promote the synthesis of all-silica Beta zeolite.

2.1. Bottom-Up Approaches

2.1.1. Seed-Assisted Synthesis

Mal and Ramaswamy [25] were in 1997 the first to report the synthesis of large-pore Sn-Beta and Al-free Sn-Beta zeolites under hydrothermal conditions. The synthesis procedure followed a three-step route where Al/Sn-Beta zeolite (Si/Sn = 78.8, Si/Al = 28.5) was initially synthesized with the assistance of Al³⁺ ions in basic media (142 °C, 10 days). Then, the Al/Sn-Beta zeolite was refluxed in acid (110 °C, 3 h) to obtain dealuminated Sn-Beta zeolite (deAl-Sn-Beta; Si/Sn = 85.4, Si/Al > 3000), which was used as seeds to synthesize Al-lean Sn-Beta zeolite (Si/Sn = 54.5, Si/Al > 4000) with a moderate crystallinity of 87%. Although the Sn-Beta zeolite was successfully synthesized under the hydrothermal condition trace Al³⁺ in the framework structure easily forms Brønsted acidic sites, which can affect catalytic performance and product selectivity.

Corma et al. [26] introduced an alternative fluoride-mediated hydrothermal procedure (140 °C, 20 days) with assistance of highly dealuminated Beta zeolite seeds to synthesize highly crystalline and defect-free Sn-Beta (Si/Sn = 125, 1.6 wt.% Sn). The Sn-Beta zeolite exhibited efficient and stable catalytic performance for Baeyer-Villiger oxidations with the Sn sites acting as discrete and isolated Lewis sites, as revealed later by solid state ^{119}Sn magic angle spinning (MAS) NMR spectroscopy [26]. Isotope labeling experiments have also later confirmed the framework Sn in Sn-Beta zeolite to be tetrahedral coordinated in the dehydrated form, but octahedral coordinated with additional water molecules as ligands in aqueous solution [19,21]. Although the hydrothermally synthesized Sn-Beta by Corma et al. showed promising catalytic properties, the long crystallization time was a downside with respect to, e.g., reproducibility and scale-up. Therefore, to shorten the crystallization time Chang et al. [32] used uniformly distributed crystalline zeolite Beta seeds in the synthesis gel, which were prepared without drying and calcination during the synthesis and dealumination processes, respectively. Their modified procedure allowed obtaining high-crystallinity Sn-Beta with a significant reduction in crystallization time from 20 to 2 days. Considering the environmental issues of the introduced fluoride, Xu et al. used *N*-cyclohexyl-*N,N*-dimethylcyclohexaammonium hydroxide as the organic structure-directing agent (OSDA) to synthesize the Sn-Beta zeolite in F^- -free medium [33]. In this direct hydrothermal synthesis method, the Na^+ ions and pure Si-Beta seeds were critical for successfully synthesizing highly crystalline Sn-Beta zeolite. The composition and sources of precursor materials may also affect the hydrothermal synthesis of Sn-Beta, and some optimizations have also been performed in this respect. In the classical hydrothermal route, tetraethyl orthosilicate (TEOS) is used as a Si source which upon hydrolysis with water forms SiO_2 and ethanol. However, evaporation of the ethanol can be difficult to control accurately, which can result in differences in the $\text{H}_2\text{O}/\text{SiO}_2$ ratio in the synthesis gel and poor reproducibility of the procedure. To circumvent this issue, Zhou et al. [34] found both fumed silica and silica sol useful as silica sources instead of TEOS to successfully synthesize Sn-Beta. Both the crystallization behavior and the morphology as well as crystal size of the formed Sn-Beta was similar to the material synthesized from TEOS. However, the Sn-Beta obtained using silica sol had fewer silanol groups and the lowest ratio of open/closed Sn sites of the materials. Kang et al. [35] also studied fumed silica as the silica source and found that traces of Na^+ ions in the fumed silica accelerated nucleation resulting in shortened crystallization time.

In the crystallization process, the amount of water present is also important as this significantly affects the concentrations of both template and silica. Generally, studies have established lower ratios of $\text{H}_2\text{O}:\text{SiO}_2$ to favor the synthesis of Sn-Beta and dramatically reduce crystallization time, but lower ratios of $\text{H}_2\text{O}:\text{SiO}_2$ also lead to the formation of more extra-framework SnO_2 which usually is undesired for catalysis [36]. The amount and type of Sn source present in the synthesis gel can also greatly influence the crystallization of Sn-Beta. Tolborg et al. [37] even found that these parameters not only drastically affected the crystallization time, but also changed the morphology of the formed Sn-Beta crystals. Thus, increasing the amount of Sn during synthesis will demand longer crystallization time and result in Sn-Beta with reduced crystallinity.

2.1.2. Dry-Gel Conversion Techniques

To shorten the crystallization time during Sn-Beta synthesis, Kang et al. [29] adopted a simple steam-assisted conversion (SAC) method where dry stannosilicate gel was successfully converted to highly crystalline Sn-Beta (Si/Sn = 93) zeolite within 5 h under 180 °C (Figure 2). Dry-gel conversion techniques such as SAC are much faster and more convenient than conventional hydrothermal procedures, but also in SAC do the content of Sn significantly affects synthesis with higher Sn loading resulting in longer crystallization time and lower crystallinity. When using stannosilicate dry gel in SAC with $\text{Si}/\text{Sn} \leq 75$, it has proved impossible to obtain Sn-Beta even after 200 h of crystallization.

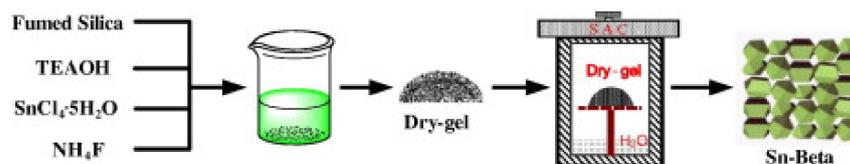


Figure 2. Illustration of the Sn-Beta zeolite preparation by SAC method. Reproduced with permission from [29]. Copyright 2012, Elsevier.

Kang et al. [38] optimized the synthesis of Sn-Beta zeolite by SAC as the amount of water in the autoclave affected the zeolite formation if condensed water dropped into the gel and altered its composition. With an improved autoclave setup and optimized synthesis parameters corresponding to a gel drying temperature of 60–100 °C and a crystallization temperature of 160–200 °C the condensation could be avoided.

2.1.3. Inter-Zeolite Transformations

Hydrothermal synthesis of Sn-Beta zeolites with high Sn content remains an eminent target in literature. Iida et al. [39] obtained mixed Sn-Si oxide composites by mechanochemical treatment and used them as precursor for hydrothermal synthesis of Sn-Beta zeolite at 170 °C under static conditions for 4 to 8 days. The strategy allowed successful incorporation of framework Sn into Sn-Beta with a relatively high Sn content (Si/Sn = 60, 3.17 wt.%). Following an analogous mechano-chemical route and combining it with inter-zeolite transformation, Zhu et al. [31] also obtained highly crystalline Sn-Beta zeolite with a relatively high Sn content (Si/Sn = 63, 3.03 wt.%) but within 3 days. Here, all-silica MWW-type crystals (ITQ-1 zeolite) were the silica source and deAl-Beta was introduced as the seeds (Figure 3). According to the crystallization mechanism, the framework similarity between the MWW crystals and deAl-Beta seeds was a key factor for the successful synthesis of the Sn-Beta zeolite.

2.2. Top-Down Approaches

Atom-planting is a post-synthetic strategy exploited to introduce Lewis acidic metals into zeolitic matrices. In the general procedure, Sn-Beta zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 1900$) have been produced by dealumination of Al-Beta with concentrated nitric acid (65 wt.%, 100 °C, 20 h, 20 mL/g) to create deAl-Beta with framework vacancies where Sn atoms were then inserted. Acid-induced dealumination was preferred instead of steaming to remove the framework Al as the latter method can also create ill-defined extra-framework Lewis acidic Al sites with undesired catalytic performance. The Sn insertion routes included both traditional gas-solid deposition (e.g., chemical vapor deposition), solid-state ion (SSI) exchange as well as liquid-phase routes (e.g., impregnation).

2.2.1. Gas-Solid Deposition

Traditional gas-solid deposition takes advantage of the low volatility of Sn precursors (e.g., SnCl_4) to accelerate the diffusion and mass transfer of Sn ions and quickly coordinate with the framework defects of deAl-Beta zeolite. For example, Li et al. [27] utilized the vapors of SnCl_4 to react with the silanols in the hydroxyl nests of highly deAl-Beta at 400–500 °C (Figure 4). The Sn species were inserted into the framework and occupied the tetrahedral coordination sites predominately with a Sn content reaching up to 6.2 wt.% (Si/Sn \approx 35). Adopting the same synthesis route, Jin et al. [40] successfully synthesized mesoporous Sn-Beta zeolites, however, the poor volatility of SnCl_4 resulted in aggregation of the Sn ions as SnO_2 species making the method less ideal.

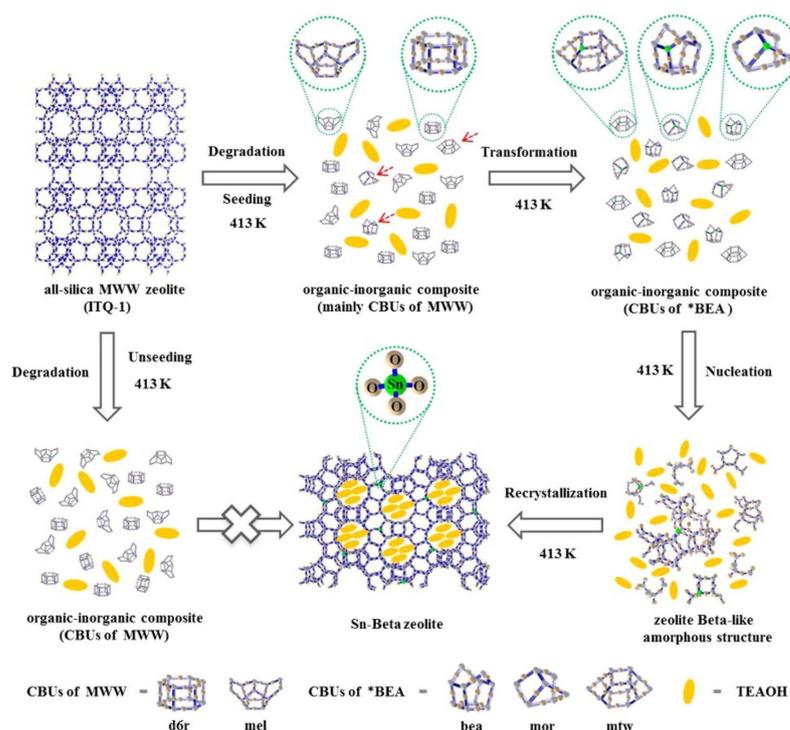


Figure 3. Schematic representation of the proposed crystallization mechanism for seed-assisted transformation of parent MMW-type zeolite to Sn-Beta. The red arrows indicate the composite building units (CBUs) of BEA* derived from the degradation of the seeds. Reproduced with permission from [31]. Copyright 2017, Elsevier.

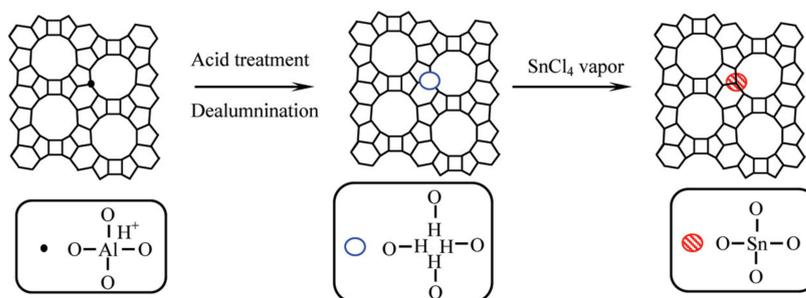


Figure 4. Strategy for post-synthesis of Sn-Beta through a combination of dealumination with solid-gas reaction (Atom-Planting Method). Reproduced with permission from [27]. Copyright 2011, American Chemical Society.

2.2.2. Solid-State Ion Exchange

The synthesis of Sn-Beta zeolite by both in-situ hydrothermal or post-synthetic strategies possesses some drawbacks, including long crystallization time, necessity of fluoride ions, and a limited amount of generated framework Sn sites. To circumvent these issues, Hammond et al. [28] developed a simple and scalable post-synthetic strategy for incorporating Sn into zeolitic frameworks using SSI exchange. Here, deAl-Beta zeolite with vacant tetrahedral sites and an appropriate Sn precursor (e.g., tin(II) acetate) were mixed by simply mechanical grinding followed by calcination at 550 °C to remove residual organic species (Figure 5). Further studies [41] also addressed the regeneration and pre-activation of Sn-Beta prepared by SSI by treatment the material in a flow of methanol at 110 °C for 0.5 h followed by calcination at 550 °C in air for 3 h. This caused the active-site environment to become more accessible, more hydrophobic, more reactive as well as more stable. Sels and coworkers [42] found that the atmosphere during heat-treatment significantly affected

the dispersion of active Sn sites in the Sn-Beta as the Sn precursor (such as tin(II) acetate) decomposes and forms Sn(II)O species under inert atmosphere. The melting point of Sn(II)O (1080 °C) is relatively low compared to that of Sn(IV)O₂ (1630 °C), causing the Sn(II)O species to migrate more which results in a good dispersion of Sn atoms [43].

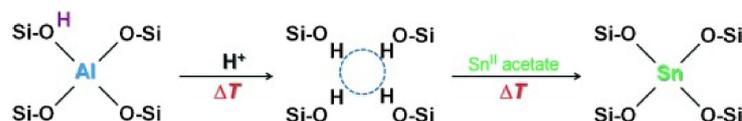


Figure 5. Schematic representation of the synthesis of Sn-Beta by the solid-state ion (SSI) exchange method. Reproduced with permission from [28]. Copyright 2012, Wiley-VCHH.

2.2.3. Liquid-Phase Routes

Dijkmans et al. [30] introduced 0.03–0.72 mmol of Sn into deAl-Beta by refluxing the material in a isopropanolic solution containing variable amounts of Sn(IV) chloride pentahydrate for 7 h (Figure 6). The obtained Sn-Beta materials with Sn loadings less than 1 wt.% exclusively featured tetrahedral framework species, while those with higher metal contents were characterized by the co-presence of SnO_x species. The restricted insertion of Sn into the framework was attributed to significantly increased diffusion resistance of isopropanol solvated Sn ions in the zeolite pores.

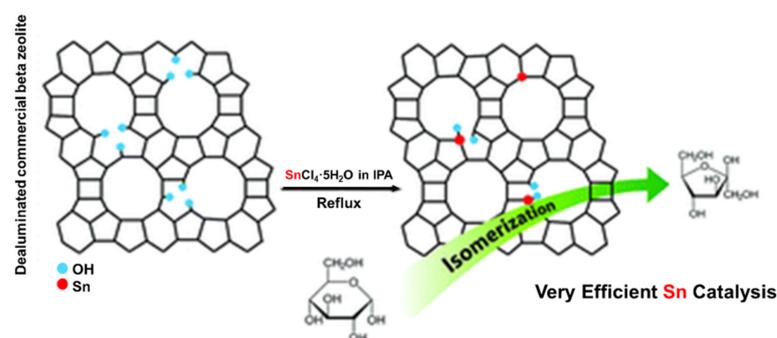


Figure 6. Schematic illustration for grafting Sn(IV) into deAl-Beta in isopropanol under reflux. Reproduced with permission from [30]. Copyright 2013, Royal Society of Chemistry.

3. Catalytic Transformations of Sugars with Sn-Beta Zeolite

3.1. Sugar Isomerization

Sn-containing zeolites exhibit pronounced performance in the catalytic isomerization of sugars with respect to both conversion and selectivity. Generally, the ratio of Lewis and Brønsted acid sites over zeolites can be adjusted by different methods such as steam/thermal treatment, element doping, and acid/base etching [44], which is directly correlated with the product distribution. Incorporation of Sn into the framework increases the Lewis acidity of zeolites, which has been reported to be efficient for the isomerization of C3–C6 sugars such as glucose, xylose, erythrose, and dihydroxyacetone.

3.1.1. Glucose-to-Fructose

Glucose-to-fructose isomerization (Figure 7) is an industrial reaction process for producing high-fructose corn syrup, where fructose is much sweeter than the other sugars, such as fructose (1.50) > sucrose (1.00) > maltose (0.5). Fructose can not only be applied as diet sugar for food but also as starting material used in the synthesis of high-value chemicals such as HMF and levulinic acid, rendering biomass sugar a promising alternative to fossil fuels. In connection with this, catalytic isomerization of glucose, as one of the key steps to yield fructose, has attracted extensive attention using Sn-modified zeolites having different framework structures such as MWW (~0.37 nm pore diameter), MFI (~0.55 nm pore diameter), MOR (~0.70 nm pore diameter), and Beta (~0.70 nm pore diameter).

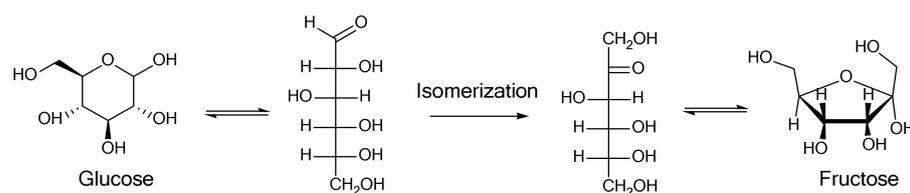


Figure 7. Schematic illustration for isomerization of glucose to fructose.

Van der Graaff et al. [45] reported that only large-pore Sn-MOR and Sn-Beta were active for the isomerization of glucose to fructose under identical conditions in water at 100 °C. With Sn-Beta, 29% yield of fructose and 5% mannose were obtained in 2 h while Sn-MOR afforded 10% fructose in 6 h. In contrast, Sn-MOR-bulk zeolite was found to yield 22% fructose and 1% mannose at a glucose conversion of 25% in water at 100 °C after 24 h thus signifying that the pore topology affected the product distribution despite the zeolites had the same Sn catalytic center. In addition, it has been found that sugar molecules are able to adsorb and react within hydrophobic channels even though bulk water is excluded from them [46], in which the porous voids should allow the traverse of reactants and products.

Sn-Beta occupies a very important position for glucose isomerization as it exhibits high selectivity and can act as a Lewis acid capable of catalyzing the isomerization of glucose in a pure aqueous medium. It is observed that the framework Sn centers are necessary for Sn-Beta to catalyze the reaction [47], but catalytic activity is not linearly related to Sn content, as the activity is likely caused by a gradual decrease in dispersion and an increase of less active condensed SnO_x species. The open site of Sn-Beta is found to be the active part for catalyzing glucose conversion to fructose, and the preparation method via stannic chloride reflux in dichloromethane solvent (60 °C) can tune the open-to-close site ratio in the framework of Sn-Beta [48]. Sn-BEC can be prepared by incorporation of Sn into the germanosilicate framework of BEC zeolite via a direct hydrothermal procedure as Sn-Beta. Zhang and co-workers [49] demonstrated that Sn-BEC (Sn/Si = 0.01 and 0.02) had a single catalyst center type and exhibits higher isomerization selectivity (65.2–69.5%) than Sn-Beta (Sn/Si = 0.01, 44.2%) in methanol. Sn-BEC (Sn/Si = 0.02) was detected to have stronger Lewis acidity, which tends to be responsible for the superior selectivity in catalytic isomerization of glucose to fructose. It should be noted that fructose and mannose reacted with the reaction medium methanol to form methyl glucoside, methyl fructoside, and methyl mannoside, respectively.

The mechanism of glucose isomerization catalyzed by Sn-Beta has been extensively scrutinized. Bermejo-Deval et al. [50] showed that Sn-Beta and Ti-Beta could catalyze the glucose isomerization like the metalloenzyme *glucose isomerase* (EC 5.3.1.5) in three steps (Figure 8) which involved: (1) ring-opening of glucose, (2) coordination of glucose to the Sn site, and (3) intramolecular hydride shift from the C2 position to the C1 position on the open glucose chain (1,2-intramolecular hydride shift, 1,2-HS) followed by ring-closure to yield the furanose product. Apart from the Lewis acidic catalyst center mentioned above, the silanol group may also play an important role in the isomerization reaction, wherein hydride transfer and subsequent proton transfer occur in a single step with lower activation energy [51]. To further study the interplay between the structure and activity of active sites in the zeolite, two molecular models (tin silsesquioxanes) were further designed [52]. The zeolite that contained an octahedral Sn site (open site) with an adjacent silanol group could selectively isomerize glucose to fructose through a 1,2-HS, while the one without an adjacent silanol group mainly produced mannose via a 1,2-intramolecular carbon shift (1,2-CS). The role of water and Na⁺ cations in the catalytic activity of Sn-BEA were also investigated [53–55]. It was found that when methanol was used as a solvent instead of water, the conversion of glucose could be increased [53]. Li and co-workers [55] compared reaction pathways both in the absence and presence of water molecules in the vicinity of the active site and found that water not only influenced the energetics of an individual

pathway, but also effectively determined the selectivity, especially in the case of Na-Sn-BEA. The authors proposed that polar water molecules were coordinated around the Na^+ cation through strong electrostatic interactions between Na^+ and the hydroxyl groups of the sugar, which results in the drop of the 1,2-CS energy barrier by about 0.4 eV, thus making the epimerization reaction more preferable compared to the isomerization reaction.

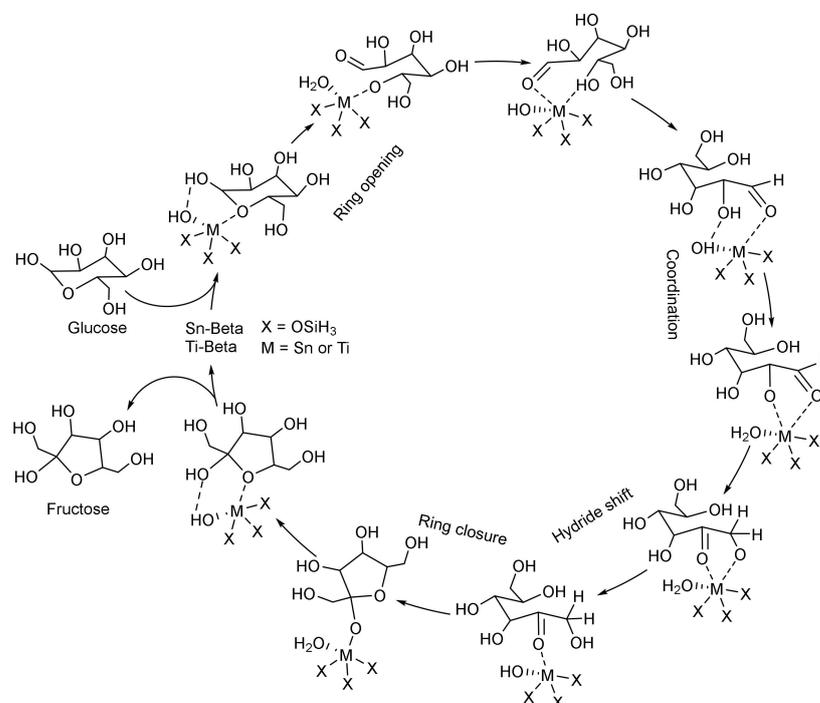


Figure 8. Mechanism of the glucose-to-fructose isomerization catalyzed by open site of Sn-Beta or Ti-Beta.

3.1.2. Xylose-to-Xylulose

FF is a biomass derivative that has the potential to be used in preparing gasoline and diesel [56]. Xylose is the most common five-carbon sugar that can be converted into FF, but the reaction does not take place under mild conditions due to the high activation barrier (124 kJ/mol). However, the isomerization of xylose to xylulose, followed by degradation to FF, can be carried out at a lower temperature in the presence of an acid catalyst [57].

Paniagua and co-workers [58] reported catalytic isomerization of xylose to xylulose with commercial zeolites (Figure 9). Two steps are involved in this reaction: (1) conversion of xylose to xylulose and methyl xyluloside in methanol, and (2) hydrolysis of methyl xylulose to xylulose after addition of water. Large-pore zeolites such as USY and Beta were active for the isomerization of xylose yielding 47% and 39% of xylulose at 100 °C after 1 h for each step, respectively. Relatively higher ratio of Brønsted to Lewis acid sites in acidic zeolites were demonstrated to be attributed to the superior activity. For example, USY (Si/Al = 6, B/L ratio = 1.07, yield: 47%) showed higher xylulose yield than USY (Si/Al = 30, B/L ratio = 0.97, yield: 4%). Based on the results, the authors speculated that the weak Lewis acid sites played an important role in the isomerization of xylose, and lower temperature could avoid sugar degradation for a longer time which was beneficial for the increase of the product yield.

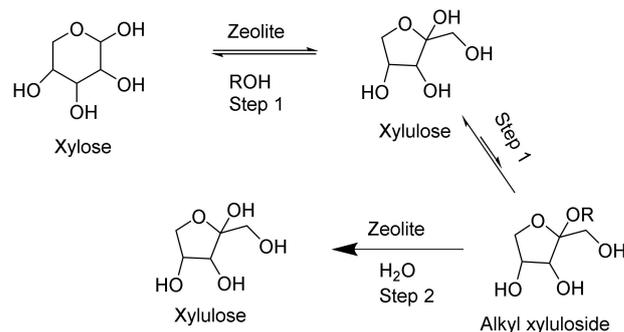


Figure 9. Reaction pathways for the conversion of xylose to xylulose and alkyl xyluloside.

Choudhary and co-workers studied the xylose-to-xylulose isomerization reaction with Sn-Beta [59]. It was found that the first step of isomerization reaction involved the opening of the ring of xylose, where the Sn-OH species in Sn-Beta was involved as an alkaline catalyst in the transfer of a proton to the oxygen of the xylose ring. Next, two-H migration reaction occurred between cyclic xyloses: (1) a proton transfer from C2 to the Sn-OH to form water; and (2) 1,2-HS after xylose combined with the Sn-Beta catalyst. The rate-limiting step of isomerization was found neither to be the ring-opening of β -furanose nor β -pyranose, but instead the 1,2-HS. Although the isomerization and epimerization are both thermodynamically and kinetically favorable, isomerization is more preferred in general.

3.1.3. Erythrose-to-Erythrulose

Methyl-4-meth-oxy-2-hydroxybutanoate is a α -hydroxy acid ester with great industrial potential, and it can be synthesized from erythrulose in high yields with homogeneous Sn-based catalysts [60]. Industrially, this reaction often involves the isomerization of erythrose to erythrulose as shown in Figure 10 [61].

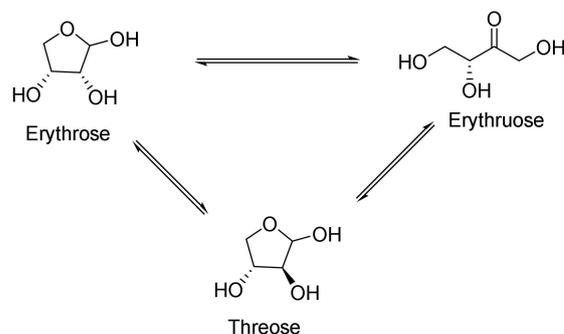


Figure 10. Schematic illustration of the conversion of tetroses by isomerization.

3.1.4. Dihydroxyacetone-to-Glyceraldehyde

The triose sugars dihydroxyacetone (DHA) and glyceraldehyde (GA) can be used to prepare lactic acid, which is useful for the production of biodegradable plastics and solvents [62] as well as commodity chemicals such as propylene glycol and acrylic acid [63]. Alkyl lactates/lactic acid can be obtained in alcohol/water solutions by isomerization of DHA and GA followed by dehydration and esterification using acidic zeolites (Figure 11). Compared with the traditional fermentation method, less purification and separation processes are required for the production of lactic acid from carbohydrates via such approaches [64].

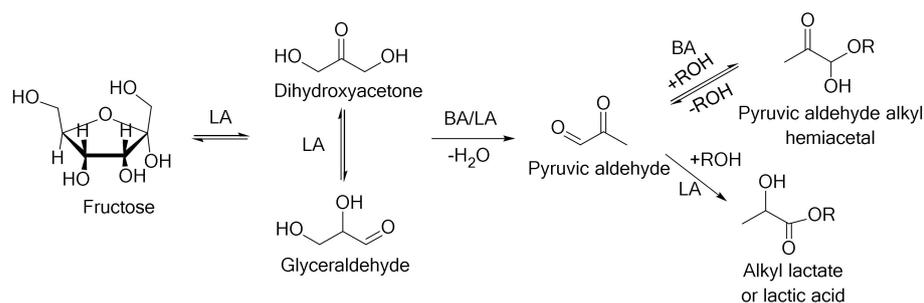


Figure 11. Reaction pathways for the conversion of dihydroxyacetone to alkyl lactates/lactic acid. LA, Lewis acid; BA, Brønsted acid.

Similar to glucose isomerization, Sn-containing zeolites, especially Sn-Beta, have reported to provide good performance in the conversion of DHA to alkyl lactates. The conversion of DHA to methyl lactate in methanol and to lactic acid in water was studied using different Beta zeotype catalyst with metals such as, e.g., Zr, Sn, Ti and Al as well as their corresponding oxides [65]. Only Sn-Beta exhibited high selectivity and yield > 99% for the formation of methyl lactate from DHA and GA under the same conditions, whereas SnO₂/Si-Beta yielded only a trace amount of methyl lactate and lactic acid. In addition, other metals oxides also had low activity for the reaction, implying that metals oxide had poor catalytic activity.

Yao et al. [66] prepared hierarchically porous and tin-rich Sn-Beta (OSF) zeolite with an acid treatment to remove the OSDA tetraethylammonium hydroxide. As compared to Sn-Beta (Nano) zeolite prepared by traditional method with remaining OSDA, Sn-Beta (OSF) had less microporous volume (0.19 cm³ g⁻¹) but a larger mesoporous volume (0.14 cm³ g⁻¹). Under the same reaction conditions (methanol, 60 °C and 4 h) the catalytic conversion of DHA into methyl lactate with Sn-Beta (Nano) and Sn-Beta (OSF) provided 86.8% and 94.4% conversion and 95.9% and 97.2% methyl lactate selectivity, respectively, implying that the hierarchical pores of Sn-Beta (OSF) were better to transport the substrate than Sn-Beta (Nano), besides the promotional role of stronger Lewis acid sites.

Sn-Beta zeolite can have both Lewis and Brønsted acid catalytic sites, which can effectively convert DHA to alkyl lactates in alcohol [28,67]. The mechanism of the reaction has been well studied, and it is widely believed that DHA, in fast equilibrium with its isomer GA, undergoes dehydration and rearrangement into pyruvic aldehyde [67]. In presence of alcohol and Brønsted acid catalytic sites, pyruvic aldehyde can be reversibly converted into the hemiacetal pyruvic aldehyde ethyl hemiacetal. Lewis acid sites and ethanol promote the conversion of pyruvic aldehyde to ethyl lactate, and the active site is most likely Sn-OH (open site) in the zeolite framework rather than tetrahedral framework Sn sites (closed sites) [67]. Dijkmans et al. [44] studied the catalytic activity of Sn⁴⁺ and Al³⁺-rich zeolites in the conversion of pyruvic aldehyde to ethyl lactate in ethanol after 15 min, and found that the yield obtained with Sn-Beta (about 70%) was ten times higher than that by Al³⁺-rich zeolite (7%). The study also showed that higher Sn content led to higher productivity, indicating that the ethyl lactate yield was correlated to the amount of Lewis acidity [31]. On the other hand, the impact on the conversion of DHA was assumed to be related to the action of Brønsted acid sites, responsible for facilitating the rate-determining step in dehydration of DHA to pyruvic aldehyde. This fact indicated that bifunctional materials containing both Brønsted and Lewis acid sites are favorable for the cascade reaction involved in the synthesis of lactates from DHA.

3.2. Sugar Dehydration

In the transformation of lignocellulosic biomass to furans derivatives, the Lewis acidic Sn sites in Sn-Beta zeolite efficiently isomerize aldoses to ketoses (see previous section), and the consecutive dehydration of ketoses to the furans derivatives are catalyzed by Brønsted acidic sites. The introduction of Brønsted acidic sites may be obtained by the

direct addition of homogeneous or heterogeneous Brønsted acid into the reaction system or, though more challenging to realize, by incorporating Brønsted acidic sites into the Sn-Beta zeolite framework. Main focus in the literature for both of these approaches have been on the transformation of sugars into mainly HMF and FF.

Sn-Beta zeolite exhibits excellent thermal and chemical stability under steam conditions so protic acid such as hydrochloric acid (HCl) can be added directly as homogeneous Brønsted into sugar solutions to facilitate dehydration. Highly efficient transformation of glucose into HMF has been achieved with high selectivity using HCl in one-pot biphasic water/tetrahydrofuran (THF) reaction system [68,69]. The HCl may also be applied for the hydrolysis of polysaccharides, cellobiose or starch into monomeric sugars and subsequently catalyze the dehydration of fructose into HMF. Here, a higher yield will be obtained at low pH and saturated aqueous salt solutions. Analogously, a combination of Sn-Beta zeolite and HCl can catalyze the isomerization and dehydration of xylose (C5 aldose) into FF in one-pot aqueous solution with a FF yield of 14.3% at a much lower temperature (110 °C) than in previous reports (>150 °C) [57].

The introduction of solid Brønsted acid catalysts such as resins can replace the homogeneous acid and improve catalyst recyclability and regenerability. Such system combining Sn-Beta zeolite with Amberlyst[®] 70 has been shown to efficiently transform glucose to HMF in monophasic reaction systems with good yields using solvents such as GVL (59%), GHL (55%), 1:1 THF:MTHF (60%), and THF (63%), respectively [70]. The solid Brønsted acid PTSA-POM (made from the copolymerization of p-toluenesulfonic acid, PTSA, and paraformaldehyde, POM) has also been introduced for the transformation of glucose to HMF due to its low cost, ease of preparation, and high Brønsted acidity. The combination of Sn-Beta and PTSA-POM achieved a good HMF yield of 60.1% at a glucose conversion of 96.3% in GVL/H₂O reaction system [71]. The presence of water significantly affected the reactivity with 10 wt.% water providing the best result. Alternatively, alcoholic solvents have also been used often as reaction media and they directly participate in the reaction by etherification of the furans in the presence of Brønsted acid. Hence, employing an ethanolic system with Amberlyst[®] 131 as the Brønsted acid in combination with Sn-Beta zeolite successfully converted glucose to 5-(ethoxymethyl)furfural (EMF) in a single reactor at 90 °C [72]. The combined catalytic system proved more stable in dioxane and the introduction of small amounts of water significantly increased the selectivity of HMF instead of EMF [73]. Subsequent studies also indicated that the presence of more Brønsted acid sites in Amberlyst[®] 15 and an appropriate amount of water in organic solvents were beneficial for the transformation of glucose to HMF and 5-(isopropoxymethyl)furfural (IMF) in 53% yield [72].

In comparison to the combined approaches, the introduction of the Brønsted acidic sites directly into the framework structure of Sn-Beta zeolite may possess advantages for sugar dehydration. When deAl-Beta zeolite is applied as seed for the synthesis of Sn-Beta traces of Brønsted acidic Al³⁺ sites will be preserved, which have a negative effect on the isomerization of glucose to fructose (see previous sections). Nevertheless, the combination of such Al³⁺ sites and Lewis acidic Sn⁴⁺ sites in Al/Sn-Beta zeolite with a suitable Sn/Al molar ratio have been reported to catalyze the one pot conversion of glucose to HMF with a conversion of 60.0% and HMF selectivity of 62.1% under optimized conditions [74]. Also, the physical pore structure of Al/Sn-Beta zeolite will affect the catalytic reactivity due to limited diffusion of reactants and products. Here, the hierarchical Sn-Beta was synthesized from hydrothermally synthesized hierarchical Al-Beta (SDA: polydiallyldimethylammonium chloride) by exposure to SnCl₄ vapor (i.e., gas-solid deposition; see previous section), and the resulting catalysts displayed good activity and afforded both higher glucose conversion (99%) and HMF selectivity (42%) than those of conventional Sn-Beta (96% and 32%, respectively) [75]. Similar catalytic performance has also been obtained at lower reaction temperature at prolonged reaction time with analogously in-situ synthesized Sn-Beta zeolites using diquatery ammonium as the SDA [76].

3.3. Sugar Fragmentation

Lactic acid/lactate salts and derived esters are chemical platform compounds with high potential and multifunctionality, which are widely used in food, pharmaceuticals, cosmetics and as biodegradable polymers and renewable solvents [77]. The fermentative conversion of biomass-derived sugars to lactic acid is the normal approach on a large scale. However, since Holm et al. [12] described that Sn-Beta zeolite could efficiently and direct catalyze common sugars to methyl lactate a lot of work have focused on these chemocatalytic processes and have been summarized several times [5,9,77–81].

The formation of lactic acid (and its derivatives) from sugars such as glucose comprise a series of reactions concerted by the Sn sites in Sn-Beta zeolites, including: (1) glucose isomerization into fructose; (2) fructose degradation into DHA and GA via retro-aldol condensation (GA can be isomerized into DHA via Sn-Beta); and (3) DHA dehydration to form the lactic acid with pyruvaldehyde as intermediate (Figure 12) [82,83]. The synthesis parameters used to prepare Sn-Beta can significantly affect its zeolitic structure and reactivity for such conversion [36]. For example, during hydrothermal synthesis a low water amount can shorten the crystallization time but create extra-framework SnO₂ and reduce the incorporation of Sn⁴⁺ into framework sites, which results in lower catalytic activity. On the other hand, a longer crystallization time will incorporate more Sn⁴⁺ species into the framework sites and generate more Lewis acid sites, though open Sn sites with a proximal silanol are unfavorable for the conversion of glucose to methyl lactate. Similar to sugar dehydration, hierarchical structures of Sn-Beta are also beneficial for obtaining higher yield of lactic acid derivatives from sugars [84,85]. Hence, hierarchical Sn-Beta zeolite synthesized with polydiallyldimethylammonium chloride as SDA gave a higher catalytic activity than that of microporous Sn-Beta and post-synthesized meso-Sn-Beta zeolites for glucose conversion, due to a combined promotional effect of mesoporosity, hydrophobicity and Lewis acidity on the retro-aldol condensation of fructose [86]. In addition, to enhance the efficiency of the catalytic transformation of glucose into lactic acid microwave irradiation was introduced for the controlled-isomerization of glucose, facilitating a very high lactic acid yield of 68.3 wt.% at 180 °C in 30 min over a “monolithic” Sn-Beta catalyst in water [87].

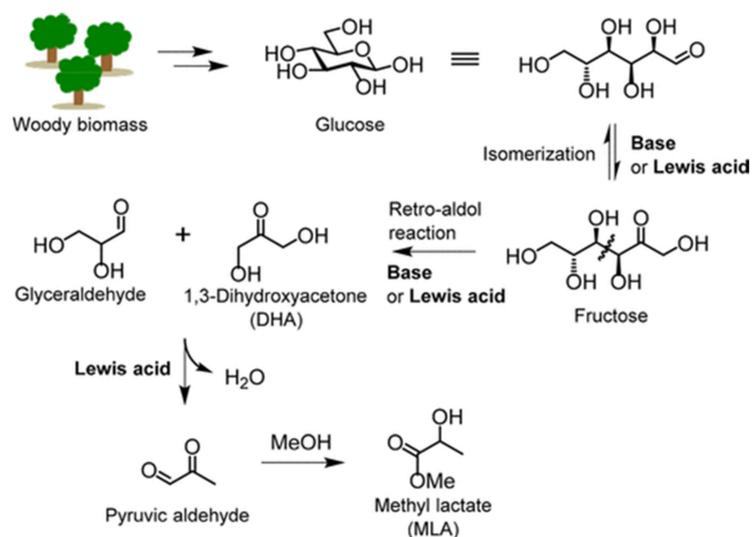


Figure 12. Reaction pathway for the conversion of glucose to methyl lactate. Reproduced with permission from [82]. Copyright 2018, American Chemical Society.

The consecutive reactions involved in the conversion of sugars to lactic acid can also be promoted by acid or base co-catalysts. Hence, for the conversion of sucrose to methyl lactate in methanol the yield was improved more than two-fold (from 20–25% to 66–71%) using both bottom-up or top-down (see previous section) synthesized Sn-Beta zeolite by

the addition of basic alkali salts to the reaction media [88]. Further experiments with calcium sulfate/carbonate as additives showed that weaker bases inhibited the effect of Brønsted acid sites present on the catalyst [89]. Various metal oxides, including MgO, TiO₂, ZrO₂, NiO, CuO, ZnO, MoO₃ and especially WO₃ also exhibited a promotion effect on the reaction system [90], and mechanistic studies indicated that fine oxide particles adsorbed on the surface of Sn-Beta and decreased silanol defects, which improved the catalytic performance. When Brønsted acid sites from H-Beta were combined with the Sn-Beta system the formation of methyl lactate from levoglucosan (pyrolysis product of sugars) was favorable as the acid sites methanolyzed levoglucosan to methyl glucosides which hydrolyzed to glucose [91].

To enhance the reactivity of Sn-Beta for the conversion sugars to lactic acid, the introduction of metal atoms into the catalyst is another strategy to improve the Lewis acidity or create base sites. Using this approach Zn, Pb, Cr, and In were introduced into the structure of Sn-Beta by the SSI method [92–95]. The introduced metal atoms had different effects; Zn and Pb created basic sites inhibiting the inevitable action of Brønsted acid, while In increased the weak Lewis acidity and decreased the strong Lewis acidity, which inhibited side reactions and enhanced the catalytic conversion of sugars to lactic acid, respectively. Oppositely, Cr imposed strong Lewis acidity promoting retro-aldol fragmentation. Liquid-phase ion exchange is a traditional method to introduce metal atoms into zeolites, and alkaline earth ions exchanged with post-synthetic Sn-Beta significantly improved the catalytic conversion of levoglucosan to lactic acid in the order Sn-Beta < Na-Sn-Beta < K-Sn-Beta < Mg-Sn-Beta < Ca-Sn-Beta [96]. The alkali ions prevented the Brønsted acid sites from initiating side reactions, and created more Lewis basic sites that could stabilize deprotonated alkoxides during the reaction. Further studies indicated that co-impregnation of deAl-Beta with Mg²⁺ and Sn⁴⁺ ions reacted with silanol nests and isolated silanols to form framework and extra-framework metal sites, which decreased the silanol defects and increased the ratio of Lewis acidity/basicity of Mg-Sn-Beta [97]. The silanol defects were found to be fewest with a Mg/Sn molar ratio of 1, which promoted the retro-aldol reaction of fructose (rate-determining step) and thus improved the selectivity to methyl lactate. Surface modification of Sn-Beta with basic organoamine groups can also enhance the activity with an effect similar to the introduction of metal atoms (i.e., reduce Brønsted acidity to diminish side reactions to by-products such as HMF) [98,99].

During the catalytic conversion of sugars with zeolites, adsorbed intermediates may undergo side reactions leading to the formation of carbonaceous deposits that will cause catalyst deactivation. The introduction of organic solvent such as GVL into aqueous glucose systems with Sn-Beta, where GVL strongly absorbs on the active Sn sites and effectively suppress the isomerization of glucose into fructose, can to a large extent circumvent such deactivation and provide high yield of lactic acid (72 wt.%) [100]. Analogously, DMSO was introduced into an aqueous glucose system and increased the fructose selectivity to 95.5% using Sn-Si/ZSM-48 [101]. Sn-Beta isomerizes glucose to fructose in methanol and in the presence of Brønsted acid sites the fructose is rapidly converted into methyl fructosides, which subsequently can release fructose and transform into methyl lactate. The addition of small amounts of water will accelerate the release process of methyl fructoside to fructose, thereby improving the catalytic performance [102]. Compared to the aqueous system, the Sn-Beta zeolite in the methanol media has much less carbon deposition, structural changes, and Sn leaching after long-term continuous operation in a trickle bed allowing continuous operation for 434 h with less than 25% loss in the yield of methyl lactate [103].

Most biomass-derived feedstocks are not simple sugars (glucose, fructose, etc.) but polysaccharides such as sucrose, hemicellulose, and cellulose. In one-pot reactions, the polysaccharides need initial hydrolysis to monosaccharides before further conversion, and this reaction is slower than for simple sugars. The introduction of acids or bases can assist the hydrolysis reaction during Sn-Beta catalyzed conversion of polysaccharide to lactic acid without increase in side reactions. This has been demonstrated for the conversion of the sugar-rich microalgae *Scenedesmus*, where formic acid induced hydrolysis of the cell wall

under controlled release of glucose [104]. Since formic acid possessed only relatively weak Brønsted acidity it was unable to dehydrate the fructofuranose intermediate to byproducts such as HMF and levulinic acid.

Sn-Beta zeolite can in addition to glucose also transform various C5 sugars into methyl lactate in methanol, though lower yields are usually obtained along with higher yields of glycolaldehyde dimethyl acetal due to formation of triose and glycolaldehyde by the retro-aldol condensation [105]. In contrast, Sn-Beta provided in water very high lactic acid yield of 70.0 wt.% from the common C5 sugar xylose [106]. The reaction pathway was by ^{13}C NMR corroborated to proceed via retro-aldol cleavage to glycolaldehyde followed by condensation to erythrose and subsequent cleavage to lactic acid and formic acid.

4. Conclusions and Perspectives

In the past two decades, the synthesis of Sn-Beta zeolites has made great progress with the development of different bottom-up and top-down synthetic approaches, which to some extent allow controlling relevant features like e.g., crystallinity and hydrophobicity. deAl-Beta zeolites have commonly been applied as seeds for the bottom-up approaches, as they significantly promote and accelerate the crystallization process during synthesis. Top-down synthetic approaches are generally more convenient for the synthesis of Sn-Beta zeolite. Here, deAl-Beta zeolites are reacted with Sn salts (e.g., tin acetate or chloride) by various gas, solid and liquid methods which can impose preferred properties such as an increased hydrophobic nature. Nevertheless, silanol defects and traces of Al^{3+} are often difficult to avoid completely using this strategy, which may impose negative effects on catalytic properties. For future syntheses strategies of Sn-Beta zeolite several aspects should be considered and improved: (1) Fluoride-assisted crystallization methods enable synthesis of highly hydrophobic Sn-Beta but the fluoride causes environmental problems and prompts the growth of undesired large crystallites, thus making fluoride-free medium preferable; (2) hydrothermal synthesis of Sn-Beta generally use none-green processes with OSDAs, and template-free or other alternative green routes should be considered instead [107]; (3) synthetic approaches to increase the framework Sn sites in Sn-Beta usually result in the formation of SnO_2 and extra-framework Sn species, which may be circumvented by the introduction of single-atom catalysts [108]; and (4) the structure of Sn-Beta affects the efficiency of sugar transformations significantly, but two-dimensional or core-shell structures may preserve the desired properties and enhance the catalytic performance [109].

Since the pivotal discovery that Sn-Beta zeolite is an efficient Lewis acid catalyst for the conversion of glucose to fructose or lactate derivatives at elevated temperature, many studies have during the last decade exploited the use of Sn-Beta for transformation of sugars. Sn-Beta can efficiently isomerize C3-C6 aldoses to ketoses and through the introduction of Brønsted acidity into the catalytic system the isomeric products can be dehydrated into furan derivatives. Analogously, the introduction of basicity can enhance the fragmentation of sugars into lactate derivatives. One strategy to introduce acidity/basicity into Sn-Beta reaction systems involves the use of added Brønsted acids or bases, which are responsible for the dehydration or fragmentation of sugars following the isomerization. Such catalytic systems provide good performance, but are less prone for recycling especially with homogeneous acids/bases. A more durable, but less developed, strategy rely on synergistic catalyzed transformation of sugars with Sn-Beta zeolites with incorporated acidic/basic sites. Such systems have proven their potential, but more control of the type and amount of the introduced acidic/basic sites are warranted. In future applications with Sn-Beta zeolite, the relationship between structures and pathways of sugar transformations should be considered and established: (1) the Lewis acidic Sn sites play a critical role in sugar isomerization, and Sn-Beta should be fabricated with a well-fined pore size suitable for the molecular diameter of C3-C6 sugars and equipped with hydrophobicity; (2) the introduction of Brønsted acid or Lewis base into systems with Sn-Beta promotes dehydration and fragmentation as subsequent reactions of sugar isomerization. Such species can be introduced as homogeneous catalyst in the reaction media or on/into Sn-Beta as heterogeneous

catalyst. Of these, the latter is preferential for continuous operation; and (3) the content and properties of catalytically active Sn sites in Sn-Beta are important parameters to regulate to control the efficiency and products of the reaction.

Overall, Sn-Beta zeolites have in recent years been established as very prospective Lewis acidic catalytic materials. Importantly, they are not limited to sugar transformations and in particular multifunctional catalysts integrated with Sn-Beta zeolites are expected to have huge potential and wider applications within biomass valorization. However, the industrialization of biomass valorization remains challenging, including the synthesis of catalysts and efficient operation. Industrial processes are usually performed in continuous operation units, and continuous reactors are accordingly good options to test the viability and catalytic performance of Sn-Beta in lab scale.

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