

Synthesis of Sn-Beta with Exclusive and High Framework Sn Content

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Sn-Beta zeolite was prepared by acid dealumination of Beta zeolite, followed by dehydration and impregnation with anhydrous SnCl₄. The formation of extraframework Sn (EFSn) species was prevented by the removal of unreacted SnCl₄ in a methanol washing step prior to calcination. The resulting Sn-Beta zeolites were characterized by X-ray diffraction, Ar physisorption, NMR, UV/Vis, and FTIR spectroscopy. These well-defined Lewis acid zeolites exhibit good catalytic activity and selectivity in the conversion of 1,3-dihydroxyacetone to methyl

Introduction

Dwindling reserves of fossil fuels and the growing environmental concerns associated with their combustion necessitates the development of new chemical processes based on renewable feedstock. Readily available lignocellulosic biomass that does not compete with food production will play an increasingly important role in sustainable chemical processes for the production of chemicals and fuels.^[1–4] The chemistry needed to upgrade lignocellulosic biomass is very different from the chemistry currently used to convert hydrocarbon-based raw materials. The selective and atom-efficient conversion of biomass to value-added compounds requires the development of new technologies and catalyst systems.

Several intermediates that can be derived from biomass and can be used in different applications have already been identified.^[4–6] Among such platform chemicals, lactic acid is promising because it is already widely used in the food industry and it can also serve as a monomer for biopolymers, such as polylactic acid, and as an intermediate in the production of other industrially important compounds, such as acrylic acid or green solvents.^[5] Lactates can be obtained from biomass by conversion of glycerol-derived trioses, such as 1,3-dihydroxy-

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lactate. Their performance is similar to a reference Sn-Beta zeolite prepared by hydrothermal synthesis. Sn-BEA zeolites that contain EFSn species exhibit lower catalytic activity; the EFSn species also catalyze formation of byproducts. DFT calculations show that partially hydrolyzed framework Sn-OH species (open sites), rather than the tetrahedral framework Sn sites (closed sites), are the most likely candidate active sites for methyl lactate formation.

acetone and glyceraldehyde;^[7–10] an alternative, performed on a commercial scale is the fermentation of glucose.^[5] To develop viable catalytic systems for these transformations, the development of benign chemocatalytic routes employing stable and versatile catalysts is desirable. Recently, the development of active Lewis acid chemocatalysts for the conversion of carbohydrates into value-added chemicals has become an important research area in the field of heterogeneous catalysis. In particular, Sn-modified large-pore Beta zeolites are highly active and selective catalysts for the conversion of carbohydrates.^[11-16] To date, Sn-Beta zeolite is the preferred catalyst in terms of activity and selectivity for the retro-aldol reaction of glucose to wards lactic acid, as well as in the isomerization of glucose to fructose, representing a key step in selective sugar-valorization paths.^[11-15]

It is generally believed that the active sites in Sn-Beta catalysts for such conversions are framework Sn atoms (FSn). Direct incorporation of Sn into the zeolite framework by hydrothermal synthesis is difficult and typically requires the use of fluoride media,^[17,18] which presents considerable environmental drawbacks. This problem is accompanied by the formation large crystallites owing to the long synthesis times, although methods have been developed to reduce these drawbacks.^[13, 19] Furthermore, the employed Sn precursor has an effect on the morphology and the catalytic performance of the zeolite.^[20] In addition to the lengthy synthesis, the hydrothermal synthesis method yields relatively large zeolite crystals, which may lead to mass-transfer limitations when relatively bulky biomass fragments are to be converted. Therefore, the introduction of Sn in smaller zeolite crystals is one way to prevent these diffusion limitations. Another problem with the fluoride-assisted method is the relatively low Sn content of the framework (<2 wt%). At a high Sn content in the gel, extrafra-

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mework Sn species (EFSn), in the form of dispersed intrazeolite Sn species as well as bulk tin oxides, are formed. It has been speculated that such EFSn species decrease the performance of Sn-Beta in carbohydrate-isomerization reactions.^[21,22]

In the view of these limitations, there has been quite some interest in the development of more-facile preparation methods for Sn-Beta catalysts.^[23-26] Specifically, indirect/postsynthesis methods that aim to introduce Sn in the framework of an already synthesized Beta zeolite have been explored (Scheme 1). In addition to their simplicity, higher amounts of



Scheme 1. Postsynthesis functionalization of zeolites with Sn.

Sn can be introduced into the framework than by direct hydrothermal synthesis. A common postsynthesis strategy involves the introduction of Sn after the removal of framework heteroatoms, such as B and Al.^[22,27-34] The direct introduction of B and Al into the Beta lattice is easier than that of Sn. The silanol nests arising from acid deboronation or dealumination provide anchor points for Sn. For instance, Li et al. used chemical vapor deposition (CVD) of SnCl₄ on dealuminated zeolites.^[27] Although more Sn can be introduced into the framework by this method, it remains difficult to limit the amount of EFSn species.^[27,28] Jin et al. reported that the presence of mesoporosity reduces the formation of EFSn species.^[29] Solid-state ion exchange has also been explored by several groups.^[22, 30, 31] By thorough grinding of a solid Sn precursor [e.g. Sn(OAc)₂ or Sn(Me₂Cl₂)] and the zeolite followed by careful calcination, Sn is dispersed in the zeolite micropores and anchored to the vacant T-sites of the dealuminated parent zeolite. Although high Sn contents of up to 10 wt% have been achieved by this method, the contribution of EFSn species increases as the Sn content is increased. Other methods include the impregnation of a dealuminated zeolite with a Sn-containing precursor, followed by calcination.^[32-34] Although facile, there is little control over Sn speciation and, usually, a considerable amount of EFSn species is formed.^[32, 34] These methods and their most important limitations are briefly summarized in the Supporting Information, Table S1. Despite the promise of these methods compared with the direct synthesis of Sn-BEA, a simple and reproducible approach to prepare Sn-Beta with exclusive framework Sn is still desirable.

Herein, we report the synthesis, characterization, and catalytic properties of a Sn-Beta zeolite by a simple and reproducible protocol for the introduction of large amounts (> 5 wt%) of Sn into the Beta framework without the formation of EFSn species. The dealuminated Beta zeolite is impregnated with anhydrous SnCl₄ under an inert atmosphere and excess SnCl₄ is removed by washing with methanol. This step is necessary to avoid the formation of EFSn species during the subsequent calcination step. The resulting Sn-Beta zeolite is substantially more active for the conversion of 1,3-dihydroxyacetone (DHA) to methyl lactate (ML) in methanol than the previously reported postsynthetically prepared Sn-Beta zeolites^[33] and also the Sn-Beta prepared by alternative hydrothermal routes.^[13] The materials were characterized by pyridine-FTIR, UV/Vis spectroscopy, solid-state NMR spectroscopy, Ar physisorption, X-ray diffraction, and elemental analysis. Mechanistic insight was obtained by exploring the importance of open versus closed Sn sites by DFT calculations of the rate-limiting H-shift step.

Results and Discussion

As a precursor for the Sn-containing zeolites, nanosized crystalline Al-containing Beta with varying Si/Al ratios (BEA-25, BEA-50, and BEA-100) were prepared according to the procedure reported by Mintova et al.^[35]

The X-ray diffraction patterns shown in Figure 1 confirm the exclusive formation of Beta zeolite. Direct calcination of the material at 550 °C (heating rate $1 \,^{\circ}$ C min⁻¹), either statically in



Figure 1. X-Ray diffraction patterns of the as-synthesized BEA-25, BEA-50, and BEA-100 and the corresponding Sn-treated materials. Sn-BEA-HF was added as reference.

air or in an artificial air flow (He/O₂=4:1), resulted in partial collapse of the zeolite lattice.^[36] The structural damage follows from the severe line broadening in the diffraction patterns (see the Supporting Information Section S2). Therefore, a milder two-step calcination procedure was employed involving heating of the as-synthesized zeolite to 400 °C for 10 h, followed by a second calcination step at 550 °C for 10 h by using heating rates of 1 °C min⁻¹ in an artificial air flow. By this approach, zeolite-framework decomposition was almost completely suppressed, as evidenced by the XRD results (Figure 1). The Si/Al ratio in the as-synthesized zeolite was different from the gel Si/Al ratio (Table 1). The final Si/Al ratios for BEA-25, BEA-50, and BEA-100 were 14, 20, and 33, respectively. These findings agree well with those in the original work of Bein and co-workers.^[35]

The textural properties of the synthesized materials were analyzed by Ar physisorption (Table 2). BEA-25, BEA-50, and BEA-100 zeolites have similar BET surface areas. The external surface

Table 1. Elemental composition of the prepared materials ^[a]								
Material	Si/Al ^[b] (Al-BEA)	Si/Al ^[c] (Sn-BEA)	Sn content [wt%]	Si/Sn	Substitution efficiency [%]			
Sn-BEA-25	14	>1500	2.81	62	23			
Sn-BEA-50	20	>1500	5.07	34	59			
Sn-BEA-100	33	>1500	3.49	51	65			
Sn-BEA-50*	20	>1500	5.88	29	n/a			
Sn-BEA-HF	-	-	1.95	95	n/a			
Sn-MCM-41	-	-	6.82	26	n/a			

[a] Determined by ICP-AES. [b] Si/Al ratio in the Al-containing zeolites after calcination. [c] Si/Al ratio in the postsynthesized Sn-BEA materials after dealumination, SnCl₄ treatment, and calcination.

Table 2. Physicochemical properties of the synthesized materials. ^[a]							
Material	S_{BET} [m ² g ⁻¹]	$V_{ m micro}$ [m ³ g ⁻¹]	$V_{\rm meso}$ [m ³ g ⁻¹]	$S_{external}$ [m ² g ⁻¹]			
AI-BEA-25	542	0.12	0.54	304			
AI-BEA-50	573	0.16	0.14	254			
AI-BEA-100	602	0.21	0.09	211			
Deal-BEA-25	508	0.07	0.47	357			
Deal-BEA-25	473	0.14	0.16	188			
Deal-BEA-100	477	0.11	0.11	263			
Sn-BEA-25	461	0.07	0.50	303			
Sn-BEA-50	483	0.15	0.19	202			
Sn-BEA-100	485	0.15	0.12	211			
Sn-BEA-50*	436	0.11	0.11	238			
Sn-BEA-HF	450	0.16	0.03	153			
[a] Determined by Ar physisorption.							

area increased with the Al content. This trend indicates that the zeolites with a higher Al content consist of smaller crystals. This is likely to be because of the higher nucleation rate when the Al content in the gel is increased. TEM analysis confirms

that smaller particles were obtained for Al-rich gel compositions (Figure 2). The obtained zeolite particles are agglomerates of smaller crystals of approximately 5 nm. This morphology is particularly pronounced for BEA-25 and BEA-50 (Figure 2 a,b). BEA-25 contains particles smaller than 50 nm (Figure 2a). The particle size of BEA-100 is approximately 150 nm (Figure 2 c).

The AI-BEA zeolites were dealuminated by treatment with 6 м aqueous HNO₃ at 110 °C for 16 h (50 mLg⁻¹). This procedure resulted in the complete removal of AI (Table 2), without affecting the crystallinity of the zeolites (see the Supporting Information Section S1). In agreement with previous reports,^[37] the acid leaching of lattice Al resulted in a small increase of the mesopore volume at the expense of the micropore volume (Table 1).

The dealuminated zeolites (Deal-BEA-X) were placed in a Schlenk flask and dehydrated under vacuum at 170 °C for 3 h. This step was necessary to avoid uncontrolled hydrolysis of the added Sn precursor. Such hydrolysis would lead to the formation of EFSn species in the micropores. After cooling to 100°C, the dehydrated zeolite powder was impregnated with excess anhydrous liquid SnCl₄ under an inert Ar atmosphere. The impregnated zeolite was then incubated for 16 h at 100 °C to allow diffusion of the grafting agent into the pores. The condensation of Sn into the framework was achieved by calcination at 550 °C (1 °C min⁻¹) for 5 h. Prior to the calcination step, the zeolites were thoroughly washed with methanol to remove excess SnCl₄. This step was essential to avoid the formation of EFSn sites.

The UV/Vis spectra (Figure 3) of Sn-BEA-25, Sn-BEA-50, and Sn-BEA-100 contained only very weak absorption features at 260 nm, characteristic for EFSn species.^[27] Incomplete removal of unreacted Sn precursor from the zeolite pores, owing to insufficient washing with methanol, led to the formation of EFSn upon calcination (Sn-BEA-50*). This formation was evident from the intense and broad absorption band at higher wavelengths (250-300 nm). The UV/Vis spectrum of Sn-BEA-50* resembles that of Sn-BEA materials prepared by high-temperature chemical vapor deposition of SnCl₄.^[27,28] Grafting of SnCl₄ to silanol nests in zeolites followed by extensive washing with methanol resulted in more-homogeneous Sn speciation. Compared with other Sn-silicate materials reported in literature,^[18, 19, 22, 27, 35, 38] the ligand-to-metal charge transfer $({\rm O}^{2-}{\rightarrow}{\rm Sn}^{4+})$ band, which is usually assigned to tetrahedrally coordinated FSn, was not observed at 210 nm but at lower wavelength (< 200 nm). This shift to shorter wavelengths has been observed before for Sn-BEA.^[21]



Figure 2. TEM images of a) BEA-25, b) BEA-50, c) BEA-100, d) Sn-BEA-25, e) Sn-BEA-50, and f) Sn-BEA-100. Scale bars = 50 nm





Figure 3. Diffuse reflectance UV/Vis absorption spectra of the synthesized materials. Absorption bands owing to framework and extraframework Sn species are indicated with f and ef, respectively.

Additional evidence for the selective incorporation of Sn into the vacant silanol nests is provided by FTIR spectroscopy. The intensity of the broad band in the range $\tilde{v} = 3500-3600 \text{ cm}^{-1}$ associated with silanol hydroxyl nests in the Deal-BEA zeolites decreased after the introduction of SnCl₄ (Figure 4).

The BEA-50 materials before and after dealumination and SnCl₄ grafting were further characterized by ¹H, ²⁹Si, and ¹¹⁹Sn NMR spectroscopy. ¹H and ²⁹Si NMR spectra (Figure 5 A and B, respectively) further demonstrate that the majority of the silanol nests reacted with SnCl₄. The reaction of Deal-BEA-50 with SnCl₄ led to a strong decrease in the relative intensity of the ¹H NMR signal at δ = 2.0 ppm corresponding to internal silanol nests (Figure 5 A). The changes in the intensity of the signal at δ = 1.8 ppm, owing to silanol groups on the external surface of the zeolite crystals, was much less pronounced. The occupation of internal silanols by Sn is further underpinned by the ²⁹Si NMR spectra shown in Figure 5 B. The respective Q³-signal at δ = -101 ppm increased upon dealumination of the parent BEA-50. This signal was reduced to its original intensity after treatment of the zeolite with SnCl₄. ¹¹⁹Sn NMR spectrosco-



Figure 4. FTIR spectra of the OH region of the dealuminated and Sn-functionalized materials after dehydration. The band generally assigned to the formation of internal silanols after dealumination is indicated in the spectrum.

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Figure 5. A) ¹H magic angle spinning (MAS) NMR spectra of dehydrated parent Al-Beta (H-BEA-50, blue line), Deal-BEA-50 (red line) and Sn-BEA-50 (green line). The spectra are normalized by weight. B) ²⁹Si direct excitation MAS NMR spectra of a) parent H-BEA-50, b) dealuminated H-(Al-)BEA-50 and c) Sn-BEA-50.

py (see Figure S4) showed that Sn species in hydrated and dehydrated materials displayed characteristic signals at $\delta = -700$ and -430 ppm, respectively, associated with Sn in tetrahedral positions of the zeolite lattice.^[21,27,39,40]

The Sn content of the modified zeolites (Table 3) was in the range of 2.81–5.07 wt% (236–427 μ mol g⁻¹). These values are lower than the values computed on the basis of the initial Al content. It is also seen that the efficiency of Sn incorporation increased when the parent zeolite was more siliceous (Table 3). The substitution efficiency, defined as the amount of Sn incorporated relative to the amount of removed Al, ranged from 23% for Sn-BEA-25, to 59% for Sn-BEA-50, and 65% for Sn-BEA-100. A tentative explanation is that the removal of a larger

Table 3. Acid site density of the synthesized materials. Quantification was performed by using the absorption coefficients reported by Datka et al. ^[41]								
Material	BAS ^[a] [µmol g ⁻¹]	LAS ^[a] [µmol g ⁻¹]	Sn content ^[b] [μmol g ⁻¹]	$A_{LAS,300} / A_{LAS,100}^{[c]}$				
Sn-BEA-25	16.0	281	236	0.26				
Sn-BEA-50	17.2	530	427	0.36				
Sn-BEA-100	16.7	306	292	0.23				
Sn-BEA-50*	3.6	392	495	0.28				
Sn-BEA-HF	11.8	118	166	0.13				
[a] Lewis (LAS) and Brønsted (BAS) acid site density determined at 200 $^\circ\text{C}.$								
[b] Number of LAS based on ICP Sn content. [c] Ratio of the band areas								
of the $v \approx 1450$ cm $^{\circ}$ signal.								

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fraction of framework sites for the Al-rich zeolites led to more extensive restructuring of the lattice. Such large defects might be more difficult to heal upon treatment with SnCl₄ compared with materials derived from the zeolites with a higher Si/Al ratio.

Infrared spectroscopy of adsorbed pyridine (Py_{ads} IR) was employed to evaluate the strength and number of Lewis and Brønsted acid sites in the Sn-modified samples (Figure 6). The



Figure 6. FTIR spectra of pyridine adsorbed on a) the synthesized Sn-modified materials and outgassed at 200 °C and b) Sn-BEA-50 followed by evacuation at 100, 200, and 300 °C. Different sites are denoted as SL (strong Lewis acid), H (H-bonded pyridine), B (Brønsted acid), and BL (Brønsted/Lewis acid).

spectra were dominated by very strong signals at $\tilde{\nu} = 1450$ and 1610 cm^{-1} , corresponding to pyridine adsorbed to strong Lewis acidic sites (SL). In addition, a weak band at $\tilde{\nu} = 1545 \text{ cm}^{-1}$ corresponding to Brønsted acid sites was observed. The intensity of this band rapidly decreased upon evacuation of the samples at elevated temperatures, indicating the weak acidity of these sites. We surmise that these sites might be unoccupied silanol nests or partially hydrolyzed framework Sn sites.

The intensities of the IR bands at $\tilde{\nu} = 1450$ and 1545 cm⁻¹ were used to estimate the amount of Lewis and Brønsted acid sites (LAS and BAS, Table 3). Sn-BEA-50 has the highest LAS content among the well-defined materials. The amount of adsorbed pyridine correlated well with the Sn content. For the materials Sn-BEA-25, Sn-BEA-50, and Sn-BEA-100, the amounts of adsorbed pyridine were 281, 530, and 306 μ mol g⁻¹, respec-



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Figure 7. Sn content versus pyridine adsorbed. The displayed values for the pyridine adsorption were determined at 200 $^{\circ}$ C.

tively. The amount of LAS correlated linearly with the Sn content in the postsynthetically modified Sn-BEA zeolites (Figure 7). The LAS densities determined from the pyridine IR measurements are higher than Sn content of the zeolites (Table 3). The extinction coefficients used to estimate the LAS content were taken to be equal to the extinction coefficients for AI LAS.^[41] We surmise that the different binding of pyridine to Sn sites may be the cause of the considerable deviations. Figure 7 also shows that Sn-BEA-50* does not follow the trend observed for the other samples. Despite its higher Sn content (Table 1), Sn-BEA-50* contained much less LAS (Table 3, Figure 7). This result suggests that some of the Sn species in this material are not accessible to pyridine, possibly because of blockage of the pores by EFSn species. The reference Sn-BEA-HF contained slightly less LAS than expected from the correlation.

The ratio of intensities of the pyridine signals owing to LAS measured at 300 and 100 °C ($A_{LAS,300}/A_{LAS,100}$, Table 3) can be used as a qualitative measure of the strength of the Lewis acid sites. The results presented in Table 3 suggest that the LAS strength of the postsynthesized Sn-BEA samples was considerably higher than that in the reference Sn-BEA-HF. We speculate that these strong LAS are partially hydrolyzed open Sn centers.^[42]

We compared the catalytic performance of the most Lewis acidic Sn-BEA-50 zeolite with Sn-BEA-HF and Sn-BEA-50* in the conversion of DHA to methyl lactate at 70 °C. The reaction profiles are shown in Figure 8. The Sn-BEA-50 and Sn-BEA-HF zeolites that predominantly contain framework Sn displayed comparable activities. The catalytic performance of Sn-BEA-50* was much lower. The complete conversion of DHA into methyl lactate was achieved after 2 h for Sn-BEA-50 and Sn-BEA-HF. On the contrary, the reaction time to achieve complete DHA conversion was 4 h for Sn-BEA-50*. The methyl lactate yield for this catalyst was also lower (86%). One of the side products was 2-hydroxy-3-methoxypropionaldehyde, which is the product of the methylation of DHA, prior to the isomerization to glyceraldehyde. Turnover number (TON), turnover frequency (TOF), and space-time yield (STY) values are given in the Supporting Information (Table S9). Sn-MCM-41, an amorphous



Figure 8. a) Conversion of DHA (dashed line) to methyl lactate (solid line) as a function of the reaction time (T=70 °C, catalyst (40 mg), 0.25 μ DHA in MeOH, 2.5 mL). b) Methyl lactate yield as a function of reaction time under the same conditions.

mesoporous Sn-containing silica with a similar Sn content as Sn-BEA-50, exhibited the lowest activity and methyl lactate selectivity (see the Supporting Information, Figure S6). The methyl lactate yield after 4 h was only 54%. The main byproduct for Sn-MCM-41 was pyruvaldehyde dimethyl acetal (PADA). Stroobants et al. reported the formation of pyruvaldehyde diethyl acetal during DHA conversion in ethanol for Sn-MCM-41.^[26] We verified that dealuminated BEA-50 (Deal-BEA-50) did not show any conversion of dihydroxyacetone after 2 h under the same conditions (70 °C, 2.5 mL 0.25 M DHA in methanol, 40 mg catalyst).

It should be noted that the performance of all of the welldefined postsynthesized zeolites was similar, regardless of the Sn content. Accordingly, the TOFs for the zeolites with a higher Sn content will be lower at the same weight-based rate (Table S9). Such activity trends have been reported before for the application of Sn-Beta in catalysis.^[34,40] The lower activity at high Sn content is usually attributed to the negative effect of EFSn species. Our work shows that such effects also occur with EFSn-free Sn-Beta, therefore, we speculate that not all Sn species are active in the reaction. This has also been suggested by Boronat et al. who studied the nature of the active Sn-sites for the Bayer–Villiger oxidation of adamantanone.^[42] This finding may be due to the different activities of open and closed Sn framework sites.

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Figure 9. Consecutive recycling experiments for Sn-BEA-HF and Sn-BEA-50. Conditions: T = 70 °C, catalyst (40 mg), 0.25 m DHA in MeOH, 2.5 mL, t = 1 h).

The reusability of Sn-BEA-50 and Sn-BEA-HF was determined by recycling experiments under different conditions (1 h, 70 $^{\circ}$ C, Figure 9). It can be seen that both catalysts retain their activity during consecutive recycles.

Our data show that not all framework Sn sites are active in isomerization catalysis. Following the speculation of Boronat et al.^[42] that only open sites are active, we undertook a computational study to compare the reaction pathway for open and closed framework Sn sites. The conversion of DHA to methyl lactate or lactic acid is generally believed to consist of three steps: dehydration of DHA to pyruvaldehyde, addition of water, and the subsequent H-shift to the lactate.^[26,43] The isomerization of 1-hydroxy-1-methoxypropanone (HMP), the hemiketal intermediate in DHA conversion, involves a H-shift reaction.^[12,26] This step has previously been considered as the rate-determining step in the overall conversion of DHA to lactates.^[43] This important elementary reaction step is also relevant to the Bayer-Villiger oxidation reaction,^[42] and the H-shift reaction in the isomerization of larger carbohydrates.^[44] Recently, an elegant experiment by Davis and co-workers involving the exchange of the slightly acidic protons at the open Sn-OH site for Na⁺ has shown the importance of such open sites for glucose isomerization.[44] We investigated HMP isomerization to methyl lactate (Scheme 2) by DFT calculations. Reaction energy



Scheme 2. H-shift of HMP to methyl lactate.

diagrams were constructed for the partially hydrolyzed SnOH [open site, $(Si_FO_FH)_3SnOH$] and for the closed site [black, $Sn(O_FSi_F)_4$]. The results of these calculations, including the optimized geometries of key intermediates and transition states, are given in Figures 10 and 11.

The first step is the adsorption of HMP by the carbonyl group (O2) to the Lewis acidic Sn center. For the closed Sn^{V} site, this results in the formation of a hydrogen bond between



Figure 10. The comparison of DFT-calculated reaction energy diagrams for the isomerization of HMP to ML following the direct Lewis acid catalyzed mechanism over the closed Sn site (black, Sn(O_FSi_F)₄) and the cooperative OH-assisted mechanism over the open SnOH site (red, $(Si_FO_F)_3SnOH)$.



Figure 11. Optimized structures and key geometrical parameters of the reaction intermediates and transition states for the isomerization of HMP to methyl lactate over the open SnOH site in a periodic Sn-BEA model (only atoms of the active site complex with DHA and those in its first coordination sphere are shown).

the O1-H hydroxyl and a vicinal lattice oxygen, which bridges between the framework Sn and Si atoms. Deprotonation of O1–H by the weakly basic lattice O site is endothermic ($\Delta E =$ 52 kJ mol⁻¹), and it results in a cationic intermediate, bidentately bound to the Sn center by the O1 and O2 atoms. This species can then be transformed to methyl lactate by a C1-C2 Hshift ($\Delta E = -78 \text{ kJ mol}^{-1}$) and O2 reprotonation ($\Delta E =$ -51 kJmol^{-1}). Because of the high endothermicity of the first deprotonation step, the overall barrier for the methyl lactate formation is 113 kJ mol⁻¹.

The reaction proceeds in a more favorable manner when it is catalyzed by the open Sn-OH site. The most significant difference is observed in the energetics of the initial O1-H deprotonation. This difference relates to the higher basicity of the terminal Sn-OH compared with that of bridging lattice oxygen atoms. Thus, initial deprotonation of HMP by Sn-OH is exothermic (-23 kJmol^{-1}) and proceeds with an activation barrier of

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only 40 kJ mol⁻¹. In this case, a water molecule is formed that binds to the Sn center. Hydrogen bonding between the coordinated water and the O2 carbonyl group further stabilizes this intermediate. The reaction proceeds by a concerted C1-C2 Hshift and protonation of the O2 site by the coordinated water molecule (Figure 11). A similar mechanism was previously proposed as the most favorable pathway for the aldose-ketose isomerization reaction by Sn-containing zeolites.^[45] The concerted one-step conversion of the O2-deprotonated HMP to methyl lactate is exothermic by -55 kJmol^{-1} and proceeds with an activation barrier of 72 kJ mol⁻¹. This value is in good agreement with the apparent activation energy determined for DHA conversion for Sn-BEA-50 zeolite (Supporting Information, S8).

Conclusions

An improved method for the preparation of nanosized Sn-Beta zeolite containing almost exclusively framework Sn-sites is reported. The method consists of the impregnation of dehydrated dealuminated Beta-zeolite with excess anhydrous SnCl4 in an inert atmosphere, followed by careful washing with methanol and calcination. The washing step is essential to avoid the formation of EFSn species. A further advantage is that larger amounts of Sn can be introduced in Sn-Beta than by other methods, such as direct fluoride-mediated Sn-Beta synthesis. The strong Lewis acid site density correlated well with the Sn content for the well-defined Sn-Beta samples. Such samples were able to rapidly convert DHA into methyl lactate without byproduct formation, attaining productivity similar to hydrothermally synthesized Sn-Beta. TOF values, however, decreased with increasing Sn-content. When EFSn sites were present, the performance of the postsynthesized materials was much lower and byproducts were formed. Nanosized Sn-Beta with exclusive framework Sn centers showed similar performance compared to Sn-Beta prepared by conventional methods and much better performance compared to Sn-MCM-41. DFT calculations supported the proposal that the open framework Sn sites act in a cooperative manner with adjacent proton-donating groups to catalyze the isomerization of 1-hydroxy-1methoxypropanone to methyl lactate. The activation barrier for this H-shift step is lower than that for the closed site, which does not contain an hydroxyl group.

Experimental Section

Chemicals

Ludox SM-30 (30 wt % SiO₂ in H₂O, Aldrich), Al(OiPr)₃ (> 98%, Aldrich), tetraethylammonium hydroxide (TEAOH, 35 wt% in H₂O, Aldrich), anhydrous SnCl₄ (99%, Aldrich), tetraethylorthosilicate (TEOS, synthesis grade, Merck), HF (40% in H₂O, Merck), SnCl₄·5H₂O (98%, Acros), and 1,3-dihydroxyacetone (DHA, dimeric form, 97%, Aldrich) were used as received without further purification.



Synthesis of Sn-containing materials

Sn-Beta zeolite synthesized in fluoride media (Sn-BEA-HF)^[18] and Sn-MCM-41^[46] were synthesized according to established procedures. Nanosized Al-Beta zeolite precursors with synthesis Si/Al ratio of 25, 50, and 100, denoted as BEA-25, BEA-50, and BEA-100, respectively, were prepared according to a modified procedure reported by Mintova et al.^[35] A solution of TEAOH in water (28.1 g) and Al(OiPr)₃ were added Ludox SM-30 (37 g) and the mixture was stirred for 20 h, after which a clear to slightly opaque (for higher amounts of Al precursor) solution was formed. The mixture was subsequently transferred to a Teflon-lined steel autoclave and placed in an oven at 100 °C for 18 days under static conditions. The resulting zeolites were collected by centrifugation, washed thoroughly with water, and dried in air. The zeolites were calcined at 400 and 550 °C (both 1 °C min⁻⁻¹, 10 h), successively. Dealumination was performed by heating in 65% HNO₃ (50 mLg⁻¹) at 110°C overnight. Residual HNO3 was removed by thorough washing with demineralized water until the pH of the washings was neutral. The resulting materials are denoted as Deal-BEA-25, Deal-BEA-50, and Deal-BEA-100. Prior to modification with Sn, the dealuminated BEA zeolites were dried in vacuo at 170 °C for 3 h in a Schlenk flask. Sn was incorporated by adding an excess of approximately three silanol nest equivalents of anhydrous SnCl₄ at 100 °C under an Ar atmosphere and the mixtures were stirred overnight. To remove unreacted SnCl_4 from the zeolite pores, the materials were thoroughly washed with methanol at least six times and dried in air. To remove residual chloride and to complete the condensation of the Sn centers into the framework, the materials were recalcined at 550 °C (1 °C min⁻¹, 5 h). The final Sn-modified catalysts are denoted as Sn-BEA-25, Sn-BEA-50, and Sn-BEA-100.

Characterization

X-ray diffraction patterns were recorded on a Bruker D4 Endeavor diffractometer by using $Cu_{K\alpha}$ radiation in the 2θ range 5–60° with a scanning speed of 0.01° s⁻¹. Elemental analyses were carried out by using a Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing. For analysis of the materials HF/HNO₃/ H₂O 1:1:1 was used as matrix. Thermogravimetric analyses to determine the water content of the solid samples were performed on a Mettler TGA/DSC-1 apparatus using 70 µL alumina crucibles. Helium was used at a gas flow rate of 40 mLmin⁻¹. Argon physisorption measurements were performed at -186°C on a Micromeritics ASAP2020 apparatus in static measurement mode. In a typical experiment, a zeolite sample (typically 100 mg) was outgassed at 200 °C for 8 h prior to the measurement. The Brunauer-Emmett-Teller equation was used to calculate the specific surface area from the adsorption data in the p/p0 range 0.05-0.35. The mesopore volume was calculated by applying the Barrett-Joyner-Halenda (BJH) method on the adsorption branch of the isotherm and the micropore volume was calculated by using the t-plot method. FTIR spectra of pyridine adsorbed to the zeolites were recorded by using a Bruker Vertex V70v system. The spectra were acquired as an average of 32 scans at a resolution of 2 cm^{-1} The samples were prepared as thin self-supporting wafers of 5-15 mg cm⁻² density and placed inside a controlled-environment infrared transmission cell. Prior to pyridine adsorption, the catalyst wafer was heated to 550 °C at a rate of 2 °C min⁻¹ under vacuum ($p < 5 \times 10^{-6}$ mbar) and maintained at this temperature for 3 h. After cooling to 100°C, pyridine was introduced in the cell in static vacuum for 30 min. Physisorbed pyridine was removed in vacuo for 30 min. The evacuated sample containing chemisorbed pyridine was subjected to a temperature-programmed desorption sequence at 100, 200, and 300 °C for 30 min, respectively, with a heating rate of 5 °C min⁻¹. FTIR spectra were recorded in situ at these temperatures. Background correction was performed by subtracting the spectrum of the dehydrated wafer recorded at 100 °C. Integration of the signals for determining the amount of Lewis and Brønsted acid sites was performed by using the Fityk curve fitting program. ¹H NMR and ¹¹⁹Sn MAS NMR spectra were recorded by using a Bruker DMX-500 NMR spectrometer with a 4 mm zirconia rotor at a spinning rate of 10 kHz. ¹H chemical shifts were referenced to Si(CH₃)₄, ¹¹⁹Sn chemical shifts were referenced to SnO₂ ($\delta = -604$ ppm).

Catalytic activity measurements

DHA was dissolved in methanol (0.25 m) and 2.5 mL of the solution, together with the catalyst (40 mg), was added to a 4 mL thick-walled glass vial. Reactions were performed at 70 °C under stirring (500 rpm) and mixtures were analyzed by GC-FID with *n*-decane as an external standard on a Shimadzu GC-17 A apparatus equipped with a Restek Rxi-5 ms column (30 m×0.25 mm, d_f =0.25 µm). Reactions used to determine the activation energy of the reaction were performed at 50, 60, and 70 °C. Identification of unknown compounds was performed on a Shimadzu QP5050 GC-MS equipped with a Stabilwax column (30 m×0.32 mm, d_f =0.5 µm). Recycle experiments were performed in a 12 mL screw-capped glass vial. The catalyst was recovered by centrifugation after each cycle, washed twice with methanol, and dried in air.

Computational details

DFT calculations were performed by using the Vienna ab initio Simulation Package (VASP 5.2).^[47] The generalized gradient exchangecorrelation PBE functional was used.^[48] The electron-ion interactions were described by the projected augmented wave (PAW) method.^[49] Geometry optimization was performed with a planewave basis set with a cut-off of 400 eV. The calculations were assumed to be converged, when the forces on each atom were less than 0.05 eV Å⁻¹. Brillouin zone-sampling was restricted to the Γ point. Optimized cell parameters for all-silica zeolite Beta are a = b = 12.66 Å, c = 26.40 Å. Two candidate active sites for Sn-Beta were considered. One is the closed Sn^{IV} site $(Sn(O_FSi_F)_4, O_F and Si_F)_4$ represent the framework oxygen and silicon atoms, respectively). The other is generated by H₂O dissociation over the framework Sn-O-Si moiety, resulting in the open (Si_FO_F)₃SnOH···HO_FSi_F active site. Sn atoms were introduced at T6 tetrahedral site of the BEA framework. The R-HMP and R-methyl lactate were used as the initial and final states to study the mechanism of the intramolecular hydrideshift reaction. The minimum reaction energy path and corresponding transition state were determined by using the nudged-elastic band method (NEB) with improved tangent estimate.^[50] The maximum energy geometry along the reaction path obtained with the NEB method was further optimized by using a quasi-Newton algorithm. In this step, only the extraframework atoms and the atoms in the first coordination sphere of Sn were relaxed. Frequency analysis of the stationary points was performed by means of the finite difference method as implemented in VASP. Small displacements (0.02 Å) were used to estimate the numerical Hessian matrix. The transition states were confirmed by the presence of a single imaginary frequency corresponding to the reaction coordinate. To account for the van der Waals (vdW) interactions between zeolite voids and carbohydrates, all calculations were carried out with the DFT-D2 method^[51] as implemented in VASP 5.2.



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- [1] J. J. Bozell, G. R. Petersen, Green Chem. 2010, 12, 539-554.
- [2] G. W. Huber, A. Corma, Angew. Chem. Int. Ed. 2007, 46, 7184–7201; Angew. Chem. 2007, 119, 7320–7338.
- [3] G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 2006, 106, 4044-4098.
- [4] A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411-2502.
- [5] M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B. F. Sels, Energy Environ. Sci. 2013, 6, 1415–1442.
- [6] H. Röper, Starch/Stärke 2002, 54, 89–99.
- [7] R. Garcia, M. Besson, P. Gallezot, Appl. Catal. A 1995, 127, 165-176.
- [8] E. Farnetti, J. Kašpar, C. Crotti, Green Chem. 2009, 11, 704–709.
- [9] N. Wörz, A. Brandner, P. Claus, J. Phys. Chem. C 2010, 114, 1164-1172.
- [10] H. J. Kim, J. Lee, S. K. Green, G. W. Huber, W. B. Kim, *ChemSusChem* 2014, 7, 1051–1054.
- [11] Y. Román-Leshkov, M. Moliner, J. A. Labinger, M. E. Davis, Angew. Chem. Int. Ed. 2010, 49, 8954–8957; Angew. Chem. 2010, 122, 9138–9141.
- [12] M. S. Holm, C. M. Osmundsen, S. Dahl, E. Taarning, Proc. R. Soc. London Ser. A 2012, 468, 2000–2016.
- [13] C.-C. Chang, Z. Wang, P. Dornath, H. J. Cho, W. Fan, RSC Adv. 2012, 2, 10475 – 10477.
- [14] M. S. Holm, S. Saravanamurugan, E. Taarning, Science 2010, 328, 602– 605.
- [15] E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, ACS Catal. 2011, 1, 408-410.
- [16] M. Moliner, Dalton Trans. 2014, 43, 4197-4208.
- [17] A. Corma, L. T. Nemeth, M. Renz, S. Valencia, *Nature* 2001, 412, 423–425.
- [18] A. Corma, M. E. Domine, S. Valencia, J. Catal. 2003, 215, 294-304.
- [19] a) Z. Kang, X, Zhang, H. Liu, J. Qiu, K. L. Yeung, Chem. Eng. J. 2013, 218, 425-432; b) Z. Kang, X. Zhang, H. Liu, J. Qiu, W. Han, K. L. Yeung, Mater. Chem. Phys. 2013, 141, 519-529.
- [20] S. Tolborg, A. Katerinopoulou, D. D. Falcone, I. Sádaba, C. M. Osmundsen, R. J. Davis, E. Taarning, P. Fristrupa, M. S. Holm, J. Mater. Chem. A 2014, 2, 20252–20262.
- [21] R. Bermejo-Deval, R. Gounder, M. E. Davis, ACS Catal. 2012, 2, 2705 2713.
- [22] C. Hammond, S. Conrad, I. Hermans, Angew. Chem. Int. Ed. 2012, 51, 11736–11739; Angew. Chem. 2012, 124, 11906–11909.
- [23] J. Wang, J. Ren, X. Liu, J. Xi, Q. Xia, Y. Zu, G. Lu, Y. Wang, Green Chem. 2012, 14, 2506–2512.

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- [24] P. Y. Dapsens, M. J. Menart, C. Mondelli, J. Pérez-Ramírez, Green Chem. 2014, 16, 589–593.
- [25] F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G. V. Baron, J. F. M. Denayer, P. P. Pescarmona, P. A. Jacobs, B. F. Sels, *J. Am. Chem. Soc.* **2012**, *134*, 10089– 10101.
- [26] L. Li, C. Stroobants, K. Lin, P. A. Jacobs, B. F. Sels, P. P. Pescarmona, Green Chem. 2011, 13, 1175–1181.
- [27] P. Li, G. Liu, H. Wu, Y. Liu, J.-g. Jiang, P. Wu, J. Phys. Chem. C 2011, 115, 3663–3670.
- [28] M. Liu, S. Jia, C. Li, A. Zhang, C. Song, X. Guo, Chin. J. Catal. 2014, 35, 723-732.
- [29] J. Jin, X. Ye, Y. Li, Y. Wang, L. Li, J. Gu, W. Zhao, J. Shi, Dalton Trans. 2014, 43, 8196-8204.
- [30] P. Wolf, C. Hammond, S. Conrad, I. Hermans, Dalton Trans. 2014, 43, 4514–4519.
- [31] B. Tang, W. Dai, G. Wu, N. Guan, L. Li, M. Hunger, ACS Catal. 2014, 4, 2801–2810.
- [32] P. Y. Dapsens, C. Mondelli, J. Jagielski, R. Hauert, J. Pérez-Ramírez, Catal. Sci. Technol. 2014, 4, 2302–2311.
- [33] Q. Guo, F. Fan, E. A. Pidko, W. N. P. van der Graaff, Z. Feng, C. Li, E. J. M. Hensen, *ChemSusChem* 2013, 6, 1352–1356.
- [34] J. Dijkmans, D. Gabriëls, M. Dusselier, F. de Clippel, P. Vanelderen, K. Houthoofd, A. Malfliet, Y. Pontikes, B. F. Sels, *Green Chem.* 2013, 15, 2777–2785.
- [35] S. Mintova, V. Valtchev, T. Onfroy, C. Marichal, H. Knözinger, T. Bein, Microporous Mesoporous Mater. 2006, 90, 237–245.
- [36] W. Kim, J.-C. Kim, J. Kim, Y. Seo, R. Ryoo, ACS Catal. 2013, 3, 192-195.
- [37] J. C. Groen, J. A. Moulijn, J. Pérez-Ramírez, J. Mater. Chem. 2006, 16, 2121–2131.
- [38] P. S. Niphadkar, A. C. Garade, R. K. Jha, C. V. Rode, P. N. Joshi, *Microporous Mesoporous Mater.* 2010, 136, 115–125.
- [39] W. R. Gunther, V. K. Michaelis, M. A. Caporini, R. G. Griffin, Y. Román-Leshkov, J. Am. Chem. Soc. 2014, 136, 6219–6222.
- [40] P. Wolf, M. Valla, A. J. Rossini, A. Comas-Vives, F. Nuñez-Zarur, B. Malaman, A. Lesage, L. Emsley, C. Copéret, I. Hermans, Angew. Chem. Int. Ed. 2014, 53, 10179–10183; Angew. Chem. 2014, 126, 10343–10347.
- [41] J. Datka, A. M. Turek, J. M. Jehng, I. E. Wachs, J. Catal. 1992, 135, 186– 199.
- [42] M. Boronat, P. Concepcion, A. Corma, M. Renz, S. Valencia, J. Catal. 2005, 234, 111 – 118.
- [43] R. S. Assary, L. A. Curtiss, J. Phys. Chem. A 2011, 115, 8754-8760.
- [44] R. Bermejo-Deval, M. Orazov, R. Gounder, S.-J. Hwang, M. E. Davis, ACS Catal. 2014, 4, 2288–2297.
- [45] G. Li, E. A. Pidko, E. J. M. Hensen, Catal. Sci. Technol. 2014, 4, 2241– 2250.
- [46] A. Corma, M. T. Navarro, L. Nemeth, M. Renz, Chem. Commun. 2001, 2190–2191.
- [47] G. Kresse, J. Hafner, Phys. Rev. B 1993, 48, 13115-13118.
- [48] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865– 3868.
- [49] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953-17979.
- [50] G. Mills, H. Jónsson, G. K. Schenter, Surf. Sci. 1995, 324, 305-337.
- [51] S. Grimme, J. Comput. Chem. 2006, 27, 1787-1799.

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Synthesis of Sn-Beta with Exclusive and High Framework Sn Content



Only in the framework! Extraframework Sn (EFSn) species in Sn-Beta zeolites have a negative impact on the activity and selectivity of the catalyst for the conversion of 1,3-dihydroxyacetone into methyl lactate. The reported method is specifically designed to avoid EFSn formation during the synthesis of Sn-Beta zeolites. In this way, the activity and selectivity of the catalysts are significantly improved.