



Effects of Alkali and Counter Ions in Sn-Beta Catalyzed Carbohydrate Conversion

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Published in:
ChemSusChem (Print)

Link to article, DOI:
[10.1002/cssc.201702413](https://doi.org/10.1002/cssc.201702413)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Elliot, S. G., Tolborg, S., Madsen, R., Taarning, E., & Meier, S. (2018). Effects of Alkali and Counter Ions in Sn-Beta Catalyzed Carbohydrate Conversion. *ChemSusChem (Print)*, 11(7), 1198-1203.
<https://doi.org/10.1002/cssc.201702413>

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Accepted Article

Title: Effects of Alkali and Counter Ions in Sn-Beta Catalyzed Carbohydrate Conversion

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To be cited as: *ChemSusChem* 10.1002/cssc.201702413

Link to VoR: <http://dx.doi.org/10.1002/cssc.201702413>

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Effects of Alkali and Counter Ions in Sn-Beta Catalyzed Carbohydrate Conversion

Samuel G. Elliot,^[a] Søren Tolborg,^[b] Robert Madsen,^[a] Esben Taarning,^{[b]*} and Sebastian Meier^{[a]*}

Alkali ions have been shown to strongly influence the catalytic behavior of stannosilicates in the conversion of carbohydrates. An effect of having alkali ions present is a pronounced increase in selectivity towards methyl lactate. Mechanistic details of this effect have remained obscure and are herein addressed experimentally through kinetic experiments and isotope tracking. Alkali ions have a differential effect in competing reaction pathways: they promote the rate of carbon-carbon bond breakage of carbohydrate substrates, but decrease the rates of competing dehydration pathways. Further addition of alkali inhibits activity of Sn-Beta in all major reaction pathways. The alkali effects on product distributions and on rates of product formation are similar, thus pointing to a kinetic reaction control and to irreversible reaction steps in the main pathways. Additionally, an effect of the accompanying basic anions is shown, supposedly facilitating the cation exchange and eliciting a different concentration-dependent effect than neutral alkali salts.

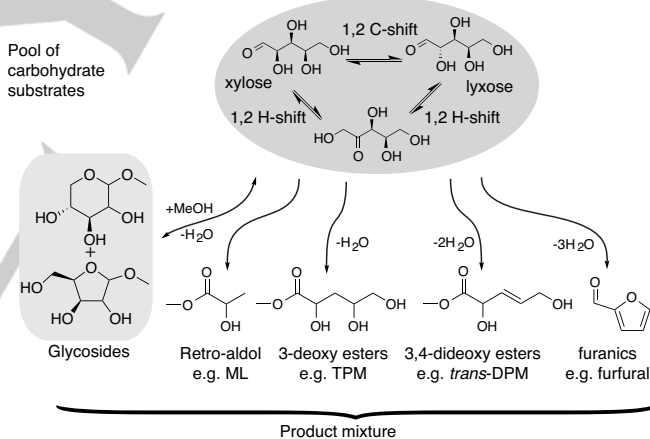
Introduction

Chemocatalytic carbohydrate conversion may be achieved by the use of zeolites, which are microporous solid materials widely used in oil refining that are projected to obtain similarly central roles in biomass refining.^[1-2] Especially zeotypes, with elements such as tin instead of aluminum incorporated in the zeolite framework, have been shown to catalyze a range of relevant reactions in the conversion of carbohydrates, including isomerization, dehydration and retro-aldol cleavage of carbohydrates.^[1, 3-4] Since carbohydrates comprise approximately 75% of all biomass on Earth, they are attractive as a feedstock for the development of sustainable processes.^[5]

Sn-Beta, a tin-containing zeotype (stannosilicate), is a particularly promising heterogeneous catalyst for carbohydrate conversion.^[4, 6] Sn-Beta is able to catalyze the isomerization and epimerization of carbohydrates at mild reaction conditions (near 100 °C),^[7-9] while higher temperatures (above 120 °C) facilitate the formation of different α -hydroxy acids/esters and furanic compounds through a combination of retro-aldol cleavage^[10-12] or condensation,^[13] and dehydration reactions.^[10, 14-18] The major products resulting from conversion of xylose by Sn-Beta above

120 °C are displayed in Scheme 1.

Recently, it has been shown that the catalytic performance of stannosilicates can be influenced by the presence of alkali cations.^[19] Low millimolar amounts of alkali ions were found to greatly increase the formation of methyl lactate in methanol (from 30% to 75%) at 160 °C using Sn-Beta.^[19-20] At lower temperatures (80 °C), alkali ions have also been reported to promote Sn-Beta catalyzed epimerization over the isomerization of carbohydrates.^[21-23] The effect of alkali ions on zeolite catalyzed reactions has been more thoroughly studied for reactions with fewer competing pathways than those of Scheme 1, using non-carbohydrate substrates. Thus, alkali exchange has been shown to enhance Baeyer–Villiger oxidation by Sn-Beta,^[24] but to lower the activity of titanosilicates in epoxidation with H₂O₂.^[25-26] These alkali effects are thought to result from exchange of protons at or in the vicinity of the catalyst active site.^[24-26] The detailed nature of the alkali effect in improving methyl lactate yield and carbohydrate epimerization, and the correlation between the two effects have hitherto remained unclear.



Scheme 1. Competing pathways observed in the conversion of pentoses catalyzed by Sn-Beta in methanol. ML = methyl lactate, TPM = 2,4,5-trihydroxypentanoic acid methyl ester, *trans*-DPM = *trans*-2,5-dihydroxy-3-pentenoic acid methyl ester, furanics = furfural and furfural dimethyl acetal.

The current study sets out to systematically study the effect of alkali salts (as demonstrated herein for potassium salts) on the divergent pathways catalyzed by Sn-Beta (Scheme 1). Quantitative high-field NMR spectroscopy was used to distinguish and quantify various reaction products without the need for purification, reference compounds or instrument calibrations.^[27] Changes in activity and selectivity of Sn-Beta were thus noninvasively probed by accurate *in situ* analysis of resultant reaction mixtures. These assays show that alkali ions are activity promoters of methyl lactate formation at moderate concentrations but inhibitors of all major Sn-Beta catalyzed pathways at higher concentrations.

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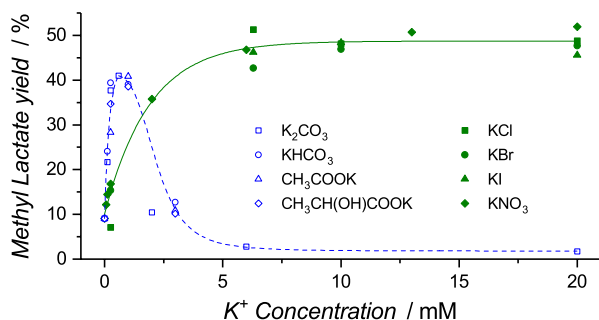


Figure 1. Methyl lactate yield as a function of potassium concentration for various salts of strong acids (filled green symbols) and salts of weak acids (open blue symbols). Reaction conditions: 0.250 g glucose, 0.100 g Sn-Beta (HT), 5 mL methanol containing up to 20 mM potassium salt, 120 °C, 19 h. Methyl lactate is considered stable under the reaction conditions (Figure S1).

Results and Discussion

A variety of potassium salts were initially probed for their impact on the formation of methyl lactate by Sn-Beta. These experiments encompassed potassium salts of weak acids and of strong acids. The experiments were conducted at mild reaction conditions (120 °C) and with long reaction times (19 h) in order to ensure full conversion. The potassium salts of weak and strong acids in a concentration range between 0 and 20 mM K^+ showed distinct effects on the methyl lactate yield (Figure 1). The yields of methyl lactate increased for salts of strong acids and reached a plateau at higher concentrations. In contrast, alkali salts of weak acids (with basic anions) generally show a steeper increase in methyl lactate yield to a well-defined optimum, followed by a subsequent decrease in yield at higher concentrations of the salt.

Mechanistic insights into the observed effect of potassium salts of strong and weak acids were subsequently sought. The effect was analyzed by probing the flux into all major reaction pathways catalyzed by Sn-Beta. The formation of the four major product classes (Scheme 1) and the methyl glycoside by-products were tracked as initial rate experiments using quantitative high-resolution NMR spectroscopy in order to obtain time-resolved kinetic data. These experiments were performed using pentose substrate rather than hexoses at higher temperatures (160 °C), due to higher obtained yields of the dehydration products and formation of fewer diastereoisomers.^[17] Reactions were performed using a microwave reactor and analyzed *ex situ* with ^{13}C and 1H - ^{13}C NMR spectroscopy. The conversion of xylose was tracked in the absence of alkali salt, in the presence of 2 mM KCl, and in the presence of 0.3 mM K_2CO_3 . The chosen concentrations are near the optimum for methyl lactate formation under these conditions (Tables S1 and S2).^[19] In addition, K_2CO_3 concentrations above and below the optimum were tested (0.1–1 mM).

Initial rate experiments were conducted for only up to two minutes at 160 °C. We observed that xylose was converted very rapidly, on the low minute timescale (Figure S2), albeit the process previously had been conducted on a time scale of hours. Both substrate and product signals showed initial linear trends with and without alkali salts, indicating that a steady state was achieved (Figure 2 and Figure S3).

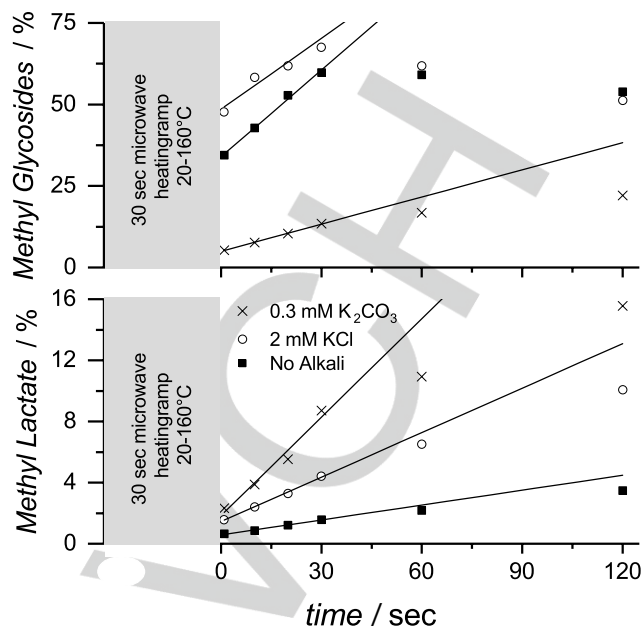


Figure 2. Initial rate experiments of methyl glycoside and methyl lactate. Signal areas were converted to molar yields by a quantitative NMR approach. Reactions consisted of 360 mg D-xylose, 90 mg Sn-Beta (PT), 5 mL methanol and 50 mg dimethyl sulfoxide (internal standard), which were heated from room temperature to 160 °C within 30 seconds (indicated by the grey box) and reacted for variable time at 160 °C. Methanol containing no additive, 2 mM KCl or 0.3 mM K_2CO_3 , was used.

The time-resolved experiments show rapid formation of glycosides already during the heating stage, both in the presence of KCl and in the absence of any added salts. In contrast, the rate of glycoside formation is suppressed approximately 4-fold for reactions performed at optimum K_2CO_3 concentrations (Figure 2). Thus, alkali salts also exhibit an effect on the formation of methyl glycosides depending on the basicity of the anion, consistent with Fischer glycosylation in the presence of weak Brønsted acidic sites. This effect is also observed for the formation of furanics and is consistent with pathway models suggesting that the formation of furanics encompasses Brønsted acid catalyzed dehydration. These observations may be explained by neutralization of Brønsted acidity by a basic anion.

Importantly, the initial rate of methyl lactate formation increases both in the presence of K_2CO_3 and of KCl (Figures 2 and 3), demonstrating the positive effect of the alkali cation on the catalytic activity of Sn-Beta towards methyl lactate. A smaller increase is observed in the presence of KCl than in the presence of K_2CO_3 . This finding is consistent with both the higher degree of free carbohydrates in the presence of K_2CO_3 (Figure 2), as a result of inhibiting Brønsted acid catalyzed pathways, and with higher exchange of cations onto the zeotype in the presence of a basic anion.^[28–29] Increased rates for the formation of methyl lactate are accompanied by reduced rates for formation of dehydration products (Figure 3). Hence, the change in selectivity is caused by higher activity of retro-aldol cleavage and slightly reduced activity for dehydration pathways.

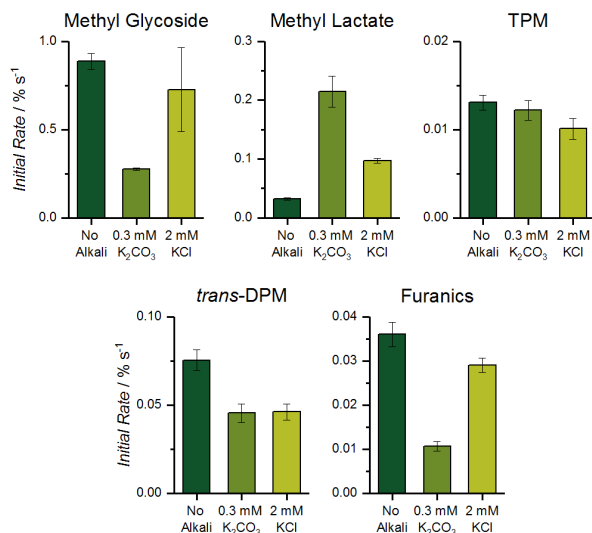


Figure 3. Overview of the effects of KCl and K_2CO_3 on the rates of formation for the designated products. Errors are calculated based on a linear fit of experimental data points.

Subsequently, the reasons for the decline in methyl lactate formation above the optimum concentration of K_2CO_3 were probed. To this end, the initial reaction rates were determined for varying concentrations of K_2CO_3 . These rates are consistent with previously reported trends in product distributions for increasing concentrations of K_2CO_3 .^[16, 27] Rates of formation for dehydration products decline upon addition of K_2CO_3 , in parallel with a drop in yield of these products upon addition of K_2CO_3 . Similarly, the highest rate of methyl lactate formation is found at the K_2CO_3 concentration that also results in the highest yield of methyl lactate (Figure 4). A well-defined optimum for the yield of methyl lactate in the presence of K_2CO_3 results from a deactivation of the catalyst at higher concentrations. Effects of base-catalyzed carbohydrate degradation are secondary and the rate of carbohydrate conversion is reduced in the presence of K_2CO_3 , and not increased through possible additional degradation reactions.

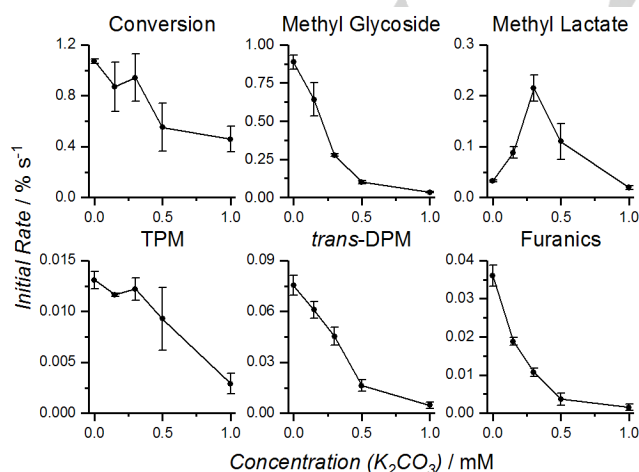


Figure 4. Initial rates of conversion and of formation for different compound classes as a function of K_2CO_3 concentration. Reaction conditions: 360 mg D-xylose, 90 mg Sn-Beta (PT), 5 mL methanol and 50 mg dimethyl sulfoxide at 160 °C. Errors are calculated based on a linear fit of experimental data points.

Thus, initial rates of conversion indicate that the catalyst kinetically favors dehydration reactions in the absence of added K_2CO_3 , but favors the formation of retro-aldol products near 0.3 mM K_2CO_3 prior to deactivation of all reaction pathways by further addition of basic alkali salt. Alkali ions thus promote methyl lactate formation at moderate concentrations but inhibit all major Sn-Beta catalyzed pathways at higher concentrations. Furthermore, the alkali effect occurs at concentrations similar to the concentrations of tin present in the catalyst (0.31 K/Sn for an experiment with 0.3 mM K_2CO_3), supporting that the alkali cation effect is related to the tin active sites.

In addition to catalyzing the formation of products shown in Figure 4, Sn-Beta had been reported to catalyze carbohydrate epimerization at temperatures near 80 °C.^[21-23] For a more complete picture of the alkali effect on Sn-Beta catalyzed reactions, we therefore also wanted to probe the effect of alkali addition on the rate of epimerization. There are two viable mechanisms that can explain the 1,2-carbon shift occurring in the epimerization of carbohydrates: 1) a retro-aldol type mechanism where the shift occurs as a consequence of a retro-aldol/aldol rearrangement (Figure 5A) and 2) a Biliik-type mechanism with concerted breakage of the C2-C3 bond and formation of a new bond between C1-C3 (Figure 5B). Both suggested reaction mechanisms involve (i) breaking of a C=O bond to form a C-O-Sn bond, (ii) breaking of a Sn-O bond to form a C=O bond and (iii) breakage of the C2-C3 bond and formation of a new bond between C1-C3.^[23, 30] Irrespective of which mechanism is responsible for the 1,2-carbon shift, epimerization and retro-aldol cleavage thus share similar reaction steps and a similar effect of alkali on both reactions could seem possible.

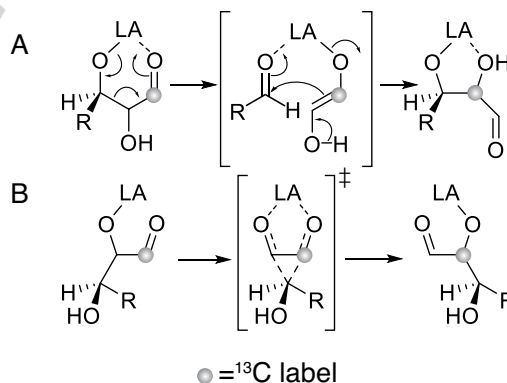


Figure 5. Comparison of 1,2-carbon shift by a retro-aldol (A) and a Biliik-type (B) cleavage mechanism.^[30] The conversion of a ^{13}C labelled C1 position to a ^{13}C labelled C2 position is indicated for both cases.

NMR spectroscopy was used to quantitatively measure isotope redistributions and compound yields to correlate the alkali effects both on epimerization and on methyl lactate formation. The 1,2-carbon shift was indirectly probed at high temperature conditions that favor the cleavage or dehydration of carbohydrates. To this end, isotopically enriched D-[1- ^{13}C] xylose was converted at 160 °C in methanol using Sn-Beta under varying concentrations of alkali salts. Isotope scrambling was quantified for all major products after five minutes of reaction.

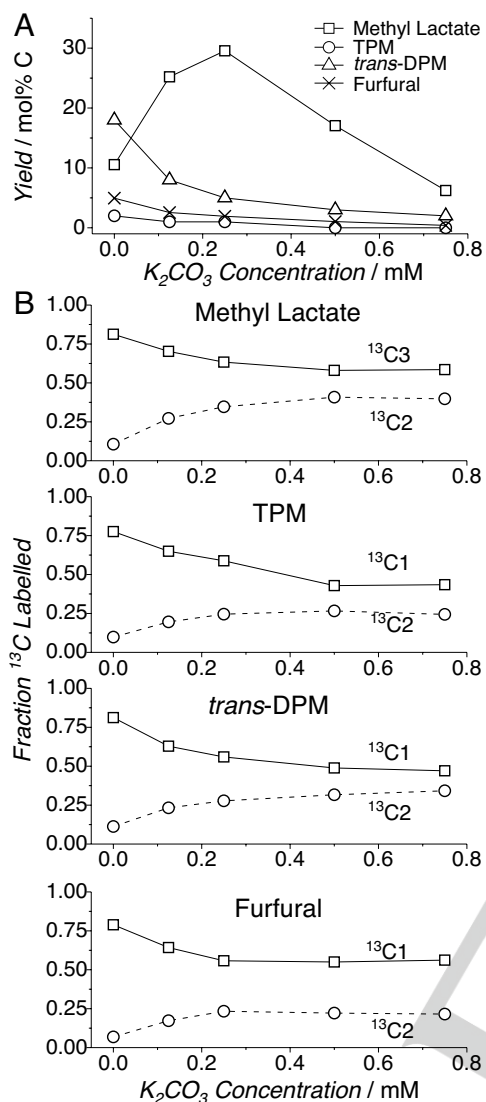


Figure 6. (A) ^{13}C distribution of the C1 and C2 positions of methyl lactate, TPM, trans-DPM and furfural (analysed in its dimethyl acetal form) at varying alkali concentrations (see Figure S4 for Methyl Glycosides). For ML, the C3 position deriving from pentose C1 is shown instead of C1. (B) Corresponding yields of methyl lactate. All reactions conducted with 36 mg D-[1- ^{13}C]-xylose, 18 mg Sn-Beta (HT), 500 μ L methanol and 5 mg dimethyl sulfoxide, which were heated to 160°C for 5 min. Methanol containing 0 mM, 0.125 mM, 0.25 mM, 0.5 mM and 0.75 mM K_2CO_3 , respectively, was used.

Experiments conducted with increasing amounts of K_2CO_3 show that epimerization and retro-aldol cleavage share a similar dependence on alkali concentrations, as expected. The product distributions are depicted in Figure 6A and the fractions of different isotopic isomers of these products are shown in Figure 6B. The product distributions (Figure 6A) in response to varying K_2CO_3 concentrations reflect the trends shown in Figure 4. The ^{13}C label in the product was primarily found at the C1 and C2 positions of all dehydration products, and at the C3 and C2 positions of methyl lactate, as the C1 position of xylose primarily gets converted to C3 of methyl lactate (Figure 6B).^[31] All major products showed a comparable trend in the distribution of isotopic isomers with increasing amounts of K_2CO_3 . Scrambling increased with K_2CO_3 concentrations for the positions deriving from C1 and C2 of xylose up to K_2CO_3 concentrations that

provide optimal methyl lactate yield (0.25 mM K_2CO_3 , 0.17 K/Sn). These observations show that the epimerization of carbohydrates by a 1,2-carbon shift^[21] also occurs under high temperature conditions that lead to significant retro-aldol cleavage and dehydration reactions. The relative product distribution of the main product categories as shown in Figure 6A thus stabilizes in the same concentration range of K_2CO_3 , where also the isotope redistribution due to epimerization (Figure 6B) stabilizes. Indirect detection of 1,2-carbon shift by stable isotope redistribution thus indicates that moderate alkali exchange accelerates epimerization by Sn-Beta, while initial rate experiments show that the same conditions also accelerate the retro-aldol cleavage but impede dehydration by Sn-Beta.

Conclusion

We employ two independent assays to evaluate the role of additives in heterogeneous catalysis. Effects of alkali metal salts on the activity and selectivity of Sn-Beta catalyzed carbohydrate conversion were probed. Isotope tracking experiments show that C-C bond breakage in epimerization and retro-aldol reactions is accelerated relative to dehydration reaction pathways in the presence of alkali ions. Epimerization and retro-aldol cleavage display a similar dependence on the alkali ion concentration. Kinetic experiments show that K_2CO_3 and KCl have differential effects on carbohydrate conversion, as K_2CO_3 suppresses Brønsted acid catalyzed reactions in the formation of methyl glycosides and furanic compounds. Both K_2CO_3 and KCl are activity promoters of retro-aldol cleavage at low alkali concentrations, indicating a modification of the active site by alkali cations. At higher concentrations of alkali metal salts containing basic anions, all major Sn-Beta catalyzed pathways are deactivated. Overall, kinetic and isotope data indicate that the alkali effect increases the selectivity for the formation of methyl lactate from carbohydrates by changing the catalyst active site to increase rates of carbon-carbon cleavage and - to a lesser extent - reduce rates of dehydration in kinetically controlled pathways.

Experimental Section

Reactions with isotope labelled xylose were conducted with a Biotage Initiator+ microwave reactor in 500 μ L glass reaction vials. Reactions were typically conducted with 18 mg Sn-Beta (Si/Sn = 200, hydrothermally synthesized), 36 mg [1- ^{13}C]-D-xylose, 500 μ L methanol and 5 mg dimethyl sulfoxide as an internal standard. Rate experiments were conducted with a Biotage Initiator+ microwave reactor in 5 mL glass reaction vials. A typical reaction was conducted with 90 mg Sn-Beta (Si/Sn = 150, post-treated), 360 mg D-xylose, 50 mg dimethyl sulfoxide as the internal standard and 5 mL methanol as well as alkali salts at concentrations as indicated. Control experiments were conducted in the presence of alkali salts but in the absence of Sn-Beta, with results shown in Figure S5.

Hydrothermally synthesized Sn-Beta (Si/Sn = 200) catalyst was prepared according to the procedure by Tolborg *et al.*, employing a target Si/Sn ratio of 200.^[32] The catalyst structure and composition was confirmed by ICP-OES (0.9 wt% Sn, Si/Sn

= 196), XRD (*BEA framework) and N₂ absorption (S_{BET} = 540 m² g⁻¹, S_{micropore} = 436 m² g⁻¹, V_{total} = 0.30 mL g⁻¹, V_{micropore} = 0.22 mL g⁻¹ calculated by the *t*-plot method). Post-treated Sn-Beta (Si/Sn = 150) catalyst was synthesized by a post-treatment method in accordance with the procedure by Hammond *et al.*^[33] The catalyst structure and composition was confirmed by ICP-OES (1.3 wt% Sn, Si/Sn = 152), XRD (*BEA framework) and N₂ absorption (S_{BET} = 688 m² g⁻¹, S_{micropore} = 555 m² g⁻¹, V_{total} = 0.43 mL g⁻¹, V_{micropore} = 0.22 mL g⁻¹ calculated by the *t*-plot method).

NMR spectra were recorded using an 800 MHz Bruker Avance III NMR spectrometer equipped with a TCI CryoProbe and a SampleJet sample handler. Quantifications were obtained with qNMR (quantitative NMR) experiments. Response factors in two-dimensional ¹H-¹³C HSQC NMR spectra were obtained for the analytes of interest by comparison to quantitative, integrated 1D ¹³C spectra. These quantitative proton decoupled ¹³C 1D spectra were acquired with recycle delays of 60 seconds using a pulse sequence that employs inverse gated decoupling. Employing response factors of ¹H-¹³C HSQC NMR experiments, far more sensitive spectra (~32-fold more sensitive) could be used to accurately and rapidly (20 min NMR experiment time) quantify the main reaction products. The spectra were processed in Bruker Topspin 3.5 pl7 software using ample zero filling in all spectral dimensions.

Acknowledgements

This work was funded by the Innovation Fund Denmark (case number 5150-00023B). 800 MHz NMR spectra were recorded on the spectrometer of the NMR center DTU supported by the Villum foundation.

Keywords: alkali effect • heterogeneous catalysis • methyl lactate • kinetics • Sn-Beta

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Layout 2:

FULL PAPER

Samuel G. Elliot, Søren Tolborg, Robert Madsen, Esben Taarning,* and Sebastian Meier*

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Effects of Alkali and Counter Ions in Sn-Beta Catalyzed Carbohydrate Conversion

Time for a promotion. Catalyst modifiers have an outstanding impact on the practicability and profitability of catalytic processes. Alkali ions, for instance, influence the catalytic properties of silicate-based materials such as zeolites in carbohydrate conversion towards handpicked products. Here, the functional role of catalyst modifiers in promoting and poisoning reaction pathways is probed.

