Alkaline-assisted stannation of beta zeolite as a scalable route to Lewis-acid catalysts for the valorisation of renewables

Author(s): Dapsens, Pierre Y.; Mondelli, Cecilia; Pérez-Ramírez, Javier

Publication Date: 2016-05-01

Permanent Link: https://doi.org/10.3929/ethz-a-010792796


Rights / License: In Copyright - Non-Commercial Use Permitted
Alkaline-assisted stannation is applied as a facile one-step post-synthetic approach for the preparation of Lewis-acid Sn-BEA from a high-silica commercial beta (BEA) zeolite. The concentration of base, tin and protective additive tetrapropylammonium as well as the nature of the tin precursor are identified as key parameters of the metallation process determining the acidic and structural properties of the stannated zeolite and, in turn, its performance in the isomerisation of bio-based substrates.

Lewis-acid solids play a prominent role in the valorisation of biomass to chemicals enabling relevant isomerisation, (retro)aldol, transfer-hydrogenation and cycloaddition reactions.[1-4] In these conversions, tin-containing high-silica zeolites have demonstrated extremely active and selective.[5-7] Among them, Sn-BEA prepared under hydrothermal conditions comprises the state-of-the-art catalyst. Nevertheless, since its synthesis is long, poorly reproducible and needs noxious fluoride ions, the development of more industrially-amenable methods has received increasing interest.[6] While a rapid and fluoride-free route based on steam-assisted dry-gel conversion has been recently reported,[8] post-synthetic strategies have been more widely explored in view of their potentially higher scalability.[6] The most followed approach is a two-step method which comprises dealumination of Al-rich BEA (bulk Si/Al ≈ 12) with a concentrated acid solution followed by tin incorporation into the as-created vacancies (i.e., silanol nests).[9-11] Tin implantation through exposure to SnCl₄ vapours at 673-773 K produced Sn-BEA materials exclusively featuring framework Sn atoms only at low loadings (ca. 1.2 wt.%).[9] Upon solid-state stannation, dealuminated BEA was ground with Sn(OAc)₂ attaining a zeolite containing ca. 10 wt.% of tin and virtually free of SnO₂ species or was treated with an organometallic precursor such as Sn(Me₂Cl₂).[10] Recently, the use of isopropanolic solutions of SnCl₄·5H₂O and of dry impregnation with SnCl₄ for liquid-phase stannation has also been demonstrated.[11] Overall, the catalysts featuring the highest degree of tin integration at lattice position displayed the best performance in the isomerisation of sugars, α-pinene and dihydroxyacetone,[9c,10] in some cases matching that of the reference Sn-BEA thanks to the higher metal loading and smaller crystal size.

Recently, our group introduced alkaline-assisted metallation as an alternative method to incorporate Lewis metals in zeolitic matrices.[12] Upon treating the zeolite in aqueous NaOH containing a soluble salt of the desired metal (Al, Ga, Sn), vacancies are created by Si extraction and healed by the added metal in one pot. In contrast to the previous approach that can only be applied to zeolites which are easily dealuminated such as BEA,[10-11,14] this strategy is more versatile since base leaching has been shown for various frameworks.[13] Indeed, tin was successfully integrated in silicalite attaining catalysts displaying similar Lewis-acid characteristic to Sn-MFI prepared under hydrothermal conditions, which proved extremely active for the isomerisation of glyoxal and dihydroxyacetone in water and methanol as well as for that of sugars.[12c,d,e]

Herein, we systematically study the effect of key preparative aspects of alkaline-assisted stannation broadening its scope of application to a commercial high-silica BEA zeolite. In particular, we investigate the impact of the strength...
of the alkaline medium, the amount of an organic zeolite protector and tin in solution and of the type of tin precursor on the process using the isomerisation of glyoxal in water as a model reaction to assess the quality of the Lewis-acid sites integrated (Scheme 1). The optimised catalyst derived is then compared to hydrothermally-synthesised Sn-BEA and evaluated in the valorisation of trioses, pentoses and hexoses.

BEA zeolite with a bulk Si/Al ratio of 220 was selected as the starting material for stannation (Table 1, entry 1) since it undergoes appreciable modification upon alkaline treatment under mild conditions[15] and its low Al content should have a negligible effect on the metalla
tation. Firstly, Sn-BEA materials featuring different crystallinity (Fig. S1 in the ESI) were prepared treating P in 0.1 M NaOH containing 0.01 M of SnCl\(_4\) and variable amounts (0-0.2 M) of tetratetrapropylammonium (TPA\(^+\)) bromide. While the sole NaOH led to the collapse of the framework (Table 1, entry 2) confirming the high sensitivity of this BEA sample to basic conditions, the presence of Sn\(^{4+}\) species was effective in partially retaining its crystalline structure (44%) while introducing tin in the solid (ca. 1.85 wt.% Table 1, entry 3). This finding uncovers that also tetravalent metal atoms protect the zeolite crystals from excessive dissolution. The further addition of TPA\(^+\) to the basic medium allowed to better preserve the crystallinity of the final zeolite (58 to 69%). The latter value corresponds to the maximum achievable based on the results obtained treating BEA with only NaOH and TPA\(^+\) (Table 1, entry 6). Interestingly, in spite of the distinct structural alterations produced, no change in metalla
tation efficiency was observed in the absence or presence of TPA\(^+\) (Table 1, entries 4-5). The performance of these stannated zeolites was assessed in the aqueous-phase conversion of glyoxal to glycolic acid since this transformation was shown to be exclusively Lewis-acid catalysed and to lead to negligible catalyst deactivation in 8-h tests, possibly due to the mild reaction temperature (363 K) and the absence of byproducts.[12c] As depicted in Fig. 1, a linear correlation was found between the TOF and the crystallinity of the samples, which indicates the benefits of a defined micropore geometry for the activity. This supports previous evidence for zeolitic and amorphous tin-containing porous materials in other Lewis-acid catalysed isomerisations.[6]

In a second step, the influence of the tin loading on the catalyst performance was evaluated. In fact, previous works have indicated that, although post-synthetic approaches enable the introduction of higher metal amounts compared to hydrothermal synthesis, more active tin sites are attained at lower tin contents. [10a,11a] For this purpose, the concentration of SnCl\(_4\) in the alkaline medium was varied keeping that of TPA\(^+\) constant (Table 1, entries 7-8). While the sample containing only ca. 1 wt.% Sn did not show a higher TOF, the catalyst containing more metal exhibited lower activity, in line with the literature.[10a,11a] Thus, a metal content of 1.5-1.8 wt.% was targeted in the subsequent preparations in analogy to hydrothermally-prepared Sn-BEA.

Since the parent zeolite already features a significant amount of defects, as evidenced by DRIFT and \(^{29}\)Si MAS NMR

| Table 1 Characterisation of the parent, alkaline-treated, stannated and hydrothermally-synthesised BEA zeolites |

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst[a]</th>
<th>Yield[b] (%)</th>
<th>Sn[c] (wt.%)</th>
<th>Crystal[d] (%)</th>
<th>(S_{\text{meso}}[e] (\text{m}^2 \text{g}^{-1}))</th>
<th>(V_{\text{meso}}[e] (\text{cm}^3 \text{g}^{-1}))</th>
<th>(V_{\text{por}}[f] (\text{cm}^3 \text{g}^{-1}))</th>
<th>(S_{\text{BET}}[g] (\text{m}^2 \text{g}^{-1}))</th>
<th>TOF (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P</td>
<td>100</td>
<td>–</td>
<td>100</td>
<td>85</td>
<td>0.19</td>
<td>0.36</td>
<td>550</td>
<td>n.a.</td>
</tr>
<tr>
<td>2</td>
<td>AT1</td>
<td>88</td>
<td>–</td>
<td>0</td>
<td>305</td>
<td>0.07</td>
<td>0.41</td>
<td>446</td>
<td>n.a.</td>
</tr>
<tr>
<td>3</td>
<td>AT1Sn1</td>
<td>87</td>
<td>1.85</td>
<td>44</td>
<td>248</td>
<td>0.11</td>
<td>0.45</td>
<td>519</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>AT1Sn1TPA1</td>
<td>82</td>
<td>1.92</td>
<td>58</td>
<td>219</td>
<td>0.17</td>
<td>0.45</td>
<td>563</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>AT1Sn1TPA2</td>
<td>86</td>
<td>1.86</td>
<td>69</td>
<td>172</td>
<td>0.24</td>
<td>0.46</td>
<td>673</td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td>AT1TPA2</td>
<td>77</td>
<td>–</td>
<td>72</td>
<td>222</td>
<td>0.21</td>
<td>0.49</td>
<td>740</td>
<td>n.a.</td>
</tr>
<tr>
<td>7</td>
<td>AT1Sn05TPA2</td>
<td>81</td>
<td>1.02</td>
<td>57</td>
<td>255</td>
<td>0.17</td>
<td>0.44</td>
<td>620</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>AT1Sn15TPA2</td>
<td>88</td>
<td>3.43</td>
<td>57</td>
<td>194</td>
<td>0.16</td>
<td>0.40</td>
<td>574</td>
<td>25</td>
</tr>
<tr>
<td>9</td>
<td>Sn05</td>
<td>98</td>
<td>0.65</td>
<td>100</td>
<td>81</td>
<td>0.17</td>
<td>0.34</td>
<td>558</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Sn05TPA2</td>
<td>99</td>
<td>0.72</td>
<td>97</td>
<td>86</td>
<td>0.17</td>
<td>0.36</td>
<td>531</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>AT2Sn05TPA2</td>
<td>59</td>
<td>1.50</td>
<td>37</td>
<td>516</td>
<td>0.06</td>
<td>0.64</td>
<td>639</td>
<td>40</td>
</tr>
<tr>
<td>12</td>
<td>AT1SnS1</td>
<td>88</td>
<td>3.29</td>
<td>25</td>
<td>241</td>
<td>0.10</td>
<td>0.43</td>
<td>444</td>
<td>63</td>
</tr>
<tr>
<td>13</td>
<td>AT3Sn4TPA2</td>
<td>81</td>
<td>1.71</td>
<td>68</td>
<td>126</td>
<td>0.15</td>
<td>0.32</td>
<td>478</td>
<td>91</td>
</tr>
<tr>
<td>14</td>
<td>Sn-BEA</td>
<td>n.a.</td>
<td>1.50</td>
<td>100</td>
<td>50</td>
<td>0.19</td>
<td>0.31</td>
<td>508</td>
<td>156</td>
</tr>
</tbody>
</table>

[a] P = Parent, ATxSn(S)xTPAx = alkaline treatment in 0. x M NaOH and in the presence of 0.x M of tin source (Sn = tin(IV) chloride and SnS = tin(II) sulphate) and of 0.0x M TPABr. Sn-BEA = hydrothermally-prepared sample. [b] Yield of solid after alkaline treatment or alkaline-assisted stannation and subsequent calcination. [c] ICP-OES. [d]XRD, based on the height of the reflection at 2\(\theta\) = 22.5°. [e]\(\text{BET}\) method. [f] Volume adsorbed at \(p/p_0\) = 0.99. [g] BET method.

---

Figure 1. TOF of stannated Sn-BEA samples prepared with 0.1 M NaOH and 0.01 M of SnCl\(_4\) in the absence or presence of various amounts of TPA\(^+\) in the conversion of glyoxal \textit{versus} their crystallinity.
sensitivities (Fig. S2 in the ESI), we also stannated samples in the sole presence of tin chloride or of this salt and TPA⁺ (Table 1, entries 9-10), i.e., mimicking the metallation of a dealuminated zeolite. In spite of a significant tin incorporation and a substantial decrease of defects, the very low TOF values highlight the critical role of the base in generating a sensible amount of active species.

The effect of the alkalinity of the medium was thus assessed. Higher concentrations of hydroxide ions are expected to generate more vacancies, thus maximising the probability of tin incorporation in the framework, but too harsh conditions undermine the structural integrity of the zeolite reducing its activity, as discussed above. A stannated material was prepared treating P with 0.2 M NaOH and the optimal TPA⁺ concentration determined earlier (Table 1, entry 11). One should note that a lower concentration of metal salt was used to prevent excessive metallation. Remarkably, despite a lower crystallinity, this sample displayed a two-fold higher turnover frequency in glyoxal isomerisation compared to AT1Sn1. It is likely that under more basic conditions, the introduction of tin in the lattice was promoted at the expense of the formation of inactive oxidic species and that this overcomes the drawback of a lower crystallinity. Additionally, a beneficial contribution by the higher mesoporosity of this sample cannot be discarded.

Lastly, the nature of the tin precursor was investigated. For this purpose, SnSO₄ was used instead of the chloride salt in the typical treatment with 0.1 M NaOH (Table 1, entry 12). The resulting material displayed lower crystallinity, double tin content and 2.5 times higher activity with respect to AT1Sn1. Accordingly, we suggest that the counter-ion of tin might play a role in the metallation process. In this respect, the addition of NaCl upon NaOH treatment of USY zeolites has been reported to significantly impact the dissolution process, leading to less crystalline materials.[16]

Based on these insights, an optimised Sn-BEA catalyst was prepared by appropriate tuning of all the key parameters, i.e., further increasing the alkalinity and using tin(II) sulphate and the maximal concentration of TPA⁺ tested (Table 1, entry 13). The TOF of this sample was significant (91 h⁻¹) but still 40% inferior to that of the reference Sn-BEA catalyst (Table 1, entry 14).

In order to rationalise this difference in activity, the tin sites in these two materials were characterised in terms of structural and acidic properties. The DR-UV/Vis spectrum of the stannated zeolite (Fig. 2a) evidences a band centred at 200 nm, generally associated with tetrahedral tin sites, and a much less intense absorption with maximum at around 280 nm, attributed to SnO₂ clusters. The hydrothermally-prepared sample produced a similar spectrum, but the contribution of oxidic species is much larger, being their absorption of equal intensity to that of framework tin sites. While the presence of SnO₂ clusters at the surface of this material has been already reported,[17] these findings appear in contrast to the activity data. The reason for this discrepancy could be the surface sensitivity of the technique, which might not probe extraframework tin sites located in the intracrystalline mesopores of the solid prepared by the top-down method. Thus, in order to shed more light into the nature of the Lewis-acid centres introduced, FTIR spectroscopy of adsorbed d₅-acetonitrile was performed since this probe molecule exclusively adsorbs on tetrahedral sites.[18] As highlighted in Fig. 2b, a band at ca. 2310 cm⁻¹ is visible in both spectra resulting from the stretching vibration of C≡N bound to tetracoordinated tin atoms. This feature is more intense for the hydrothermally-prepared sample. Integration of the peaks followed by normalisation by the tin content for the two samples points to a 1.6 times higher amount of framework sites in the reference zeolite. This ratio roughly corresponds to the difference in TOF values between the catalysts, thus pointing to framework metallation efficiency as the key parameter for activity, as previously suggested.[19] Still, an additional contribution of the greater surface hydrophobicity of the hydrothermally-synthesised zeolite cannot be excluded.

Finally, the ability of stannated BEA to isomerise other relevant bio-based compounds was evaluated. Fig. 3 displays the TOF calculated in the conversion of glyoxal, pyruvaldehyde, xylene and glucose to glycolic acid, lactic acid, xylulose and fructose, respectively, at 383 K. The higher reactivity of pyruvaldehyde compared to glyoxal is in line with previous evidence over the reference Sn-BEA.[11a] Although
literature studies indicate the propensity of glucose to diffuse in the BEA pores,[20] the lower TOF values determined in the conversion of the sugars suggest the existence of mass transfer limitations. In this respect, we hypothesise that tin oxide species, present in greater amount compared to hydrothermally-synthesised Sn-BEA, might hamper the diffusion/access of the bulkier pentose and hexose in the pores.

Experimental

BEA zeolite (Tosoh Corp., HSZ-980HOA, bulk Si/Al = 220, protonic form) was used as received for post-synthetic modification. The latter comprised alkaline treatment in aqueous NaOH (0.1-0.2 M, 3.8 cm³ per gram of dried zeolite) or alkaline-assisted stannation in an NaOH solution (0.1-0.2 M, 3.8 cm³ per gram of dried zeolite) containing SnCl₄·5H₂O (Sigma-Aldrich, 98%, 0.005-0.015 M) or SnSO₄·H₂O (Acros, 98%, 0.01-0.04 M) and, in certain cases, tetrapropylammonium bromide (TPABr, ABCR, 98%, 0.01 M). All treatments were performed at 338 K for 30 min in an Easymax™ 102 reactor (Mettler Toledo). Owing to the difficult solubilisation of tin(II) sulphate, the alkaline solution containing this precursor was heated at 318 K for 1 h and then filtered to remove insoluble hydroxystannate species prior to the addition of the zeolite. The resulting metallosilicates were converted into their protonic form according to a reported procedure.[12c] Hydrothermally-prepared Sn-BEA was synthesised following the recipe in example 2 of [21]. Characterisation and catalytic testing were performed as described in the ESI. The turnover frequencies (TOF) were calculated based on the mole of product formed per hour and per mole of Sn after 30 s (glyoxal at 363 K) or 15 (all substrates at 383 K) min of reaction.

Acknowledgments

This work was supported by the Swiss National Science Foundation (Project Number 200021-140496). G.M. Lari is thanked for experimental input.

Notes and references

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland.

E-mails: cecilia.mondelli@chem.ethz.ch; jpr@chem.ethz.ch
Fax: +41 44 6331405; Tel: +41 44 6337120

†Electronic Supplementary Information (ESI) available: Characterisation and testing protocols; XRD patterns and ²⁹Si MAS NMR and DRIFT spectra of selected zeolites. See DOI: 10.1039/c000000x/

1. Catalyst characterisation

The tin content in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Horiba Ultra 2 instrument equipped with a photomultiplier tube detector. Prior to the measurements, the materials were digested in an acidic mixture (HCl-HNO₃-HF) at 343 K for 12 h. Nitrogen sorption at 77 K was performed using a Quantachrome Quadrasorb-SI analyser on degassed samples (10⁻¹ mbar, 573 K, 3 h). Powder X-ray diffraction (XRD) was measured using a PANalytical X’Pert PRO-MPD diffractometer with Ni-filtered Cu Kα radiation (λ = 0.1541 nm). Data were recorded in the 5-70° 2θ range with an angular step size of 0.05° and a counting time of 7 s per step. UV/Vis spectroscopy was carried out in diffuse reflectance mode using an Ocean Optics Maya2000-Pro spectrometer. Spectra were collected in the 200-600 nm range, with an integration time of 150 ms and accumulating 32 scans. The UV-VIS spectra of the stannated and hydrothermally-prepared Sn-BEA samples were corrected for the absorption of the framework (signal at ca. 225 nm) by subtracting the spectra of the commercial and hydrothermally-prepared BEA zeolites, respectively. Fourier transform infrared (FTIR) spectroscopy measurements of adsorbed d₃-acetonitrile were conducted using a Bruker IFS66 spectrometer equipped with a liquid N₂-cooled mercury cadmium telluride (MCT) detector. Self-supporting zeolite wafers (20 mg, 5 ton cm⁻², 1 cm²) were pretreated at 10⁻¹ mbar and 693 K for 4 h. After cooling down to room temperature, the sample was saturated with d₃-acetonitrile vapour and then evacuated at room temperature (15 min). Spectra were recorded in the 4000-650 cm⁻¹ range with a resolution of 4 cm⁻¹ by co-addition of 32 scans. Diffuse-reflectance Fourier transform infrared (DRIFT) spectroscopy was performed using a Bruker Vertex 70 spectrometer equipped with a high-temperature DRIFT cell (Harrick) and an MCT detector. Spectra were recorded in the range of 4000-400 cm⁻¹ under N₂ flow and at 473 K by co-addition of 200 scans with a resolution of 4 cm⁻¹. Prior to the measurements, the samples were dried at 673 K under N₂ flow for 4 h. ²⁹Si cross-polarisation magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra were recorded using a Bruker AVANCE 700 III HD NMR spectrometer equipped with a 4-mm probe head and 4-mm ZrO₂ rotors at 139.1 MHz. Spectra were measured using a spinning speed of 10 kHz, 6144 accumulations, 1 ms pulses, a recycle delay of 10 s and Q8M8 as a reference.
2. Catalytic testing

Catalytic tests were conducted in batch mode under autogenous pressure in 15-cm³ thick-walled glass vials (Ace, pressure tubes, front seal) dipped in an oil bath heated at the desired reaction temperature. For the runs at 363 K, the vials were loaded with 4 cm³ of a 4 wt.% glyoxal (ABCR, 40 wt.% aqueous solution) solution and a catalyst mass corresponding to 1.37 mg of Sn. For the tests at 383 K, 8 cm³ of a 0.33 M solution of glyoxal, pyruvaldehyde (Sigma-Aldrich, 40 wt.% aqueous solution), D-xylose (Sigma-Aldrich, >99%) or D-glucose monohydrate (ABCR, 99%) and a catalyst mass corresponding to 0.67 mg of Sn were applied. The reactions were quenched using an ice bath and the catalyst was removed from the mixture by means of a Chromafil Xtra 0.25 μm syringe filter. The reactants and products were analysed by high-performance liquid chromatography (HPLC) using a Merck LaChrom system equipped with a Biorad Aminex HPX-87C column heated at 353 K and a refractive index detector (Hitachi Chromaster model 5450) set at 303 K, using an aqueous eluent of 0.005 M H₂SO₄ (pH 2.30) flowing at 0.6 cm³ min⁻¹. Quantification was obtained by integration of their respective peaks using butan-2-one (Merck, 99.5%) as an internal standard. In the case of xylulose, the response factor of xylose was applied.