

Simple and Scalable Preparation of Highly Active Lewis Acidic Sn-β**

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Lewis acids are a versatile class of catalysts that exhibit remarkable activity for a number of essential transformations, including oxidations and isomerizations.^[1] Although homogeneous analogues are well-established, heterogeneous catalysts offer several advantages for the development of more sustainable technology in terms of facile downstream processing and process intensification. Of particular interest are Lewis acid doped zeolites, some of which exhibit remarkable activity, selectivity, and lifetime for a number of processes.^[2] The development of TS-1 (a Ti^{IV}-doped MFI-type zeolite) is, for instance, viewed as one of the greatest breakthroughs in sustainable chemistry in the last few decades, having resulted in a “greener” process for the epoxidation of propylene,^[3] amongst others. Promising results have also been obtained in the development of Sn^{IV}-doped zeolite β, which has shown unparalleled activity and selectivity for the isomerization of glucose to fructose and the Baeyer–Villiger oxidation of ketones to lactones using H₂O₂ as green oxidant.^[3,4]

Lewis acid doped zeolites are typically obtained by direct incorporation of the Lewis acid into the framework during hydrothermal synthesis.^[2–4] However, it remains a challenge to obtain a significant number of isolated sites within the structures, without the undesirable formation of metal oxide particles which are significantly less active. Moreover, even under optimized conditions, the incorporation of large Lewis acidic centers, such as Sn^{IV}, typically leads to a significant retardation of the zeolite nucleation, and hence long synthesis timescales (up to 40 days) and unfavorably large crystals. To facilitate the crystallization process, additives, such as HF, are also commonly added to the synthesis gel, posing additional practical and environmental limitations. This, in combination with the limited amount of active metal that can be incorporated into the structures (under 2 wt.%) currently limits the large-scale applicability of these otherwise promising materials.

With these limitations in mind, we aimed to develop a convenient post-synthetic route for the incorporation of various Lewis acid centers into zeolitic frameworks. An attractive route involves the incorporation of the desired transition-metal ions into the vacant tetrahedral (T)-sites of a pre-dealuminated zeolite. Not only does this approach avoid the long synthesis times associated with the conventional hydrothermal synthesis routes, but it also allows for the synthesis of a material with significantly smaller crystallite sizes than possible through direct synthesis. As a proof of

concept, we focus on the preparation of Sn-β. This material has tremendous potential,^[4] equivalent to TS-1, but industrial implementation is currently hampered by the tedious synthesis procedure.

Preliminary work focused on the efficient dealumination of a parent Al-β zeolite. Although steaming is a well-known method for removing framework Al³⁺, it has the disadvantage of leaving behind ill-defined extra-framework Lewis acidic Al³⁺ species, which could affect the catalytic performance of the material. In view of this problem, an acidic pre-treatment with HNO₃ (13 M, 100 °C, 20 h, 20 mL g⁻¹) was performed to extract and remove the aluminum quantitatively.^[5] The results in Table 1 show indeed that nearly all Al³⁺ can be removed,

Table 1: Physicochemical properties of the materials.^[a]

Entry	Catalyst	Treatment	S _{BET} [m ² g ⁻¹]	V _{micro} [cm ⁻³ g ⁻¹]	SiO ₂ /Al ₂ O ₃	SiO ₂ /SnO ₂
A	H-β	–	600	0.17	25	–
B	deAl-β	H ⁺	620	0.18	> 1900	–
C	Sn/deAl-β	H ⁺ /SSIE	610	0.17	> 1900	32
D	Sn/deAl-β	H ⁺ /SSIE	600	0.17	> 1900	16

[a] H-β = commercial H-β-zeolite, deAl-β = dealuminated β-zeolite, Sn/deAl-β = Sn-β-zeolite, prepared by SSIE, S_{BET} = Brunauer-Emmett-Teller surface area, V_{Micro} = micropore volume.

without destruction of the framework or significant alterations to its textural properties. The removal of framework Al is exemplified by the loss of the Brønsted acidity, that is, the sharp IR signal at 3610 cm⁻¹ (Figure 1 A,B). In its place, a broad absorbance around 3500 cm⁻¹ appears, confirming the successful formation of silanol nests and vacant T-sites for the incorporation of Sn^{IV}.^[6]

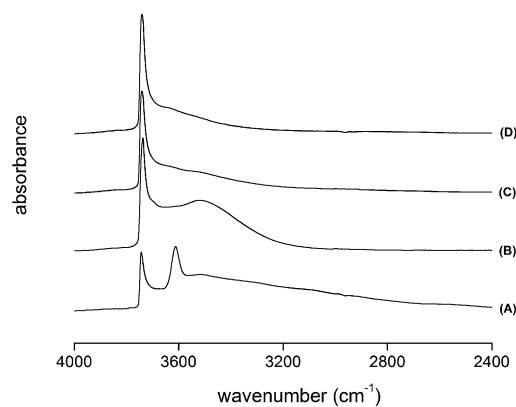


Figure 1. IR spectra of A) H-β, B) dealuminated β (deAl-β), C) 5 wt % Sn/deAl-β, and D) 10 wt % Sn/deAl-β (see Table 1).

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Subsequently, methods of introducing Sn^{IV} into the vacant T-sites were considered. Although liquid-phase routes (e.g. impregnation) offer a convenient and scalable route for the deposition of tin, the solvation shell surrounding the tin cations could potentially lead to significant diffusion limitations within the zeolite micropores, negatively affecting the incorporation of tin and resulting in poor dispersion. Furthermore, hydrolysis of the tin precursor may also result in the partial formation of bulk oxide species in the final material. Although traditional gas–solid deposition (e.g. chemical vapor deposition; CVD) offers exciting possibilities of incorporating “naked” metal atoms into the T-sites, the low volatility of typical Sn precursors (e.g. SnCl₄) results in difficulties grafting sufficient quantities of Sn into the final material. Moreover, previous work has demonstrated that a multitude of Sn species are formed by SnCl₄ grafting, the majority of which appear to be extra-framework species or bulk tin oxides.^[7] The catalytic activity of such materials is therefore rather poor.

Solid-state ion-exchange (SSIE) was therefore considered to be an interesting route for incorporating the desired amount of metal into the structure, with both high dispersion and homogeneity. The procedure simply involves mechanical grinding of dealuminated zeolite and the appropriate precursor, in this case tin(II)acetate, prior to calcination at 550 °C for removal of the residual organic species.

A combination of spectroscopic techniques was used to determine the nature of the Sn species generated post-synthetically. The incorporation of Sn into the dealuminated framework can be detected by IR spectroscopy as a result of the closure of the silanol nests (Figure 1 C,D). Diffuse reflectance spectroscopy also reveals a sharp UV absorbance around 216 nm, even for very high initial loadings of tin(II)acetate (Figure 2 a, spectrum B); this signal is characteristic of isolated, tetrahedral Sn^{IV} species within the zeolite framework. No SnO₂ could be detected with UV/Vis or Raman spectroscopy (Figure 2 b). It should be noted that the UV/Vis spectra of the post-synthetically prepared samples are almost identical to that of a reference Sn-β sample prepared by direct hydrothermal synthesis (Figure 2 a, spectrum A). This spectroscopic data indicates that Sn^{IV} sites similar to those of Sn-β are obtained even at around eight-times the total loading.

The catalytic efficiency of the prepared materials was evaluated for the Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ (Table 2). As can be seen, the SSIE of Sn^{IV} into dealuminated β (entries 1 and 2) results in the formation of an active catalyst, comparable in both yield and turnover number (TON) to that reported for hydrothermally synthesized materials.^[4b] Interestingly, the 5 and 10 wt % Sn/deAl-β show comparable activity per Sn^{IV} site, but lead to a different lactone selectivity. We attribute this selectivity to the presence of un-closed silanol nests in the 5 wt % sample, resulting in the presence of residual Brønsted acid sites. Such sites are capable of catalyzing the formation of 6-hydroxycaproic acid by acid-catalyzed hydrolysis, as confirmed by lactone stability studies. At higher Sn loadings, a larger fraction of the silanol nests are closed, thus decreasing the number of available Brønsted acid sites and resulting in increased

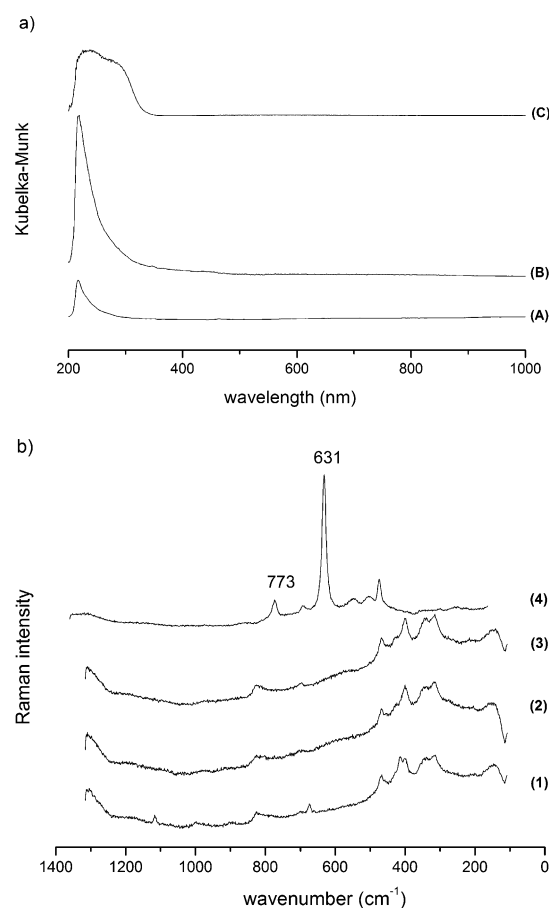


Figure 2. a) UV/Vis spectra of A) conventional Sn-β (1.5 wt %), B) 10 wt % Sn/deAl-β, and C) 10 wt % Sn(O₂)/deAl-β. b) Raman spectra of 1) deAl-β, 2) 5 wt % Sn/deAl-β, 3) 10 wt % Sn/deAl-β, and 4) bulk SnO₂.

Table 2: Catalytic activity of various tin-containing samples for the Baeyer–Villiger oxidation of cyclohexanone.^[a]

Entry	Catalyst	Conv. [%]	Selec. [%]	Yield [%]
1	5 wt % Sn/deAl-β	35.0	75	26.2
2	10 wt % Sn/deAl-β	41.1	93	38.2
3	10 wt % Sn/deAl-β (3 ×) ^[b]	39.8	91	36.2
4	10 wt % Sn(O ₂)/deAl-β	0	–	0
5	10 wt % Sn/β	0	–	0

[a] Cyclohexanone in 1,4-dioxane (0.33 M), H₂O₂ (30 wt % solution, H₂O₂/ketone = 1.5), Sn content = 1 mol %, 90 °C, 4 h. [b] Third use of the catalyst.

selectivity. Importantly, the catalyst was also found to be reusable (entry 3), confirming that the Sn sites and catalyst structure are highly stable under the reaction conditions.

To further substantiate the hypothesis that isolated, tetrahedral Sn^{IV} species are indeed the active sites formed in the post-synthetic material, we verified that the dispersion of SnO₂ into/onto the dealuminated framework (Table 2,

entry 4) leads to zero catalytic activity. Similarly, the dispersion of tin(II)acetate into/onto a non-dealuminated framework (Table 2, entry 5) also leads to an inactive material; clearly, when the formation of framework Sn^{IV} sites is prohibited (either by an inappropriate precursor or the lack of vacant framework sites), an inactive catalyst is obtained.

To confirm the heterogeneous nature of the catalytic reaction, a hot-filtration test was performed,^[8] demonstrating that removal of the catalyst after 1 h (i.e., after ca. 15% conversion) leads to complete termination of the reaction (Figure 3).

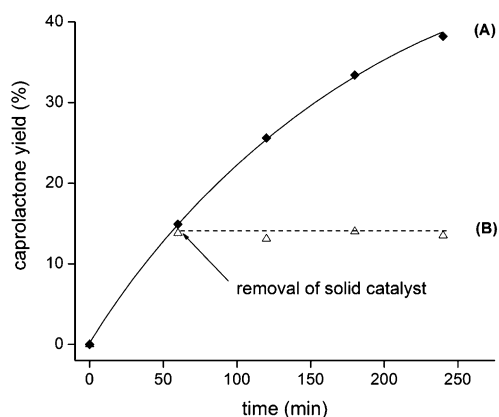


Figure 3. A) Time-dependent formation of ϵ -caprolactone in the presence of 10 wt% Sn/deAl- β , and B) hot-filtration test for the catalyst (conditions, see Table 2).

Comparing the SSIE synthesized material with the hydrothermally prepared material, shows both give comparable levels of lactone- and H₂O₂-based selectivity (Table 3).

Table 3: Comparison of post-synthetic and hydrothermal routes.^[a]

Entry	Catalyst	S(lactone) [%]	S(H ₂ O ₂) [%]	STY ^[b]	Ref.
1	1.5 wt% Sn- β	> 98	> 95	374	[4b]
3	10 wt% Sn/deAl- β	93	> 95	1075	this work

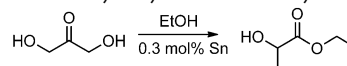
[a] Comparison under identical experimental conditions; 0.33 M ketone in 1,4-dioxane, 90°C, 3 h. [b] Space-time-yield calculated as "g (lactone produced) kg⁻¹ (catalyst) h⁻¹".

However, the Sn/deAl- β is significantly more productive, as shown by the approximately three-fold increase in the observed space-time-yield (STY). This increase is predominantly due to the successful incorporation of such high quantities of Sn^{IV}, without causing significant unwanted side effects, such as agglomeration, increased crystallite sizes, and leaching. This improved reaction efficiency, in combination with the facile and scalable synthesis procedure is expected to promote the industrial applicability of Sn- β .

To explore the general applicability of the post-synthetic material, we studied the conversion of the triose sugar dihydroxyacetone into ethyl lactate, a convenient building

block towards renewable and biodegradable solvents and polymers.^[9] Recently, it has been reported that tin(IV)-containing compounds are amongst the most active and selective materials for these reactions,^[10] and that a combination of Lewis acidity and mild Brønsted acidity is advantageous for this reaction.^[11] As can be seen from the results in Table 4, along with proceeding at exceptional levels of

Table 4: Conversion of dihydroxyacetone into ethyl lactate.



Entry	Catalyst	S(lactate) (%)	TON	STY ^[a]	Ref.
1	3.9 wt% Sn/MCM-41	98	30	195	[10]
2	1.6 wt% Sn- β	> 99	120	70	[12]
3	Sn-carbon-silica	100	350	200	[11]
4	10 wt% Sn/deAl- β	> 99	250	1050	this work

[a] Calculated as "g (lactone produced) kg⁻¹ (catalyst) h⁻¹".

selectivity, the 10 wt% Sn/deAl- β catalyst is significantly more productive than the benchmark materials in terms of turnover numbers and space-time-yield.

In conclusion, a convenient route for the preparation of Lewis acidic Sn- β has been developed. In addition to exhibiting comparable or higher levels of catalytic activity and selectivity to the state-of-the-art materials, significantly higher space-time-yields can be obtained through the preparation of a high-metal-content material. Furthermore, the developed procedure requires significantly less synthesis time and produces no toxic waste in comparison to the benchmark process. We expect such a straightforward approach to facilitate the utilization of the same or similar materials on a large scale.

Experimental Section

Commercial zeolite H- β (ZeoChem) was dealuminated by treatment in HNO₃ solution (13 M) at 100°C for 20 h (20 mL g⁻¹ (zeolite)). SSIE was performed by grinding the appropriate amount of tin(II)acetate with the required amount of dealuminated zeolite for 15 min. Samples were calcined in an air flow at 550°C. Conventional Sn- β was synthesized according to the original procedure of Corma et al.^[4b] FT-IR spectroscopy was performed on a self-supporting wafer using a Bruker Alpha Spectrometer in transmission mode (resolution of 2 cm⁻¹). Intensities were normalized to the Si-O-Si overtones of the zeolite framework. UV/Vis analysis was performed with an Ocean Optics UV/Visible Spectrophotometer in diffuse reflectance mode. Si, Al, and Sn contents were determined by ICP-AES. Porosimetry measurements were performed on a Micromimetics 2000 apparatus. The samples were degassed prior to use (275°C, 3 h). Adsorption isotherms were obtained at 77 K and analyzed using BET and t-plot methods.

Baeyer–Villiger oxidation of cyclohexanone was carried out in a 50 mL round-bottomed flask equipped with a reflux condenser. The vessel was charged with the reactant solution (5 mL, 0.33 M cyclohexanone in 1,4-dioxane) and the desired amount of catalyst (corresponding to 1 mol% Sn relative to ketone). The vessel was heated to the reaction temperature (90°C) for 15 min, prior to the addition of H₂O₂ at a final concentration of 0.5 M (H₂O₂/ketone = 1.5) and stirred vigorously for the required reaction period. Samples were taken periodically and quantified by GC-FID against a biphenyl

internal standard (30 m FFAP column). H₂O₂ concentrations were determined by titration against Ce⁴⁺. The conversion of dihydroxyacetone (DHA) into ethyl lactate was performed in an autoclave reactor at 20 bar N₂ pressure. The vessel was charged with DHA solution (25 mL; 0.4 M in EtOH plus 0.3 mol% Sn, relative to DHA), and the reaction performed at 90 °C. The reactant and product were quantified against a biphenyl internal standard by means of GC-FID (30 m FFAP column) and HPLC (nucleodur 100–5 NH₂-RP column).

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