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Supporting Information

Tracking the solid-state incorporation of Sn into the framework of dealuminated zeolite beta, and consequences for catalyst design

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Keywords Zeolite synthesis · Catalyst preparation · *In situ* spectroscopy · Lewis acid catalysis · Biomass Conversion ·

22 pages in total, including 35 figures and 2 tables.

Table of contents.

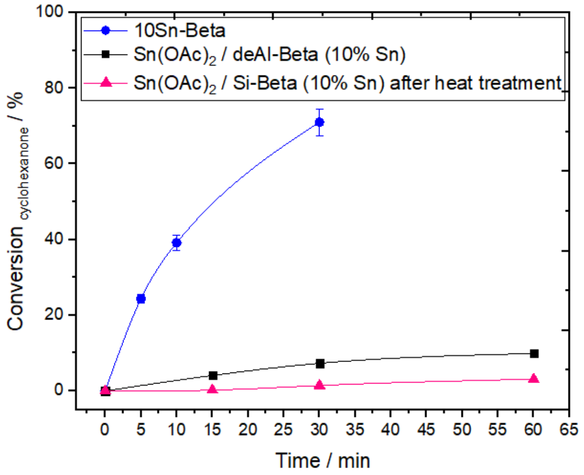


Figure S1. Comparison of catalytic performances for Meerwein–Ponndorf–Verley reaction of cyclohexanone to cyclohexanol over i) 10Sn-Beta (blue circles), ii) $Sn(OAc)_2$ / deAl-Beta mixture (black squares), and iii) $Sn(OAc)_2$ / Si-Beta mixture after heat treatment (magenta triangles), with 10 wt. % of Sn. Reaction conditions: 0.2 M cyclohexanone and 0.01 M biphenyl in 2-butanol, 373 K.

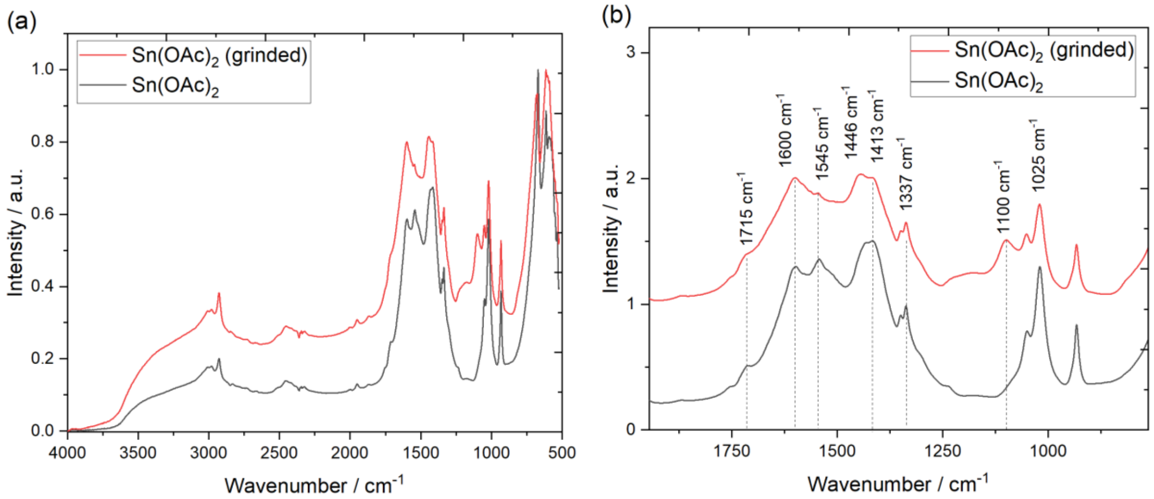


Figure S2. (a) DRIFT spectra of grinded (red line) and pure (black line) $Sn(OAc)_2$. (b) DRIFT spectra of grinded (red line) and pure (black line) $Sn(OAc)_2$ in the region 2000-750 cm^{-1}.

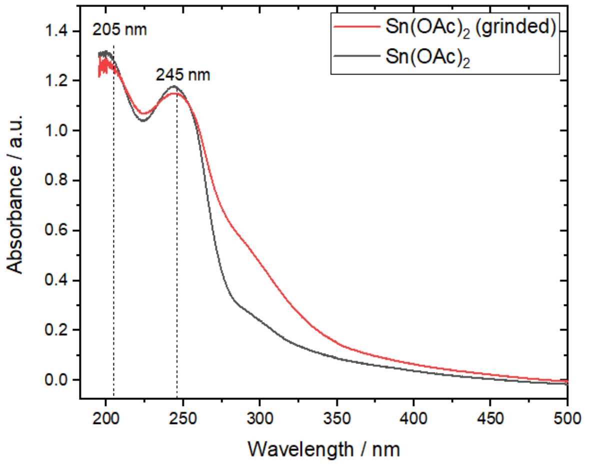


Figure S3. DRUV-Vis spectra of grinded (red line) and pure (black line) Sn(OAc)$_2$.

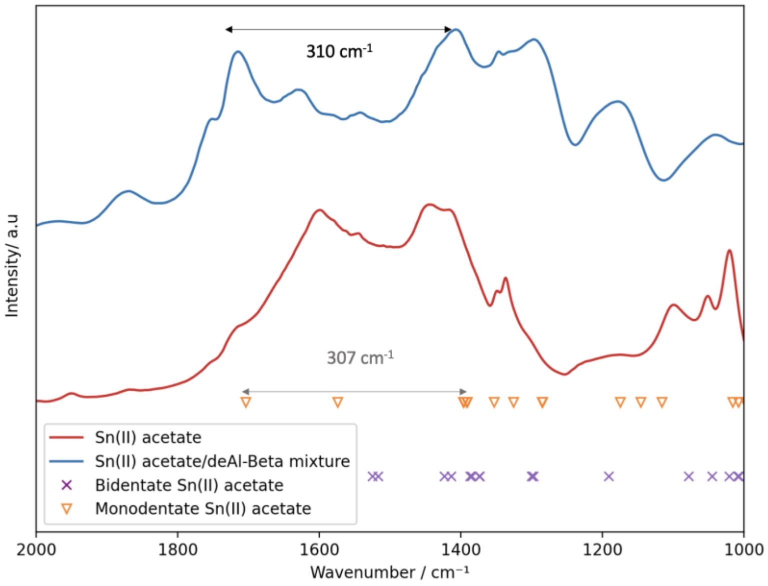


Figure S4. Experimental DRIFT spectra of grinded Sn(OAc)$_2$ (red line) and Sn(OAc)$_2$/deAl-Beta mixture with 10 wt. % of Sn (blue line) compared with computer simulated vibrational modes for bidentate Sn(OAc)$_2$ (purple crosses) and monodentate Sn(OAc)$_2$ (orange triangles), showing Δ value of Sn(OAc)$_2$ [νCO_{asym} - νCO_{sym}] from experimental DRIFT spectra and simulation.

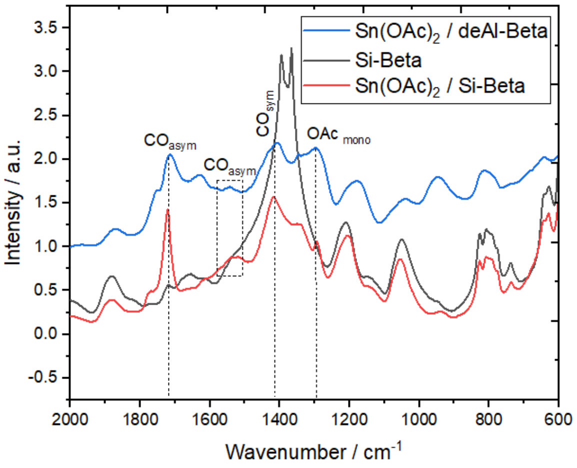


Figure S5. DRIFT spectra of i) 10Si-Beta (black line), ii) $Sn(OAc)_2$ / Si-Beta mixture with 10 wt. % of Sn (red line), and iii) $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % of Sn (blue line).

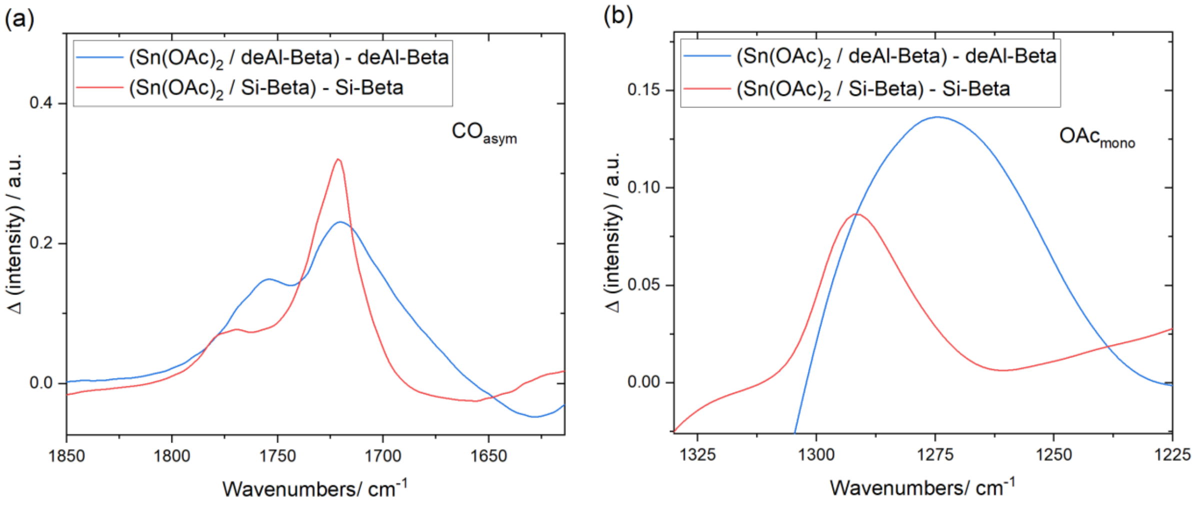


Figure S6. Differential DRIFT spectra obtained through subtraction of i) $Sn(OAc)_2$ / deAl-Beta mixture and deAl-Beta alone (blue line) and ii) $Sn(OAc)_2$ / Si-Beta mixture and Si-Beta alone (red line): (a) CO asymmetric stretching region; (b) vibrational band(s) of monodentate acetate groups.

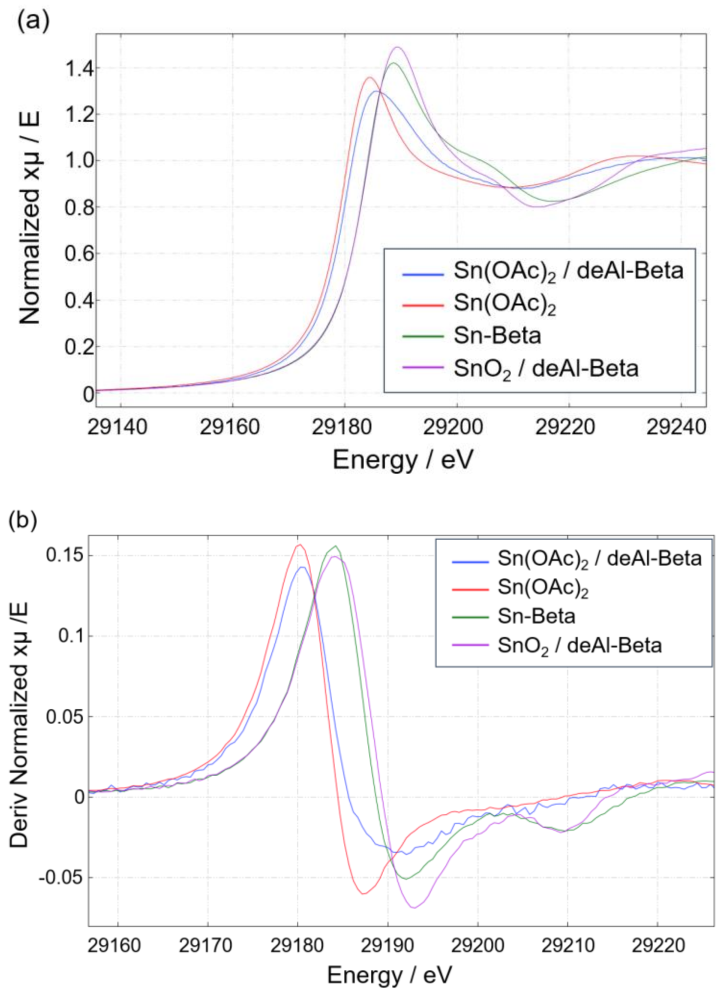


Figure S7. (a) Sn K edge XANES spectra and (b) normalised intensity of the maxima of the first derivative of Sn K edge XANES of: i) pure $Sn(OAc)_2$ (red line), ii) $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % of Sn (blue line), iii) Sn (IV) oxide / deAl-Beta mixture (purple line), and iv) 10Sn-Beta anhydrous (green line).

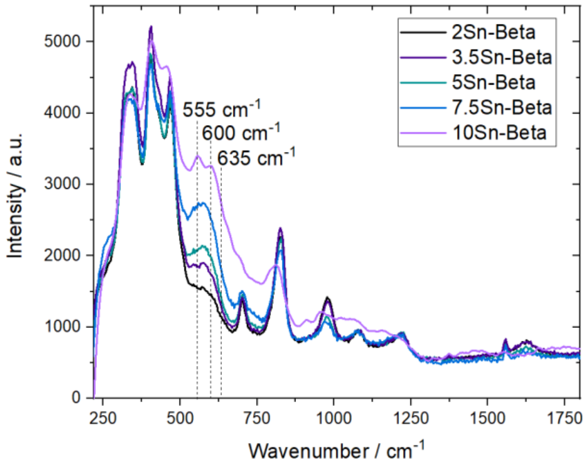


Figure S8. Raman spectra of Sn-Beta with various Sn loadings (2-10 wt. % of Sn) obtained using a 266 nm excitation wavelength.

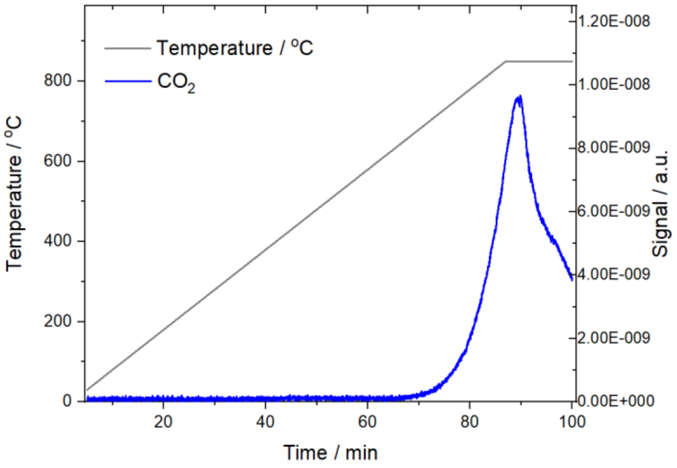


Figure S9. TPD-MS profile during calcination of $CaCO_3$. The black line represents the temperature over time whilst the blue line represents the evolution of CO_2 (TPD signal) over time.

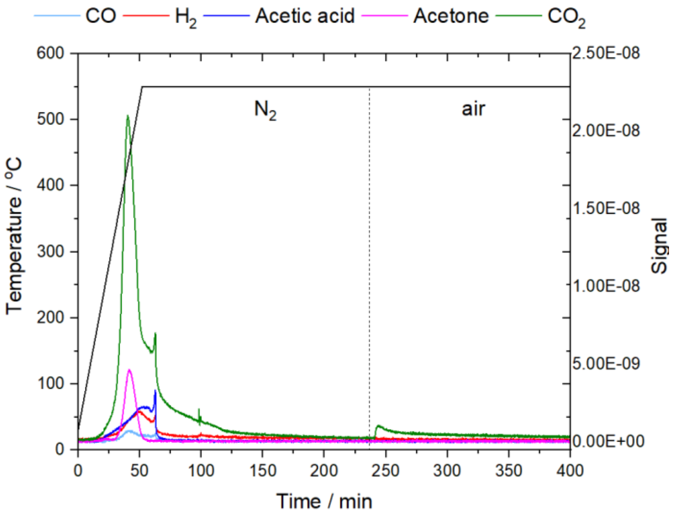


Figure S10. TPD-MS profile during calcination of $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % Sn loading. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow, 3 hours at 550 °C in N_2 flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

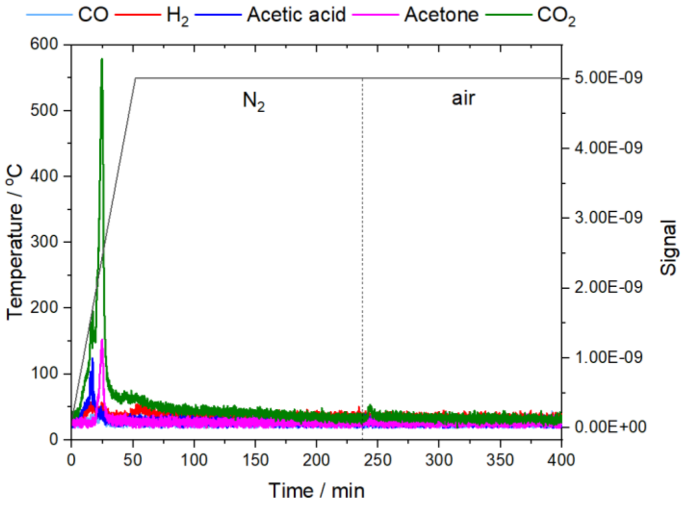


Figure S11. TPD-MS profile during calcination of pure $Sn(OAc)_2$. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow, 3 hours at 550 °C in N_2 flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

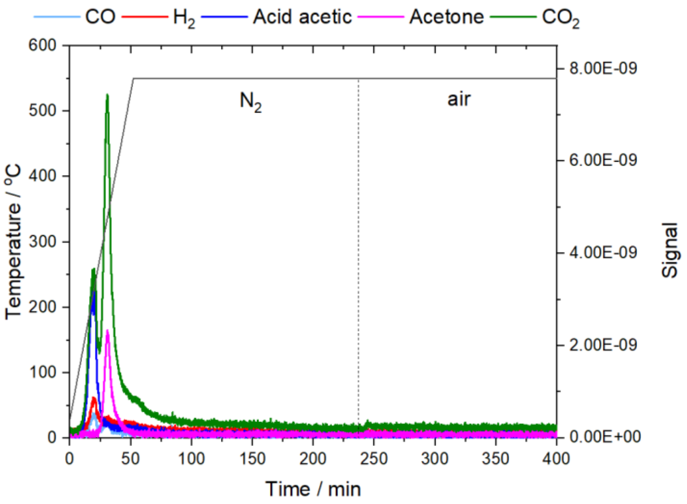


Figure S12. TPD-MS profile during calcination of $Sn(OAc)_2$ / Si-Beta mixture with 10 wt. % Sn loading. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow, 3 hours at 550 °C in N_2 flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

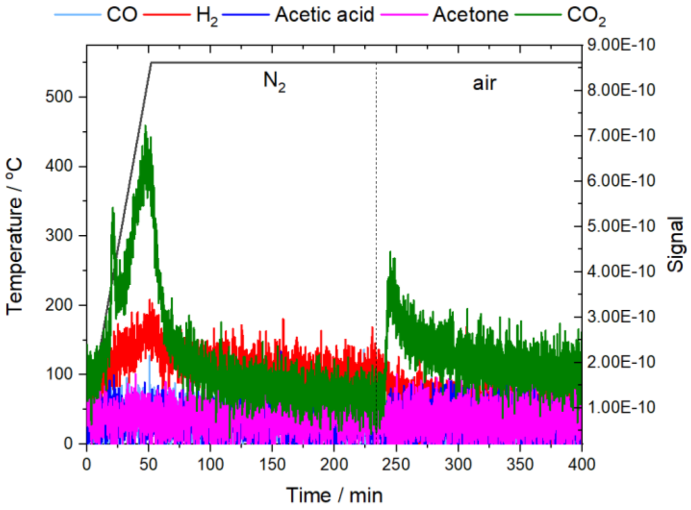


Figure S13. TPD-MS profile during calcination of deAl-Beta. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow, 3 hours at 550 °C in N_2 flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

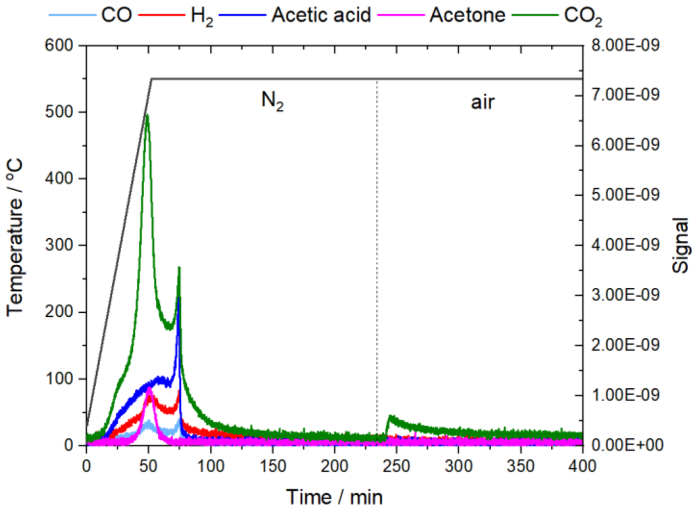


Figure S14. TPD-MS profile during calcination of deAl-Beta pre-treated with acetic acid. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow, 3 hours at 550 °C in N_2 flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

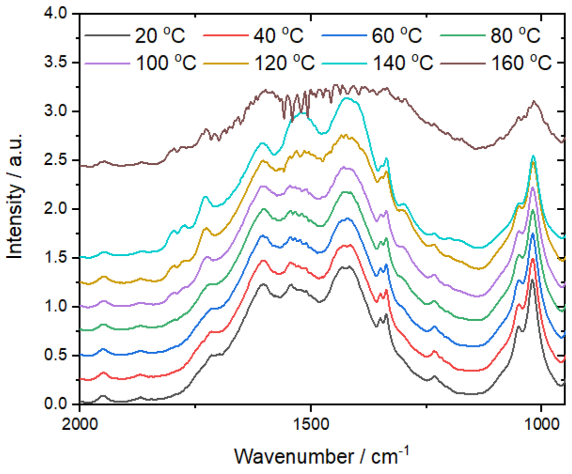


Figure S15. *In situ* DRIFT spectra during calcination of $Sn(OAc)_2$: range 2000-900 cm^{-1}. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow.

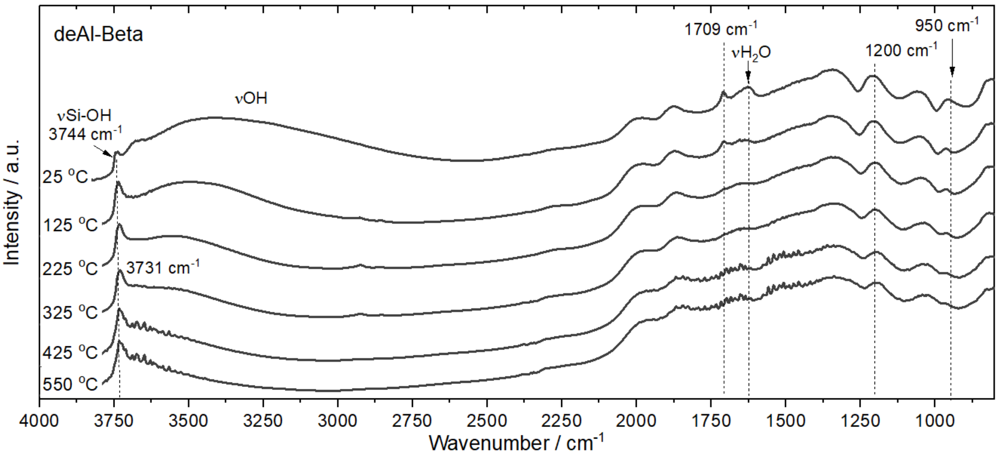


Figure S16. *In situ* DRIFT spectra during calcination of deAl-Beta. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow.

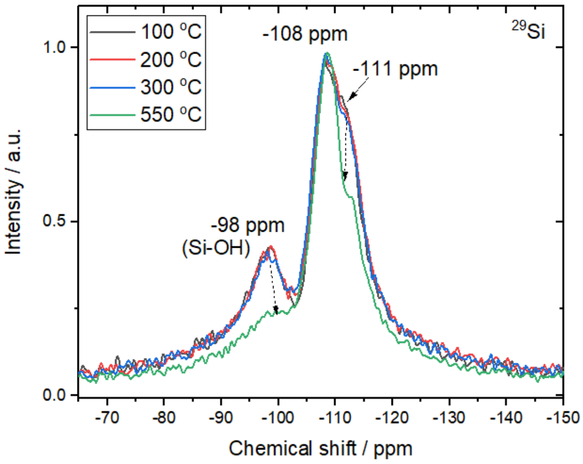


Figure S17. ^{29}Si MAS NMR of $Sn(OAc)_2$/deAl-Beta with 10 wt. % Sn loading, heated at different temperatures in the range 100-550 °C. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow. Samples were removed from the furnace at various temperatures, cooled, and analysed for ^{29}Si MAS NMR.

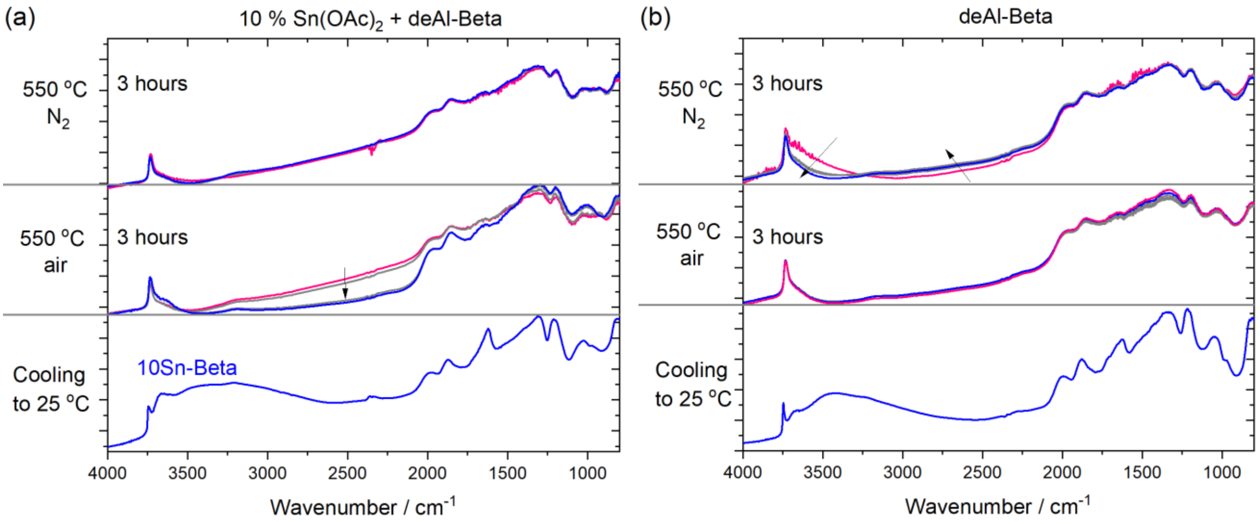


Figure S18. *In situ* DRIFT spectra of (a) $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % Sn loading and (b) deAl-Beta alone during i) first isotherm stage (550 °C, N_2 flow, top spectra), ii) second isotherm stage (550 °C, air flow, central spectra) and, cooled to room temperature (post heat treatment, bottom spectra).

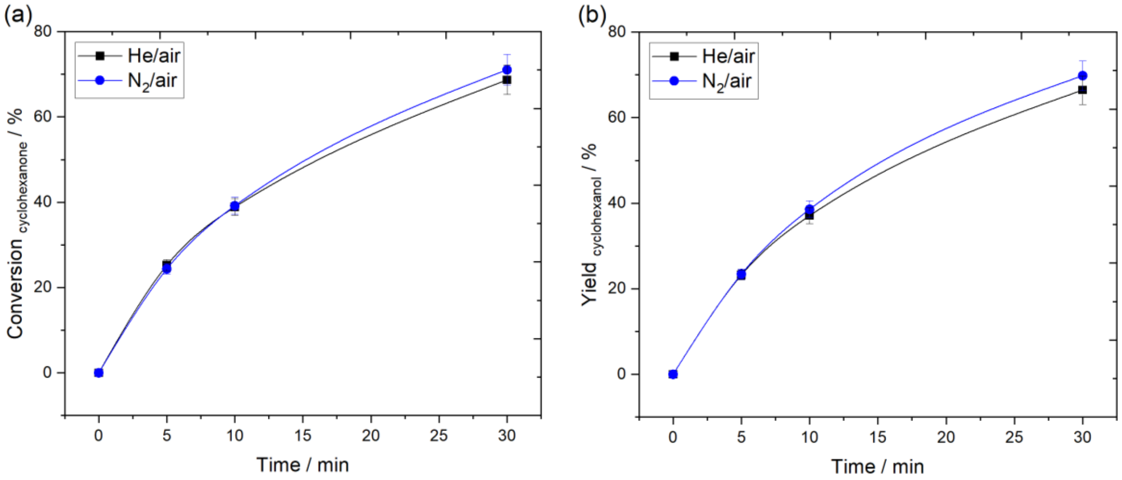


Figure S19. Comparison catalytic performances for Meerwein–Ponndorf–Verley reaction of cyclohexanone to cyclohexanol over 10Sn-Beta prepared i) using N_2 (blue circles) and, ii) He (black squares) as inert gas: (a) conversion of cyclohexanone over time; (b) yield of cyclohexanol over time. Calcination conditions: 10 °C min^{-1} ramp rate in inert gas flow, 3 hours at 550 °C in inert gas flow, and 3 hours at 550 °C in air flow. Reaction conditions: 0.2 M cyclohexanone and 0.01 M biphenyl in 2-butanol, 100 °C, Sn:cyclohexanone molar ration equal to 1:100.

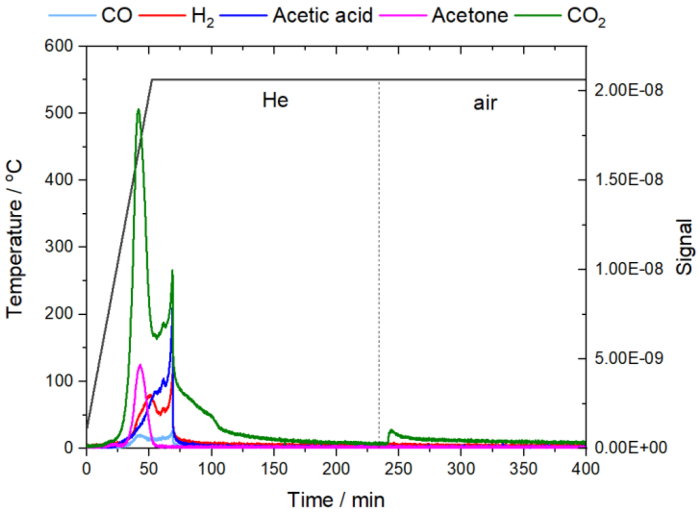


Figure S20. TPD-MS profile during calcination of 10Sn-Beta prepared using helium flow as inert gas. Calcination conditions: 10 °C min^{-1} ramp rate in He flow, 3 hours at 550 °C in He flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

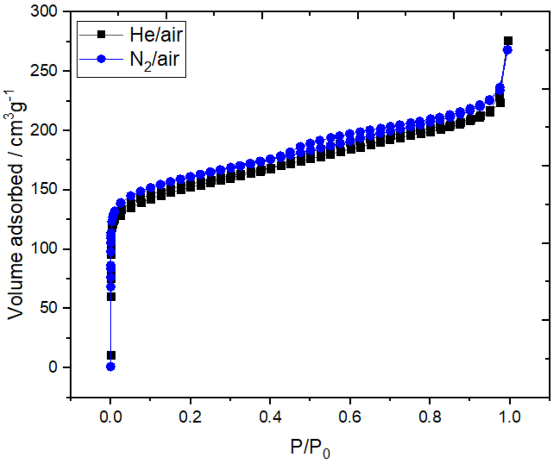


Figure S21. Nitrogen physisorption of 10Sn-Beta prepared i) using N_2 (blue circles) and, ii) He (black squares) as inert gas. Samples were prepared calcining $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % of Sn loading, under following conditions: 10 °C min^{-1} ramp rate in inert gas flow, 3 hours at 550 °C in inert gas flow, and 3 hours at 550 °C in air flow.

Table S1. Textural properties of 10Sn-Beta prepared i) using N_2 and, ii) He as inert gas. Samples were prepared calcining $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % of Sn loading, under following conditions: 10 °C min^{-1} ramp rate in inert gas flow, 3 hours at 550 °C in inert gas flow, and 3 hours at 550 °C in air flow.

Sample	t-plot			BET	DFT Method	
	Micropore volume (cm^3g^{-1})	Micropore area (m^3g^{-1})	External Surface area (m^3g^{-1})	Surface Area	Pore Volume	Surface Area
(N_2/air)10Sn-Beta	0.219	416.785	92.459	509.243	0.35	890.774
(He/air)10Sn-Beta	0.207	396.02	94.51	490.529	0.34	874.349

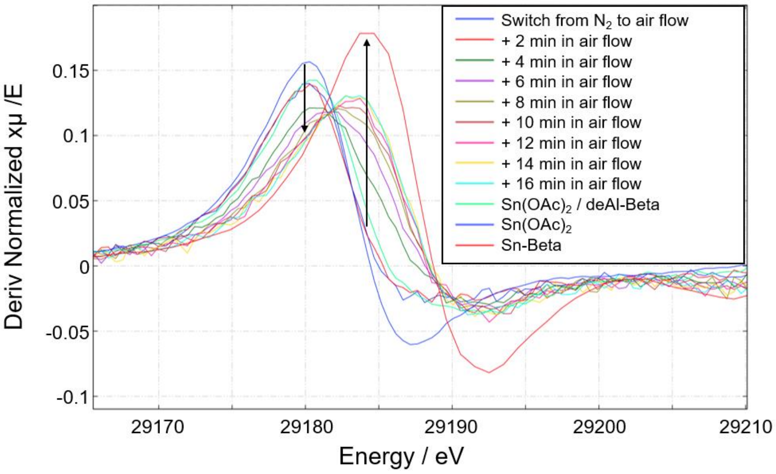


Figure S22. *In situ* XAS analysis of 10Sn-Beta synthesis. Normalised intensity of the maxima of the first derivative of selected Sn K edge XANES spectra obtained during heat treatment of $Sn(OAc)_2$/deAl-Beta with 10 wt. % of Sn, to yield 10Sn-Beta. Normalised intensity of the maxima of the first derivative of Sn K edge XANES spectra of pure Sn(OAc)2 (blue line) included for reference. Calcination conditions: 10 °C min^{-1} ramp rate in He flow, 3 hours at 550 °C in He flow, and 3 hours at 550 °C in air flow.

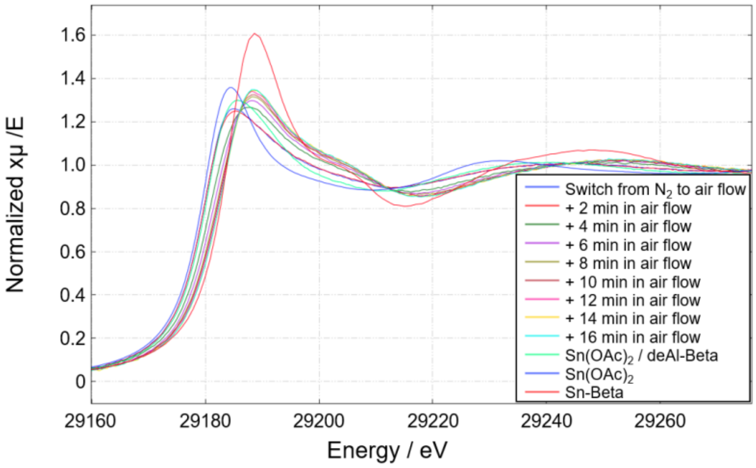


Figure S23. *In situ* XAS analysis of 10Sn-Beta synthesis. Normalised intensity of selected Sn K edge XANES spectra obtained during heat treatment of $Sn(OAc)_2$/deAl-Beta with 10 wt. % of Sn, to yield 10Sn-Beta. Normalised intensity Sn K edge XANES spectra of pure $Sn(OAc)_2$ (blue line) included for reference Calcination conditions: 10 °C min^{-1} ramp rate in He flow, 3 hours at 550 °C in He flow, and 3 hours at 550 °C in air flow.

Table 2. EXAFS fitting data obtained during synthesis of 10Sn-Beta.[a] Calcination conditions: 10 °C min^{-1} ramp rate in He flow, 3 hours at 550 °C in He flow, and 3 hours at 550 °C in air flow.

Entry	Sample	Flow	Time / min	Coordination number (Sn)	R / Å (Sn-O)	$2\sigma^2$ / Å^2	E_t /eV	R-factor
1	$Sn(OAc)_2$	/		3.9 (0.4)	2.161 (0.013) 2.885 (0.024)	0.011 (0.0019)	7 (1)	0.0087
2	$Sn(OAc)_2$ / deAl-Beta (prior heat treatment)	/	0	4.2 (0.6)	2.087 (0.015)	0.01 (0.0028)	6 (1)	0.0233
3	$Sn(OAc)_2$ / deAl-Beta (during heat treatment)	N_2	175	3.3 (0.5)	2.043 (0.019)	0.0124 (0.0032)	6 (2)	0.0146
4	″	N_2	231	3.3 (0.5)	2.045 (0.018)	0.0125 (0.0031)	6 (2)	0.0126
5	″	Air	233	3.2 (0.5)	2.038 (0.02)	0.0117 (0.0032)	6 (2)	0.0158
6	″	Air	235	3.3 (0.5)	2.046 (0.018)	0.0126 (0.003)	6 (2)	0.0121
7	″	Air	237	3.3 (0.5)	2.046 (0.021)	0.0128 (0.0036)	6 (2)	0.0172
8	″	Air	239	3.4 (0.5)	1.998 (0.016)	0.0099 (0.0025)	5 (2)	0.0123
9	″	Air	241	3.5 (0.4)	1.981 (0.014)	0.0094 (0.0024)	6 (1)	0.0111
10	″	Air	243	3.4 (0.4)	1.962 (0.014)	0.0072 (0.0021)	4 (2)	0.0119
11	″	Air	245	3.8 (0.4)	1.965 (0.011)	0.0088 (0.0018)	5 (1)	0.0069
12	″	Air	247	3.8 (0.3)	1.961 (0.092)	0.0071 (0.0014)	4 (1)	0.0054
13	″	Air	249	4 (0.5)	1.956 (0.012)	0.0075 (0.0019)	5 (1)	0.0091
14	″	Air	251	4 (0.4)	1.956 (0.01)	0.0071 (0.0016)	3 (1)	0.006
15	″	Air	253	4 (0.4)	1.955 (0.011)	0.0069 (0.0017)	3 (1)	0.0071
16	10Sn-Beta after cooling	/	413	4.8 (0.3)	1.959 (0.006)	0.0074 (0.0008)	2 (1)	0.0026

[a] Fitting parameters: $S^2_0=1$ as deduced by SnO_2 and $Sn(OAc)_2$ standard; Fit range $2.5<k<13$, $1<R<4$; Number of independent points=19. Values in parenthesis give the experimental error.

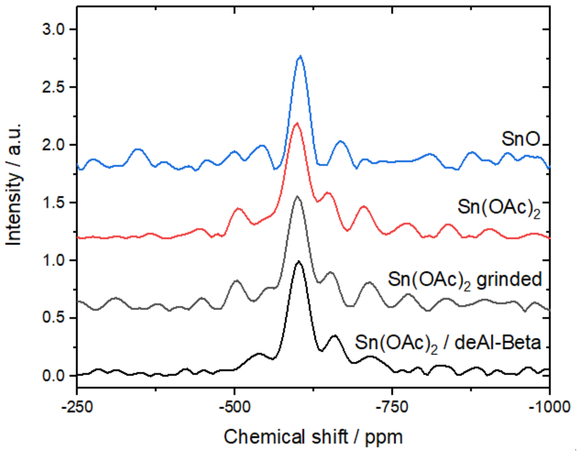


Figure S24. ^{119}Sn DE CPMG MAS NMR of (from top to bottom) i) pure Sn (II) oxide (SnO), ii) pure Sn(OAc)$_2$, iii) grinded Sn(OAc)$_2$, and iv) Sn(OAc)$_2$ / deAl-Beta mixture with 10 wt. % Sn loading.

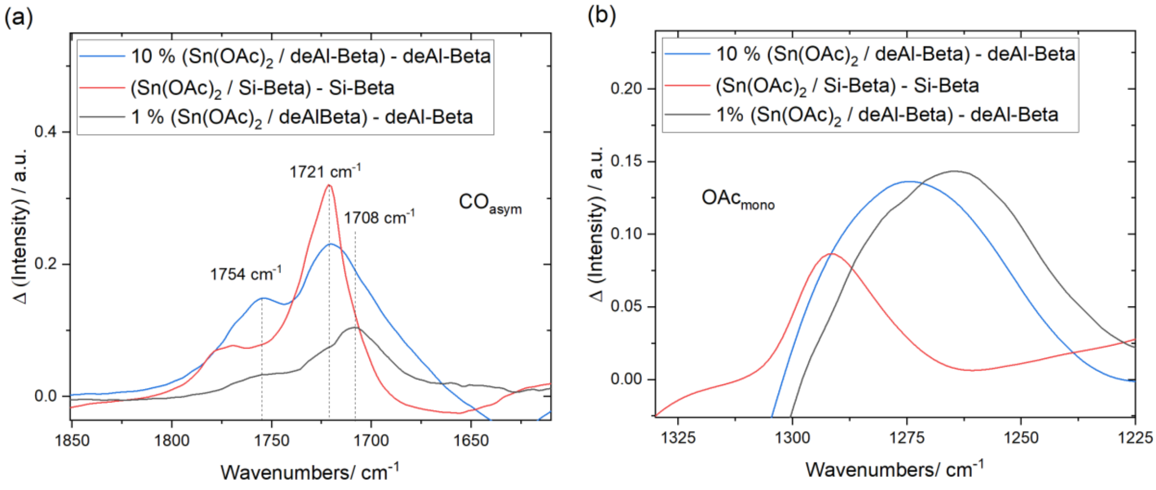


Figure S25. Differential DRIFT spectra obtained through subtraction of i) Sn(OAc)$_2$ / deAl-Beta mixture with 10 wt. % of Sn and deAl-Beta alone (blue line), ii) Sn(OAc)$_2$ / Si-Beta mixture and Si-Beta alone (red line), and iii) Sn(OAc)$_2$ / deAl-Beta mixture with 1 wt. % of Sn and deAl-Beta alone (black line): (a) CO asymmetric stretching region; (b) vibrational band(s) of monodentate acetate groups.

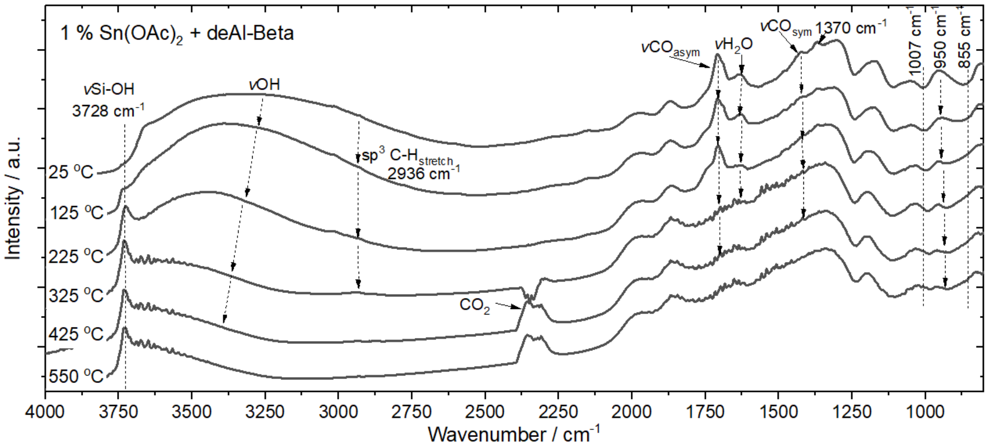


Figure S26. *In situ* DRIFT spectra during heat treatment of Sn(OAc)$_2$/deAl-Beta with 1 wt. % Sn loading. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow.

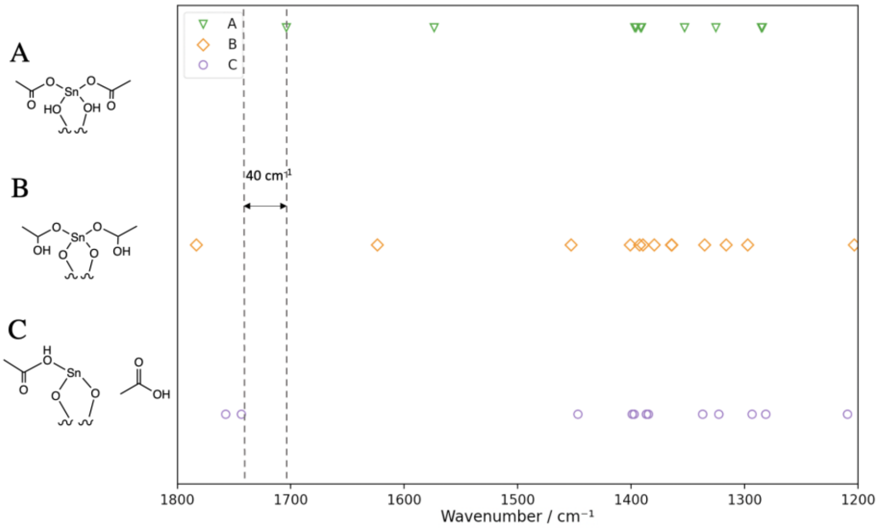


Figure S27. Simulated vibrational modes of the different permutations of acetate ligand and acetic acid ligand.

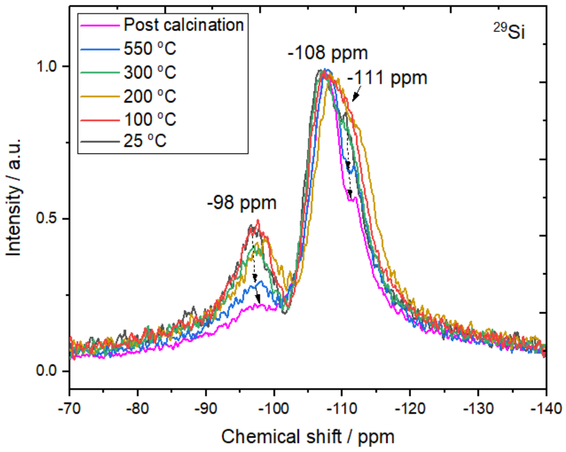


Figure S28. ^{29}Si MAS NMR of Sn(OAc)$_2$/deAl-Beta with 1 wt. % Sn loading, heated at different temperatures in the range 100-550 °C. Calcination conditions: 10 °C min^{-1} ramp rate in N$_2$ flow. Samples were removed from the furnace at various temperatures, cooled, and analysed for ^{29}Si MAS NMR.

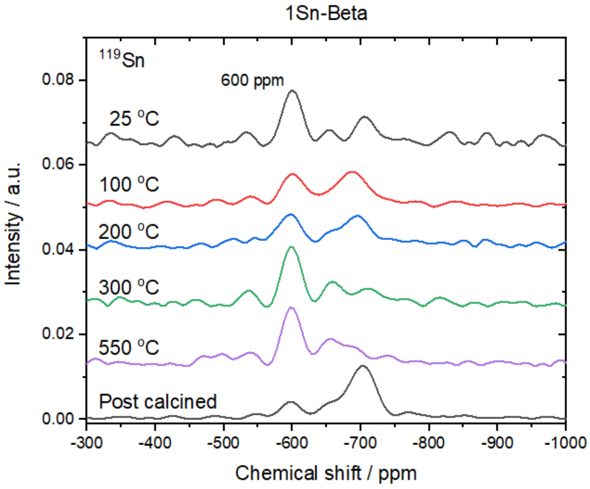


Figure S29. ^{119}Sn MAS DE CPMG NMR of i) 1Sn-Beta, and ii) Sn(OAc)$_2$/deAl-Beta with 1 wt. % Sn loading, heated at different temperatures in the range 100-550 °C.

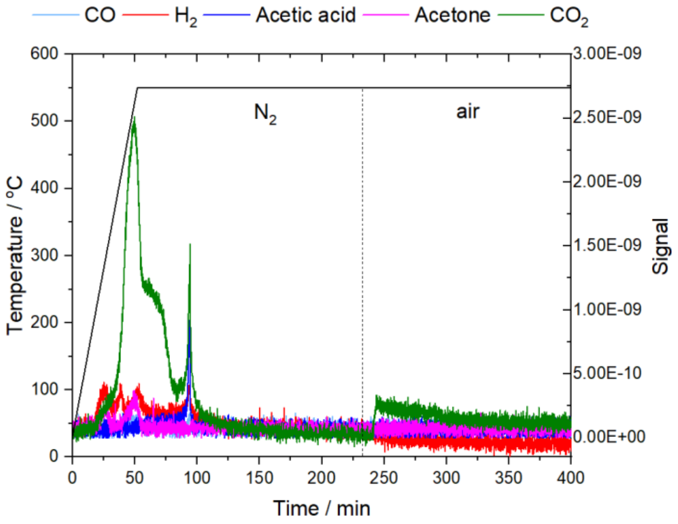


Figure S30. TPD-MS profile during calcination of $Sn(OAc)_2$ / deAl-Beta mixture with 1 wt. % Sn loading. Calcination conditions: 10 °C min^{-1} ramp rate in N_2 flow, 3 hours at 550 °C in N_2 flow, and 3 hours at 550 °C in air flow. The black line indicates the temperature.

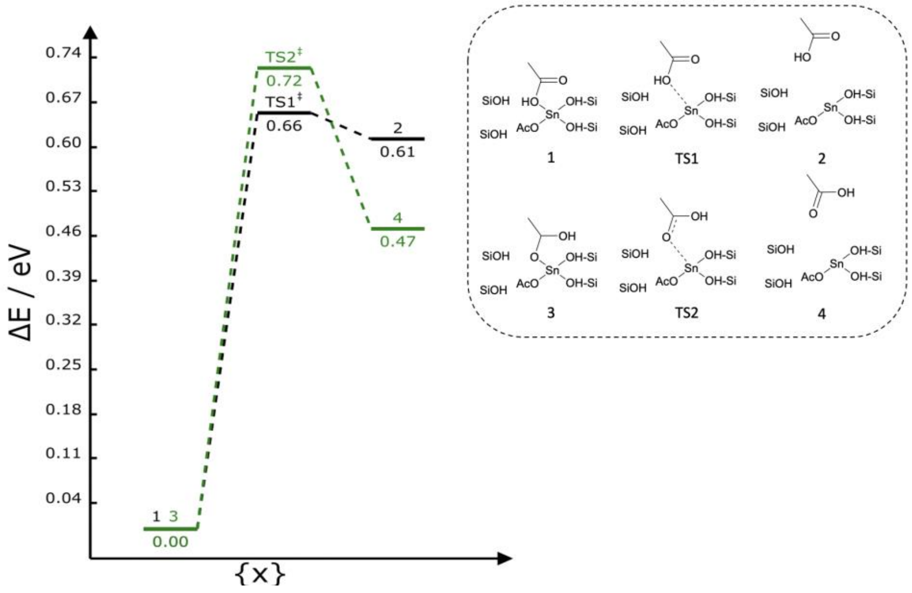


Figure S31: Reaction barriers calculated for the formation of acetic acid.

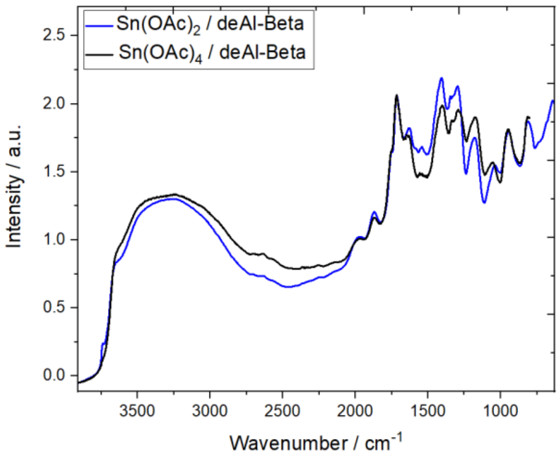


Figure S32. DRIFT spectra of i) $Sn(OAc)_2$ / deAl-Beta mixture with 10 wt. % of Sn (blue line), and ii) $Sn(OAc)_4$ / deAl-Beta mixture with 10 wt. % of Sn (black line).

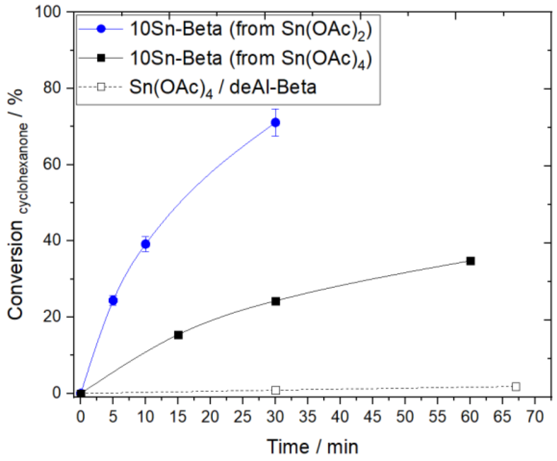


Figure S33. Comparison catalytic performances for Meerwein–Ponndorf–Verley reaction of cyclohexanone to cyclohexanol over i) 10Sn-Beta prepared using $Sn(OAc)_2$ as metal source (blue circles), ii) $Sn(OAc)_4$ / deAl-Beta mixture with 10 wt. % of Sn (IV) (empty squares, dotted line), and iii) 10Sn-Beta prepared using $Sn(OAc)_4$ as metal source (black squares). Reaction conditions: 0.2 M cyclohexanone and 0.01 M biphenyl in 2-butanol, 100 °C, Sn:cyclohexanone molar ration equal to 1:100.

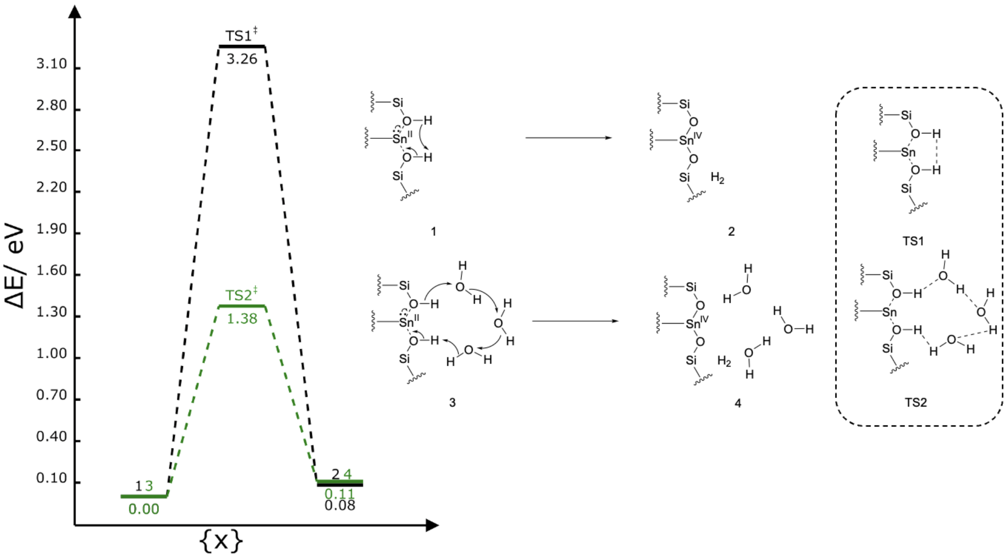
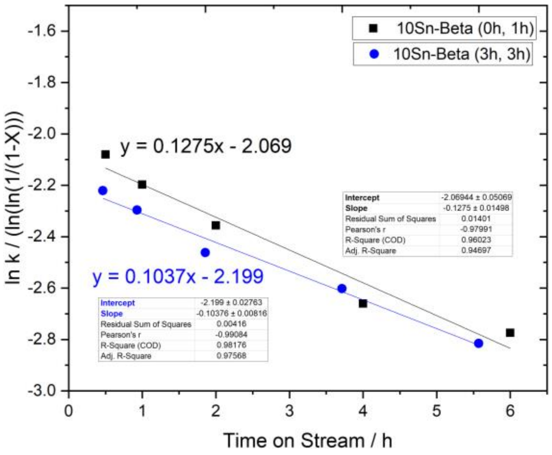


Figure S34. Reaction barriers calculated for the oxidation of Sn from +2 to +4 and corresponding mechanisms transition states i) via direct release of H_2 from geminal Si-OH centres (black lines, top scheme), and ii) in the presence of a network of water molecules (green lines, bottom scheme).



Intercept	-2.06944 ± 0.05069
Slope	-0.1275 ± 0.01498
Residual Sum of Squares	0.01401
Pearson's r	-0.97991
R-Square (COD)	0.96023
Adj. R-Square	0.94697

Intercept	-2.199 ± 0.02763
Slope	-0.10376 ± 0.00816
Residual Sum of Squares	0.00416
Pearson's r	-0.99084
R-Square (COD)	0.98176
Adj. R-Square	0.97568

Figure S35. Levenspiel plots for rapidly synthesised (0h N_2, 1h air isotherm) and conventional (3h N_2, 3h air isotherm) 10Sn-Beta. Experiments performed in 1 wt. % glucose in methanol solution using 100 mg of catalyst at 110 °C at a flow rate of 1 mL min^{-1}.