

## Supporting Information for

# Confinement Effects in Lewis Acid-Catalyzed Sugar Conversion: Steering Toward Functional Polyester Building Blocks

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# I. Catalyst preparation

## Sn-, Ti- and Zr- $\beta$ via hydrothermal synthesis procedure

Sn- $\beta$  was prepared according to a method provided by Zhang *et al.*<sup>1</sup> 2.7 g of large pore silica gel (Alfa Aesar) were dissolved with 9.94 g of a tetraethylammonium hydroxide solution (~40 wt%, Sigma Aldrich) under stirring for 2 hours. Subsequently, 0.032 g of SnCl<sub>4</sub>.5H<sub>2</sub>O (98%, Sigma-Aldrich) dissolved in 0.075 g of distilled water were added drop-wise under stirring and the mixture was stirred for another hour. Afterwards 1 g of NH<sub>4</sub>F dissolved in 0.375 g of distilled water was added to the mixture under vigorous stirring, along with 1.32 mL ethanol. Finally, the mixture was stirred for another 30 min. and resulted in a gel with a composition of 1SiO<sub>2</sub>:0.002SnO<sub>2</sub>:0.6TEAOH:0.6NH<sub>4</sub>F:6.5H<sub>2</sub>O:0.5EtOH. The gel was transferred to a Teflon lined autoclave and was heated for crystallization at 423 K for 10 days. Ti- $\beta$  and Zr- $\beta$  were synthesized according to the same procedure, but using equimolar amounts of Titanium(IV) ethoxide or Zirconium(IV) oxychloride octahydrate as metal precursor respectively.

## Sn- $\beta$ deAl via post-treatment procedure

Sn- $\beta$  deAl was prepared according a procedure described by our group.<sup>2,3</sup> For this, a commercial  $\beta$  zeolite (CP814E, Zeolyst International, Si/Al = 25) was dealuminated by stirring it in a 7.2 M aqueous nitric acid solution at 353 K overnight. Afterwards, the powder was filtered, rinsed thoroughly with deionized water and dried overnight at 333 K. Prior to Sn grafting, the powder was activated overnight at 423 K to remove physisorbed water. Then, the activated sample was suspended in dry isopropanol (100 mL g<sub>catalyst</sub><sup>-1</sup>) and 27 mmol of SnCl<sub>4</sub>.5H<sub>2</sub>O per g of support was added. The solution was refluxed under N<sub>2</sub> for 7 hours and afterwards filtered, rinsed with isopropanol and dried at 333 K.

## Sn-MFI

Sn-MFI was prepared according to Mal *et al.*<sup>4</sup> For this, 18.93 g of tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich) were mixed with a solution of 0.254 g SnCl<sub>4</sub>.5H<sub>2</sub>O (98%, Sigma Aldrich) in deionized water (6.06 g) and was stirred for 30 min. Then, 40 g of a 20 wt% solution of tetrapropylammonium hydroxide (TPAOH, 1.0 M in water, Sigma Aldrich) were added drop-wise under continuous stirring and left to react for another hour. Finally, 16.96 g of deionized water was added under vigorous stirring. A clear gel was obtained with a molar composition of 1SiO<sub>2</sub>:0.008SnO<sub>2</sub>:0.44TPAOH:34.3H<sub>2</sub>O. The gel was transferred to a Teflon lined autoclave and was put in an oven at 433 K for 3 days to crystallize.

### **Sn-MCM-41**

The ordered mesoporous Sn-MCM-41 was prepared according to Li *et al.*<sup>5</sup> Typically, 12.3 mL of a tetramethylammonium silicate solution (20 wt% in water) were added to 26 g of a 25 wt% aqueous solution of cetyltrimethylammonium bromide (98%, Sigma Aldrich) and was stirred for 50 min. Subsequently, a solution of 0.334 g SnCl<sub>4</sub>.5H<sub>2</sub>O (98%, Sigma Aldrich) in 1.048 g deionized water was added and the gel was stirred for another 10 min. Finally, 6.52 mL of TEOS (98%, Sigma Aldrich) were added and the resulting gel was stirred for 2.5 h. The gel was transferred to a Teflon-lined autoclave and heated at 413 K for 16 h.

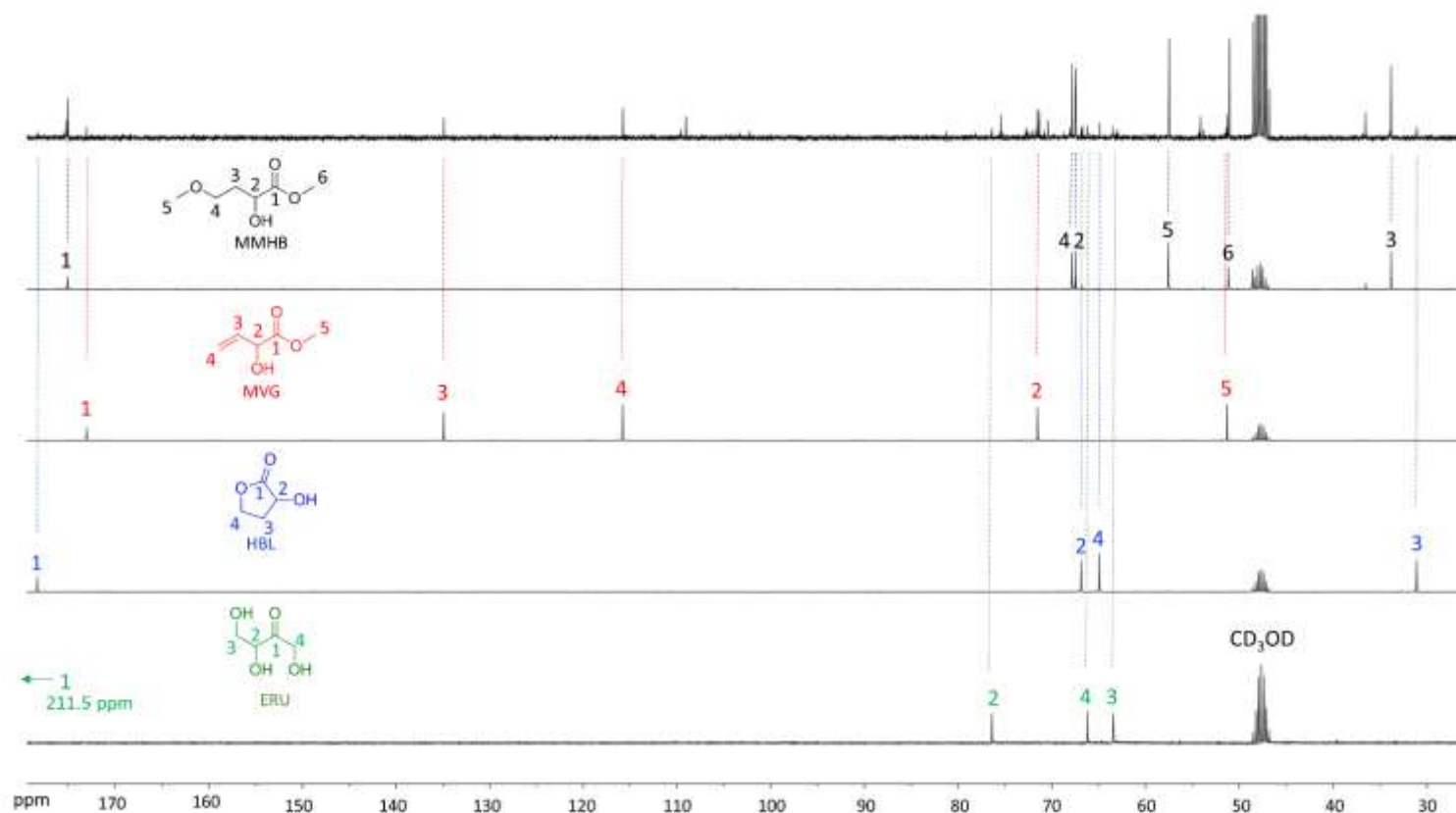
### **Sn-SBA-15**

Sn-SBA-15 was prepared according to a procedure described by Ramaswamy *et al.*<sup>6</sup> For this, 4.0 g of Pluronic P-123 (PEG,PPG,PEG polymer, MW = 5800 g mol<sup>-1</sup>, Sigma Aldrich) was dissolved in 30.0 g of water. Then, 0.5 g of a 37 wt% HCl solution, diluted with 70 g of water, was added and the mixture was stirred for 2 h. Afterwards, 9.0 g of TEOS and 0.302 g of SnCl<sub>4</sub>.5H<sub>2</sub>O dissolved in 1.0 g of water were added dropwise and the mixture was stirred for another 24 h at 313 K to obtain a gel with an approximate composition of 1 SiO<sub>2</sub>:0.02SnO<sub>2</sub>:0.016P123:0.14Cl<sup>-</sup>:134H<sub>2</sub>O. Finally, the gel was transferred to a Teflon-lined autoclave and was heated for 24 h at 373 K.

### **Post-synthesis treatment**

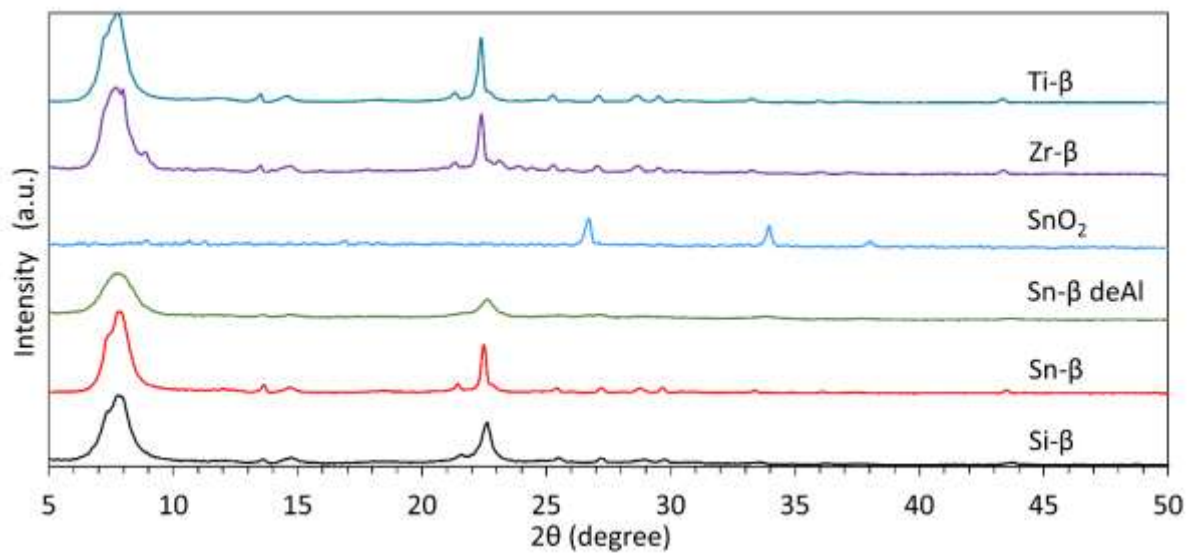
After synthesis of the hydrothermal catalysts, the autoclaves were quenched in a water bath, the solid materials were filtered, washed thoroughly with deionized water and dried overnight at 333 K in air. The obtained powders were calcined at 823 K for 6 hours (heating rate: 1 K min<sup>-1</sup>) in static air to remove all organic compounds. For Sn-β deAl an alternative calcination procedure was used: 3 K min<sup>-1</sup> to 473 K, dwell 6 hours, 3 K min<sup>-1</sup> to 823 K, dwell 6 hours.

## II. Figures

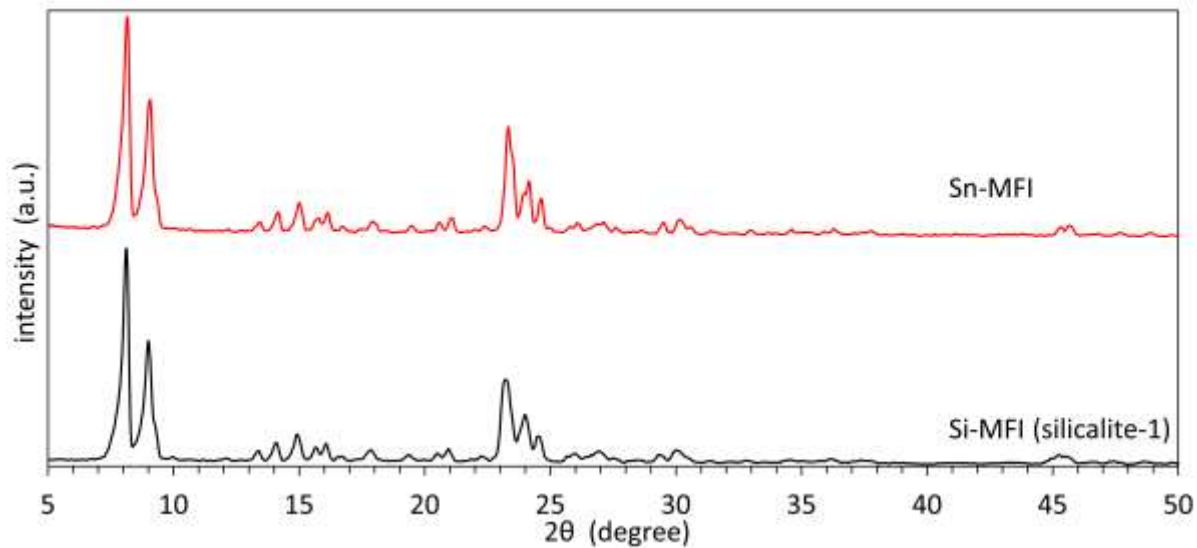


**Figure S1.** <sup>13</sup>C-NMR spectra of the product mixture obtained after reacting ERU with Sn-β in methanol at 363 K (top) and of pure compounds dissolved in CD<sub>3</sub>OD for comparison. Reaction conditions: 2.5 mmol ERU, 100 mg Sn-β, 5 mL methanol, 5 h reaction time.

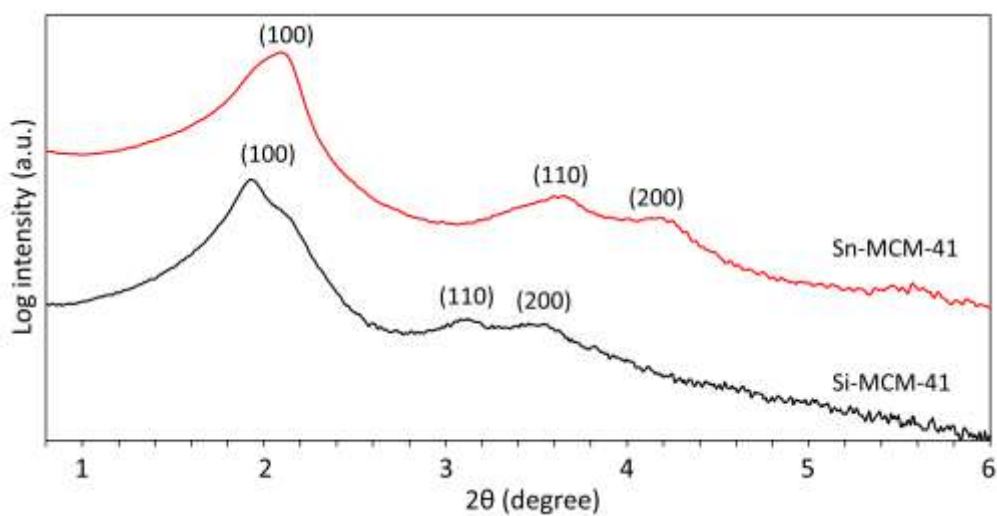
To obtain the <sup>13</sup>C-NMR sample, 1 mL of the product mixture was evaporated by a mild N<sub>2</sub> flow. Afterwards, 0.6 mL of CD<sub>3</sub>OD was added to the residu. To obtain a <sup>13</sup>C-NMR spectrum of MMHB, 5 mmol ERU was reacted with 10 mol% of SnCl<sub>4</sub>·5H<sub>2</sub>O in methanol (4 mL) for 5 hours at 363 K. Then, 1 mL of the product mixture was evaporated by a mild N<sub>2</sub> flow. Afterwards, 0.6 mL of CD<sub>3</sub>OD was added to the residu. The signal of the carbonyl group of ERU falls at 211.5 ppm, but is not shown in this figure.



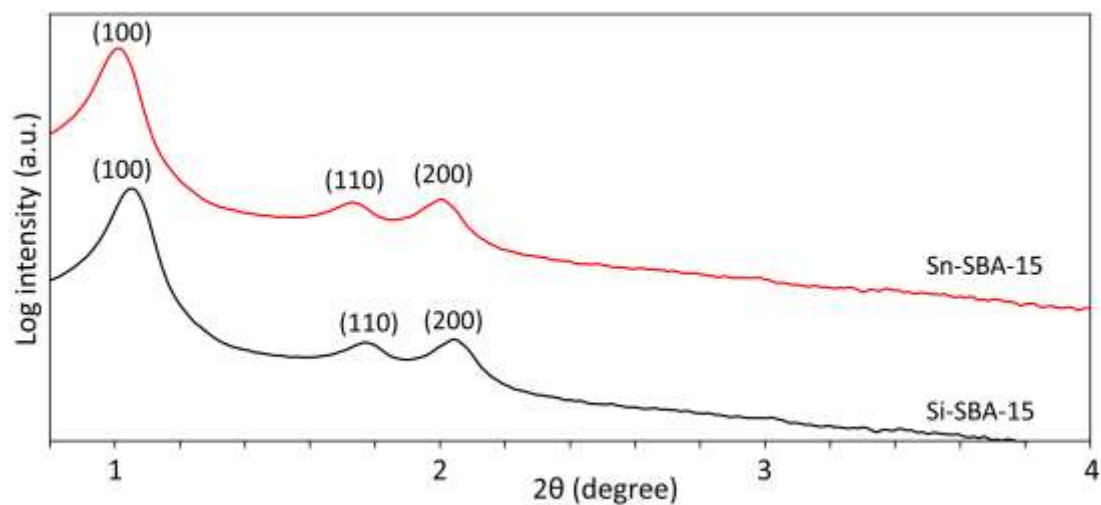
**Figure S2.** Powder XRD patterns of Si-β, Sn-β, Sn-β deAl, SnO<sub>2</sub>, Zr-β and Ti-β. Diffraction lines have been offset for clarity.



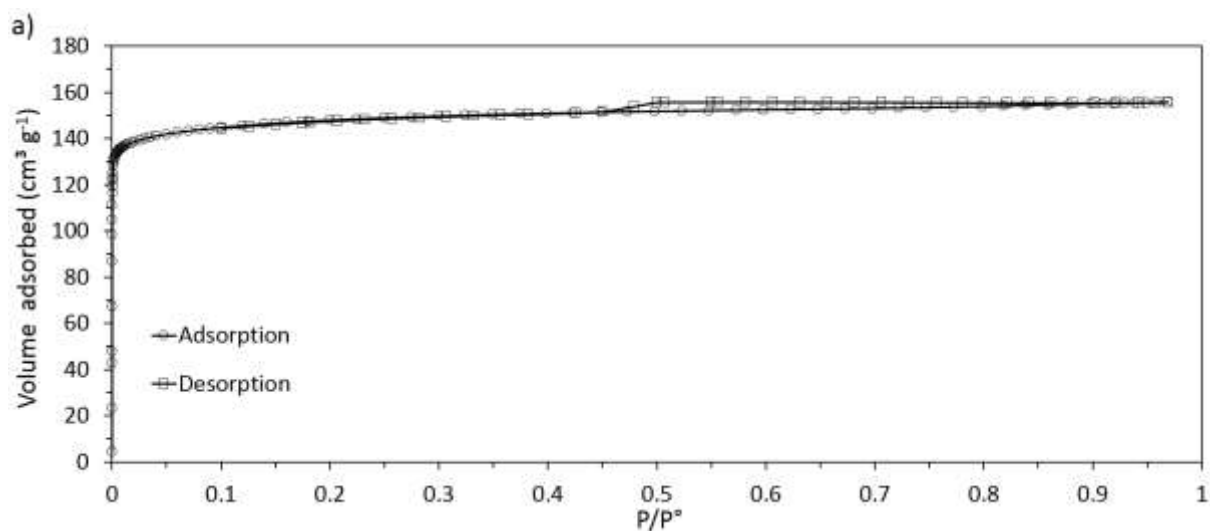
**Figure S3.** Powder XRD patterns of Si-MFI and Sn-MFI. Diffraction lines have been offset for clarity.



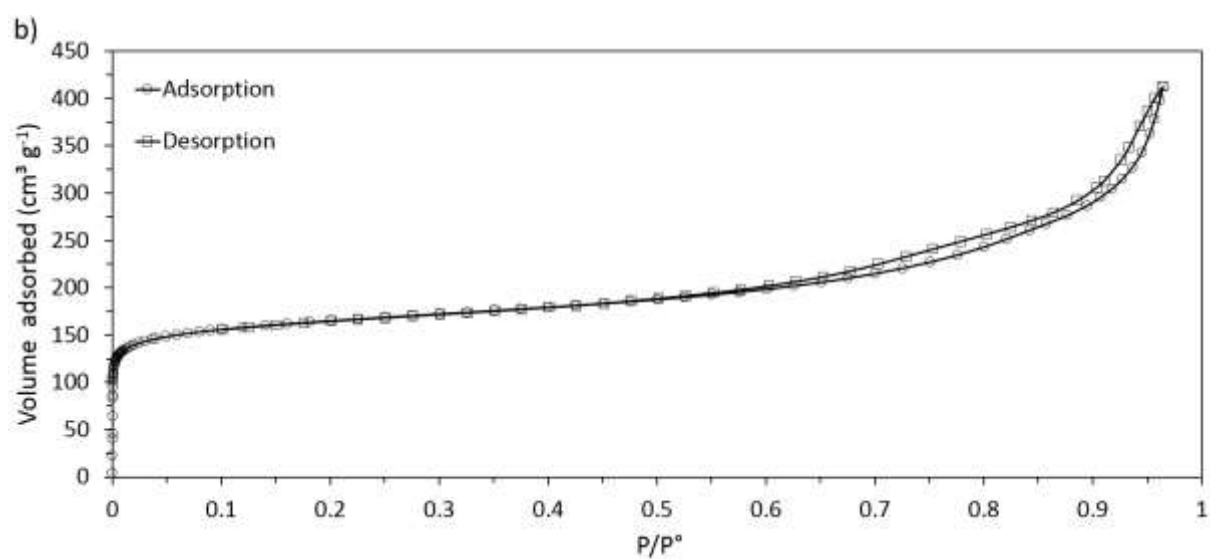
**Figure S4.** Small angle X-ray diffraction patterns of Si-MCM-41 and Sn-MCM-41. Diffraction lines have been offset for clarity. The (100), (110) and (200) reflections arise from the mesoporous ordering.



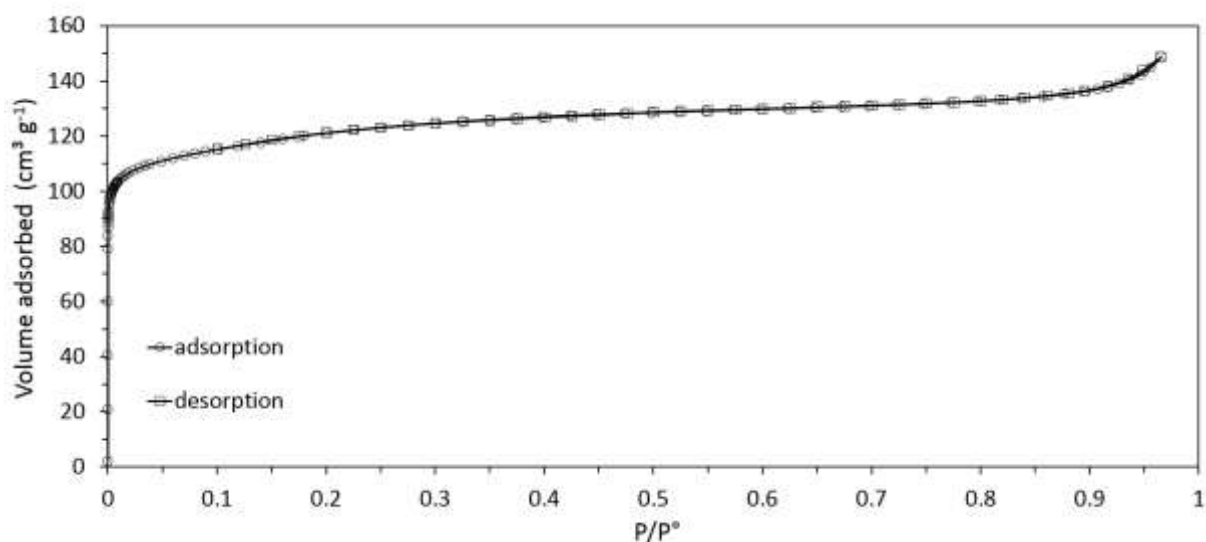
**Figure S5.** Small angle X-ray diffraction patterns of Si-SBA-15 and Sn-SBA-15. Diffraction lines have been offset for clarity. The (100), (110) and (200) reflections arise from the mesoporous ordering.



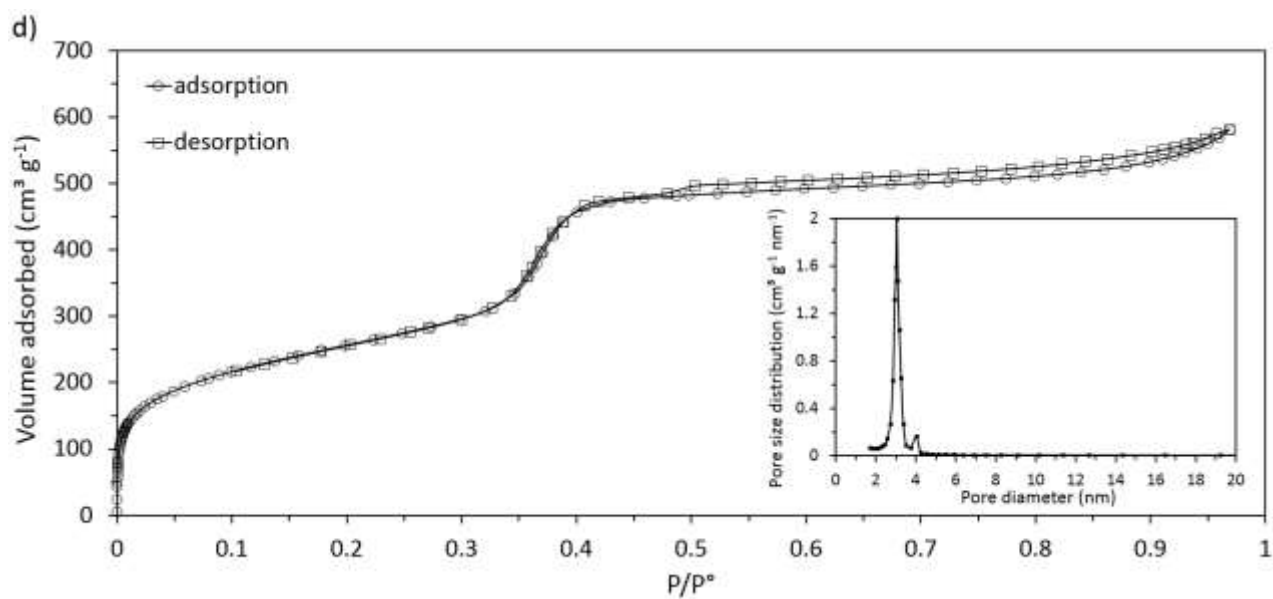
**Figure S6.**  $\text{N}_2$ -adsorption (circles) and desorption (squares) isotherms of  $\text{Sn-}\beta$ .  $P$ , pressure of adsorbent;  $P^\circ$  saturation pressure (1 atm).



**Figure S7.**  $\text{N}_2$ -adsorption (circles) and desorption (squares) isotherms of  $\text{Sn-}\beta \text{ deAl}$ .  $P$ , pressure of adsorbent;  $P^\circ$  saturation pressure (1 atm).

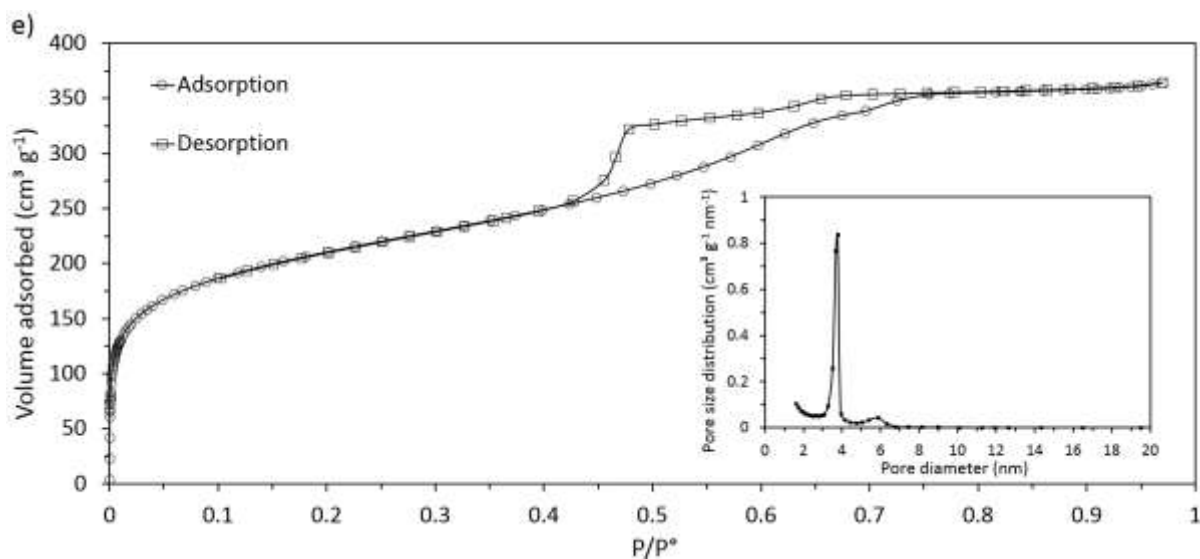


**Figure S8.** N<sub>2</sub>-adsorption (circles) and desorption (squares) isotherms of Sn-MFI. P, pressure of adsorbent; P<sup>o</sup> saturation pressure (1 atm).

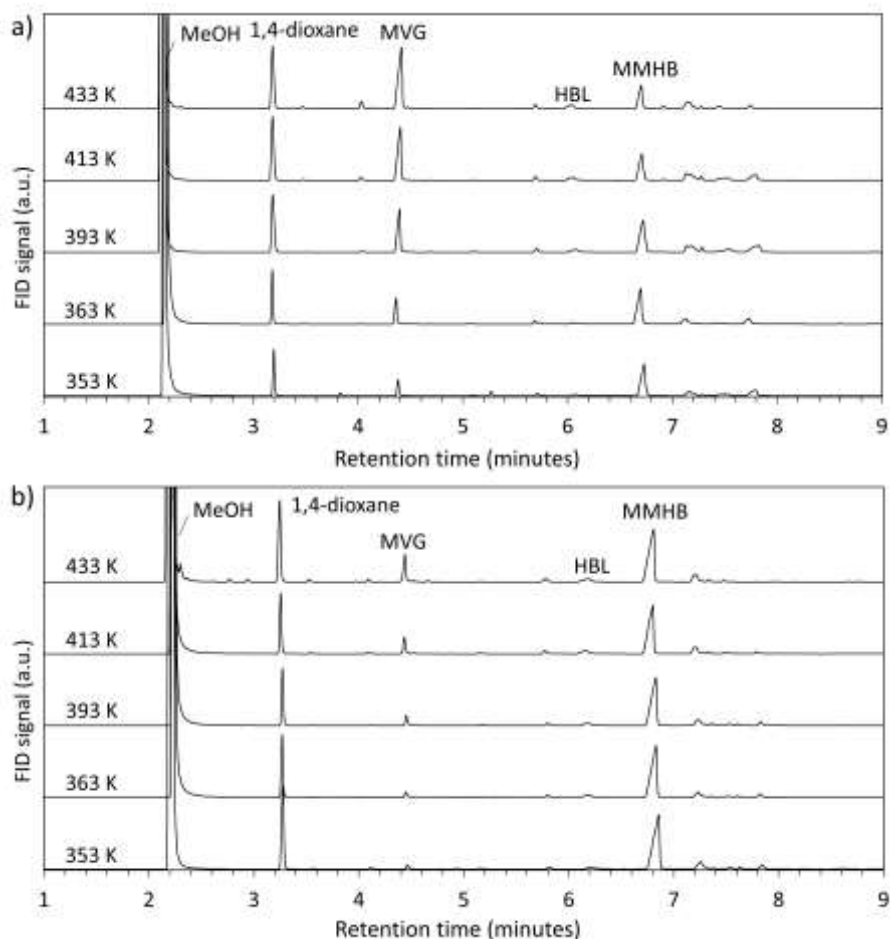


**Figure S9.** N<sub>2</sub>-adsorption (circles) and desorption (squares) isotherms and corresponding pore size distribution of Sn-MCM-41. P, pressure of adsorbent; P<sup>o</sup> saturation pressure (1 atm).

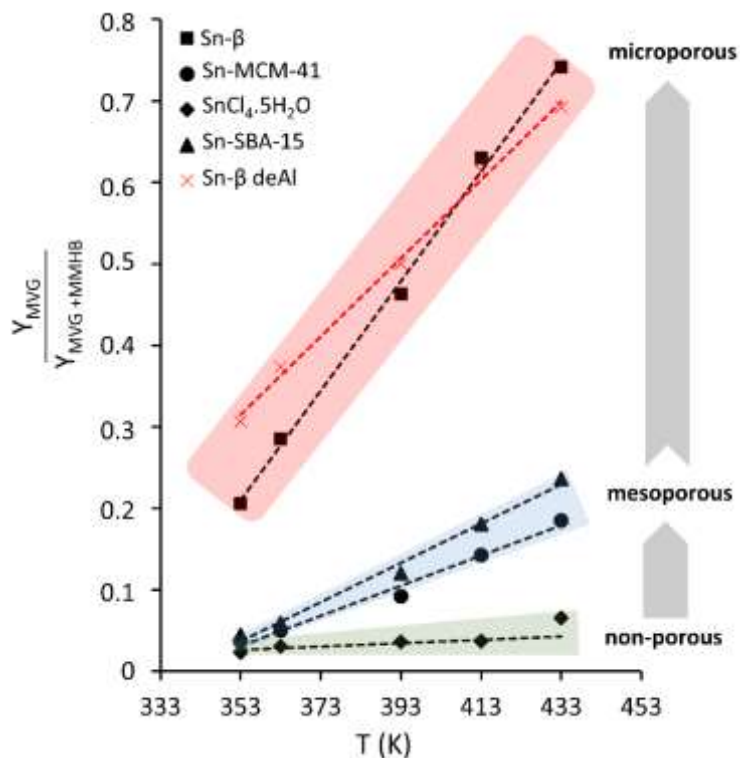




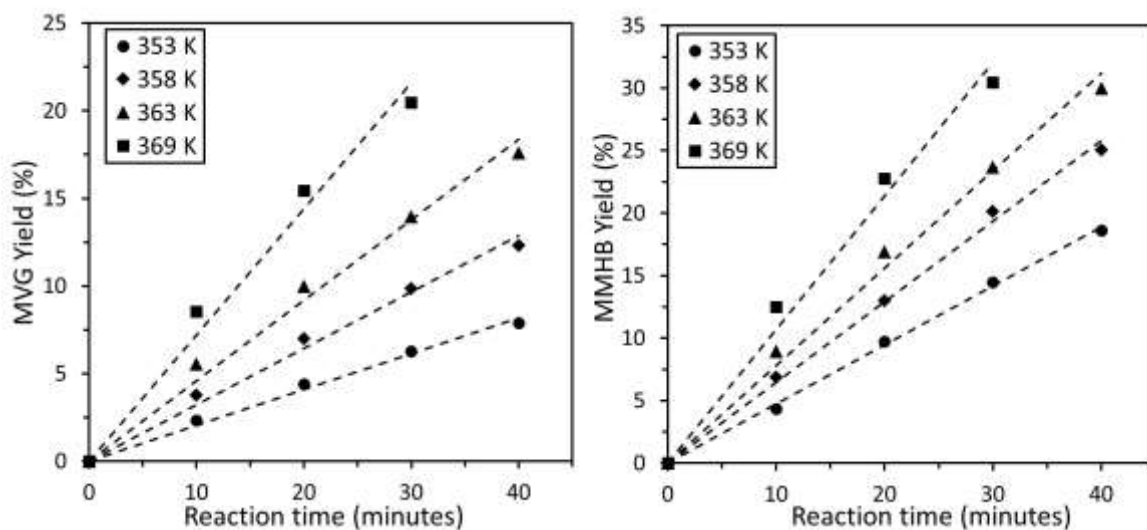
**Figure S10.**  $N_2$ -adsorption (circles) and desorption (squares) isotherms and corresponding pore size distribution of Sn-SBA-15. P, pressure of adsorbent;  $P^\circ$  saturation pressure (1 atm).



**Figure S11.** GC chromatograms of the product mixture after the conversion of ERU in methanol at different temperatures with a) Sn- $\beta$  and b) Sn-MCM 41.

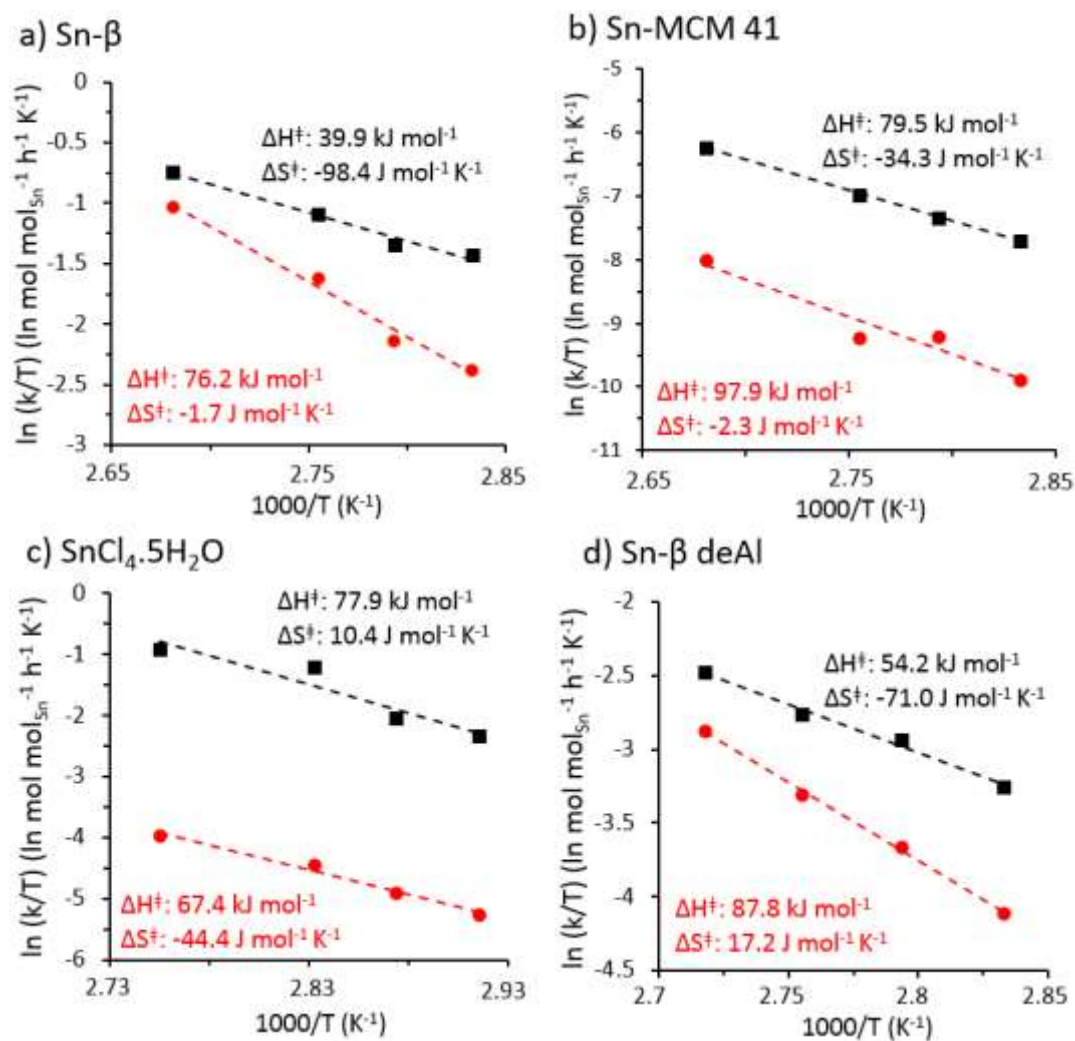


**Figure S12.** Comparison of the influence of temperature on the selectivity towards MVG, compared to the total amount of MVG and MMHB produced for hydrothermal Sn- $\beta$  and Sn- $\beta$  deAl.

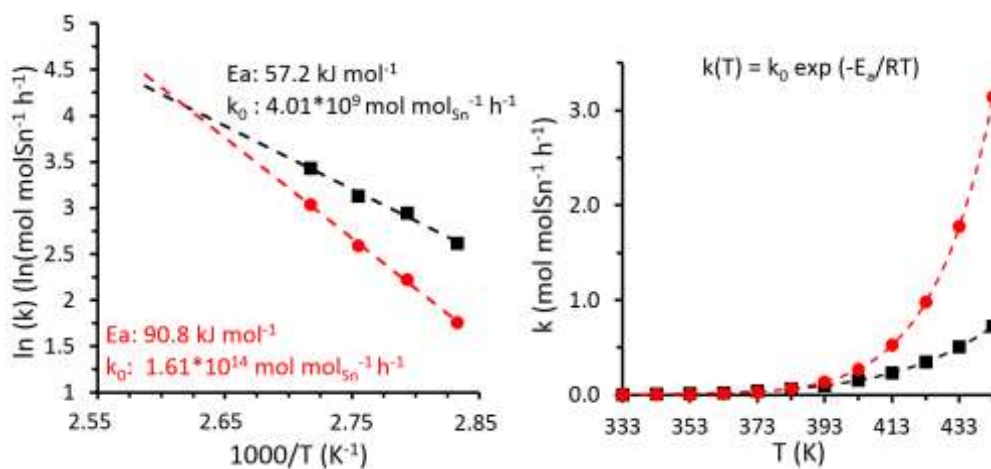


**Figure S13.** Kinetic plots at various temperatures for the conversion of ERU to MVG (left) and MMHB (right) with Sn- $\beta$  deAl in methanol. Reaction conditions: 1,25 mmol ERU, 100 mg catalyst, 50 mg 1,4-dioxane (internal standard), 5 mL methanol.

*Note:* For continuous sampling, the reaction was cooled using an ice bath and the reaction timer was paused. When the reactor was cold, a sample was taken using a syringe equipped with a needle through the septum of the crimp cap. Then, the reactor was put back in the heated copper block and the reaction timer was started again.



**Figure S14.** Eyring-Polanyi plots for the conversion of ERU to MVG and MMHB with a) Sn- $\beta$ , b) Sn-MCM-41, c) SnCl<sub>4</sub>·5H<sub>2</sub>O and d) Sn- $\beta$  deAl.  $\Delta H^\ddagger$  was calculated from the slope (which is expressed as  $-\Delta H^\ddagger/T$ ).  $\Delta S^\ddagger$  was derived from the intercept, which equals  $(\ln(k_b/T) + (\Delta S^\ddagger/R))$ .



**Figure S15.** Arrhenius plot for the conversion of ERU to MVG and MMHB1 (left) and calculated reaction rates for both products at different reaction temperatures (right) for Sn- $\beta$  deAl.

### III. Tables

**Table S1.** Conversion of dihydroxyacetone (DHA) to methyl lactate (MLA) using different Sn-based heterogeneous catalysts.<sup>a</sup>

Entry	Catalyst <sup>b</sup>	Catalyst [mg]	DHA [mmol]	Reaction time [h]	MLA yield [%]	Ref.
1	Sn- $\beta$	100	1.25	5	>99	7
2	Sn- $\beta$ deAl	75	1	7.5	95	3
3	Sn-MFI	80	1.25	20	94	8
4	Sn-MCM-41	200	2	6	98	5
5	Sn-SBA-15	80	1.25	24	78	8

<sup>a</sup>Different reaction conditions were used for each catalyst to compare with literature values. All reactions were performed at 363 K in methanol with 50 mg of 1,4-dioxane as internal standard. <sup>b</sup>Details on composition can be found in table 2 in the original manuscript.

**Table S2.** Estimated kinetic diameters ( $\sigma$ ) of substrates and products used in this study compared to pore sizes of the tested catalysts.<sup>a</sup>

Compound	MW [g mol <sup>-1</sup> ]	$\sigma$ [Å]	Pore size [Å]			
			MFI 5.5-6	$\beta$ 6.6-6.7	MCM-41 > 20	SBA-15 >20
			$\sigma < \text{pore size?}$			
DHA	90	5.5	yes	yes	yes	yes
MLA	104	5.8	yes	yes	yes	yes
ERU	120	6.1	no	yes	yes	yes
MVG	116	6.0	no	yes	yes	yes
MMHB	134	6.3	no	yes	yes	yes
HBL	104	5.8	yes	yes	yes	yes

<sup>a</sup>Kinetic diameters were calculated by the empirical formula  $\sigma = 1.234 (M_w)^{1/3}$ , where  $M_w$  is the molecular weight in g mol<sup>-1</sup>.

*Note:* Although this formula was originally derived for aromatic hydrocarbons<sup>9</sup>, it was recently shown that for oxygenates, there is a good agreement (<2 % average difference) between literature values of kinetic diameter and those determined by this empirical correlation. Thus, this suggests that using this approximation for determining the kinetic diameter of oxygenates is reasonable.<sup>10</sup> The results from this table suggests that all compounds can freely diffuse in the pores of the Sn- $\beta$ , Sn-MCM-41 and Sn-SBA-15 catalysts. In Sn-MFI however, DHA and MLA can diffuse freely, whereas the kinetic diameter of the more bulky ERU, MVG and MMHB exceed or are equal to the maximum of the pore size range. This suggests diffusion limitation of ERU or products derived thereof might inhibit higher product yields.

**Table S3.** Conversion of ERU to C<sub>4</sub>-AHAs with Sn-β deAl at various temperatures<sup>a</sup>

Catalyst	T K]	Yield [%]			Conversion [%]
		MVG	MMHB	HBL	
Sn-β deAl	353	19	43	7	94
	363	24	47	5	93
	393	27	27	7	96
	413	35	22	8	90
	433 <sup>b</sup>	45	20	5	94

<sup>a</sup>Reaction conditions: 1.25 mmol ERU, 100 mg catalyst, 5 mL methanol, 50 mg 1,4-dioxane, 5h reaction time. <sup>b</sup>Sample taken after 1 h reaction time.

## IV. References

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