Electronic Supplementary Information for

Fluoride-free and low concentration template synthesis of hierarchical Sn-Beta zeolites: efficient catalyst for conversion of glucose to alkyl lactate

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1. Experimental

1.1. Materials

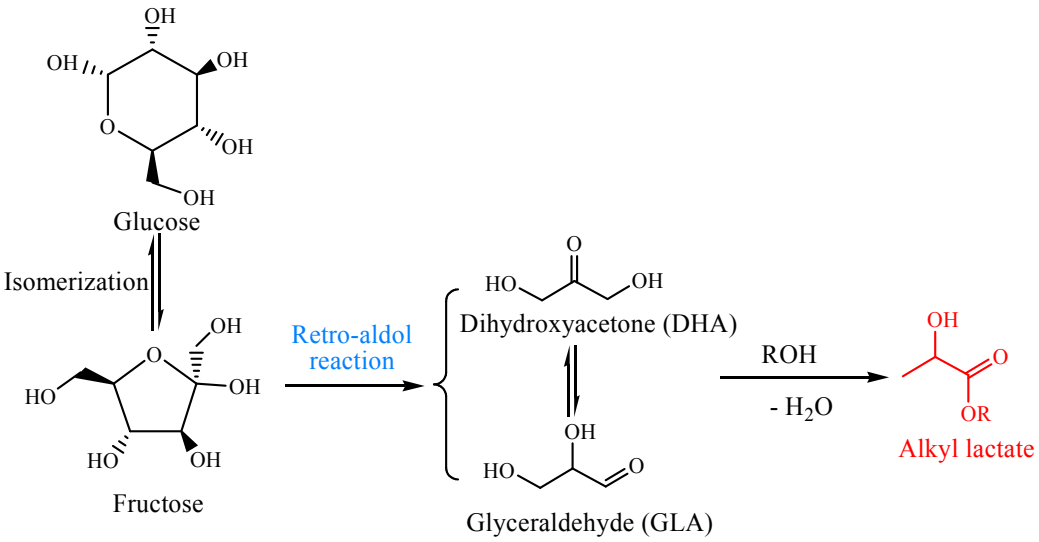
The parent Al-Beta zeolites with Si/Al ratio of 38.1, 19.5 and 13.8 were purchased from Nankai University Catalyst Co. (China). Nitric acid (65-68%), hydrofluoric acid (40%), $SnCl_4 \cdot 5H_2O$, methanol, ethanol, *n*-buthanol and naphthalene were purchased from commercial resources (AR grade). Tetraethyl orthosilicate (TEOS, AR grade), tetraethylammonium hydroxide (TEAOH, 25% aqueous solution) and ethyl lactate were purchased from Aladdin Reagent Co. (China). 1,3-Dihydroxyacetone dimer (97%, DHA), xylose and *n*-butyl lactate were obtained for J & K Scientific Ltd, China. Methyl lactate (> 98%, MLA) was purchased from TCI Shanghai, China. Glucose monohydrate was of analytic grade and purchased from Tianjin Fengchuan Chemical Reagent Factory. Fructose (99%) was purchased from Aladdin Reagent Co. (China). Mannose and sucrose were purchased from SCRC, Ltd. All chemicals were used as purchased without further purification.

1.2. Hydrothermal synthesis of Sn-Beta zeolite in fluoride medium

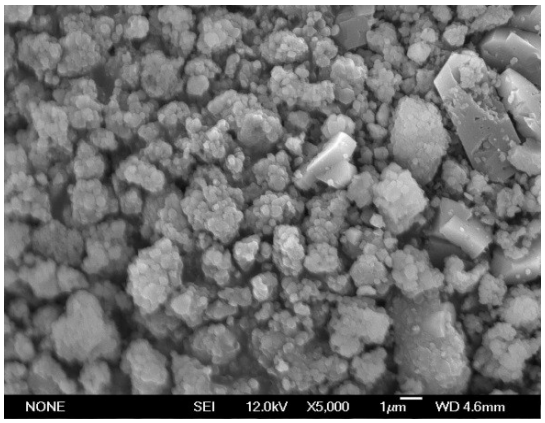
Sn-Beta zeolite synthesized directly by the hydrothermal method was designated as Sn-Beta-F. The hydrothermal method described in reference [1] was adopted to prepare Sn-Beta-F. 10.74 g TEOH (25% aqueous solution) was mixed with 6.98 g TEOS in a plastic beaker. After stirring for 90 min, 0.74 g $SnCl_4$ solution (0.14 g $SnCl_4 \cdot 5H_2O$ dissolved in 0.6 g H_2O) was added dropwise and white precipitate appeared. The mixture was continued to stir until EtOH and H_2O (total weight loss of 10.08 g) was evaporated. Then, 0.89 g HF (40% aqueous solution) was added, and the

dense gel was formed. Finally, the above dealuminated Beta seeds (0.083 g, ~4 wt% compared to the theoretical zeolite amount) were suspended in deionized water (0.58 g), sonicated and added into the dense gel. The molar ratio of the resulting gel was as follows: 0.008 SnO_2: 1 SiO_2: 0.54 TEAOH: 0.54 HF: 7.5 H_2O. The gel was mixed homogeneously, transferred to a stainless steel autoclave lined with PTFE, and crystallized statically at 140 °C for 30 days. After crystallization, the autoclave was cooled down to room temperature quickly and the products were isolated by centrifugation. The products were washed three times with deionized water and dried at 100 °C overnight. The dried powder was calcined in muffle furnace at 550 °C for 8 h to remove carbonaceous residues.

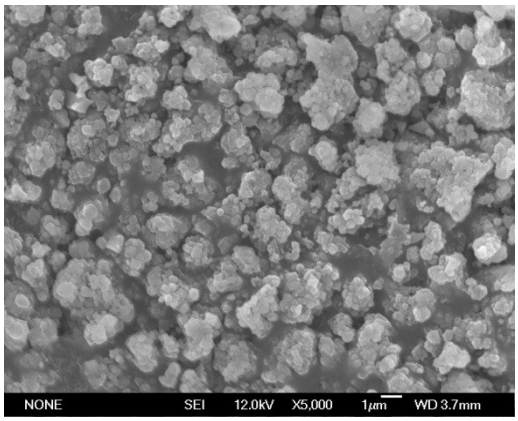
2. Additional results



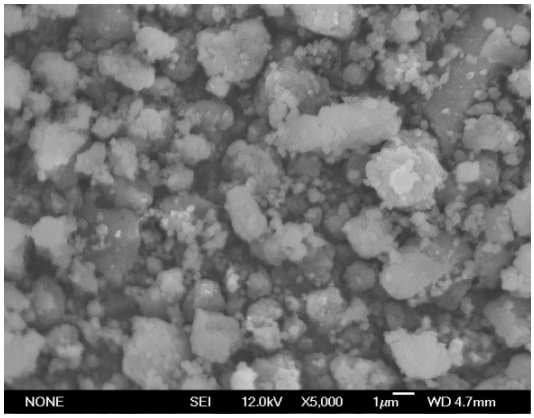
Scheme S1 Proposed reaction pathway for the conversion of C_6 carbohydrate to alkyl lactate [1,2].



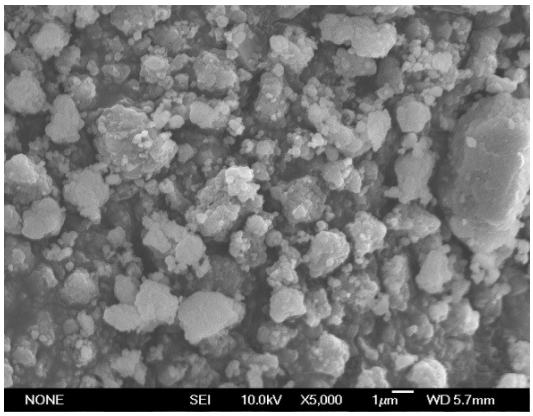
Al-Beta



deAl-Beta



$x = 0.05$



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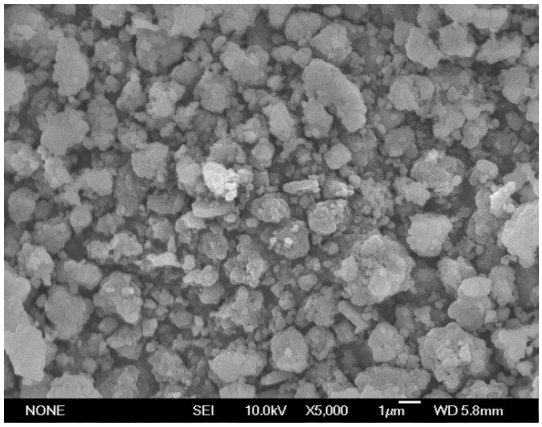

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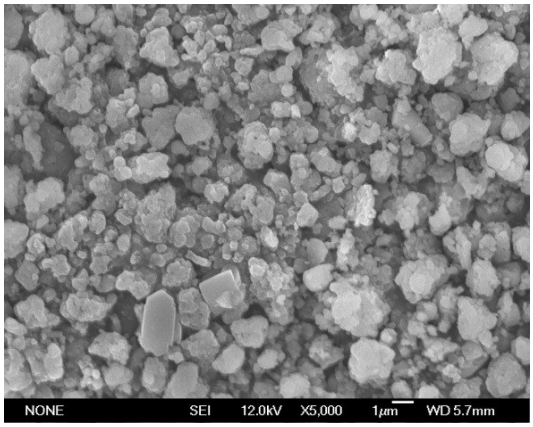

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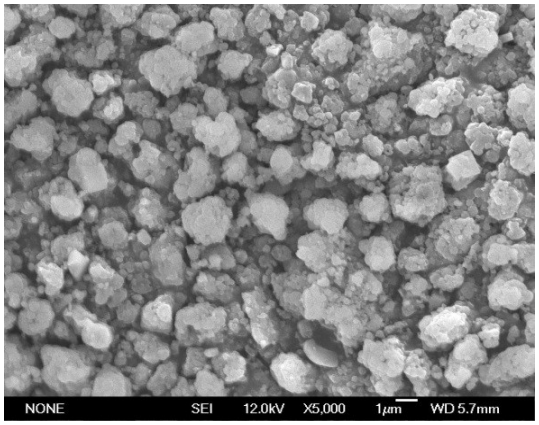
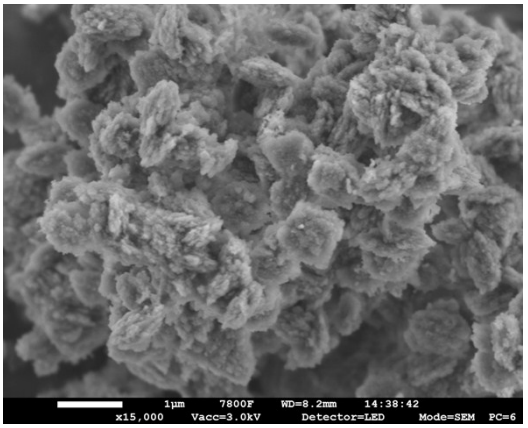




x = 0.4 Sn-Beta-F

Fig. S1 SEM pictures of Al-Beta, deAl-Beta, Sn-Beta-H-x (x represents the concentration of TEAOH.) and Sn-Beta-F.

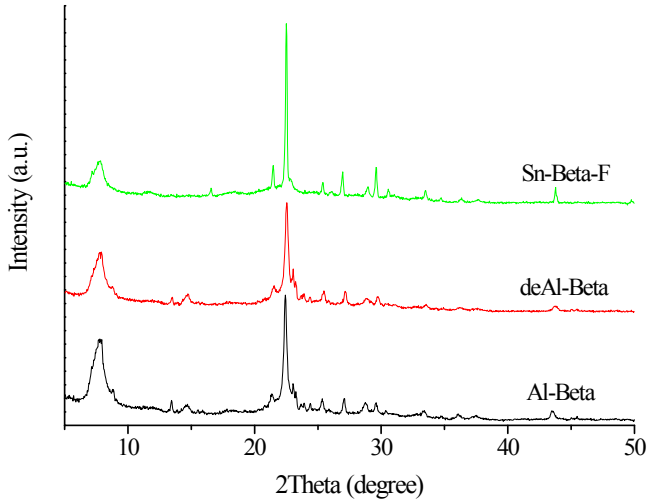


Fig. S2 XRD patterns of Al-Beta, deAl-Beta and Sn-Beta-F.

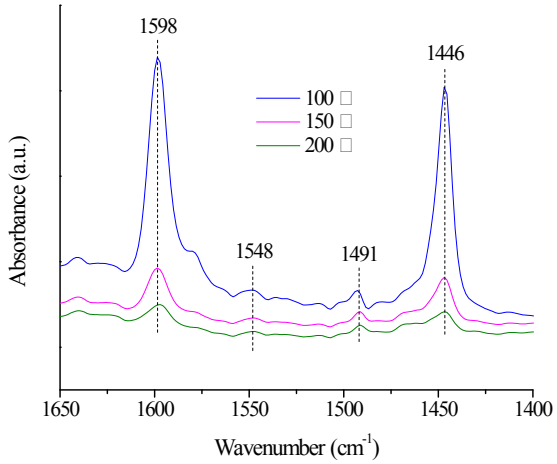


Fig. S3 FT-IR spectra of pyridine adsorbed on deAl-Beta. The bands at 1446 cm^{-1} and 1598 cm^{-1} correspond to hydrogen-bonded pyridine.

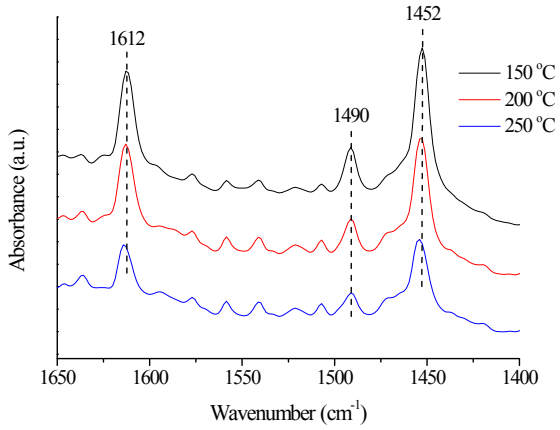
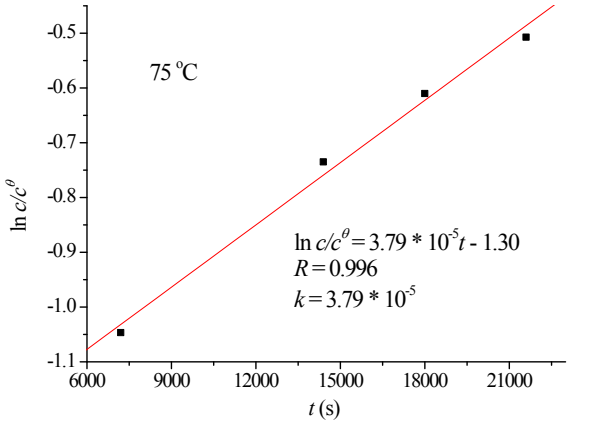
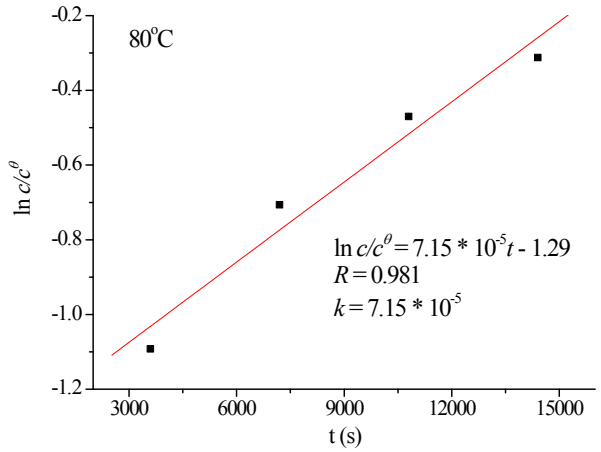


Fig. S4 FT-IR spectra of pyridine adsorbed on Sn-Beta-F.





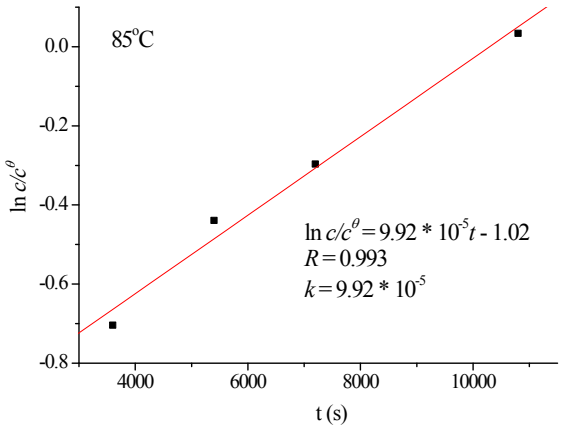
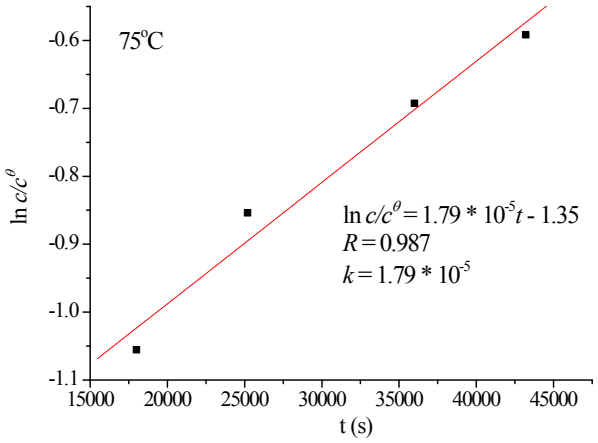
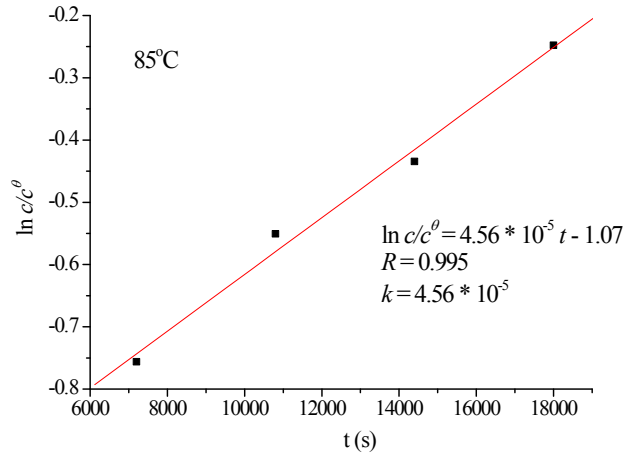


Fig. S5 Kinetic analysis of MLA formation from fructose in methanol in the presence of Sn-Beta-H-0.3.





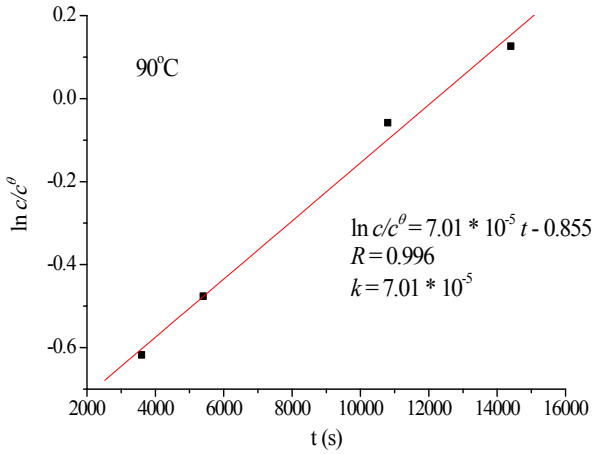


Fig. S6 Kinetic analysis of MLA formation from fructose in methanol in the presence of Sn-Beta-F.

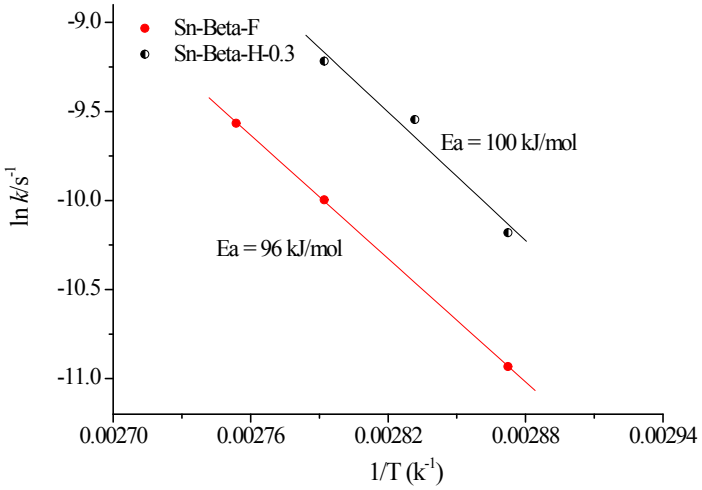


Fig. S7 Arrhenius plots of the retro-aldol of fructose over Sn-Beta-H-0.3 and Sn-Beta-F.

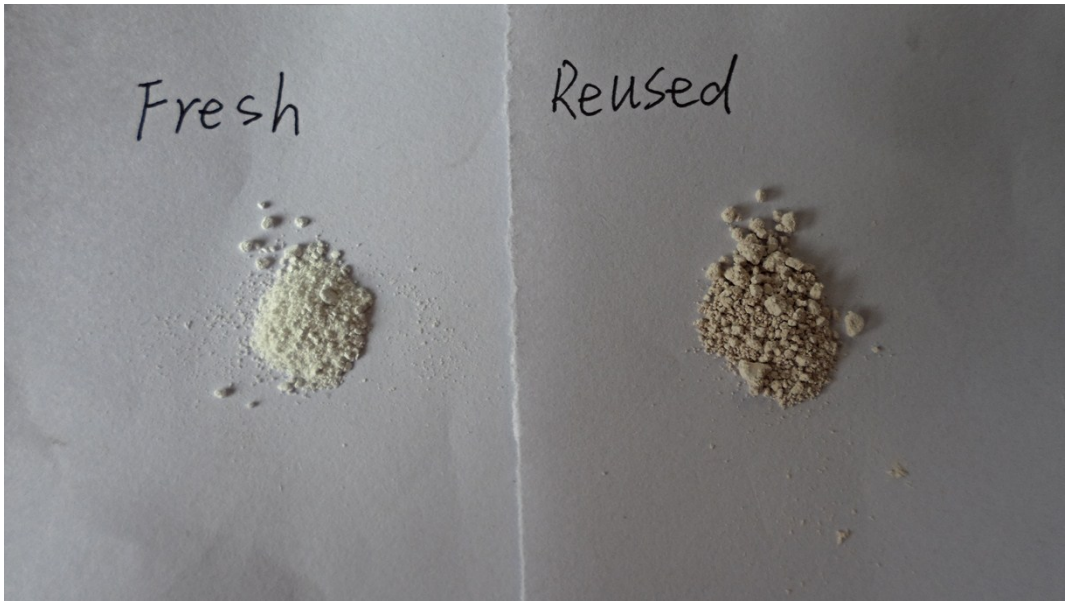


Fig. S8 Photos of fresh and reused Sn-Beta-H-0.3.

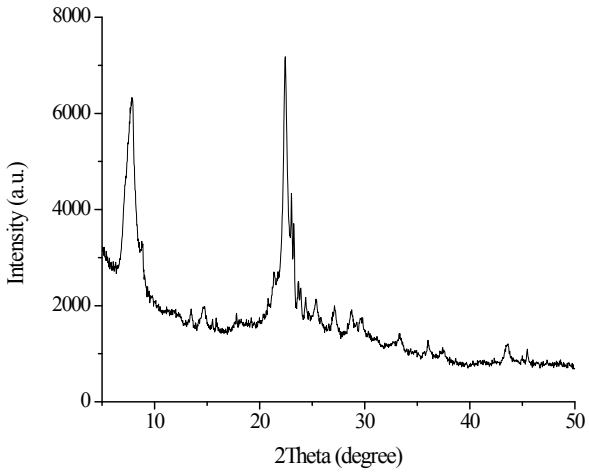


Fig. S9 XRD pattern of reused Sn-Beta-H-0.3.

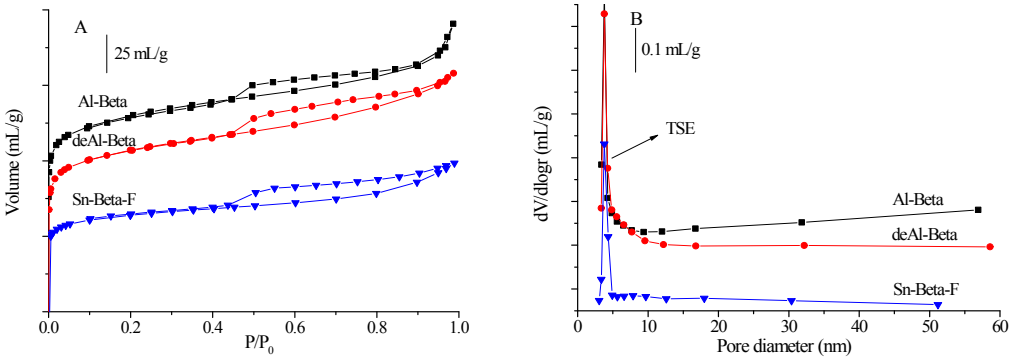
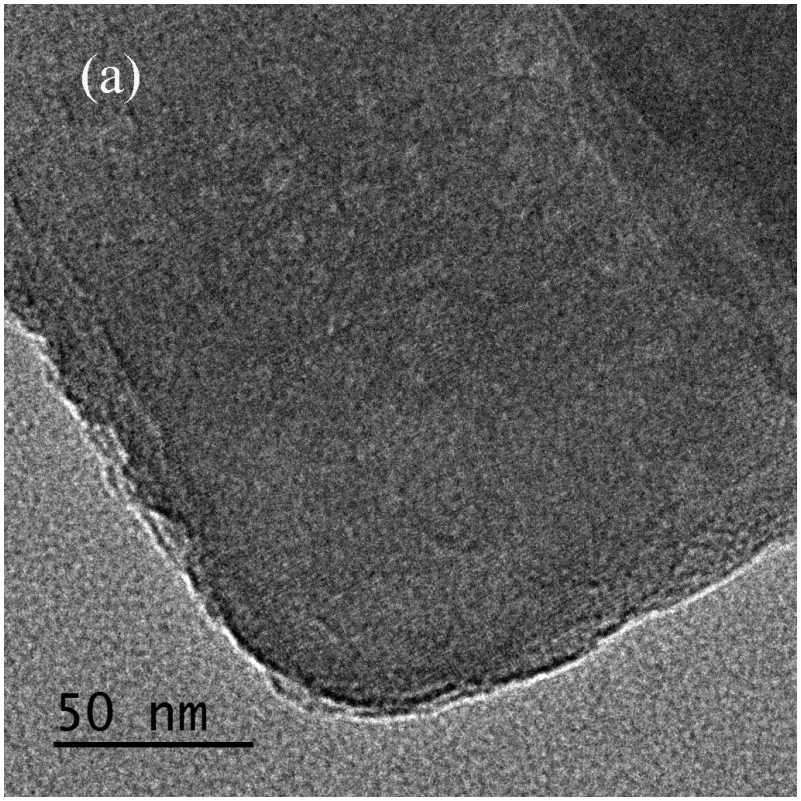
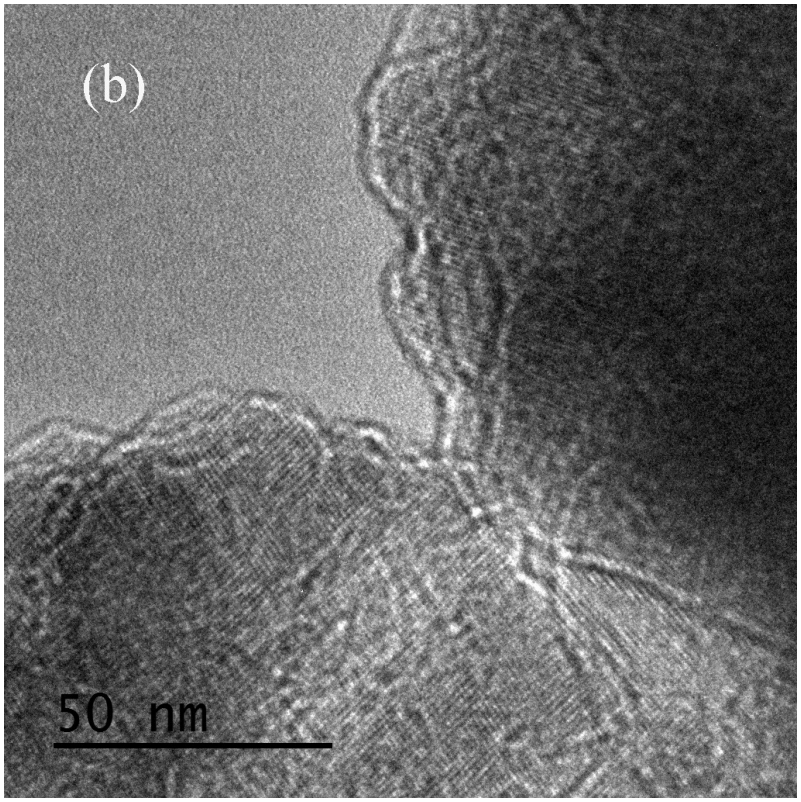


Fig. S10 N_2 isotherms (A) and BJH-derived pore size distributions (B) of Al-Beta,

deAl-Beta and Sn-Beta-F.





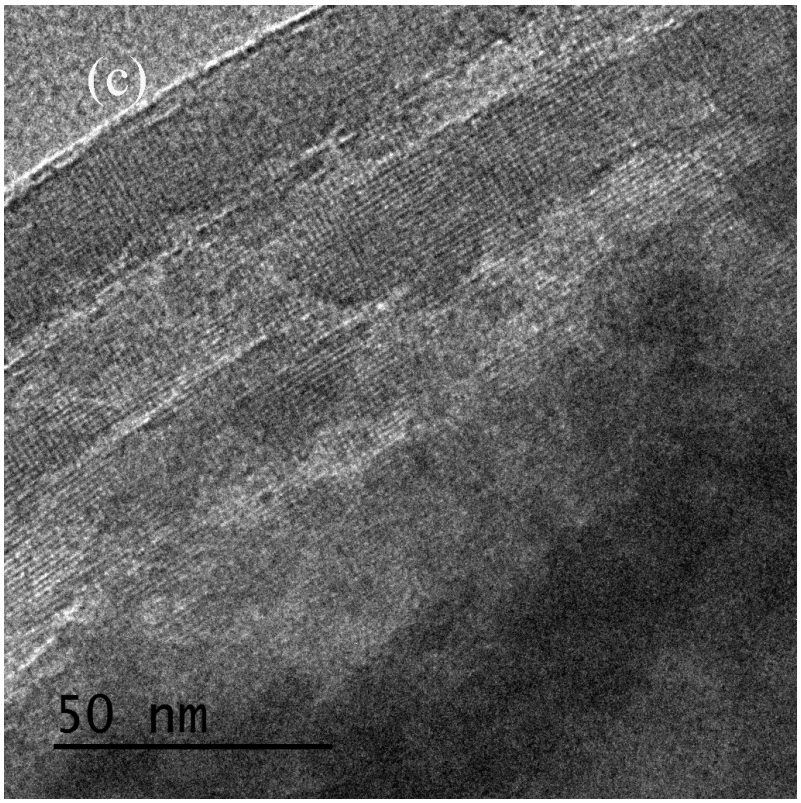


Fig. S11 TEM images of (a) Sn-Beta-H-0.2, (b) Sn-Beta-H-0.3 and (c) Sn-Beta-H-0.4.

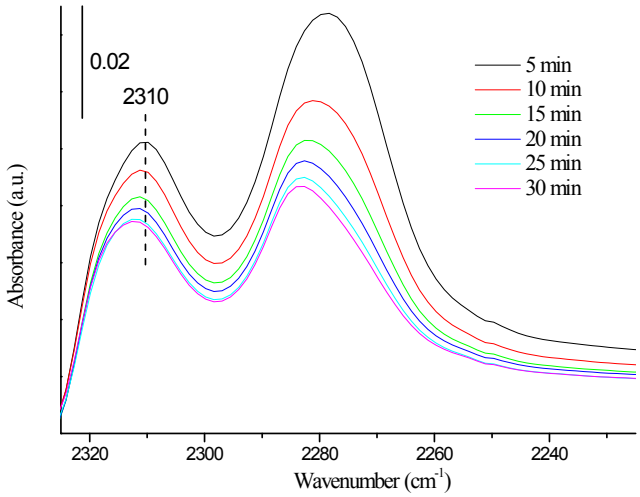


Fig. S12 FT-IR spectra of CD_3CN adsorbed on Sn-Beta-F. The spectra were measured after saturation of CD_3CN on the samples followed by different desorption times at 25 ^oC.

Table S1 TG results of Sn-Beta zeolites

Sample	Weight loss at different temperature region (wt%)			Total weight loss (wt%)
	I (<200 °C)	II (200-350 °C)	III (>350 °C)	
Sn-Beta-H-0.05	2.2	3.2	3.5	8.9
Sn-Beta-H-0.1	2.0	7.0	4.4	13.4
Sn-Beta-H-0.2	1.8	9.0	5.2	16.0
Sn-Beta-H-0.3	2.0	9.1	5.0	16.1
Sn-Beta-H-0.4	1.9	9.1	4.8	15.8
Sn-Beta-F	3.0	12.0	4.0	19.0

Table S2 Lewis acid density of Sn-Beta-H-0.3 and Sn-Beta-F

Sample	Lewis acid density (μmol/g)		
	150 °C	200 °C	250 °C
Sn-Beta-H-0.3	331	245	158
Sn-Beta-F	280	225	176

Table S3 Comparison of pseudo-yield of retro-aldol reaction of fructose over Sn-Beta zeolites[a]

Catalyst	Yield of MLA (%)[a]		Pseudo-yield of retro-aldol reaction (%)[b]
	From fructose	From DHA	
Sn-Beta-H-0.3	17	89	19
Sn-Beta-F	8	93	9

[a] Reaction conditions: 0.124 g carbohydrate, 80 mg catalyst, 5 mL methanol, 0.5 MPa

N_2, 90 °C, 5 h.

[b] Pseudo-yield of retro-aldol reaction = (yield of MLA from fructose)/(yield of MLA from DHA).

Table S4 Yield (%) of methyl lactate from glucose over Sn-Beta zeolites[a]

Entry	Sample	From Al-Beta with Si/Al of 13.8	From Al-Beta with Si/Al of 19.5
1	Al-Beta	3	3
2	deAl-Beta	16	10
3	Sn-Beta-H-0.05	32	36
4	Sn-Beta-H-0.1	46	46
5	Sn-Beta-H-0.2	57	55
6	Sn-Beta-H-0.3	59	56
7	Sn-Beta-H-0.4	54	56
8[b]	Sn-Beta-H-0.3		60

[a] Reaction conditions: 0.124 g glucose, 80 mg catalyst, 5 mL methanol, 0.5 MPa N_2, 160 °C, 10 h.

[b] Hydrothermally treated with solid to liquid ratio of 1 g/5 mL.

Reference

1 M. S. Holm, S. Saravanamurugan and E. Taarning, *Science*, 2010, **328**, 602–605.

2 L. Zhou, L. Wu, H., X. Yang, Y. Su, T. Lu and J. Xu, *J. Mol. Catal. A: Chem.*, 2014, **388–389**, 74–80.