

Supplementary information

**Production of liquid fuel intermediates from furfural via aldol condensation over
Lewis acid zeolite catalysts**

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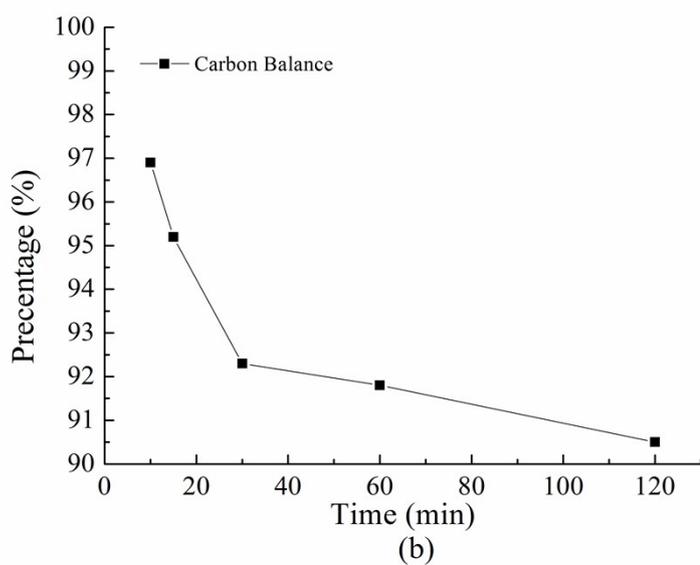
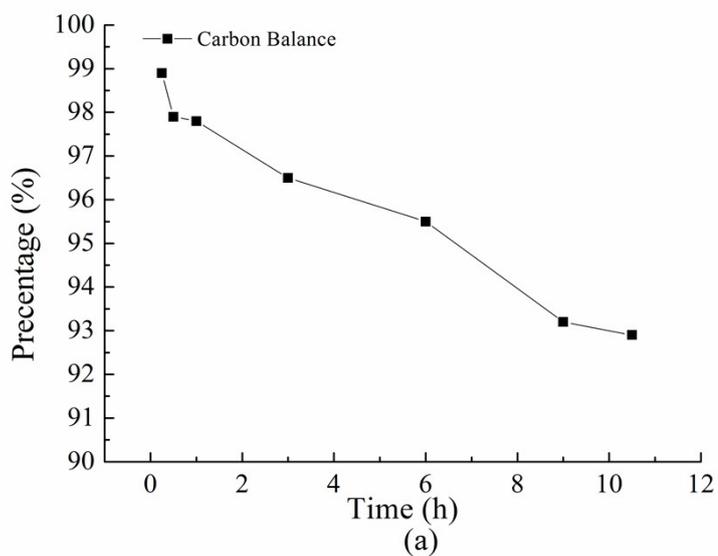


Fig.S1 Carbon balance over Sn-MFI (a) and Sn-Beta (b).

The carbon balance decreased from 98.9% to 92.9% over Sn-MFI and 96.9% to 90.5% over Sn-Beta with the reaction time increasing, respectively. The results indicated Sn-Beta produced more side reactions compared with Sn-MFI.

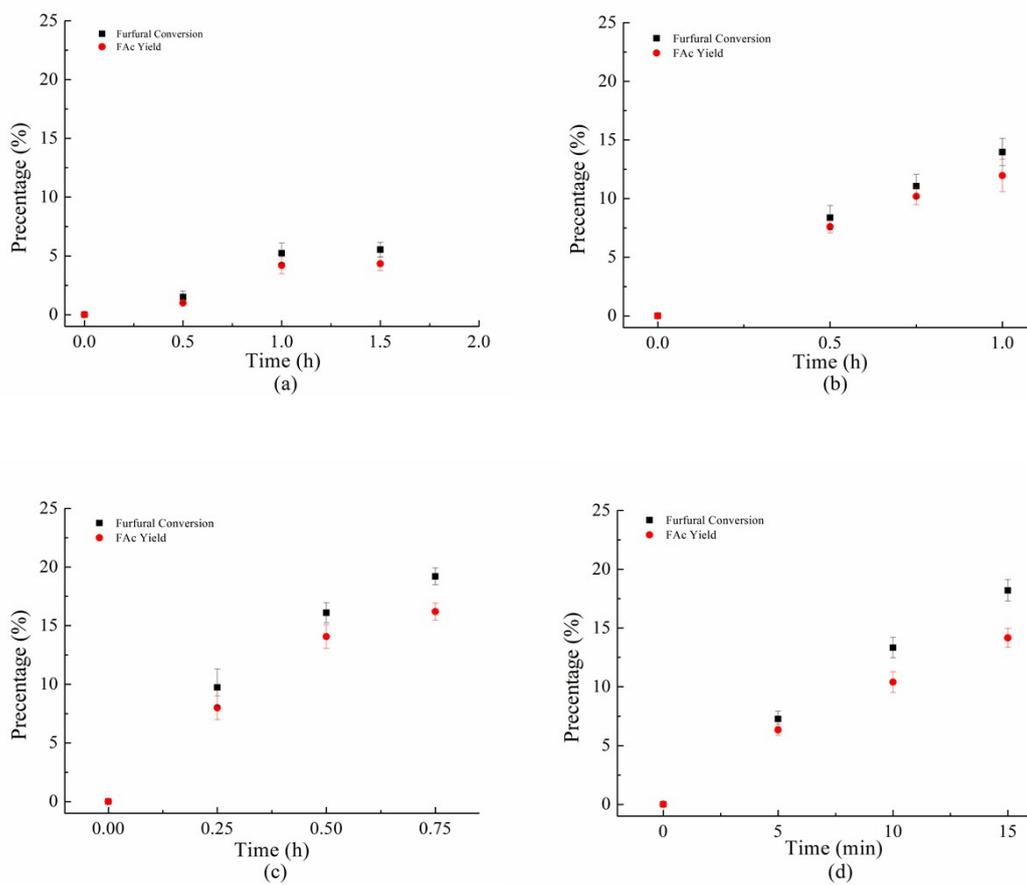


Fig.S2 Reaction kinetics data over Sn-MFI lower than 20%: (a)100°C, (b)120°C, (c)140°C, (d)160°C.

The experiment was repeated three times to obtain the error bar.

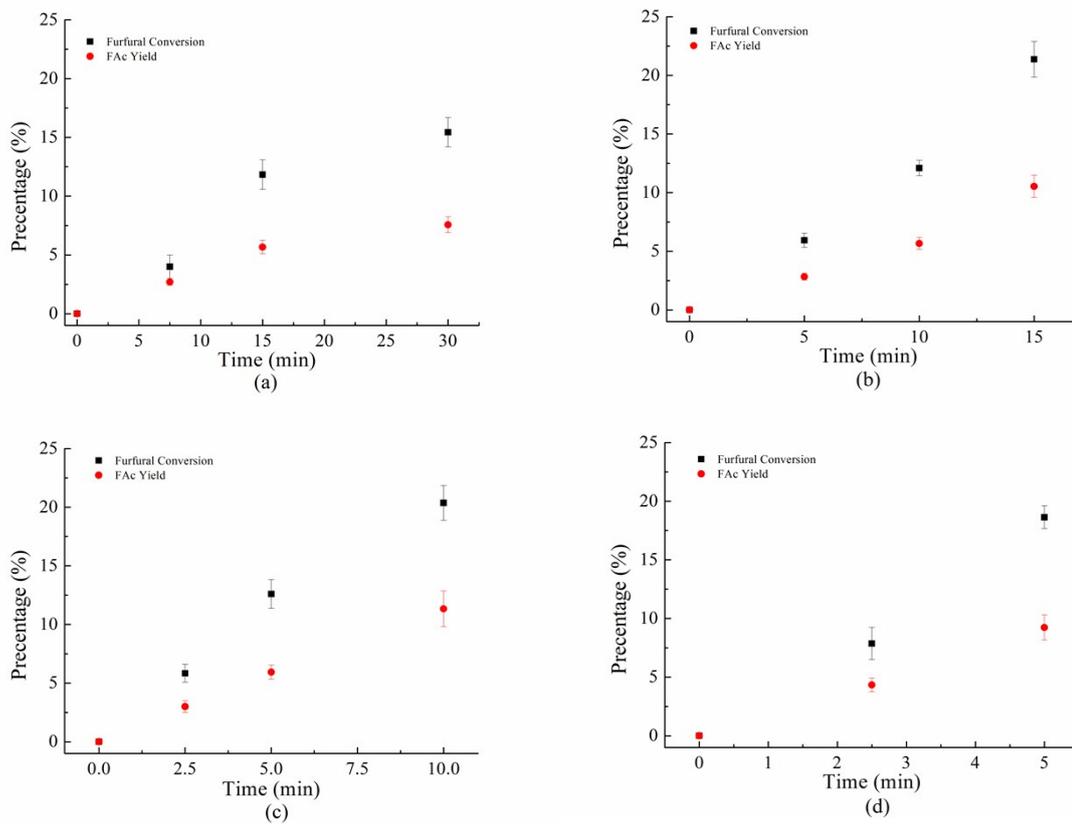


Fig.S3 Reaction kinetics data over Sn-Beta lower than 20%: (a)100°C, (b)120°C, (c)140°C, (d)160°C.

The experiment was repeated three times to obtain the error bar.

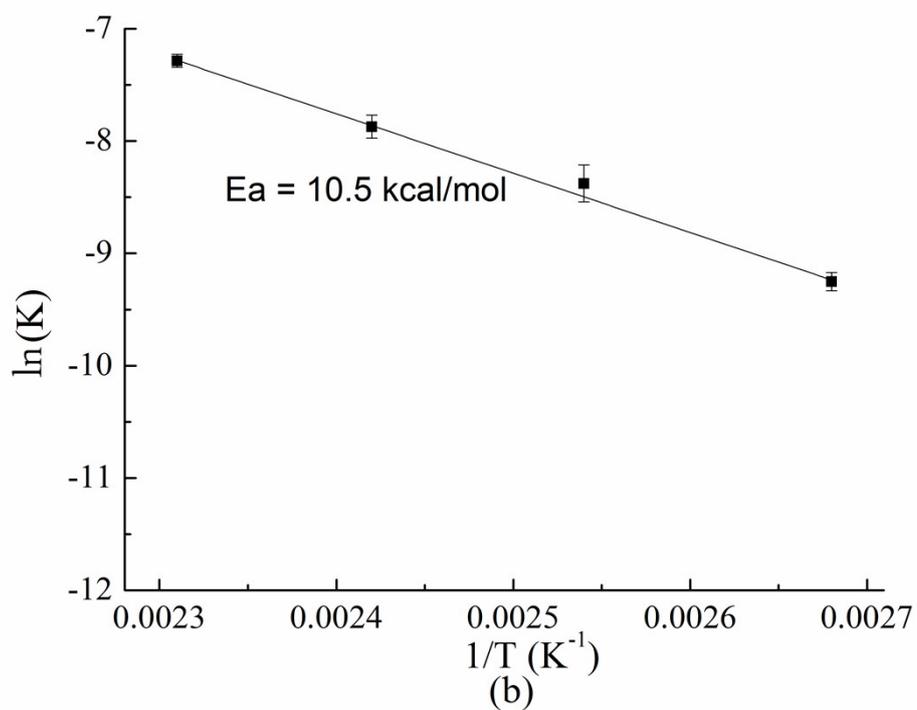
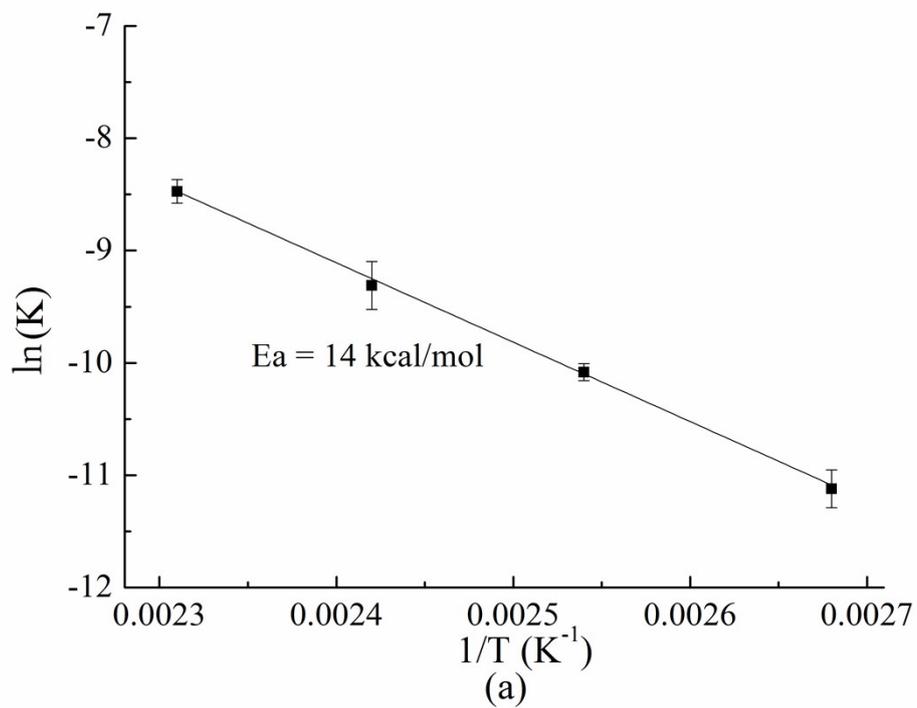


Fig.S4 The activation energy of aldol condensation reaction between furfural and acetone (a) catalyzed by Sn-MFI and (b) catalyzed by Sn-Beta

Identification of the presence of F₂A in the reaction mixture.

Reaction product F₂A, 1,5-bis-(2-furanyl)-1,4-pentadien-3-one, was identified in the reaction medium with a GC-MS by assignation of their fragmentation patterns, although they were not contained in the reference spectral library. Fig.S4 showed the corresponding mass spectrometry fragmentation patterns of this compounds, which was according with previous literature¹. Its response factors were assumed to be similar of that of Phenyl salicylate.

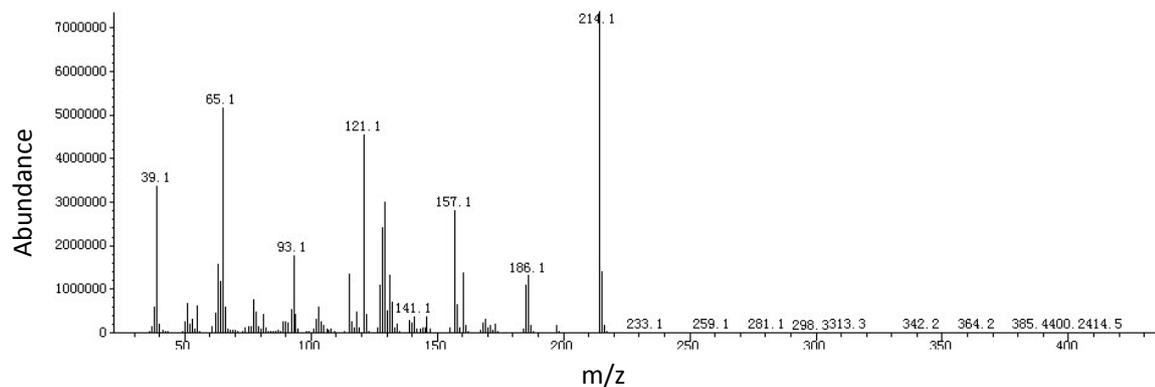


Fig.S5 MS fragmentation pattern of F₂A.

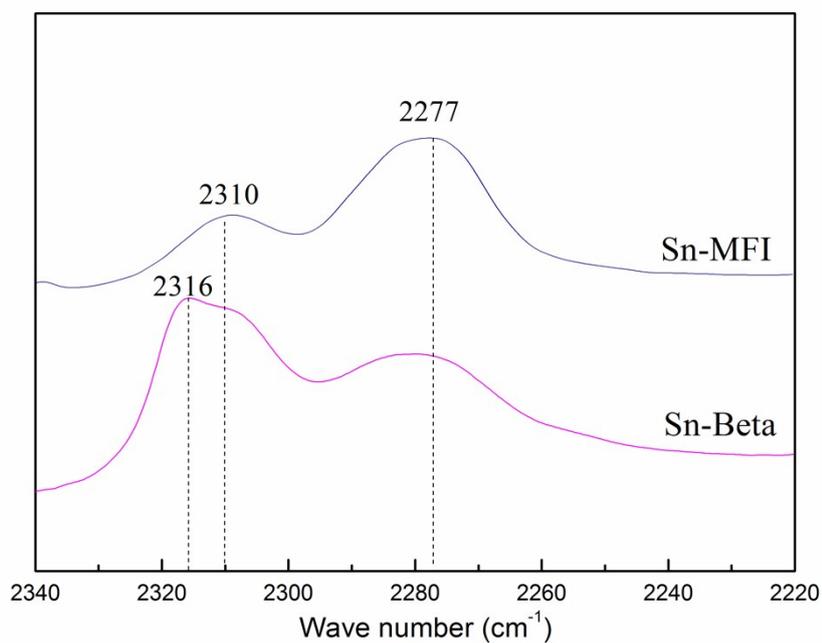


Fig. S6 FT-IR spectra of Sn-MFI and Sn-Beta after adsorbing deuterated acetonitrile. The FT-IR spectra of Sn-MFI and Sn-Beta displayed bonds near 2277 cm^{-1} , in accord with the $\nu(\text{C}\equiv\text{N})$ stretching mode of acetonitrile adsorbed on the silanol groups. The bonds close 2310 cm^{-1} and 2316 cm^{-1} were united with CD_3CN tied to isomorphously substituted Sn Lewis acid sites of Sn-MFI and Sn-Beta, respectively. The total Tin sites can be considered as the active sites for the aldol condensation between furfural and acetone.

Table.S1 The difference in the selectivity to aldol products over Sn-Beta in the absence and presence of water at the same furfural conversion

Furfural conversion (%)	Selectivity without water (%)		Selectivity with water (%)	
	FAc	F ₂ Ac	FAc	F ₂ Ac
87	44	23	46	18
50	52	28	42	0
40	45	20	28	0

Table.S2 the reaction rate based per Sn site for Sn-MFI and Sn-Beta ($\text{mol}_{\text{furfural consumed}} \cdot \text{mol}_{\text{Sn}}^{-1} \cdot \text{h}^{-1}$)

Sn-MFI				
	160°C	140°C	120°C	100°C
60min			12.5	4.7
45min		22.8	13.2	
30min		28.7	15.0	2.6
15min	65.0	34.6		
10min	69.8			
5min	78.5			
Sn-Beta				
	160°C	140°C	120°C	100°C
30min				27.5
15min			76.4	42.1
10min		107.1	63.5	
7.5min				28.5
5min	200.0	135.5	63.4	
2.5min	167.9	123.2		

Reference

1 I. Sádaba, M. Ojeda, R. Mariscal, R. Richards and M. L. Granados, Catal. Today, 2011, 167(1), 77-83.