Electronic Supplementary Information for

Conversion of dihydroxyacetone to methyl lactate catalyzed by highly active hierarchical Sn-USY at room temperature

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Contents:

1. Preparation of SnO_2 and Sn-β

SnO_2 was prepared by calcination of $Sn(OH)_4$ at 640 °C for 4 h, which was synthesized through precipitation of aqueous $SnCl_4$ solution with NaOH. X-ray diffraction (XRD) (Fig. S1) showed that the prepared SnO_2 is in tetragonal structure.

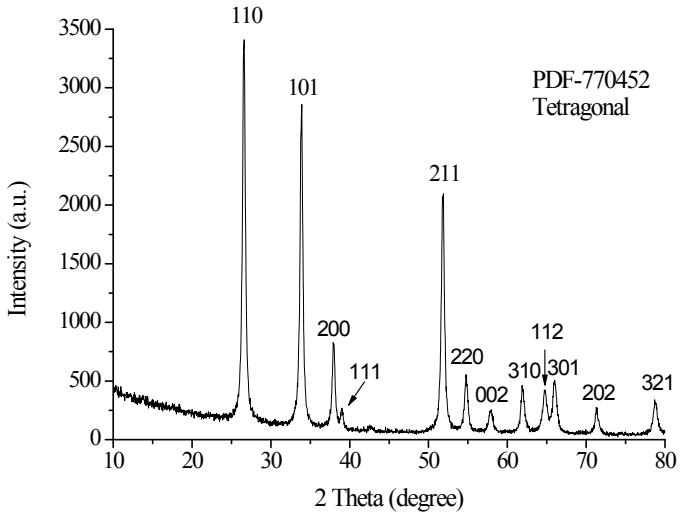


Fig. S1 XRD pattern of bulk SnO_2.

Sn-β zeolite was synthesized by the hydrothermal method as following:

(1) *Preparation of dealuminated β seeds*

The dealuminated β seeds were prepared from H-β zeolite with Si/Al of 38.1 purchased from Nankai University Catalyst Co. (China). The parent H-β zeolite was dealuminated with nitric acid (13 mol L^{-1}, 20 mL g^{-1} zeolite) at 100 °C for 20 h. Then the solid was separated by filtration and washed with deionized water until the filtrate was neutral. Finally, the solid was dried at 100 °C to obtain dealuminated β seeds.

(2) Synthesis of Sn-β

The hydrothermal method described in references [2,3] was adopted to synthesize Sn-β. 10.74 g tetraethyl ammonium hydroxide (TEAOH, 25% aqueous solution) was

mixed with 6.98 g TEOS in a plastic beaker. After stirring for 100 min, 0.74 g $SnCl_4$ solution (0.14 g $SnCl_4 \cdot 5H_2O$ dissolved in 0.60 g H_2O) was added dropwise and white precipitate appeared. The mixture was continued to stir until 10.08 g H_2O and EtOH was evaporated. Then, 0.89 g HF (40% aqueous solution) was added, and the dense gel was formed. Finally, the above dealuminated β seeds (0.083 g, ~4 wt% compared to the theoretical zeolite amount) were suspended in demineralized 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 with a mortar, transferred to a closed Teflon vessel in a stainless steel autoclave, and crystallized statically at 140 °C for 30 days. After crystallization, the autoclave was cooled down to room temperature and the products were isolated by centrifugation. The products were washed three times with demineralized 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. XRD patterns (Fig. S2) of the as-synthesized and calcined Sn-β zeolites confirmed that the synthesized sample was in pure BEA structure [4]. The ratio of *n*Si/*n*Sn determined by X-ray fluorescence (XRF) is 177. The Ultraviolet-visible (UV-vis) spectra of Sn-β and SnO_2 were shown in Fig. S3. SnO_2 showed a wide range adsorption in the range from 200-500 nm. An adsorption band at 220 nm was observed for Sn-β and no adsorption related to SnO_2 was observed; it indicated that tin was incorporated into the framework of BEA.

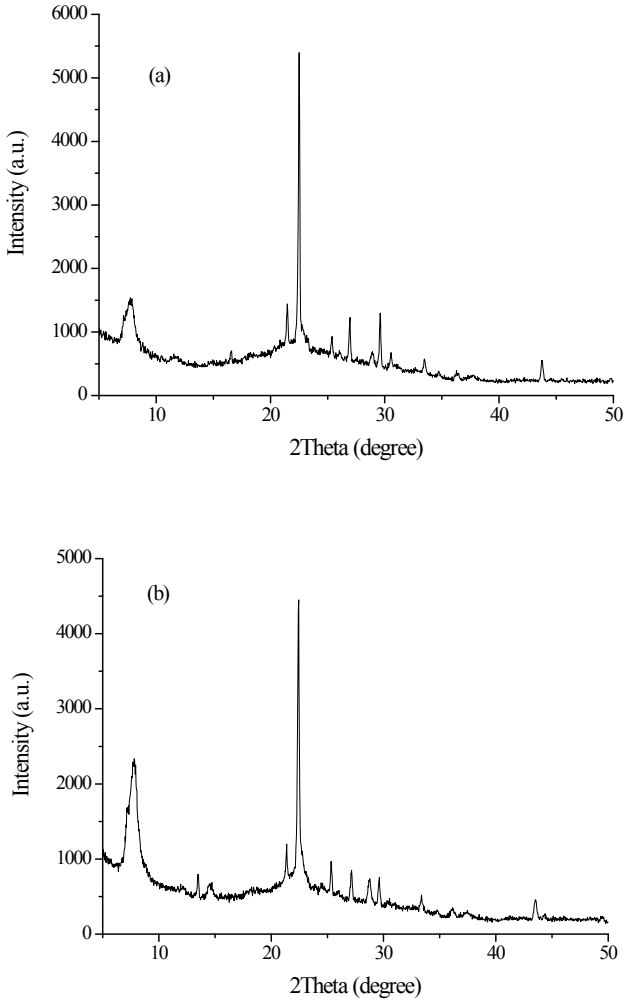


Fig. S2 XRD patterns of (a) as-synthesized and (b) calcined Sn-β.

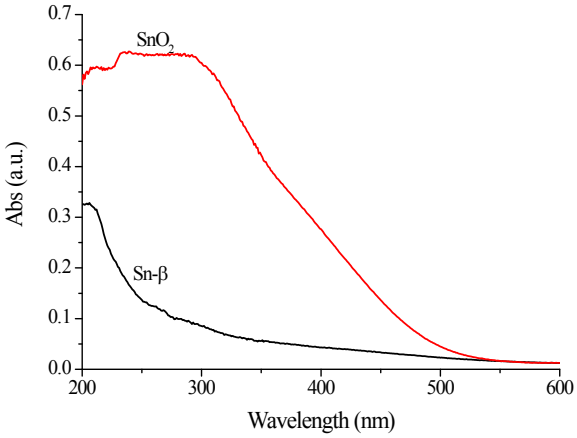


Fig. S3 UV-vis spectra of SnO_2 and Sn-β.

2. Additional Results

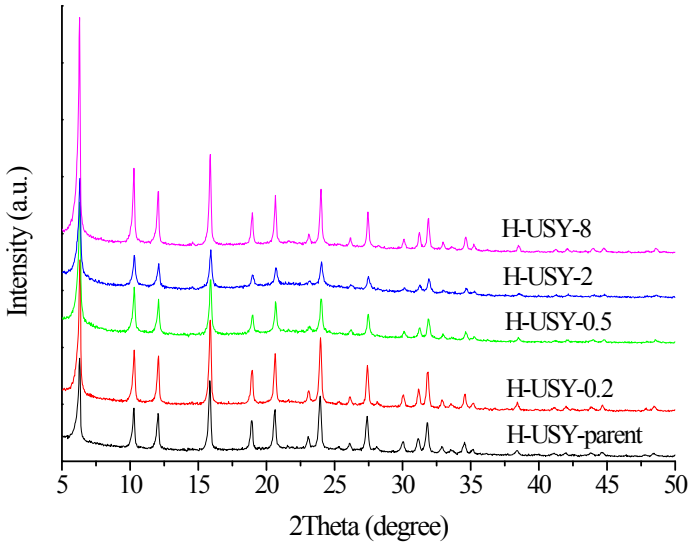


Fig. S4 XRD patterns of the parent and acid-treated H-USY zeolites.

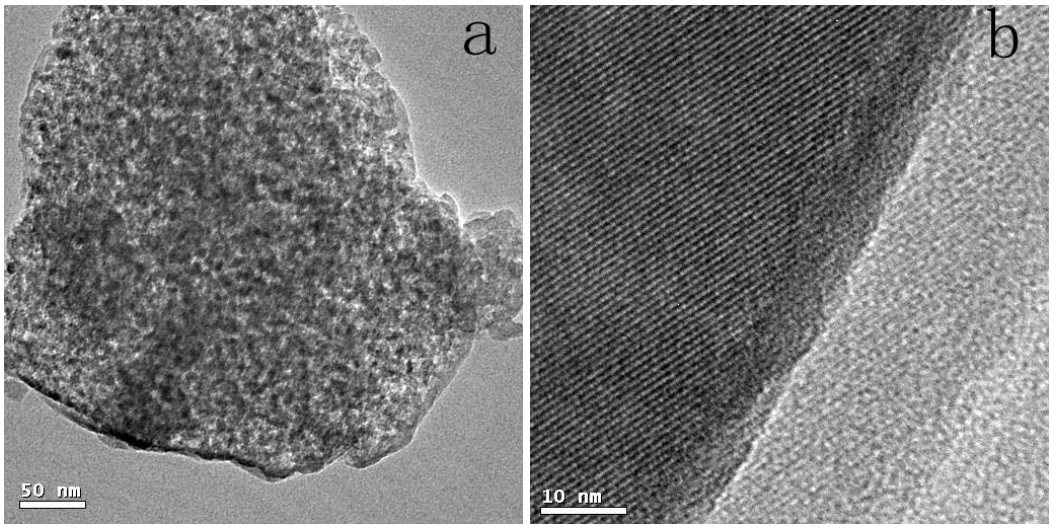
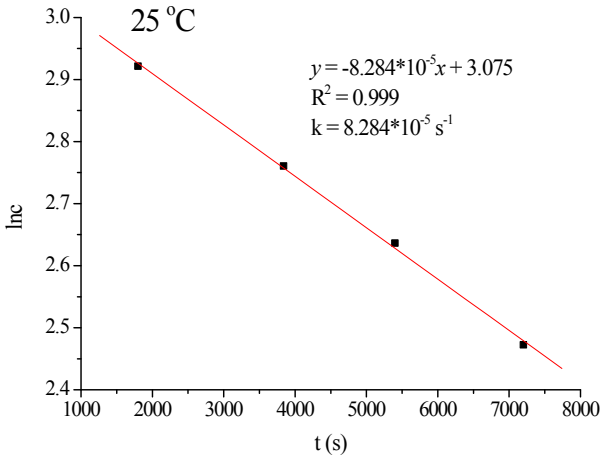


Fig. S5 TEM (a) and HRTEM (b) images of Sn-USY-8.


25 °C
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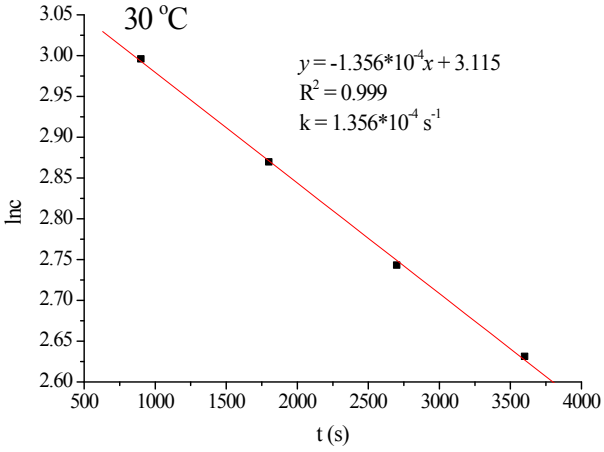
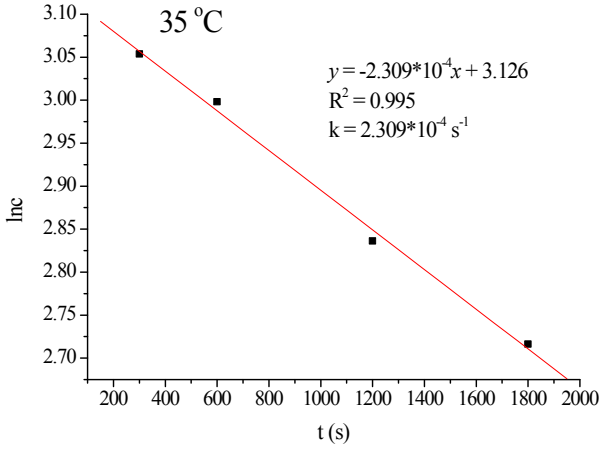
R2 = 0.999
k = 8.284*10-5 s-1
lnc
t (s)


30 °C
y = -1.356*10-4x + 3.115
R2 = 0.999
k = 1.356*10-4 s-1
lnc
t (s)


35 °C
y = -2.309*10-4x + 3.126
R2 = 0.995
k = 2.309*10-4 s-1
lnc
t (s)

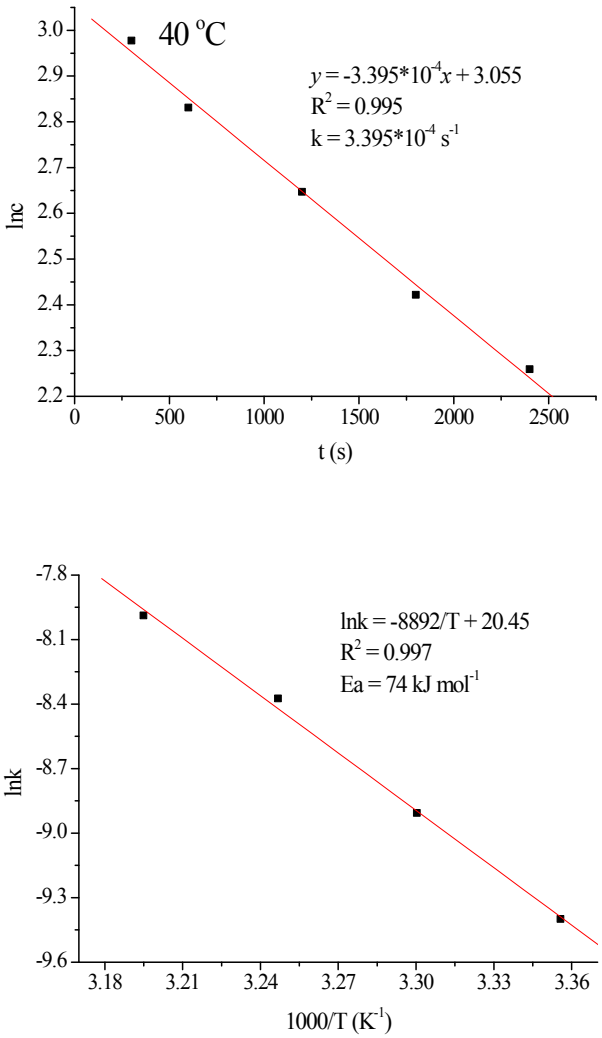
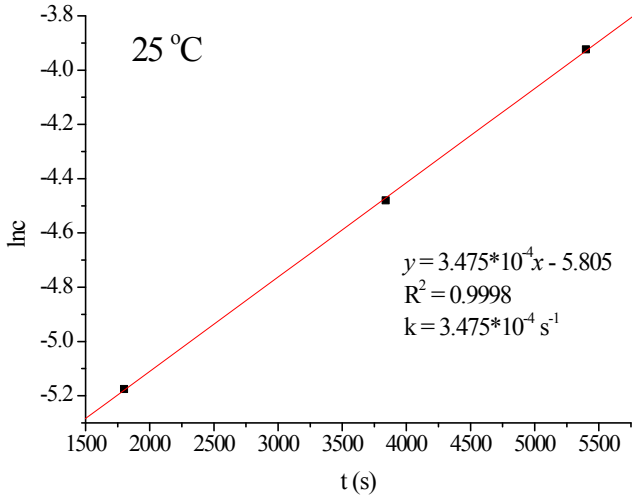
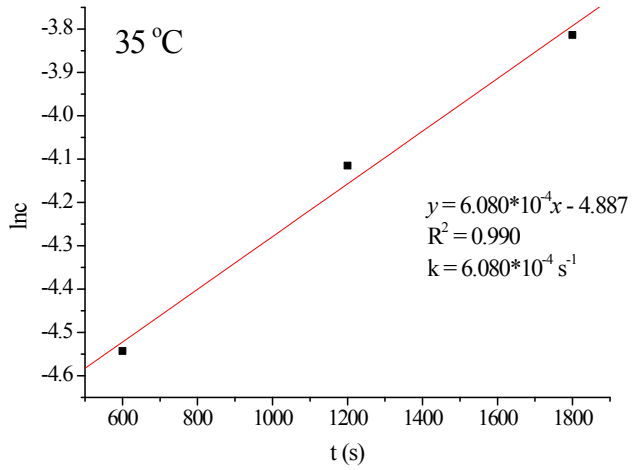
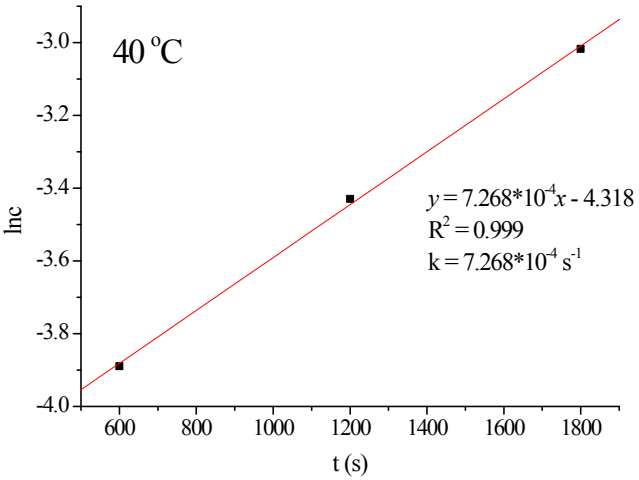


Fig. S6 Kinetic analysis of DHA conversion in methanol in the presence of Sn-USY-8 catalyst and Arrhenius plot (The X-axis is multiplied by 1000).


25 °C
lnc
t (s)
y = 3.475*10^-4 x - 5.805
R^2 = 0.9998
k = 3.475*10^-4 s^-1


35 °C
lnc
t (s)
y = 6.080*10^-4 x - 4.887
R^2 = 0.990
k = 6.080*10^-4 s^-1


40 °C
lnc
t (s)
y = 7.268*10^-4 x - 4.318
R^2 = 0.999
k = 7.268*10^-4 s^-1

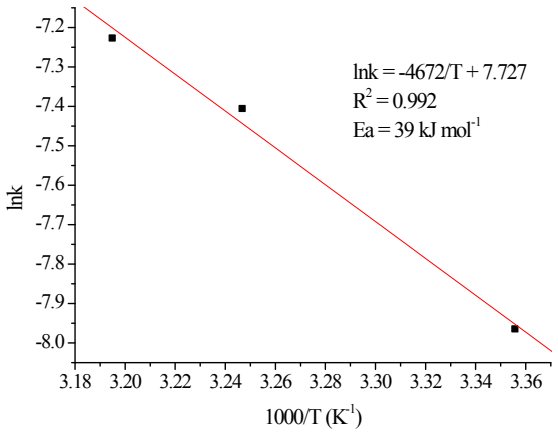


Fig. S7 Kinetic analysis of MLA formation in methanol in the presence of Sn-USY-8 catalyst and Arrhenius plot (The X-axis is multiplied by 1000).

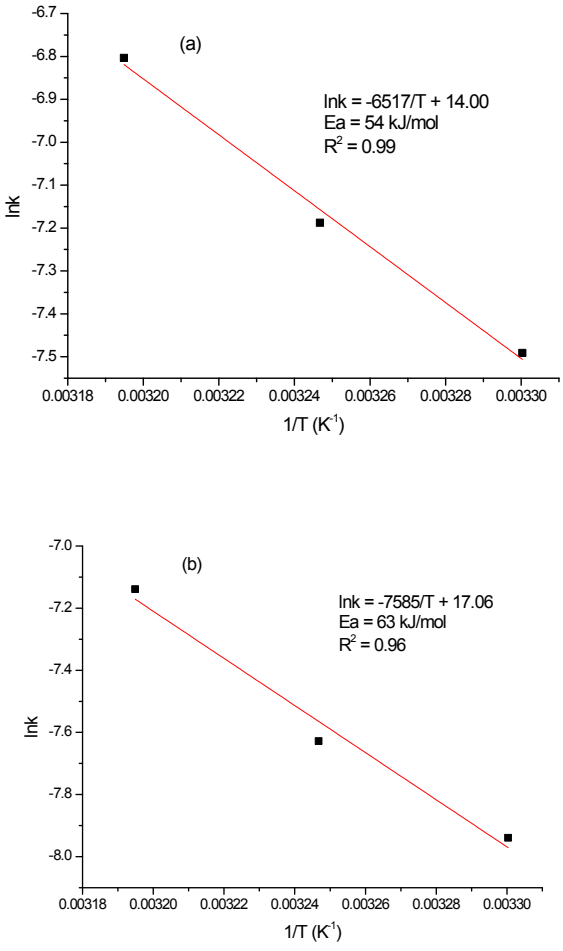
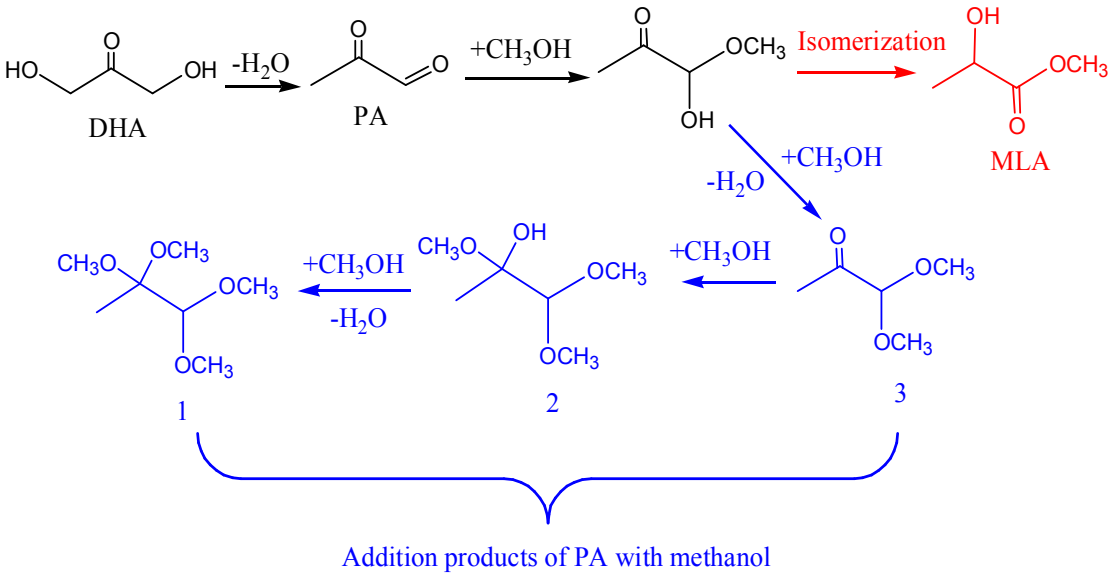


Fig. S8 Arrhenius plots for MLA formation over (a) Sn-Beta-P and (b) Sn-Beta-F in methanol.



Scheme S1. Possible by-products of DHA conversion in methanol.

Table S1 Ratio of Lewis/Brønsted acid sites for Sn-USY

Sample	Ratio of Lewis/Brønsted acid sites[a]
Sn-USY-parent	2.0
Sn-USY-0.2	3.9
Sn-USY-0.5	11.9
Sn-USY-2	15.6
Sn-USY-8	20.4

[a] The ratio is calculated using the method described in literature [5].

3. GC and HPLC Traces

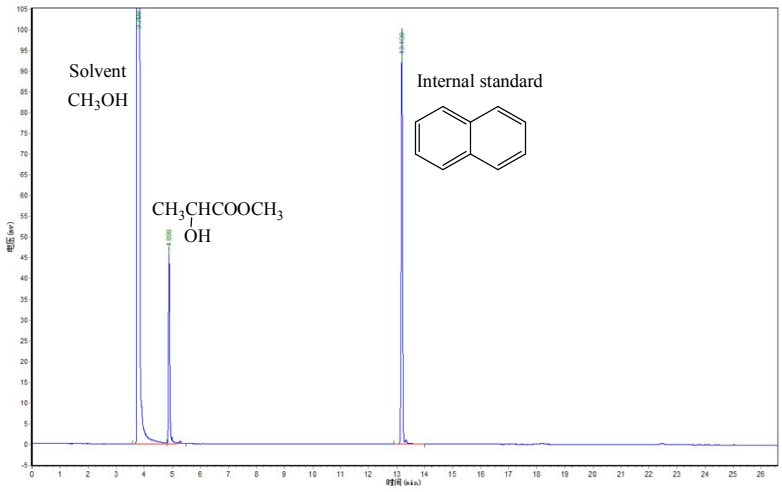


Fig. S9 GC trace of reaction mixture (Table 2, entry 2).

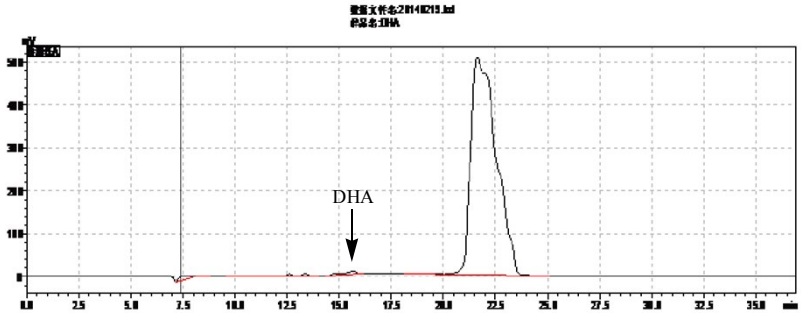


Fig. S10 HPLC trace of reaction mixture (Table 2, entry 2).

References

[1] C. Hammond, S. Conrad and I. Hermans, *Angew. Chem. Int. Ed.*, 2012, **51**, 1.

[2] A. Corma, L. T. Nemeth, M. Renz and S. Valencia, *Nature*, 2001, **412**, 423.

[3] M. S. Holm, S. Saravanamurugan and E. Taarning, *Science*, 2010, **328**, 602.

[4] R. Otomo, T. Yokoi, J. N. Kondo and T. Tatsumi, *Appl. Catal. A*, 2014, **470**, 318.

[5] M. Guisnet, P. Ayrault, C. Coutanceau, M. F. Alvarez and J. Datkac, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 1661.