Electronic Supplementary Information for

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

Xiaomei Yang\(^a\), Lin Wu\(^a\), Zhen Wang\(^a\), Jingjing Bian\(^a\), Tianliang Lu\(^b\), Lipeng Zhou*\(^a\),
Chen Chen\(^c\) and Jie Xu\(^c\)

\(^a\) College of Chemistry and Molecular Engineering, Zhengzhou University, 100 Kexue Road,
Zhengzhou 450001, P. R. China

\(^b\) School of Chemical Engineering and Energy, Zhengzhou University, 100 Kexue Road,
Zhengzhou 450001, P. R. China

\(^c\) State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian
Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian
116023, P. R. China

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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.

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$_4$·5H$_2$O dissolved in 0.60 g H$_2$O) was added dropwise and white precipitate appeared. The mixture was continued to stir until 10.08 g H$_2$O and EtOH was evaporated. Then, 0.89 g HF (40% aqueous solution) was added, and the dense gel was formed. Finally, the above dealumined 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$_2$O. 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 SnO₂ 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
\[ y = -8.284 \times 10^3 x + 3.075 \]
\[ R^2 = 0.999 \]
\[ k = 8.284 \times 10^3 \text{ s}^{-1} \]

30 °C
\[ y = -1.356 \times 10^4 x + 3.115 \]
\[ R^2 = 0.999 \]
\[ k = 1.356 \times 10^4 \text{ s}^{-1} \]

35 °C
\[ y = -2.309 \times 10^5 x + 3.126 \]
\[ R^2 = 0.995 \]
\[ k = 2.309 \times 10^5 \text{ s}^{-1} \]
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).
$y = 3.475 \times 10^3 x - 5.805$

$R^2 = 0.9998$

$k = 3.475 \times 10^3 \text{ s}^{-1}$

$y = 6.080 \times 10^4 x - 4.887$

$R^2 = 0.990$

$k = 6.080 \times 10^4 \text{ s}^{-1}$

$y = 7.268 \times 10^5 x - 4.318$

$R^2 = 0.999$

$k = 7.268 \times 10^5 \text{ s}^{-1}$
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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio of Lewis/Brønsted acid sites&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-USY-parent</td>
<td>2.0</td>
</tr>
<tr>
<td>Sn-USY-0.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Sn-USY-0.5</td>
<td>11.9</td>
</tr>
<tr>
<td>Sn-USY-2</td>
<td>15.6</td>
</tr>
<tr>
<td>Sn-USY-8</td>
<td>20.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> The ratio is calculated using the method described in literature [5].
3. GC and HPLC Traces

![Graph showing GC trace of reaction mixture (Table 2, entry 2).](image1)

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

![Graph showing HPLC trace of reaction mixture (Table 2, entry 2).](image2)

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

References


