Supporting Information

Temperature Responsive Zn-based Catalysts for Efficient Catalytic Conversion of Biomass-derived Carbohydrates to Ethyl Lactate

Jiangang Wang a, Jinghua Wang a,b, Yifan Liu a, Tihang Liu a, Zhaobin Pang a, Hongyou Cui a*, Yuan Zhang a, Feng Song a

a School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo, 255091, China

b Shandong Lunan Coal Chemical Research Institute of Engineering and Technology, Zaozhuang University, Zaozhuang, 277160, China

Email: cuihy@sdut.edu.cn
Experimental

Materials and Reagents

ZnCl$_2$ (99%), ZnO (99%), Zn(OH)$_2$ (98%), glucose (98%), glucose monohydrate (98%), D-fructose (99%), mannose (99%), sucrose (99%), ethyl lactate (EL, 99%), methylglyoxal (MG, 40%), glyceraldehyde (GLA, 90%), tetraethyl orthosilicate (TEOS, 99%), 1,1,2-triethoxyethane (TEE, 99%), NH$_3$·H$_2$O (28%) and Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$, AR) were purchased from Macklin Reagent Co. 1,3-dihydroxyacetone (DHA, 98%) was bought from Bide Reagent Co. Anhydrous alcohol (99.9%) was got from Tianjin Fuchen Chemical Reagent. All the chemicals were used without further purification.

Catalyst preparation

The procedure used for the preparation of porous silicon (SiO$_2$) was similar to that of SBA-15. Briefly, 4.0 g of P$_{123}$ was firstly dissolved in 150 mL of HCl solution (1.6 mol/L) and then 8.5 g of TEOS was added and vigorously stirred at 35°C for 24 h. The mixture was subjected to crystallization in a Teflon-lined autoclave at 120°C for 48 h. The resulting precipitate was recovered by filtration and sufficiently washed with water, and subsequently subjected to calcination at 550°C for 6 h in air in order to remove the template.

For the preparation of the ZnSi-$x$ ($x$=1, 2, 3 or 4) samples, the following procedure was used. To a glass conical flask was added 4.0 mmol anhydrous ZnCl$_2$ and 5.0 ml deionized water under stirring condition to form a homogeneous solution. And then 2.5 g prepared porous silica was added and allowed to sufficient impregnation. Afterwards, diluted NH$_3$·H$_2$O solution was added dropwise until pH= 3.5 and followed by drying at 150 °C. The resultant solid was sufficiently washed with ethanol to remove the unreacted ZnCl$_2$, and dried at 105 °C overnight. The prepared catalysts were denoted as ZnSi-1, ZnSi-2, ZnSi-3 and ZnSi-4 respectively, which corresponded to the added ZnCl$_2$ amounts of 4.0, 5.0, 6.0 and 8.0 mmol, separately.

Catalyst characterization

X-ray diffraction (XRD) patterns were collected on Bruker AXS D8 Advance at a scanning range of 5-80° (scanning speed 0.05°/min, Cu Kα radiation). TEM characterization was conducted on a Tecnai G2 F20 S-TWIN electron microscope (accelerating voltage 20-200 kV, resolution≤0.19
nm, lattice resolution ≤ 0.102 nm). ICP-OES data was acquired with an Agilent 725 ES atomic emission spectrometer (Detection accuracy ≥ 0.1 ppm). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo-Fisher ESCALAB Xi+ spectrometer with monochromatic Al K\textalpha radiation. In order to reduce the deviation, the characteristic peaks of different elements were corrected with C1s electron binding energy (284.8 eV) as the standard.

The textural property of each sample was measured by N\textsubscript{2} adsorption-desorption using a Micromeritics ASAP2046 apparatus. Prior to the test, the sample was vacuumized at 200 °C for 12 h to remove the impurity and water adsorbed on the catalyst surface, and then subject to adsorption at -196 °C. The external surface area and volume of the micropores were estimated by the t-plot method. The pore size distribution curve was calculated according to adsorption isotherm data by the BJH method.

The acidity of the sample was determined with AutoChem II 2920 chemisorption instrument. Prior to NH\textsubscript{3}-TPD, the sample was subject to heat treatment at 200 °C for 75 min under a He flowrate of 50 ml/min and followed by cooling to 120 °C. After that, mixed gas of NH\textsubscript{3} (10%) and He (90%) was charged at a flowrate of 30 ml/min for 60 min, and then purged with pure helium for another 30 min. Finally, the sample was heated to 600 °C at heating rate of 10 °C/min under helium atmosphere to complete NH\textsubscript{3} desorption. The used detector was a thermal conductivity detector.

The basicity of the samples was also measured with the AutoChem II 2920 chemisorption instrument. Prior to CO\textsubscript{2}-TPD, the sample was subject to heat treatment at 200 °C for 75 min under a He flowrate of 50 ml/min and then cooling to 50 °C. Mixed gas (10% CO\textsubscript{2} + 90% He) was charged for 60 min at a flowrate of 30 ml/min, and then switched to further purge with pure helium for another 60 min. Finally, the sample was heated to 600 °C at 10 °C/min in helium atmosphere to complete CO\textsubscript{2} desorption.

To determine the acid type, the Py-IR spectra were recorded on Thermo Fisher Nicolet iS10. Firstly, 50 mg sample was pretreated under reduced pressure at 350 °C for 2 h. After being cooled to room temperature, the sample was allowed to saturadely adsorb pyridine vapor. The sample wafer was then switched to desorption at 100 °C. Upon cooling to room temperature again, the spectrum was collected.
**Catalytic activity**

All the catalytic experiments were carried out in a 100 ml stainless steel (Hastelloy C276) autoclave equipped with a mechanic stirrer. In a typical experiment, 0.2 g reaction substrate, 0.04 g catalyst and 40 ml ethanol were loaded into the autoclave. Prior to test, the autoclave was evacuated with pure N\textsubscript{2} gas to remove air inside and then pressurized to 2.0 MPa. The stirring speed was fixed at 500 rpm which had been confirmed to ably eliminate the external diffusion limitation. The reaction temperature was controlled within an accuracy of ±1°C. Upon completing the reaction, the autoclave was quenched immediately with tape water. All the experiments were done in triplicate and the reported results are the average.

**Analysis**

Quantitative determination of fructose, DHA, GLA and MG in the reaction mixture was performed by HPLC (Waters e2695), which was equipped with a Rezex ROA-Organic Acid H\textsuperscript{+} column: 8% (7.8 mm × 150 mm) and a differential refraction detector (Waters 2414). The elution phase used was 2.5 mmol/L sulfuric acid at a flowrate of 0.6 ml/min. The column temperature was fixed at 55 °C.

Quantitative determination of EL and TEE was conducted with gas chromatography (GC, Agilent 6890), which was equipped with an FID detector and a capillary column (DB-1701, 60 m × 0.25 mm × 0.25 µm). 2-octanone was used as the internal standard.

The conversion (X), product yield (Y) and selectivity (S) were calculated based on the following equations:

\[
X = \frac{n_0 - n}{n_0} \times 100\% \quad (1)
\]

\[
Y = \frac{n_i}{n_i^t} \times 100 \quad (2)
\]

\[
S = \frac{Y}{X} \times 100\% \quad (3)
\]

Where \(n_i\), \(n_i^t\) are the actually formed and theoretical moles of the product \(i\), respectively; \(n_0\) and \(n\) are the moles of the initial and unreacted substrates, respectively.

The productivity of the catalyst was defined as following equation:
\[ \text{Productivity} = \frac{n_{EL}}{t \times m_{\text{cat}}} \times 1000 \quad (4) \]

Where \( n_{EL}, t, \) and \( m_{\text{cat}} \) are formed EL in unit of millimole, reaction time (h), and catalyst mass (g), respectively.

**DFT Calculation**

All the chemical structures were optimized at the B3LYP/Genecp level of theory using the Gaussian16 package\(^{11} \), where Genecp denotes the combination of the 6-31G(d) basis set for C, H, O F and Cl atoms, and the LANL2DZ basis set for Zn atoms. Frequency analysis was carried out at the same level with Geometry optimizations. Single-point energy calculations were conducted using at the B3LYP/Def2-TZVP level of theory. The SMD model was used to take the solvation effect of ethanol into account. The transition states were confirmed to have exactly one imaginary frequency, while the other compounds had no imaginary frequency. Furthermore, intrinsic reaction coordinate (IRC) analyses were performed to verify that the transition states were the first-order saddle points on the potential energy surfaces. The Gibbs free energy of the compound was calculated according to the following equation:

\[ \Delta G = G_0 + G_s \quad (5) \]

Where \( G_0 \) was the thermal correction to Gibbs free energy, and \( G_s \) was Gibbs free energy of the compound calculated by large basic set.
Fig. S1 Enlarged HRTEM images of ZnSi-2 (e), ZnSi-3(g) and ZnSi-4(i)
Fig. S2 TG of ZnSi-2 (a); the mass spectra of ZnSi-2 pyrolysis products (b); the TPD characterization for catalysts in absence of CO₂/NH₃ gas adsorption (c)
Fig. S3 Py-IR spectra of the samples
Fig. S4 Effect of reaction temperature on conversion fructose to EL

Reaction condition: 0.04 g 10%-Zn/SBA-15, 0.20 g fructose in 40 ml ethanol, 220°C, 60 min,

2 MPa N₂
Fig. S5 time course profile of conversion of glucose or glucose monohydrate to EL.

Reaction condition: 0.04 g ZnSi-2, 0.20 g substrate in 40 ml ethanol, 220°C, 2 MPa N₂.
Fig. S6 Concentration of H⁺ proton variation as function of temperature of 0.04 g ZnSi-2 in glycol or glycol aqueous solution (solid line, temperature rise; dash line, temperature drop)
Fig. S7 A typical GC-MS of the reaction product under the catalysis of ZnSi-2
Fig. S8 Leaching loss of Zn with cycles
Fig. S9 N\textsubscript{2} adsorption-desorption isotherms of the spent ZnSi-2
Fig. S10 TEM image of the spent ZnSi-2
Fig. S11 TG of the samples
Table S1 Species and contents of impurities desorbed from ZnSi-2

<table>
<thead>
<tr>
<th>m/z</th>
<th>Chemicals</th>
<th>Percentage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>H₂O</td>
<td>95.1</td>
</tr>
<tr>
<td>35</td>
<td>HCl</td>
<td>0.21</td>
</tr>
<tr>
<td>44</td>
<td>CO₂</td>
<td>4.68</td>
</tr>
<tr>
<td>No.</td>
<td>Product</td>
<td>Solvent</td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>1</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>2</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>3</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>4</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>5</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>8</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>9</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>10</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>11</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>12</td>
<td>ML</td>
<td>MeOH</td>
</tr>
<tr>
<td>13</td>
<td>EL</td>
<td>EtOH</td>
</tr>
<tr>
<td>14</td>
<td>EL</td>
<td>EtOH</td>
</tr>
<tr>
<td>15</td>
<td>EL</td>
<td>EtOH</td>
</tr>
<tr>
<td>16</td>
<td>EL</td>
<td>EtOH</td>
</tr>
</tbody>
</table>

Table S2 Comparison with results reported in the literature for conversion glucose to lactate.
References