Supporting Information

Di ionic multifunctional porous organic frameworks for efficient CO$_2$ fixation at mild and co-catalyst free conditions

Dingxuan Ma,a Jixin Li,b Kang Liu,*a Baiyan Li,b Chunguang Li,b and Zhan Shi*b

a. Laboratory of Eco-chemical Engineering, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, People’s Republic of China.
b. State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, People’s Republic of China

E-mail: liukang28@126.com; zshi@mail.jlu.edu.cn
I Synthesis

POF-Zn-X

Scheme S1. Ion exchange for the preparation of POF-Zn\(^{2+}\)-X\(^-\).

Activated POF-DI (0.5 g) was dispersed in 20 mL of 0.2 M methanol solution of corresponding halide salts. After the mixture was stirred for 12 h, the residue was filtered. Repeated the above step three times, the precipitate was washed with anhydrous methanol (20 ml) five times and dried at 100 °C under vacuum to afford the goal product.

POF-DI& ZnCl\(_2\)

Activated POF-DI (150 mg) and ZnCl\(_2\) (20 mg) were mixed uniformity, and then used as the catalyst.

II Characterization Details

Table S1. Elemental Analysis

<table>
<thead>
<tr>
<th></th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>S%</th>
<th>Na%</th>
<th>Zn%</th>
<th>S/Zn mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>POF-DI</td>
<td>52.72</td>
<td>4.872</td>
<td>16.90</td>
<td>5.709</td>
<td>5.74</td>
<td>0</td>
<td>/</td>
</tr>
<tr>
<td>POF-Zn(^{2+})-Cl(^-)</td>
<td>47.44</td>
<td>4.392</td>
<td>14.55</td>
<td>4.923</td>
<td>0.106</td>
<td>4.48</td>
<td>2.245</td>
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<tr>
<td>POF-Zn(^{2+})-Br(^-)</td>
<td>46.74</td>
<td>4.302</td>
<td>14.38</td>
<td>4.607</td>
<td>0.143</td>
<td>4.23</td>
<td>2.226</td>
</tr>
<tr>
<td>POF-Zn(^{2+})-I(^-)</td>
<td>46.33</td>
<td>4.221</td>
<td>14.22</td>
<td>4.564</td>
<td>0.117</td>
<td>4.04</td>
<td>2.309</td>
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</tbody>
</table>
Fig S1. TGA data of POF-DI.

Fig S2. PXRD patterns of POF-DI, POF-Zn$^{2+}$-Cl$^{-}$, POF-Zn$^{2+}$-Br$^{-}$ and POF-Zn$^{2+}$-I$^{-}$. 
Fig S3. SEM and TEM images of POF-DI.

Fig S4. Pore-size distribution profiles of POF-DI, POF-Zn$^{2+}$-Cl$^{-}$, POF-Zn$^{2+}$-Br and POF-Zn$^{2+}$-I$^{-}$. 
Fig S5. Comparison of IR spectra of the as-made POF-Zn$^{2+}$-Cl\textsuperscript{-} sample and the POF-Zn$^{2+}$-Cl\textsuperscript{-} after catalysis cycles.

Fig S6. Comparison of IR spectra of the as-made POF-Zn$^{2+}$-Br\textsuperscript{-} sample and the POF-Zn$^{2+}$-Br\textsuperscript{-} after catalysis cycles.
Fig S7. Comparison of IR spectra of the as-made POF-Zn$^{2+}$-I sample and the POF-Zn$^{2+}$-I after catalysis cycles.

Fig S8. Comparison of SEM of the as-made POF-Zn$^{2+}$-Cl, POF-Zn$^{2+}$-Br, POF-Zn$^{2+}$-I (a-c) and the POF-Zn$^{2+}$-Cl, POF-Zn$^{2+}$-Br, POF-Zn$^{2+}$-I after catalysis cycles (d-f).
Fig S9. N₂ adsorption/desorption isotherms of POF-DI, POF-Zn²⁺-Cl⁻, POF-Zn²⁺-Br⁻ and POF-Zn²⁺-I⁻ after catalysis cycles. BET surface areas of POF-Zn²⁺-Cl⁻, POF-Zn²⁺-Br⁻ and POF-Zn²⁺-I⁻ are 494 m²g⁻¹, 312 m²g⁻¹ and 286 m²g⁻¹.

Table S2. A comparison table for the present POF-Zn catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Co-catalyst</th>
<th>Temperature (°C)</th>
<th>Pressure(MPa)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>POF-Zn²⁺-I⁻</td>
<td>None</td>
<td>60</td>
<td>1</td>
<td>99</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>Zn/Hazo-POP-1</td>
<td>TABA</td>
<td>100</td>
<td>3</td>
<td>98</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Bp-Zn@MA</td>
<td>TABA</td>
<td>100</td>
<td>1</td>
<td>99</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>P-POF-Zn</td>
<td>TABA</td>
<td>100</td>
<td>1.5</td>
<td>99</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>Zn@ah-PMF</td>
<td>TABA</td>
<td>100</td>
<td>2</td>
<td>99</td>
<td>4</td>
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<tr>
<td>6</td>
<td>PAF-ZnBr₂</td>
<td>TABA</td>
<td>90</td>
<td>1</td>
<td>95</td>
<td>5</td>
</tr>
</tbody>
</table>
III Characterization Data of Catalytic Products

$^1$H NMR Spectra of Catalytic Products

Propylene carbonate ($\text{CD}_2\text{O}, 400$ MHz)

4-Ethyl-1,3-dioxolan-2-one ($\text{CD}_2\text{O}, 400$ MHz)
4-Propyl-1,3-dioxolan-2-one (CDCl$_3$, 400 MHz)

4-Butyl-1,3-dioxolan-2-one (CDCl$_3$, 400 MHz)
1,3-Dioxolan-2-one (CD$_3$O, 400 MHz)

4-(chloromethyl)-1,3-dioxolan-2-one (CD$_3$O, 400 MHz)
4-(Bromomethyl)-1,3-dioxolan-2-one (CDCl₃, 400 MHz)

4-phenyl-1,3-dioxolan-2-one (CD₂O, 400 MHz)
4-(phenoxymethyl)-1, 3-dioxolan-2-one (CDCl₃, 400 MHz)

1, 3-Benzodioxol-2-one (CDCl₃, 400 MHz)
GC-MS Analysis of Catalytic Products
References