Supporting Information

Novel catalyst PTMA-PILC: structural properties and catalytic performance for the bioethanol dehydration to ethylene

Xianmei Xie*, Zheng Li, Baoru Li, Xu Wu, Xia An

S1. Experimental

1.1 Catalyst characterization

The X-ray diffraction diagrams were recorded over powder sample on Riga ku D/max-2500 instrument (40 KV, 100 mA) using Cu Kα radiation (λ = 0.154056 nm) at a scanning speed of 0.13 °/s, with the scanning range of 4-35 °.

FT-IR spectra of the samples were performed on a Perkin-Elmer 1730 Infrared Fourier Transform Spectrometer between 400-4000 cm⁻¹ region. One milligram of sample and 300 mg of KBr were used in the preparation of the pellets.

The surface area and pore size distribution were determined from nitrogen adsorption-desorption isotherm data by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods using a Micro-meritics ASAP 2020 instrument. The isotherms were measured at 77 K using N₂. Prior to determining the isotherms, the samples were degassed at 100 °C in vacuum (≈30 Pa) for 70 min.

The temperature-programmed desorption of NH₃ (NH₃-TPD) was carried out between 10 and 750 °C using Autochem II 2920 (Micromeritics Instruments). Prior to adsorption, the sample (0.04 g) was calcined under the N₂ flow of 50 mL/min at 300 °C for 1 h and then cooled to 50 °C. After that, it was treated by 10% NH₃/He for 30 min. The nature and strength of acid sites were evaluated by IR spectroscopy of pyridine. For this analysis the sample was preheated at 300 °C for 2 h under vacuum pressure. Pyridine adsorption was run at room temperature during 30 min. Desorption was realised in vacuum at 150 °C and infrared spectra were recorded after thermal treatment.

Thermogravimetric analysis (TG) was performed on a NETZSCH-STA 409C thermobalance. Around 5 mg of sample at particle sizes of 100– 200 mesh was used for each experimental and the heating temperature in the TG was in the range of 25–800 °C, with the heating rate in the range of 25–800 °C, and the heating rate was controlled at 10 °C/min. Nitrogen was used as the carrier gas in the TG which flow rate was fixed at 100 mL/min.

The microstructures of catalysts was investigated using transmission electron microscope (TEM, JEM-1011).

1.2 Catalytic performances test

The fixed-bed micro-reactor used for the catalytic performance tests is shown as Fig. 1 and the reaction of ethanol dehydration to ethylene was used to evaluate the catalytic behaviours of the solids. 1.0 g catalysts were dispersed in 3.0 g silica sand and loaded in the middle of a stainless steel reactor. The reactor was purged by nitrogen flow for 60 min, and the liquid reactant containing water and ethanol with the volume ratio of 7:3 was injected by a pulse micro-liquid pump into a vaporizer and subsequently passed into the reactor with the LHSV of 0.65 h⁻¹. The temperatures of the vaporizer and the reactor were controlled by the thermocouples. Outlet products were condensed and separated by a gas-liquid separator. The gas concentrations were quantified on-line by a haixin 950 gas chromatograph equipped with a FID and a TCD detector and two packed columns (GDX-401, TDX-01). The liquid products were analyzed off-line on another gas chromatograph equipped with a Porapack Q column. Ethanol conversion was denoted as C_{ethanol} and Si represents the product distribution of i, they were calculated according to Eq. (S1) and (S2):

\[
C_{\text{ethanol}} = \frac{n(\text{ethanol}_{\text{in}}) - n(\text{ethanol}_{\text{out}})}{n(\text{ethanol}_{\text{in}})} \times 100\% \quad \text{(S1)}
\]

\[
S_i = \frac{n(P_i)}{\sum_{i=1}^{n} n(P_i)} \times 100\% \quad \text{(S2)}
\]

S2. Reaction mechanism of ethanol dehydration

On OH-rich metal oxide surfaces, the following pathways have been proposed:

1. Diethyl ether formation:

\[
\begin{align*}
C_2H_5OH + OH^- (s) & \rightarrow C_2H_5O^-(s) + H_2O \\
C_2H_5OH + C_2H_5O^- (s) & \rightarrow (C_2H_5)_2O + OH^- (s)
\end{align*}
\]

2. Ethylene:

\[
2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O
\]
2. Ethene formation:
\[ \text{C}_2\text{H}_5\text{OH} + \text{OH}^- (s) \rightarrow \text{C}_2\text{H}_4\text{O}^- (s) + \text{H}_2\text{O} \]
\[ \text{C}_2\text{H}_5\text{O}^- (s) \rightarrow \text{C}_2\text{H}_2 + \text{OH}^- (s) \]
\[ \text{C}_2\text{H}_4\text{OH} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2\text{O} \]

On OH- poor surfaces, the following mechanisms have been suggested:

1. Diethyl ether formation:
\[ 2\text{C}_2\text{H}_5\text{OH} + 2\text{O}^{2-} (s) \rightarrow 2\text{C}_2\text{H}_5\text{O}^- (s) + 2\text{OH}^- (s) \]
\[ 2\text{C}_2\text{H}_5\text{O}^- (s) \rightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{O}^{2-} (s) \]
\[ 2\text{OH}^- (s) \rightarrow \text{H}_2\text{O} + \text{O}^{2-} (s) \]
\[ 2\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O} \]

2. Ethene formation:
\[ \text{C}_2\text{H}_5\text{OH} + \text{O}^{2-} (s) \rightarrow \text{C}_2\text{H}_5\text{O}^- (s) + \text{OH}^- (s) \]
\[ \text{C}_2\text{H}_5\text{O}^- (s) \rightarrow \text{C}_2\text{H}_4 + \text{OH}^- (s) \]
\[ 2\text{OH}^- (s) \rightarrow \text{H}_2\text{O} + \text{O}^{2-} (s) \]
\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

Table S1. The compositions of Na-MMT

<table>
<thead>
<tr>
<th>Sample (wt%)</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>MgO</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>TiO₂</th>
<th>SiO₂</th>
<th>Loss on ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MMT</td>
<td>19.55</td>
<td>2.58</td>
<td>1.71</td>
<td>0.68</td>
<td>3.63</td>
<td>4.06</td>
<td>0.08</td>
<td>0.07</td>
<td>0.06</td>
<td>61.18</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table S2. Textural characteristics of different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Pore Size/nm</th>
<th>SiO₂ (wt%)ᵃ</th>
<th>Al₂O₃ (wt%)ᵃ</th>
<th>P₂O₅ (wt%)ᵃ</th>
<th>MoO₃ (wt%)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MMT</td>
<td>21</td>
<td>3.7</td>
<td>61.18</td>
<td>19.55</td>
<td>0.08</td>
<td>--</td>
</tr>
<tr>
<td>AT-MMT</td>
<td>335</td>
<td>9.1</td>
<td>77.49</td>
<td>9.85</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PILC</td>
<td>301</td>
<td>3.7</td>
<td>70.49</td>
<td>14.99</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PTMA-PILC</td>
<td>253</td>
<td>3.4</td>
<td>65.27</td>
<td>15.92</td>
<td>0.227</td>
<td>2.383</td>
</tr>
</tbody>
</table>

ᵃThe content of SiO₂, Al₂O₃, P₂O₅ and MoO₃ over the montmorillonites was determined by XRF.

Table S3. The acid distributions on different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature</th>
<th>Weak acid amount (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MMT</td>
<td>90</td>
<td>0.086</td>
</tr>
<tr>
<td>AT-MMT</td>
<td>90</td>
<td>0.112</td>
</tr>
<tr>
<td>PILC</td>
<td>90</td>
<td>0.175</td>
</tr>
<tr>
<td>PTMA-PILC</td>
<td>93</td>
<td>0.178</td>
</tr>
</tbody>
</table>
Fig. S1. Reaction equipment for the Ethanol dehydration to ethylene

Fig. S2. Schematic diagram of Al$_{13}^{3+}$ in the midst of structure unit layer of PILC (a)
S3 References