A highly efficient Nafion-H catalyst for vapour phase carbonylation of dimethoxymethane

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Experimental Section

Preparation of catalysts
Nafion-H catalyst: Nafion-H resin powder (<200 mesh, commercially available from Aldrich) was mixed with silica powder by mechanical mixture. The Nafion-H resins loading in the catalyst were 60 wt.%. The obtained mixture was pressed to pellets, then, crushed, sieved to 40–60 mesh particles.

Polystyrenesulfonic acid resins catalysts: Polystyrenesulfonic acid resins, which were purchased from Dandong Mingzhu Special Type Resin Co., Ltd., were used without further treatment.

H-faujasite catalysts: Zeolite samples were obtained commercially with different Si/Al ratios in H\(^+\) form (Si/Al=4.3, Nankai University catalyst Co., Ltd.; Si/Al=15, Si/Al =40, Zeolyst). The zeolite samples were calcined in static air at 723 K for 4 h, and then, pelletized, crushed, sieved to 40–60 mesh size for activity test.

Sample Preparation for \(^1\)H MAS NMR
Prior to the pyridine-\(d_5\) adsorption and NMR experiments, all the samples were dehydrated at 120 °C for 12 h under vacuum condition(<1×10\(^{-2}\) Pa). When the samples were cooled to ambient temperature, the pyridine-\(d_5\) was introduced from a vacuum line at room temperature. Then, the overloaded pyridine-\(d_5\) was removed at 313 K for 10 min in vacuum. After adsorption of pyridine-\(d_5\), the sealed samples were transferred into a NMR rotor under a dry nitrogen atmosphere in a glovebox.

Solid-State NMR Experiments
\(^1\)H MAS NMR spectra were recorded on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm MAS probe with resonance frequencies of 600.13 MHz. The pulse width was 2.2 µs for a \(\pi/4\) pulse, and 32 scans were accumulated with a 10 s recycle delay. Samples were spun at 12 kHz, and chemical shifts were referenced to adamantane at 1.74 ppm.
Catalytic test

DMM (commercially available from Aldrich) carbonylation reactions were performed in a continuous-flow fixed-bed stainless steel reactor. Typically, 0.1 g of catalyst was loaded into a reactor tube (8 mm internal diameter). The sample was then heated to 120 °C for an hour under nitrogen atmosphere (30 ml min⁻¹) to remove residual water and then cooled to the reaction temperature. DMM was carried into reactor by carbon monoxide, which was bubbled through a stainless steel saturator containing liquid DMM isothermally held at 20 °C. The chemical inert nitrogen was introduced to the reaction system to adjust the partial pressure of CO. The reaction effluent was analyzed by gas chromatography (Agilent 7890) equipped with a flame ionization detector. The DMM conversion and MMAc selectivity were calculated with the followed equations.

\[
\text{DMM Conversion} = \left[1 - \frac{3C_{\text{DMM}}}{3C_{\text{DMM}} + 2C_{\text{DME}} + 2C_{\text{MF}} + C_{\text{methanol}} + 3C_{\text{MMAc}}} \right] \times 100\% \tag{1}
\]

\[
\text{MMAc selectivity} = \left[\frac{3C_{\text{MMAc}}}{2C_{\text{DME}} + 2C_{\text{MF}} + C_{\text{methanol}} + 3C_{\text{MMAc}}} \right] \times 100\% \tag{2}
\]

where \( C_i \) was the molar concentration of compound \( i \) in the reaction effluent and \( n \) was the number of carbon derived from DMM.

Figure SI 1 the effect of Si/Al ratio on the DMM conversion (△ Si/Al=40; ○Si/Al=15;
and selectivity to MMAc (▲Si/Al=40; ●Si/Al=15; ■Si/Al=4.3) at the same reaction condition (catalyst weight = 0.1 g, reaction pressure = 30.0 atm, reaction temperature = 110°C, DMM partial pressure = 0.42 atm, CO stream = 85 ml min⁻¹).

Table SI 1 the catalytic performance over various sulfonic acids with different acid strength

<table>
<thead>
<tr>
<th>Sulfonic Acids</th>
<th>$H_0^a$</th>
<th>Selectivity</th>
<th>Conversion</th>
<th>Rate of MMAc Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃SO₃H</td>
<td>-14.1</td>
<td>92.8</td>
<td>27.0</td>
<td>12.6</td>
</tr>
<tr>
<td>C₄F₉SO₃H</td>
<td>-13.2</td>
<td>91.7</td>
<td>20.2</td>
<td>10.6</td>
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<tr>
<td>H₂SO₄</td>
<td>-12.0</td>
<td>90.0</td>
<td>10.5</td>
<td>4.4</td>
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<tr>
<td>CH₃SO₃H</td>
<td>-7.8</td>
<td>88.9</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>CH₃CH₂SO₃H</td>
<td>&gt;-7.8</td>
<td>72.9</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
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<tr>
<td>p-CH₃C₆H₄SO₃H</td>
<td>+0.55</td>
<td>79.2</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>p-CH₃CH₂C₆H₄SO₃H</td>
<td>&gt;0.55</td>
<td>76.1</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
</tr>
</tbody>
</table>

a: $H_0$, value of Hammett acidity function