Supporting Information

Catalytic self-etherification of 5-hydroxymethylfurfural to 5,5′(oxy-bis(methylene))bis-2-furfural over zeolite catalysts: Effect of pore structure and acidity

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HMF conversion, OBMF yield, and products selectivity were defined as follow:

\[
\text{HMF Conversion (mol\%) =} \frac{\text{Moles of reacted HMF}}{\text{Moles of added HMF}} \times 100\%
\]

\[
\text{OBMF Yield (mol\%) =} \frac{\text{Moles of formed OBMF}}{\text{Moles of added HMF}/2} \times 100\%
\]

\[
\text{OBMF Selectivity (mol\%) =} \frac{\text{OBMF Yield}}{\text{HMF Conversion}} \times 100\%
\]

**Table S1.** Physical properties of the used samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m(^2)·g(^{-1}))(^{[a]})</th>
<th>(V_{\text{micro}}) (cm(^3)·g(^{-1}))(^{[b]})</th>
<th>(V_{\text{meso}}) (cm(^3)·g(^{-1}))(^{[c]})</th>
<th>Weight loss (wt%)(^{[d]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>14</td>
<td>0</td>
<td>0.04</td>
<td>12.6</td>
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<tr>
<td>HMZ</td>
<td>149</td>
<td>0.01</td>
<td>0.37</td>
<td>17.4</td>
</tr>
<tr>
<td>Beta</td>
<td>87</td>
<td>0</td>
<td>0.54</td>
<td>22.3</td>
</tr>
<tr>
<td>MCM-22</td>
<td>151</td>
<td>0</td>
<td>1.41</td>
<td>26.2</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Determined by BET method. \(^{[b]}\) Estimated using the t-plot method. \(^{[c]}\) Determined by a subtraction of total pore volume at a relative pressure of \(P/P_0=0.99\) from the Microporous pore volume obtained from the t-plot. \(^{[d]}\) Calculated by TG.

**Table S2.** Product distribution of HMF self-etherification on the different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of HMF (%)</th>
<th>Selectivity (%)</th>
<th>OBMF</th>
<th>THB</th>
<th>MF</th>
<th>FMF</th>
<th>unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>22.5</td>
<td></td>
<td>33.3</td>
<td>/</td>
<td>/</td>
<td>1.53</td>
<td>65.17</td>
</tr>
<tr>
<td>HMZ</td>
<td>96.8</td>
<td></td>
<td>95.97</td>
<td>0.08</td>
<td>/</td>
<td>/</td>
<td>3.95</td>
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<tr>
<td>Beta</td>
<td>75.8</td>
<td></td>
<td>70.18</td>
<td>1.13</td>
<td>7.33</td>
<td>4.47</td>
<td>16.89</td>
</tr>
<tr>
<td>MCM-22</td>
<td>84</td>
<td></td>
<td>67.86</td>
<td>0.66</td>
<td>7.71</td>
<td>2.92</td>
<td>20.85</td>
</tr>
</tbody>
</table>

Reaction condition: 18 mL 4-clorotoluene, 1.0 g HMF, 0.5 g catalyst, 100°C and 8h reaction. THB: 1,2,4-Trihydroxybenzene; MF: 5,5'-Methylendi-2-furaldehyd; FMF: 5-(2-furaldehyde)methyl formate. The selectivity of other products was determined by GC with area normalization method.
**Figure S1.** The $^1$H NMR spectrum of the HMF (solvent: CDCl$_3$).

**Figure S2.** Mass spectrum of the HMF.
**Figure S3.** The $^1$H NMR spectrum of the OBMF (solvent: CDCl$_3$).

**Figure S4.** Mass spectrum of the OBMF product.
Figure S5. Mass spectrum of the 5,5'-Methylendi-2-furaldehyd (MF) product.

Figure S6. Mass spectrum of the 5-(2-furaldehyde)methyl formate (FMF) product.
Figure S7. Mass spectrum of the 1,2,4-Trihydroxybenzene (THB) product.

Figure S8. The initial rate of catalyst under the different agitation speed.
Figure S9. The reusability of catalysts (without of regeneration) in self-etherification of HMF to OBMF.

Reaction conditions: 18 mL 4-clorotoluene, 1.0 g HMF, 0.5 g catalyst, 100°C and 2h reaction.
**Figure S10.** The color of fresh and used catalysts.
Figure S11. TG-DTG curves of the used catalysts.
**Figure S12.** Catalytic performances of the catalysts in self-etherification of HMF to OBMF (a, b) and effect of reaction temperature on the OBMF selectivity (c) and yield (d) over the different catalysts (4h reaction). Reaction conditions: 18 mL 4-clorotoluene, 1.0 g HMF, 0.5 g catalyst, 90°C.
Figure S13. NH$_3$-TPD curves of the Beta, HMZ, and modified catalysts.

Figure S14. The reusability of HMZ sample in self-etherification of HMF to OBMF.