Appendix A. Supplementary data:

Effects of support on bifunctional one-step synthesis of methylal via methanol oxidation catalyzed by Fe-Mo-based catalyst

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Table S1. Specific surface areas and pore structure data of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo:Fe(2) / HY zeolite</td>
<td>225.31</td>
<td>3.34</td>
<td>0.146</td>
</tr>
<tr>
<td>Mo:Fe(2) / Al₂O₃</td>
<td>313.52</td>
<td>2.13</td>
<td>0.109</td>
</tr>
<tr>
<td>Mo:Fe(2) / HZSM-5 (40)</td>
<td>325.32</td>
<td>2.15</td>
<td>0.110</td>
</tr>
<tr>
<td>Mo:Fe(2) / HZSM-5 (80)</td>
<td>316.47</td>
<td>2.28</td>
<td>0.099</td>
</tr>
<tr>
<td>Mo:Fe(2) / SiO₂</td>
<td>309.88</td>
<td>2.23</td>
<td>0.089</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Weak acid</td>
<td></td>
<td>Stronger acid</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------</td>
<td>------------</td>
<td>---------------</td>
</tr>
<tr>
<td></td>
<td>T(°C)</td>
<td>NO.(µmol·g⁻¹)</td>
<td>T(°C)</td>
</tr>
<tr>
<td>Mo:Fe(2) / HY zeolite</td>
<td>200</td>
<td>651.93</td>
<td>500</td>
</tr>
<tr>
<td>Mo:Fe(2) / Al₂O₃</td>
<td>200</td>
<td>158.89</td>
<td>375</td>
</tr>
<tr>
<td>Mo:Fe(2) / HZSM-5 (40)</td>
<td>225</td>
<td>814.74</td>
<td>475</td>
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<td>Mo:Fe(2) / HZSM-5 (80)</td>
<td>200</td>
<td>659.83</td>
<td>450</td>
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<tr>
<td>Mo:Fe(2) / SiO₂</td>
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<tr>
<td>catalyst</td>
<td>Lewis(^a)</td>
<td>Brönsted(^b)</td>
<td>B/L(^c)</td>
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<td>Mo-Fe (2)/HY zeolite</td>
<td>1.12</td>
<td>4.81</td>
<td>4.29</td>
</tr>
<tr>
<td>Mo-Fe (2)/Al(_2)O(_3)</td>
<td>1.10</td>
<td>3.44</td>
<td>3.13</td>
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<tr>
<td>Mo-Fe (2)/HZSM-5 (40)</td>
<td>1.87</td>
<td>4.46</td>
<td>2.39</td>
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<td>Mo-Fe (2)/HZSM-5 (80)</td>
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<td>4.11</td>
<td>4.52</td>
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<tr>
<td>Mo-Fe (2)/SiO(_2)</td>
<td>1.14</td>
<td>0</td>
<td>0</td>
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<td>HZSM-5 (40)</td>
<td>0.99</td>
<td>4.67</td>
<td>4.72</td>
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\(^a\)Lewis’ range: 1432–1460 cm\(^{-1}\). \(^b\)Bands’ range: 1510–1560 cm\(^{-1}\). \(^c\)Brönsted/Lewis bands ratio.
**Table S4.** Specific surface areas and pore structure data of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
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</thead>
<tbody>
<tr>
<td>Mo:Fe(2)/HY zeolite</td>
<td>225.31</td>
<td>3.34</td>
<td>0.146</td>
</tr>
<tr>
<td>Mo:Fe(2)/HZSM-5 (40)</td>
<td>325.32</td>
<td>2.15</td>
<td>0.110</td>
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<tr>
<td>Mo:Fe(2)/HZSM-5 (80)</td>
<td>316.47</td>
<td>2.28</td>
<td>0.099</td>
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<tr>
<td>Mo:Fe(2)/HY zeolite+HZSM-5(80)</td>
<td>231.88</td>
<td>3.49</td>
<td>0.160</td>
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<tr>
<td>Mo:Fe(2)/HZSM-5 (40+80)</td>
<td>321.37</td>
<td>2.13</td>
<td>0.099</td>
</tr>
<tr>
<td>Mo:Fe(2)/HZSM-5 (80+80)</td>
<td>305.32</td>
<td>2.18</td>
<td>0.094</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Weak acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td>T/°C</td>
<td>NO.(µmol·g⁻¹)</td>
<td>T/°C</td>
</tr>
<tr>
<td>Mo:Fe(2)/HY zeolite+HZSM-5(80)</td>
<td>225</td>
<td>1136.4</td>
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<tr>
<td>Mo:Fe(2)/HZSM-5 (40+80)</td>
<td>175</td>
<td>515.2</td>
<td>275</td>
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<tr>
<td>Mo:Fe(2)/HZSM-5 (80+80)</td>
<td>175</td>
<td>639.3</td>
<td>275</td>
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**Table S5.** The NH3-TPD results of the catalysts
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<th>catalyst</th>
<th>Lewis</th>
<th>Brönsted</th>
<th>B/L</th>
<th>total</th>
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<tbody>
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<td>Mo:Fe(2)/HY zeolite+HZSM-5 (80)</td>
<td>1.21</td>
<td>4.22</td>
<td>3.49</td>
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<td>1.62</td>
<td>4.19</td>
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<td>Mo:Fe(2) /HZSM-5 (80+80)</td>
<td>1.23</td>
<td>4.71</td>
<td>3.82</td>
<td>5.94</td>
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</tbody>
</table>

*aBands’ range: 1432~1460 cm\(^{-1}\).*\(^{b}\)Bands’ range: 1510~1560 cm\(^{-1}\).*\(^{c}\)Brönsted/Lewis bands ratio.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methanol conversion (%)</th>
<th>DMM</th>
<th>FA</th>
<th>MF</th>
<th>DME</th>
<th>CO₂</th>
<th>Yield</th>
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</thead>
<tbody>
<tr>
<td>Mo-Fe (2) /HZSM-5 (20)</td>
<td>30.81</td>
<td>48.28</td>
<td>8.9</td>
<td>40.03</td>
<td>2.02</td>
<td>0.77</td>
<td>14.05</td>
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<td>Mo-Fe (2) /HZSM-5 (60)</td>
<td>25.71</td>
<td>62.77</td>
<td>9.11</td>
<td>24.67</td>
<td>2.91</td>
<td>0.54</td>
<td>16.14</td>
</tr>
<tr>
<td>Mo-Fe (2) /HZSM-5 (100)</td>
<td>21.89</td>
<td>70.01</td>
<td>10.1</td>
<td>14.34</td>
<td>5.14</td>
<td>0.41</td>
<td>16.73</td>
</tr>
<tr>
<td>Mo-Fe (2) /HZSM-5 (80+20)</td>
<td>60.77</td>
<td>60.1</td>
<td>6.10</td>
<td>26.83</td>
<td>6.66</td>
<td>0.31</td>
<td>36.52</td>
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<td>Mo-Fe (2) /HZSM-5 (80+60)</td>
<td>80.17</td>
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<td>5.61</td>
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<td>3.01</td>
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<td>Mo-Fe (2) /HZSM-5 (80+100)</td>
<td>84.41</td>
<td>85.77</td>
<td>2.60</td>
<td>8.12</td>
<td>3.51</td>
<td>0.29</td>
<td>72.39</td>
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</table>
Fig. S1. Scheme of oxidation/dehydration of methanol
**Fig. S2.** FTIR spectra of pyridine adsorbed on the ZSM-5 (40) and Mo: Fe (2) / HZSM-5 (40) catalysts.
Fig. S3. Variation of methanol conversion with W/F for different catalysts.