A general post-synthetic modification approach of amino-tagged metal-organic frameworks to access efficient catalysts for the Knoevenagel condensation reaction

Yi Luan, Yue Qi, Hongyi Gao, RADOELIZO S. Andriamitantsoa, Nannan Zheng and Ge Wang*

Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, People’s Republic of China
General Information.

Characterization.

The phase composition of the samples was investigated by X-ray powder diffraction (XRD, M21X, Cu Kα radiation, λ=0.154178 nm). The morphology and structure of the as-obtained product were characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Thermogravimetric analysis (TG) was conducted by Netzsch STA449F at a heating rate of 10 °C/min under the N₂ flow. The specific surface areas were calculated by nitrogen sorption-desorption isotherms using a Micromeritics ASAP 2420 adsorption analyzer. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. Fourier transform infrared spectroscopy (FTIR) was acquired on Nicolet 6700 using the KBr pellet technique. The results were analyzed by gas chromatography-mass spectrometry using an internal standard (GC-MS, Agilent7890/5975C-GC/MSD, HP5-MS column, Ar carrier gas, 200 ºC). Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates.

General procedure for Knoevenagel condensation reaction of aldehyde and malononitrile

In a typical reaction, to a 5 mL reaction vessel was added 1.0 mmol benzaldehyde and 1.5 mmol malononitrile in 2 mL of toluene. To the reaction was then added 1.0 mol% of catalyst. The heterogeneous solution was stirred at room temperature (23 ºC) for 2 h. The final yield and selectivity of the Knoevenagel condensation product was analyzed by GC-MS using n-dodecane as the internal standard.
Figure S1. FTIR of MOF5, IRMOF-3 and IRMOF-3-RNH$_2$

Figure S2. FTIR of UiO-66, UiO-66-NH$_2$ and UiO-66-NH-RNH$_2$
Figure S3. Al-53, Al-MIL-53-NH$_2$ and Al-MIL-53-NH-RNH$_2$

Figure S4. Cr-MIL-101, Cr-MIL-101-NH$_2$ and Cr-MIL-101-NH-RNH$_2$
Figure S5. Nitrogen adsorption/desorption isotherms of IRMOF-3

Figure S6. Nitrogen adsorption/desorption isotherms of IRMOF-3-RNH₂
Figure S7. Nitrogen adsorption/desorption isotherms of UiO-66-NH₂

Figure S8. Nitrogen adsorption/desorption isotherms of UiO-66-NH-RNH₂
Figure S9. Nitrogen adsorption/desorption isotherms of Al-MIL-53-NH$_2$

Figure S10. Nitrogen adsorption/desorption isotherms of Al-MIL-53-NH-RNH$_2$
Figure S11. Nitrogen adsorption/desorption isotherms of Cr-MIL-101-NH$_2$, BET surface area of 1039 m$^2$ g$^{-1}$ (a), 1452 m$^2$ g$^{-1}$ (b), and 1989 m$^2$ g$^{-1}$ (c).
Figure S12. Nitrogen adsorption/desorption isotherms of Cr-MIL-101-NH-RNH$_2$, BET surface area of Cr-MIL-101-NH-RNH$_2$-1, 717 m$^2$ g$^{-1}$ (a), Cr-MIL-101-NH-RNH$_2$-2 751 m$^2$ g$^{-1}$ (b), and Cr-MIL-101-NH-RNH$_2$-3 1175 m$^2$ g$^{-1}$ (c).
Figure S13. TGA of MOF5, IRMOF-3 and IRMOF-3-RNH$_2$

Figure S14. TGA of UiO-66, UiO-66-NH$_2$ and UiO-66-NH-RNH$_2$
**Figure S15.** Al-53, Al-MIL-53-NH$_2$ and Al-MIL-53-NH-RNH$_2$

**Figure S16.** Cr-MIL-101, Cr-MIL-101-NH$_2$ and Cr-MIL-101-NH-RNH$_2$
Figure S17. ESI-MS (negative mode) of IRMOF-3-RNH$_2$

Figure S18. ESI-MS (negative mode) of UiO-66-NH-RNH$_2$
Figure S19. ESI-MS (negative mode) of Al-MIL-53-NH-RNH₂

Figure S20. ESI-MS (negative mode) of Cr-MIL-101-NH-RNH₂
Catalytic material recycling characterizations

**Figure 21.** SEM images of recycled UiO-66-NH-RNH₂

**Figure 22.** The XRD patterns of (a) fresh UiO-66-NH-RNH₂, (b) recycled UiO-66-NH-RNH₂.
Figure 23. Benzaldehyde vs. \textit{n}-dodecane internal standard for GC analysis

Figure 24. 2-benzylidenemalononitrile vs. \textit{n}-dodecane internal standard for GC analysis
Figure S25. Full 1H NMR of MOFs, a) digested UiO-66, b) digested IRMOF-3-RNH₂, c) digested UiO-66-NH-RNH₂, d) digested Al-MIL-53-NH-RNH₂.
Figure S26. $^1$H NMR of 2-methylaziridine
Fig. S27 SEM images of amino-tagged and basic modified MOF catalysts. (a) IRMOF-3, (b) IRMOF-3-RNH₂, (c) UiO-66-NH₂, (d) UiO-66-NH-RNH₂, (e) Al-MIL-53-NH₂, (f) Al-MIL-53-NH-RNH₂, (g) Cr-MIL-101-NH₂, (h) Cr-MIL-101-NH-RNH₂.
Fig. S28 Conversion vs. time employing Cr-MIL-101-NH-RNH$_2$ MOF catalyst.
Table S1. A comparison of catalytic activity of different catalysts in Knoevenagel condensation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Mol%</th>
<th>Time</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>PS-MCM-41</td>
<td>1</td>
<td>3 h</td>
<td></td>
<td></td>
<td>110</td>
<td>70%</td>
<td>70</td>
<td>23</td>
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<tr>
<td>2</td>
<td>MCM zeolite</td>
<td>17</td>
<td>3 h</td>
<td>Toluene</td>
<td>80</td>
<td>85%</td>
<td>5.0</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>SBA-15 zeolite</td>
<td>17</td>
<td>3 h</td>
<td>Toluene</td>
<td>80</td>
<td>88%</td>
<td>5.2</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Nitrided ITQ-2</td>
<td>17</td>
<td>3 h</td>
<td>Toluene</td>
<td>80</td>
<td>95%</td>
<td>5.6</td>
<td>1.9</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>MgO</td>
<td>17</td>
<td>25 h</td>
<td>Toluene</td>
<td>80</td>
<td>45%</td>
<td>2.6</td>
<td>0.1</td>
<td>2</td>
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<tr>
<td>6</td>
<td>mesoporous CeₓZr₁₋ₓO₂</td>
<td>10</td>
<td>50 min</td>
<td>Ethanol</td>
<td>80</td>
<td>82%</td>
<td>8.2</td>
<td>9.9</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>ZIF-8</td>
<td>5</td>
<td>3 h</td>
<td>Toluene</td>
<td>r.t.</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>ZIF-9</td>
<td>5</td>
<td>4 h</td>
<td>Toluene</td>
<td>r.t.</td>
<td></td>
<td></td>
<td></td>
<td>19</td>
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<tr>
<td>9</td>
<td>TMU-5</td>
<td>2</td>
<td>30 min</td>
<td>H₂O</td>
<td>r.t.</td>
<td>100%</td>
<td>50</td>
<td>100</td>
<td>6</td>
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<tr>
<td>10</td>
<td>[Gd₂(tnbd)₃·(DMF)₄]·4DMF·3H₂O</td>
<td>10</td>
<td>20 min</td>
<td>Benzene</td>
<td>r.t.</td>
<td>96%</td>
<td>9.6</td>
<td>48</td>
<td>7</td>
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<tr>
<td>11</td>
<td>Pd(cpna)₂·2DMF·6H₂O</td>
<td>3</td>
<td>24 h</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>100%</td>
<td>33.3</td>
<td>1.4</td>
<td>8</td>
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<tr>
<td>12</td>
<td>DETA-MIL-101</td>
<td>Not indicated</td>
<td>0.5-2 h</td>
<td>Toluene</td>
<td>r.t.</td>
<td>18-98%</td>
<td>-</td>
<td>9-108</td>
<td>9</td>
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<tr>
<td>13</td>
<td>UiO-66-NH-RNH₂</td>
<td>1</td>
<td>2 h</td>
<td>Toluene</td>
<td>r.t.</td>
<td>99%</td>
<td>99</td>
<td>50</td>
<td>This work</td>
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<tr>
<td>14</td>
<td>Cr-MIL-101-NH-RNH₂</td>
<td>1</td>
<td>20 min</td>
<td>Toluene</td>
<td>r.t.</td>
<td>88%</td>
<td>88</td>
<td>264</td>
<td>This work</td>
</tr>
<tr>
<td>15</td>
<td>Cr-MIL-101-NH-RNH₂</td>
<td>1</td>
<td>5 min</td>
<td>Toluene</td>
<td>r.t.</td>
<td>33%</td>
<td>33</td>
<td>396</td>
<td>This work</td>
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a The mole percentage of PS-MCM-41, MCM zeolite, SBA-15 zeolite, Nitrided ITQ-2, ZIF-8, ZIF-9, TMU-5, DETA-MIL-101 (entries 1-4, 7-9 and 12) was calculated based on the active nitrogen.

b The mole percentage of MgO, mesoporous CeₓZr₁₋ₓO₂, [Gd₂(tnbd)₃·(DMF)₄]·4DMF·3H₂O, Pd(cpna)₂·2DMF·6H₂O was calculated based on the metal content (entries 5-6, 10-11).

c The mole percentage of our catalyst (entries 13-15) was calculated based on the alkyl amino group, which indicates substrate per active center.

Gas-chromatogram Mass-spectrum

Table 3, Entry 1,

Catalyzed by UiO-66-NH-RNH$_2$

Catalyzed by Al-MIL-53-NH-RNH$_2$

Catalyzed by Cr-MIL-101-NH-RNH$_2$
Table 3, Entry 2

Catalyzed by UiO-66-NH-RNH$_2$

Catalyzed by Al-MIL-53-NH-RNH$_2$

Catalyzed by Cr-MIL-101-NH-RNH$_2$
### Table 3, Entry 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CN</th>
<th>O</th>
<th>n-dodecane</th>
</tr>
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<tbody>
<tr>
<td>Uio-66-NH-RNH₂</td>
<td>CN</td>
<td>O</td>
<td>n-dodecane</td>
</tr>
<tr>
<td>Al-MIL-53-NH-RNH₂</td>
<td>CN</td>
<td>O</td>
<td>n-dodecane</td>
</tr>
<tr>
<td>Cr-MIL-101-NH-RNH₂</td>
<td>CN</td>
<td>O</td>
<td>n-dodecane</td>
</tr>
</tbody>
</table>

Catalyzed by Uio-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 3, Entry 4

Catalyzed by UiO-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 3, Entry 5

Catalyzed by UiO-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 3, Entry 6

Catalyzed by UiO-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 3, Entry 7

Catalyzed by UiO-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 3, Entry 8,

Catalyzed by UiO-66-NH-RNH$_2$

Catalyzed by Al-MIL-53-NH-RNH$_2$

Catalyzed by Cr-MIL-101-NH-RNH$_2$
Table 3, Entry 9

Catalyzed by UiO-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 3, Entry 10,

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Retention Time (min)</th>
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<tbody>
<tr>
<td>n-dodecane</td>
<td>11.938</td>
</tr>
<tr>
<td>Catalyzed by UiO-66-NH-RNH$_2$</td>
<td>4.415, 15.165</td>
</tr>
<tr>
<td>Catalyzed by Al-MIL-53-NH-RNH$_2$</td>
<td>4.415, 15.165</td>
</tr>
<tr>
<td>Catalyzed by Cr-MIL-101-NH-RNH$_2$</td>
<td>4.415, 15.165</td>
</tr>
</tbody>
</table>
Table 3, Entry 11

Catalyzed by UiO-66-NH-RNH₂

Catalyzed by Al-MIL-53-NH-RNH₂

Catalyzed by Cr-MIL-101-NH-RNH₂
Table 4, Entry 1.

Catalyzed by UiO-66-NH-RNH₂

Table 4, Entry 2.

Catalyzed by UiO-66-NH-RNH₂