Supporting Information

Direct Synthesis of Pyrroles via Heterogeneous Catalytic Condensation of Anilines with Bioderived Furans

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1. Materials

1.1 Catalytic materials

H-ZSM-5 (18), H-BEA (12.5), H-MOR (12.5), H-Y (2.6), H-Y (3.2), H-Y (5) were supplied by NanKai University Catalyst Co. Ltd. (Tianjin, China). CeO₂ was supplied by Evonik. MgO was supplied by Alfa Aesar. Commercially available reagents and solvents (Sigma-Aldrich) were used with further purification.

1.2 Catalyst preparation

Preparation of ZrO₂: ZrO₂ powder was prepared by a conventional precipitation method following the reported procedure.[S1] Briefly, 12.9 g ZrOCl₂·8H₂O was dissolved in 200 mL deionized water at room temperature, the pH was adjusted to 9.0 by dropwise addition of NH₃·H₂O (2.5 M). The resultant hydro gel was washed with deionized water until free of chloride ions. The precipitate was then dried at 110 °C overnight and calcined at 400 °C for 2 h in air. The BET surface area of the resultant material was 110 m²·g⁻¹ (Micromeritics TriStar 3000). The crystal phase of ZrO₂ was composed of 56 % monoclinic phase and 44 % tetragonal phase.

Preparation of Nb₂O₅: Nb₂O₅ powder was prepared by calcination of niobium oxalate at 500 °C for 4 h under air.[S2]

Preparation of SiO₂-Al₂O₃: SiO₂-Al₂O₃ powder was prepared by the addition of TEOS into water containing nitric acid, aluminium nitrate (Si/Al = 1) with vigorous stirring. After the solution became homogeneous it was sealed in a plastic container, and kept at 50 °C for 20 h for gelation. The obtained gel was dried at 50 °C for 1 week and then heated at 600 °C for 2 h.[S3]
2. Supplementary Data

*Table S1.* The influence of acid strength on the yield of the target pyrrole.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Si/Al ratio</th>
<th>Desorption temperature of acid site type 1 (°C)</th>
<th>Desorption temperature of acid site type 2 (°C)</th>
<th>Pyrrole yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H-ZSM-5</td>
<td>18</td>
<td>213</td>
<td>412</td>
<td>34</td>
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<tr>
<td>2</td>
<td>H-MOR</td>
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<td>419</td>
<td>9</td>
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<tr>
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<td>H-BEA</td>
<td>12.5</td>
<td>193</td>
<td>314</td>
<td>63</td>
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<tr>
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<td>H-Y</td>
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</tr>
<tr>
<td>5</td>
<td></td>
<td>3.2</td>
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<tr>
<td>6</td>
<td></td>
<td>5</td>
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</table>

*Table S2.* The relative ratio of Bronsted acid to Lewis acid.

<table>
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<th>Entry</th>
<th>Catalyst</th>
<th>Si/Al ratio</th>
<th>B/L ratio</th>
<th>Pyrrole yield (%)</th>
</tr>
</thead>
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<td>12.5</td>
<td>1:0.63</td>
<td>9</td>
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<td>H-BEA</td>
<td>12.5</td>
<td>1:5.49</td>
<td>63</td>
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<td>2.6</td>
<td>1:0.43</td>
<td>96</td>
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<td>5</td>
<td>1:0.78</td>
<td>85</td>
</tr>
</tbody>
</table>

*Figure S1.* XRD patterns of various zeolite samples.
Figure S2. Recycling results of H-Y (2.6) in condensation of 2,5-dimethylfuran with m-methylaniline. Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol m-methylaniline, 2 mL toluene, 150 mg H-Y (2.6), 150 °C, 5 bar N₂, 0.7 h.

Figure S3. NH₃-TPD profiles of various zeolite samples.

Figure S4. FTIR spectra of pyridine adsorbed onto the various zeolite samples.
Figure S5. Time-course plot for the direct condensation of 2,5-dimethylfuran with m-methylaniline. Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol m-methylaniline, 2 mL toluene, 150 mg H-Y (2.6), 150 °C, 5 bar N₂, 0.7 h.

Figure S6. Results of mechanistic studies. Plot of ln(rate) versus ln([2,5-dimethylfuran]) and ln([m-methylaniline]).

Figure S7. Arrhenius plot for H-Y (2.6) catalyzed direct condensation of 2,5-dimethylfuran with m-methylaniline.
Scheme S1. Determination of the role of acid type by selective poisoning experiment. Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol m-methylaniline, 2 mL toluene, 150 mg H-Y (2.6), 0.5 mmol additive, 150 °C, 5 bar N₂, 0.5 h

\[ \text{without base: 96% yield} \]
\[ \text{with pyridine: 8% yield} \]
\[ \text{with 2,6-lutidine: 13% yield} \]

Scheme S2. Large-scale condensation of 2,5-dimethylfuran with m-methylaniline under neat condition. Reaction conditions: 100 mmol 2,5-dimethylfuran, 100 mmol m-methylaniline, 150 mg H-Y (2.6), 180 °C, 5 bar N₂, 18 h

Scheme S3. Traditional synthetic route for Pyrvinium.[S4]
3. $^1$H-NMR and $^{13}$C-NMR spectra of products

(Scheme 1, entry 1).$^{[58]}$ $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 7.45-7.35 (m, 3H), 7.19 (d, $J = 7.2$ Hz, 2H), 5.90 (s, 2H), 2.02 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 138.9, 128.9, 128.6, 128.1, 127.5 105.6, 12.9.

(Scheme 1, entry 2). $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 6.96 (d, $J = 7.2$ Hz, 2H), 6.70 (d, $J = 7.2$ Hz, 1H), 5.86 (s, 2H), 3.64 (br s, 2H), 2.01 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 145.8, 129.6, 129.0, 115.1, 104.9, 12.9; HRMS (ESI) calculated for C$_{12}$H$_{14}$N$_2$ [M+H]$^+$ 187.1230, observed 187.1238.

(Scheme 1, entry 3). $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 7.21 (t, $J = 8.0$ Hz, 1H), 6.70 (ddd, $J = 8.0$, 2.4, 0.8 Hz, 1H), 6.59 (ddd, $J = 8.0$, 2.4, 0.8 Hz, 1H), 6.51 (t, $J = 2.0$ Hz, 1H), 5.87 (s, 2H), 3.73 (br s, 2H), 2.04 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 147.0, 140.0, 129.7, 128.7, 118.4, 114.8, 114.3, 105.3, 12.9; HRMS (ESI) calculated for C$_{12}$H$_{14}$N$_2$ [M+H]$^+$ 187.1230, observed 187.1237.

(Scheme 1, entry 4).$^{[58]}$ $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 7.24 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 5.89 (s, 2H), 2.41 (s, 3H), 2.02 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 137.4, 136.3, 129.6, 128.8, 127.9, 105.4, 21.1, 12.9.

(Scheme 1 entry 5). $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 7.31 (t, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 2H), 5.88 (s, 2H), 2.39 (s, 3H), 2.02 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100
(Scheme 1, entry 6).\textsuperscript{[57]} \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 8.35 (d, J = 8.8 \text{ Hz}, 2H), 7.39 (d, J = 8.8 \text{ Hz}, 2H), 5.96 (s, 2H), 2.08 (s, 6H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz): \delta 146.7, 144.7, 128.8, 128.5, 124.5, 107.4, 13.1.

(Scheme 1, entry 7).\textsuperscript{[58]} \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 7.12 (d, J = 8.4 \text{ Hz}, 2H), 6.96 (d, J = 8.4 \text{ Hz}, 2H), 5.88 (s, 2H), 3.85 (s, 3H), 2.01 (s, 6H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz): \delta 158.8, 131.7, 129.2, 129.0, 114.2, 105.2, 55.4, 12.9.

(Scheme 1, entry 8).\textsuperscript{[58]} \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 7.42 (d, J = 8.0 \text{ Hz}, 2H), 7.14 (d, J = 8.0 \text{ Hz}, 2H), 5.90 (s, 2H), 2.02 (s, 6H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz): \delta 137.5, 133.5, 129.4, 129.2, 128.6, 106.0, 12.9.

(Scheme 1, entry 9). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 8.66 (d, J = 4.0 \text{ Hz}, 1H), 8.53 (s, 1H), 7.58 (d, J = 7.6 \text{ Hz}, 1H), 7.43 (dd, J = 7.2, 4.8 \text{ Hz}, 1H), 5.94 (s, 2H), 2.04 (s, 6H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz): \delta 149.3, 148.8, 135.6, 135.5, 128.9, 123.7, 106.6, 13.0; HRMS (ESI) calculated for C\textsubscript{11}H\textsubscript{12}N\textsubscript{2} [M+H]\textsuperscript{+} 173.1073, observed 173.1081.

(Scheme 1, entry 10).\textsuperscript{[59]} \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 7.91 (d, J = 8.0 \text{ Hz}, 2H), 7.52 (\text{quint}, J = 7.6 \text{ Hz}, 2H), 7.45 (s, 1H), 7.41 (t, J = 6.4 \text{ Hz}, 1H), 7.14 (d, J = 8.0 \text{ Hz}, 1H), 6.01 (s, 2H),
1.89 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 135.8, 134.2, 131.9, 129.8, 128.5, 128.0, 127.2, 126.5, 126.2, 125.3, 123.3, 105.4, 12.5.

(Scheme 1, entry 11).$^{[8,10]}$ $^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.49 (br s, 1H), 5.73 (d, $J = 2.8$ Hz, 2H), 2.19 (s, 6H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 128.1, 105.7, 12.9.

(Scheme 2, entry 1).$^{[8,11]}$ $^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.44-7.38 (m, 4H), 7.26-7.22 (m, 1H), 7.09 (t, $J = 2.0$ Hz, 2H), 6.35 (t, $J = 2.0$ Hz, 2H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 140.8, 129.5, 125.6, 120.5, 119.3, 110.4.

(Scheme 2, entry 2). $^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.43 (t, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 6.77 (s, 1H), 6.20 (s, 1H), 6.04 (s, 1H), 2.21 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 140.4, 129.4, 129.0, 126.8, 125.7, 121.3, 108.1, 108.0, 12.9; HRMS (ESI) calculated for C$_{11}$H$_{11}$N [M+H]$^+$ 158.0964, observed 158.0955.

(Scheme 2, entry 3). $^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.44-7.40 (m, 2H), 7.35-7.29 (m, 3H), 6.74 (t, $J = 6.4$ Hz, 1H), 6.22 (t, $J = 3.2$ Hz, 1H), 6.07 (quint, $J = 0.8$ Hz, 1H), 2.55 (q, $J = 3.6$ Hz, 2H), 1.15 (t, $J = 7.6$ Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 125 MHz): δ 140.4, 135.6, 129.0, 127.0, 126.1, 121.5, 107.9, 106.0, 20.1, 13.3; HRMS (ESI) calculated for C$_{12}$H$_{13}$N [M+H]$^+$ 172.1121, observed 172.1122.

(Scheme 2, entry 4). $^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.42 (t, $J = 8.0$ Hz, 2H), 7.33-7.27 (m, 3H), 6.70 (s, 1H), 6.09 (s, 1H), 2.12 (s, 3H), 2.10 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 140.7, 129.0, 126.5, 125.6, 125.2, 119.9, 116.2, 109.8, 11.5, 10.5; HRMS (ESI) calculated for C$_{12}$H$_{13}$N [M+H]$^+$ 172.1121, observed 172.1135.
Reference
