Supporting Information

Methylation of Amines, Nitrobenzenes and Aromatic Nitriles with Carbon Dioxide and Molecular Hydrogen

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1. Table S1. Catalyst screening using mono-methylation of aniline as model reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Al : Cu/mol : mol</th>
<th>Con./%</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>---</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Cu</td>
<td>---</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>CuO</td>
<td>---</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>Cu₂O</td>
<td>---</td>
<td>4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>6</td>
<td>Al₂O₃-Cu</td>
<td>1 : 1</td>
<td>3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>7</td>
<td>Al₂O₃-CuO</td>
<td>1 : 1</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Al₂O₃-Cu₂O</td>
<td>1 : 1</td>
<td>3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>9</td>
<td>Al₂O₃-Cu-Cu₂O</td>
<td>1 : 0.9 : 0.1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>CuAlOₓ</td>
<td>1 : 1</td>
<td>95 (97[a])</td>
<td>86(82[a])</td>
</tr>
</tbody>
</table>

Reaction conditions: 1.0 mmol aniline, 50 mg catalyst, 2 mL hexane, 3.0 MPa CO₂, 6.0 MPa H₂, 160 °C, 24 h. The yields were obtained by GC-FID using biphenyl as external standard. [a] yield at the 3rd run.

2. Figure S1. XPS diffraction patterns of prepared CuAlOₓ
3. **Figure S2.** XRD diffraction patterns of prepared Cu-Al-Ox

![XRD diffraction patterns](image)

4. **Figure S3.** BJH Desorption patterns of prepared Cu-Al-Ox

![BJH Desorption patterns](image)
5. **Figure S4.** TEM (left) and HR-TEM (right) images of CuAlOx catalyst sample after use.

6. **Figure S5.** Line-scan EDS analysis across the catalyst after use.
7. **Scheme S1.** The methylation reaction of aniline in a large scale.

\[
\begin{align*}
\text{NH}_2 & + \text{CO}_2 + \text{H}_2 & \xrightarrow{\text{cat 150 mg}} & \text{NH}_2 + \text{H}_2\text{O} + \text{NH}_3 \\
10 \text{ mmol} & & & \text{Y }= 64\% & \text{Y }= 3\% & \text{Y }= 3\%
\end{align*}
\]

Reaction conditions: 10 mmol amine, 150 mg catalyst, 5 mL hexane, 3.0 MPa CO\text{2}, 6.0 MPa H\text{2}, 160 °C, 24 h.

8. **Scheme S2.** The hydrogenation of nitrobenzene and benzonitrile.

\[
\begin{align*}
\text{No}_2 & \xrightarrow{\text{Con } = 100\%} \text{NH}_2 \\
\text{CN} & \xrightarrow{\text{Con } = 97\%} \text{NH}_2 + \text{NH}_3
\end{align*}
\]

Reaction conditions: 1.0 mmol nitrobenzene or nitrile, 50 mg catalyst, 2 mL hexane, 6.0 MPa H\text{2}, 160 °C, 12 h.
9. $^1$H and $^{13}$C NMR spectra of the isolated compounds

N-methylaniline: (Table 1, Entry 1) (GC purity 98%); The typical procedure for the N-methylation of aniline was followed: 95 mg aniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO$_2$, and 3.0 MPa CO$_2$ and 6.0 MPa H$_2$ were introduced. The reaction was reacted at 160 °C for 24 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (150 : 1) to give a brown liquid (88.5 mg, 81% yield).
N,N-dimethylaniline: (Table 1, Entry 8) (GC purity 99%); The typical procedure for the N,N-dimethylation of aniline was followed: 94 mg aniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (200 : 1) to give a brown liquid (94 mg, 77% yield).
4-methoxy-N-methoxylaniline: (Table 1, Entry 3) (GC purity 98%); The typical procedure for the N-methylation of 4-methoxylaniline was followed: 125 mg 4-methoxylaniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 6.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 24 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (130 : 1) to give a brown solid (103 mg, 74% yield).
4-methoxy-N,N-dimethoxylaniline: (Table 1, Entry 10) (GC purity 99%); The typical procedure for the N,N-dimethylation of 4-methoxylaniline was followed: 122 mg 4-methoxylaniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into an 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (185 : 1) to give a brown solid (123 mg, 82% yield).
1-(4-methoxyphenyl)-N,N-dimethylmethanamine: (Table 1, Entry 14) (GC purity 97%); The typical procedure for the N,N-dimethylation of (4-methoxyphenyl)methanamine was followed: 140 mg (4-methoxyphenyl)methanamine, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (5 : 1) to give a brown liquid (116 mg, 69% yield).
2-methyl-1,2,3,4-tetrahydroisoquinoline: (Table 2, Entry 8) (GC purity 97%); The typical procedure for the N-methylation of 1,2,3,4-tetrahydroisoquinoline was followed: 134 mg 1,2,3,4-tetrahydroisoquinoline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 24h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ ethyl acetate (5 : 1) to give a brown liquid (130 mg, 87% yield).
1,3-bis(1-methylpiperidin-4-yl)propane: (Table 2, Entry 12) (GC purity 97%); The typical procedure for the N-methylation of 1,3-di(piperidin-4-yl)propane was followed: 213 mg 1,2,3,4-tetrahydroisoquinoline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 24h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (3 : 1) to give a brown liquid (181 mg, 75% yield).
N-methylaniline: (Table 3, Entry 1) (GC purity 98%); The typical procedure for the N,N-dimethylation of nitrobenzene was followed: 125 mg nitrobenzene, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 170 °C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (200 : 1) to give a brown liquid (98 mg, 80% yield).
N-methylaniline: (Table 3, Entry 3) (GC purity 98%); The typical procedure for the
N,N-dimethylation of 1-methoxy-4-nitrobenzene was followed: 155 mg
1-methoxy-4-nitrobenzene, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL
autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced.
The reaction was reacted at 170 °C for 48 h under magnetic stirring. The title compound was
obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl
acetate (185 : 1) to give a brown liquid (125 mg, 82% yield).
1-(4-methoxyphenyl)-N,N-dimethylmethanamine: (Table 3, Entry 6) (GC purity 98%); The typical procedure for the N,N-dimethylation of 4-methoxybenzonitrile was followed: 135 mg 4-methoxybenzonitrile, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction was reacted at 170 °C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60°C)/ethyl acetate (5 : 1) to give a brown liquid (65 mg, 39% yield).