Supporting information

Ball-milling synthesized hydrotalcite supported Cu-Mn mixed oxide under solvent-free conditions: an active catalyst for aerobic oxidative synthesis of 2-acylbenzothiazoles and quinoxalines

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1. General Information

All reagents were purchased from commercial suppliers and used without further purification. Hydrophobic hydrotalcite (Mg$_6$Al$_2$(CO$_3$)(OH)$_{16}$·4H$_2$O, CAS No: 11097-59-9) was purchased from Sigma-Aldrich and used directly in the catalyst preparation. Hydrophilic HT was synthesized according to the literature procedure.[1] All experiments were carried out under air or using O$_2$ balloon. Flash chromatography was carried out with Merck silica gel 60 (200-300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. $^1$H NMR and $^{13}$C NMR (400 and 100 MHz respectively) spectra were recorded in CDCl$_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz.

The planetary ball mill (QM-3SP, Scheme S1) with 4 agate balling pots (100 mL) was purchased from Laibu Technology limited Company, China (website: http://www.nju-qm.com). The grinding is carried out in the agate balling pots containing agate balls with different sizes (5~15 mm diameter). When the pots rotate vigorously, the balls and the raw materials in pots go up along the pot wall under the centrifugal force and friction, and then free fall or roll down. The grinding of the raw is mainly due to the impact of the agate balls and the stripping effect.

Scheme S1. The planetary ball mill used in preparation of Cu-Mn/HT.
2. Catalysts preparation

**Cu-Mn/HT-W1 prepared via wet-impregnation.** 1.5 g of Cu(NO$_3$)$_2$·3H$_2$O (theoretical loading: 8wt% to HT) and 0.225 g of Mn(NO$_3$)$_2$·4H$_2$O (theoretical loading: 2wt% to HT) were dissolved into 40 mL of EtOH. 5 g of HT was added into the as-prepared mixed metal solution with stirring at room temperature. The mixture was stirred for 24 h. After that, the solution was removed by distillation under reduced pressure and the resulting solid was dried in oven at 80 °C for 5 h and calcined in muffle furnace at 350 °C for 2 h.

**Cu-Mn/HT-G prepared via physical grinding.** 1.5 g of Cu(NO$_3$)$_2$·3H$_2$O (theoretical loading: 8wt% to HT) and 0.225 g of Mn(NO$_3$)$_2$·4H$_2$O (theoretical loading: 2wt% to HT) and 5 g of HT were added to an agate mortar, and the mixture was grinded using a pestle by hand for 30 minutes. Then, the resulting powders were directly calcined in muffle furnace at 350 °C for 2 h.

3. Characterizations of materials

3.1. Analysis methods

Nitrogen adsorption-desorption measurements were performed at 76 K using an ASAP 2020M analyzer utilizing the BET model for the calculation of specific surface areas. The element contents of samples were determined by ICP-AES (ContrAA 700). The crystal phase and composition were determined by power X-ray diffraction using a X-Pert PRO X-ray diffractometer with Cu Ka radiation in the 2θ range of 10–90°. The morphologies of the samples were characterized by a TF20 transmission electron microscope and SM-5600LV or Quanta 250 FEG scanning electron microscope. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS Ultra DLD high performance electron spectrometer using nonmonochromatized Al Kα excitation source (hv = 1486.6 eV). Binding energies were calibrated by using the contaminant carbon (C 1s = 284.6 eV).
3.2. Characterizations of HT materials

From the XRD patterns, we can see that ball-milling did not change the crystal structure of original HT. Calcination at 350 °C would make HT release CO₂ and H₂O, which transfer it into MgO-Al₂O₃ oxides partially (Figure S1).[2] Moreover, from the SEM images of HT materials, ball-milling or calcination did not change its morphology and all HT materials exhibited uniform layered morphology (Figure S2).

![XRD patterns HT materials](image1)

**Figure S1.** XRD patterns HT materials.

![SEM images HT materials](image2)

**Figure S2.** SEM images of HT materials.
3.3. Characterizations of Cu-Mn/HT

The morphology of Cu-Mn/HT catalysts prepared by different methods was investigated by transmission electron microscope (TEM). From Figure S3, metal aggregation was obvious on Cu-Mn/HT-G, which might result from crude grinding by hand. In the case of Cu-Mn/HT-WI, well-dispersed metal particles were observed on the catalyst. Towards Cu-Mn/HT made by ball-milling, there is no obvious metal aggregation phenomenon and metal particles dispersed very well.

Figure S3. TEM images of Cu-Mn/HT-G (A and B), Cu-Mn/HT-WI (C and D) and Cu-Mn/HT (E and F).
X-ray photoelectric spectroscopy was employed to examine the surface properties of Cu and Mn of the catalysts. From Figure S4, there is no difference of metal oxidative state caused by preparation methods.

![Figure S4. XPS patterns of Cu 2p and Mn 2p of catalysts.](image)

4. Optimization of reaction conditions

Table S1. Optimization of oxidative synthesis of 2-acylbenzothiazole over different catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Metal wt% on HT</th>
<th>Oxidant</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
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<td></td>
<td></td>
<td>Cu</td>
<td>Mn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Cu/HT</td>
<td>2</td>
<td>-</td>
<td>O₂</td>
<td>12</td>
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<td>O₂</td>
<td>12</td>
</tr>
<tr>
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<td></td>
<td>H₂O₂</td>
<td>12</td>
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<tr>
<td>4</td>
<td>Cu-Mn/HT</td>
<td>8</td>
<td>1</td>
<td>O₂</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Cu-Mn/HT</td>
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<td>O₂</td>
<td>12</td>
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<tr>
<td>6</td>
<td>Cu-Mn/HT</td>
<td>8</td>
<td>2</td>
<td>H₂O₂</td>
<td>12</td>
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<tr>
<td>7</td>
<td>Cu-Mn/HT</td>
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<td>2</td>
<td>air</td>
<td>12</td>
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<tr>
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<td>2</td>
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<tr>
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<td>8</td>
<td>2</td>
<td>6</td>
<td>70</td>
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<tr>
<td>11</td>
<td>Cu-Mn oxide + HT</td>
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<td>2</td>
<td>O₂</td>
<td>12</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1a (0.2 mmol), 2a (0.2 mmol), catalyst (20 mg), EtOH (1 mL), 70 °C.
* NMR yields using anisole as internal standard.
* 50 uL of H₂O₂ was used.
* Under air (1 atm).
* Physical mixture of Cu-Mn oxide (5 mg) and HT (20 mg) was used.

5. **Hot filtration experiment**

Hot-filtration experiment between a-hydroxyacetophenone 1a and 2-aminothiophenol 2a was carried out. After the reaction performed for 2 h, the catalyst was removed by filtration from the reaction medium, and the NMR yield of 3a was roughly 45% of NMR yield. Meanwhile, the filtrate was kept running, and no more product was detected (Figure S5). The filtrate was further analyzed by ICP-AES, which shows that metal species, including Cu and Mn, were hardly observed.

![Figure S5. Reaction profiles.](image)

6. **Recycling experiment**

After each run, the catalyst was isolated by filtration and stirred in 0.5 M Na₂CO₃ solution under reflux conditions for 24 h. Next, the catalyst was filtrated from the solution and dried followed by calcination at 350 °C for 2 h for the next run. The reconstruction of HT occurs via a simple dissolution-reprecipitation mechanism.[2]
7. Spectrum data of products

benzothiazol-2-yl(phenyl)methanone$^{[3]}$ (3a)

Yellow solid, isolated yield 86%, m.p. 99-102 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.56 (d, $J$ = 8.4 Hz, 2H), 8.25 (d, $J$ = 7.6 Hz, 1H), 8.05 (d, $J$ = 8.4 Hz, 1H), 7.68 (t, $J$ = 7.6 Hz, 1H), 7.63-7.53 (m, 4H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 185.2, 167.0, 153.7, 136.9, 134.8, 133.8, 131.2, 128.4, 127.5, 126.8, 125.6, 122.1.

(5-chlorobenzothiazol-2-yl)(phenyl)methanone$^{[3]}$ (3b)

Yellow solid, isolated yield 90%, m.p. 125-127 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.55 (d, $J$ = 7.9 Hz, 2H), 8.24 (s, 1H), 7.94 (d, $J$ = 8.6 Hz, 1H), 7.69 (t, $J$ = 7.6 Hz, 1H), 7.61-7.50 (m, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 185.0, 168.9, 154.6, 135.2, 134.6, 134.2, 133.0, 131.3, 128.6, 128.3, 125.2, 123.1.

benzothiazol-2-yl(naphthalen-2-yl)methanone$^{[3]}$ (3c)

Yellow solid, isolated yield 82%, m.p. 166-168 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 9.39 (s, 1H), 8.48 (d, $J$ = 8.5 Hz, 1H), 8.34 (d, $J$ = 8.1 Hz, 1H), 8.12 (d, $J$ = 8.1 Hz, 1H), 8.07 (d, $J$ = 7.9 Hz, 1H), 8.01 (d, $J$ = 8.6 Hz, 1H), 7.95 (d, $J$ = 7.7 Hz, 1H), 7.67-7.56 (m, 4H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 185.0, 167.4, 153.9, 135.9, 134.4, 132.5, 132.1, 130.2, 129.0, 128.8, 128.3, 127.8, 127.6, 126.9, 126.7, 125.8, 125.7, 122.2.
benzothiazol-2-yl(4-bromophenyl)methanone\cite{3} (3d)

Yellow solid, isolated yield 88\%, m.p. 121-123 °C. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.48 \) (d, \(J = 8.5\) Hz, 2H), 8.24 (d, \(J = 8.0\) Hz, 1H), 8.01 (d, \(J = 8.1\) Hz, 1H), 7.70 (d, \(J = 8.6\) Hz, 2H), 7.62-7.56 (m, 2H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 184.1, 166.7, 153.7, 137.0, 133.5, 133.1, 132.5, 131.6, 131.2, 129.5, 124.8, 122.3\).

benzo[\(d\)]thiazol-2-yl(3-chlorophenyl)methanone\cite{3} (3e)

Yellow solid, isolated yield 85\%, m.p. 98-100 °C. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.50 \) (d, \(J = 8.5\) Hz, 2H), 8.26 (d, \(J = 8.1\) Hz, 1H), 8.04 (d, \(J = 7.7\) Hz, 1H), 7.73 (d, \(J = 8.2\) Hz, 2H), 7.66-7.57 (m, 2H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 184.1, 166.7, 153.8, 137.1, 133.6, 132.7, 132.2, 131.8, 129.5, 128.8, 127.8, 127.0, 125.8, 122.2\).

benzothiazol-2-yl(4-methoxyphenyl)methanone\cite{3} (3f)

Yellow solid, isolated yield 75\%, m.p. 99-102 °C. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.64 \) (d, \(J = 8.6\) Hz, 2H), 8.23 (d, \(J = 8.3\) Hz, 1H), 8.01 (d, \(J = 7.9\) Hz, 1H), 7.59-7.51 (m, 2H), 7.04 (d, \(J = 8.8\) Hz, 2H), 3.92 (s, 3H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 183.4, 167.9, 164.4, 153.8, 136.8, 133.8, 127.7, 127.4, 126.8, 125.5, 122.1, 113.9, 55.6\).

(5-chlorobenzothiazol-2-yl)(4-methoxyphenyl)methanone\cite{3} (3g)
Yellow solid, isolated yield 80%, m.p. 105-107 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.62 (d, $J$ = 7.6 Hz, 2H), 8.21 (s, 1H), 7.91 (d, $J$ = 8.4 Hz, 1H), 7.49 (d, $J$ = 8.4 Hz, 1H), 7.03 (d, $J$ = 7.6 Hz, 2H), 3.92 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 182.8, 169.7, 154.5, 135.0, 134.4, 132.8, 127.3, 123.0, 114.6, 114.1, 113.6, 113.2, 55.4.

benzothiazol-2-yl(thiophen-3-yl)methanone$^{[3]}$ (3h)

Yellow solid, isolated yield 65%, m.p. 99-102 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.81 (d, $J$ = 3.8 Hz, 1H), 8.28 (d, $J$ = 8.1 Hz, 1H), 8.04 (d, $J$ = 8.1 Hz, 1H), 7.88 (d, $J$ = 4.8 Hz, 1H), 7.63-7.57 (m, 2H), 7.31 (d, $J$ = 4.0 Hz, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 176.9, 166.5, 153.6, 139.7, 137.4, 137.0, 136.7, 128.2, 127.6, 126.9, 126.3, 122.3.

2-phenylquinoxaline$^{[4]}$ (5a)

Yellow solid, isolated yield 96%, m.p. 123-125 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 9.34 (s, 1H), 8.22-8.08 (m, 4H), 7.83-7.70 (m, 2H), 7.63-7.47 (m, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 151.8, 143.3, 142.2, 141.5, 136.7, 130.2, 130.1, 129.6, 129.5, 129.1, 129.1, 127.5.

3-phenylpyrido[3,4-b]pyrazine (5b)
White solid, isolated yield 95%, m.p. 134-136 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 9.57$ (s, 1H), 9.45 (s, 1H), 8.87 (d, $J = 5.7$ Hz, 1H), 8.25 (d, $J = 4.1$ Hz, 2H), 7.99 (d, $J = 5.6$ Hz, 1H), 7.62 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 155.8$, 154.2, 147.8, 145.0, 144.8, 136.6, 135.7, 131.3, 129.3, 128.0, 121.8.

2,3-diphenylquinoxaline$^4$ (5c)

[Image of 2,3-diphenylquinoxaline]

Yellow solid, isolated yield 95%, m.p. 92-95 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.19$ (dd, $J = 6.4$, 3.4 Hz, 2H), 7.77 (dd, $J = 6.4$, 3.4 Hz, 2H), 7.60-7.45 (m, 4H), 7.41-7.30 (m, 6H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 153.4$, 141.2, 139.0, 129.9, 129.8, 129.2, 128.8, 128.3.

2,3-bis(4-methoxyphenyl)quinoxaline$^4$ (5d)

[Image of 2,3-bis(4-methoxyphenyl)quinoxaline]

White solid, isolated yield 95%, m.p. 105-107 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.16$ (dd, $J = 6.2$, 3.4 Hz, 2H), 7.75 (dd, $J = 6.2$, 3.4 Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 4H), 6.92 (d, $J = 8.1$ Hz, 4H), 3.86 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 160.1$, 153.0, 141.0, 132.4, 131.6, 131.2, 129.0, 113.7, 55.3.

(2,3-diphenylquinoxalin-6-yl)(phenyl)methanone (5e)

[Image of (2,3-diphenylquinoxalin-6-yl)(phenyl)methanone]

White solid, isolated yield 92%, m.p. 99-102 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.59$ (s, 1H), 8.33 (s, 2H), 7.96 (d, $J = 7.7$ Hz, 2H), 7.68 (t, $J = 7.3$ Hz, 1H), 7.64-7.52 (m, 7H), 7.49-7.35 (m, 7H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 195.8$, 155.1, 154.6, 143.0, 140.1, 138.6, 138.5, 138.2, 137.1, 132.8, 132.5, 130.1, 129.9, 129.9, 129.8, 129.7, 129.4, 129.1, 128.6, 128.5, 128.4.

ethyl 2-oxo-2-phenylacetate$^5$ (6)
Colorless liquid, isolated yield 95%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.02 (d, $J$ = 7.3 Hz, 2H), 7.67 (t, $J$ = 7.4 Hz, 1H), 7.52 (t, $J$ = 7.7 Hz, 2H), 4.46 (q, $J$ = 7.1 Hz, 2H), 1.43 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 186.4, 163.7, 134.8, 132.4, 130.0, 128.8, 62.3, 14.1.

2,2'-disulfanediyldianiline$^6$ (7)

Yellow solid, isolated yield 95%, m.p. 90-92 °C. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.17-7.14 (m, 4H), 6.71 (d, $J$ = 8.4 Hz, 2H), 6.59 (t, $J$ = 7.1 Hz, 2H), 4.34 (s, 4H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 148.5, 136.7, 131.5, 118.6, 118.1, 115.1.

Reference:
8. Copy of $^1$H NMR and $^{13}$C NMR Spectra for Products
3c

3e