# **Supporting Information**

# Mechanochemical NaCl-Mediated Synthesis of Porous Cu<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub> Catalyst for Knoevenagel Condensation

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#### 1. Materials and methods

### 1.1 Materials.

Chemicals involved in the material synthesis were used directly without further purification if no specification. Copper(II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O; > 98%, Energy Chemicals), Sodium chloride (NaCl; AR, > 99.5%, Macklin Chemicals), Sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O; AR, Energy Chemicals), Malononitrile (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>; 98%, Aladdin), Benzaldehyde (C<sub>7</sub>H<sub>6</sub>O, 98%, Macklin), p-Tolualdehyde (C<sub>8</sub>H<sub>8</sub>O; 97%, Rhawn), p-Anisaldehyde (C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>; 98%, Aladdin), 4-Fluorobenzaldehyde (C<sub>7</sub>H<sub>5</sub>FO; 98%, Aladdin), 4-Chlorobenzaldehyde (C<sub>7</sub>H<sub>5</sub>ClO; 98%, Aladdin),4-Bromobenzaldehyde (C<sub>7</sub>H<sub>5</sub>BrO; 97%, Rhawn), 4-Nitrobenzaldehyde (C<sub>7</sub>H<sub>5</sub>NO<sub>3</sub>; 98%, dingchem), p-Hydroxybenzaldehyde (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>; 98%, Aladdin), Veratraldehyde (C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>; >99%, Macklin), Cinnamaldehyde (C<sub>9</sub>H<sub>8</sub>O; 97%, Rhawn), 1-napthaldehyde (C<sub>1</sub>H<sub>8</sub>O, 98%, Macklin), 2-formylofuran (C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>; 98%, Macklin)

#### **1.2 Experimental section**

In order to examine the universality of Cu<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub> in Knoevenagel condensation

reaction, another 11 different aromatic aldehyde substrates were employed under the same reaction conditions. 1 mmol aromatic aldehyde substrates and 1.2 mmol malononitrile were dissolved in 15 mL deionized water, then 15 mg  $Cu_xMo_{1-x}O_y$ -M as catalyst was added into the above reaction solution. After a period of stirring, the appropriate amount of the mixture was extracted with ethyl acetate and analyzed by GC to determine yield. The product was confirmed by <sup>1</sup>H-NMR.

## **1.3 Characterization**

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 focus diffraction spectrometer with Cu K $\alpha$  radiation (1.54056 Å). The diffraction data was collected with a 2 theta range from 10° to 80° with a scan rate of 6 degrees min<sup>-1</sup>. The Brunauer–Emmett–Teller surface area was investigated by N<sub>2</sub> adsorption-desorption isotherms measured at –196 °C using a Micromeritics TriStar II 3020 Version 3.02 analyzer. Before the measurements, the sample was degassed under vacuum at 180 °C for 5 h. Scanning electron microscopy (SEM) was carried out on a field emission scanning electron microscope (FESEM, Zeiss Gemini 500).High–angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) images were obtained using a Nion UltraSTEM 100 with a probe aberration correction.

**1.4 General Remarks.** <sup>1</sup>H spectra were recorded at 500 MHz using CDCl<sub>3</sub> or  $(CD_3)_2SO$  as solvents. Chemical shifts are reported as  $\delta$  values relative to internal chloroform multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*) are reported in Hertz (Hz). The product formation was monitored by <sup>1</sup>H NMR using aliquots containing the solvent mixture. All commercial reagents and solvents were obtained from the commercial provider and used without further purification.

# **2.Figures and Tables**

#### Table S1. The SSAs of Cu<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub>-M under different conditions

Entry	NaCl (g)	Washing	SSA
		time(min)	
1	1.2	5	61

2	1.2	10	111
3	1.2	30	135
4	1.2	60	116
6	0.6	30	96
7	2.4	30	88



Figure S1. The UV-vis spectrum of NaCl, CuCl<sub>2</sub>, NaCl+CuCl<sub>2</sub> (ball milling NaCl and CuCl<sub>2</sub>)

The UV-vis spectrum of NaCl, CuCl<sub>2</sub>, NaCl/CuCl<sub>2</sub> was shown in Figure S1. NaCl had no UV absorption from 200 nm to 800nm. CuCl<sub>2</sub> had UV absorption peaks at 200~400 nm and 600~800 nm, and the UV absorption peaks of NACl+CuCl<sub>2</sub> did not shift significantly, indicating that the chemical environment of Cu had not changed. Therefore CuCl<sub>x</sub> (x> 2) was absent.



Figure S2. XRD patterns of the Cu<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub>-M and Cu<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub>-M-300



**Figure S3.** N<sub>2</sub> adsorption-desorption isotherms of Fe<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub>-M; the corresponding pore size distribution obtained from the adsorption branch



Figure S4. XRD patterns of the Fe<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub>-M



Figure S5. N<sub>2</sub> adsorption-desorption isotherms of CaCO<sub>3</sub>

# **3.Analytical Data of Products**

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.91 (d, *J* = 7.5 Hz, 2H), 7.78 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H).



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.65 (s, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H).



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, 2H), 7.72 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H).



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.00 – 7.92 (m, 2H), 7.76 (s, 1H), 7.27 – 7.17

(m, 2H).



<sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 7.87 (d, J = 8.8 Hz, 2H), 7.74 (s, 1H), 7.53 (d, J = 8.8 Hz, 2H).



<sup>1</sup>H NMR (500 MHz, Chloroform-d) ,δ 7.78–7.76 (m, 2H), 7.73 (s, 1H), 7.70–7.67 (m, 2H).



<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.72 (s, 1H), 8.43 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 8.9 Hz, 2H).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 11.07 (s, 1H), 8.31 (s, 1H), 7.96 – 7.82 (m, 2H), 7.08 – 6.82 (m, 2H).



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.2 Hz, 2H), 7.35 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H).



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 3H), 7.51 – 7.43 (m, 3H), 7.29 (d, *J* = 3.4 Hz, 2H).

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 1.7 Hz, 1H), 7.52 (s, 1H), 7.34 (d, *J* = 3.8 Hz, 1H), 6.71 (dd, *J* = 3.8, 1.8 Hz, 1H).



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 8.26 (d, 1H), 8.09 (d, 1H), 7.94 (d, 2H), 7.68–7.59 (m, 3H).



**Figure S6.** <sup>1</sup>H NMR spectra of 2-benzylidenemalononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S7.** <sup>1</sup>H NMR spectra of 2-(4-methoxybenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S8.** <sup>1</sup>H NMR spectra of 2-(4-methylbenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



Figure S9. <sup>1</sup>H NMR spectra of 2-(4-fluorobenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on

Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S10.** <sup>1</sup>H NMR spectra of 2-(4-chlorobenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S11.** <sup>1</sup>H NMR spectra of 2-(4-bromobenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S12.** <sup>1</sup>H NMR spectra of 2-(4-nitrobenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S13.** <sup>1</sup>H NMR spectra of 2-(4-hydroxybenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: (CD<sub>3</sub>)<sub>2</sub>SO



**Figure S14.** <sup>1</sup>H NMR spectra of 2-(3,4-dimethoxybenzylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S15.** <sup>1</sup>H NMR spectra of 2-(3-phenylallylidene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S16.** <sup>1</sup>H NMR spectra of 2-(furan-2-ylmethylene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>



**Figure S17.** <sup>1</sup>H NMR spectra of 2-(naphthalen-1-ylmethylene)malononitrile. <sup>1</sup>H NMR was recorded on Bruker 500 MHz; Solvent: CDCl<sub>3</sub>