Supporting Information

# Facile Synthesis of CuMnO<sub>x</sub> Catalyst based on Mechanochemical Redox for Efficient and Stable CO Oxidation

Jiafeng Bao, Xiaolan Duan and Pengfei Zhang\*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240,

China

\*Corresponding Author:

Prof. Pengfei Zhang

(Phone: +86-21-54742893; Fax: +86-21-54742898; Email: chemistryzpf@sjtu.edu.cn)

# **1.** Catalysts Preparation

The copper manganese oxide obtained by Mechanochemical redox-based method was denoted as CuMnO<sub>x</sub>-MR. In a typical process, 2.9700 g of CuCl and 0.8000 g of NaOH were added to a stainless steel reactor (50 mL) along with 20 stainless steel balls (4×diameter 1.0 cm; 6×diameter 0.6 cm; 10×diameter 0.2 cm). The reactor was placed in a high-speed ball miller (MSK-SFM-3 DESK-TOP HIGH-SPEED VIBARTING BALL MILL) and the reactants were ball milled for 30 min at a frequency of 50 Hz. When the first ball milling finished, 1.5800 g of KMnO<sub>4</sub> was added to the reactor, the molar ratio of CuCl and KMnO<sub>4</sub> is 3:1. The mixture was ball milled for another 30 min, the resulting solids were washed in 80 mL deionized water for three times and dried in a vacuum oven at 100°C for 12 h. The Cu<sub>2</sub>Mn<sub>1</sub>O<sub>x</sub>-MR, Cu<sub>1</sub>Mn<sub>1</sub>O<sub>x</sub>-MR and Cu<sub>1</sub>Mn<sub>2</sub>O<sub>x</sub>-MR were fabricated following the procedure stated above, except changing the molar ratio of CuCl and KMnO<sub>4</sub> into 2:1, 1:1 and 1:2 respectively.

The copper manganese oxide obtained by the Sol-Gel method was denoted as  $CuMnO_x$ -SG. In a typical process, 2.7240g of Copper acetate, 1.2250 g of Manganese acetate and 1.0000 g of citric acid were added to 60 mL of deionized water. The mixture was stirred for 1 h at room temperature and then dried at 80°C for 12 h to obtain a sticky solid. Finally, the resulting solid was calcined at 350°C for 2 h in air condition.

Control samples obtained by solid-phase combustion were named as  $CuO_x$  and  $MnO_x$ . In a typical process, Copper acetate (Manganese acetate) was calcined at 350°C for 2 h with a heating rate of 5°C/min. After mortar grinding the  $CuO_x$  and  $MnO_x$  compound with 3:1 molar rate for 10 min, the  $3CuO_x \cdot MnO_x$ -MG was prepared. And the  $3CuO_x \cdot MnO_x$ -BM was obtained by ball milling the  $CuO_x$  and  $MnO_x$  samples with the same 3:1 molar ratio in the high-speed ball miller (MSK-SFM-3

### DESK-TOP HIGH-SPEED VIBARTING BALL MILL) for 30 min.

#### 2. Catalysts Characterization

X-ray diffraction (XRD) patterns of the catalyst were obtained on a D8 Advance Diffractometer with Cu K $\alpha$  (-10~168°) radiation. Each sample was scanned at a rate of 6° min<sup>-1</sup>, over a range of 2 $\theta$  from 20° to 70°.

Specific surface areas and the pore size distributions of the catalysts were obtained by  $N_2$  adsorption - desorption measured at the 77K on a Micromeritics TriStar II 3020 Version 3.02 analyzer. The catalysts were degassed under vacuum at 453K for 12 hours prior to testing. The specific surface areas were calculated from the isotherms using the BET method. The pore size distributions were visualized from the adsorption part according to the BJH model.

The actual copper and manganese contents in the CuMnO<sub>x</sub>-MR were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

Scanning Transmission Electron Microscopy (STEM) images of the CuMnO<sub>x</sub>-MR were obtained on a Talos F200X system which was equipped with a Super-X energy-dispersive X-ray analysis (EDX) device, operating at 200 kV.

X-ray Photoelectron Spectroscopy (XPS) was used to analyze the surface of CuMnO<sub>x</sub>-MR. All spectra were collected using Al K $\alpha$  radiation.

Field Emission Scanning Electron Microscope (FE-SEM) was applied to compare the surface morphology of CuMnO<sub>x</sub>-MR and CuMnO<sub>x</sub>-SG.

The Raman spectrum were measured through Senterra R200-L Dispersive Raman Microscope with 532 nm excitation wavelength.

Temperature-programmed reduction by hydrogen (H2-TPR) was tested on a Micromeritics

Autochem II 2920 instrument equipped with a thermal conductivity detector (TCD). The catalyst was pretreated in Ar at 300°C for 30 minutes and then cooled to room temperature. For TPR measurements, the temperature was raised from room temperature to 600°C with the heating rate of  $5^{\circ}$ C/min in 10 % H<sub>2</sub>/Ar.

# **3.** Catalytic Performance Test

Catalyst performance was evaluated in a fix-bed U-shaped quartz reactor at atmosphere pressure. 30 mg catalyst mixed with 100 mg quartz sand was used for each measurement under a flow rate of 10 mL min<sup>-1</sup>, which corresponds to a Gas Hourly Space Velocity (GHSV) of 20000 mL  $h^{-1}$  g<sup>-1</sup>. The feed gases contain 1vol % CO, 19.9vol % O<sub>2</sub> and 79.1vol % N<sub>2</sub>. The effluent gas was analyzed using an online gas chromatograph (GC2060), with an FID detector. The feed gase CO and product CO<sub>2</sub> can be detected in real time.

To evaluate the catalyst's resistance to water vapor, the feed gas was firstly passed into constant temperature water at 30°C, and then introduced into the catalyst bed.

In order to test the activity of the catalyst in the  $SO_2$  environment, the feed gas was mixed with  $SO_2$  before entering the U-shaped tube.

CO conversion was calculated using the following expression:

CO conversion =  $([CO]_{in} - [CO]_{out}) / [CO]_{in} \times 100$ 

[CO]<sub>in</sub> and [CO]<sub>out</sub> represent the inlet and outlet amount of CO.



Figure S1. The pore size distributions of CuMnO<sub>x</sub>-MR, CuMnO<sub>x</sub>-SG, CuO<sub>x</sub> and MnO<sub>x</sub>.



Figure S2. The XRD patterns of CuMnO<sub>x</sub>-MR, CuMnO<sub>x</sub>-SG, CuO<sub>x</sub> and MnO<sub>x</sub>.



**Figure S3.** Raman spectra of  $CuMnO_x$ -SG (top) and  $CuMnO_x$ -MR (bottom) using the 532 nm radiation for excitation.



Figure. S4 Catalytic performance of the  $CuMnO_x$ -MR,  $Cu_2Mn_1O_x$ -MR,  $Cu_1Mn_1O_x$ -MR and  $Cu_1Mn_2O_x$ -MR catalysts during CO oxidation reaction.



Figure. S5 O 1s XPS spectra of Cu MnO<sub>x</sub>-MR-100h reaction.



Figure S6. The SEM images of (a)  $CuMnO_x$ -MR and (b)  $CuMnO_x$ -MR-100h reaction.



**Figure S7.** The SEM images of (a) CuMnO<sub>x</sub>-MR and (b) CuMnO<sub>x</sub>-SG.

 Table S1 Comparison of CO catalytic activity over Cu-Mn catalysts.

Catalysis	The temperature of CO conversion at 90% (°C)
CuMnOx-MR (Our work)	140
Cu/CeO <sub>2</sub> -NC	1551
Cu <sub>2</sub> O	1502
CuO	225 <sup>3</sup>
Cu(5-methylisophthalate)	1504
MnO <sub>2</sub>	210 <sup>5</sup>
Mn <sub>3</sub> O <sub>4</sub> /CNT	2006
LaAl <sub>0.2</sub> Mn <sub>0.8</sub> O <sub>3</sub>	1707
Ce-Mn/Al <sub>2</sub> O <sub>3</sub> -873	1808

Table S2 Comparison of CO catalytic activity over CuMnO<sub>x</sub>-MR and noble metal catalysts.

Catalysis	The temperature of CO conversion at 90% (°C)
CuMnOx-MR (Our work)	140
Pd@SiO <sub>2</sub> -RM	1259
Pt-Ni(O)/SiO <sub>2</sub>	155 <sup>10</sup>
Au/Al <sub>2</sub> O <sub>3</sub>	15011
Au/TiO <sub>2</sub>	100 <sup>12</sup>

#### References

- M. Lykaki, E. Pachatouridou, S. A. C. Carabineiro, E. Iliopoulou, C. Andriopoulou, N. Kallithrakas-Kontos, S. Boghosian and M. Konsolakis, *Appl. Catal. B Environ.*, 2018, 230, 18-28.
- 2. B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro and S. O'Brien, *Nano Lett.*, 2006, **6**, 2095-2098.
- 3. M. F. Luo, J. M. Ma, J. Q. Lu, Y. P. Song and Y. J. Wang, J. Catal., 2007, 247, 127-127.
- 4. R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, J. Am. Chem. Soc., 2007, **129**, 8402-+.
- 5. G. Z. Chen, F. Rosei and D. L. Ma, *Adv. Funct. Mater.*, 2012, **22**, 3914-3920.
- 6. J. W. Xiao, L. Wan, X. Wang, Q. Kuang, S. Dong, F. Xiao and S. Wang, *J. Mater. Chem. A*, 2014, **2**, 3794-3800.
- 7. S. Cimino, L. Lisi, S. De Rossi, M. Faticanti and P. Porta, *Appl. Catal. B Environ.*, 2003, **43**, 397-406.
- 8. P. Venkataswamy, D. Jampaiah, F. J. Lin, I. Alxneit and B. M. Reddy, *Appl. Surf. Sci.*, 2015, **349**, 299-309.
- J. Ying, H. Peng, X. Xu, R. Wang, F. Yu, Q. Sun, W. Liu, Z. Gao and X. Wang, *Catal. Sci. Technol.*, 2016, 6, 5405-5414.
- 10. W. Liu, L. Zhang, T. Dong, H. Peng, Z. Wang, N. Zhang, X. Wang and P. Wu, *Chemcatchem*, 2018, **10**, 4134-4142.
- 11. R. Lu, L. He, Y. Wang, X.-Q. Gao and W.-C. Li, *Chin. J. Catal.*, 2020, **41**, 350-356.
- 12. H. Schreyer, R. Eckert, S. Immohr, J. de Bellis, M. Felderhoff and F. Schuth, *Angew. Chem. Int. Ed.*, 2019, **58**, 11262-11265.