# Single-ion copper doping greatly enhances catalytic activity

# of manganese oxides via electronic interactions †

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## **Experimental Section**

### 1.1. Catalyst Preparation.

Cu<sub>1</sub>/MnO<sub>2</sub> was synthesized via solid-phase reaction. In brief, KMnO<sub>4</sub> (0.79 g, 0.005 mol), MnSO<sub>4</sub>·H<sub>2</sub>O (1.2675 g, 0.0075 mol) and CuSO<sub>4</sub>·5H<sub>2</sub>O (1.25 g, 0.005 mol) sieved through 40-80 mesh were ground in a mortar quickly with the addition of 1-2 drops of water till the solids were almost dry. Then the steps of adding deionized water and grinding were repeated till all the solids in the mortar turned into brownish black. The obtained solids were washed with deionized water till the filtrate was colorless, dried at 110 °C for 12 h, and then calcined at 400 °C for 4 h in a mu  $\Box$  e furnace. The synthesis of  $\alpha$ -MnO<sub>2</sub> followed the similar procedure as Cu<sub>1</sub>/MnO<sub>2</sub>, while the chemical reagents were KMnO<sub>4</sub> (0.79 g, 0.005 mol) and MnSO<sub>4</sub>·H<sub>2</sub>O (1.2675 g, 0.0075 mol). CuO/MnO<sub>2</sub> series catalysts were prepared using the conventional incipient wetness method. Typically, $\alpha$ -MnO<sub>2</sub> mass ratio of 3.79%, 5.69%, or 7.58%. The slurry was heated in a water bath at 80 °C to remove the water. The obtained solids were dried and then calcined at 400 °C for 4 h in a mu  $\Box$  e furnace. CuO was purchased from Sinopharm Chemical Reagent Co., Ltd.

#### 1.2. Catalyst Characterization.

Powder X-ray di  $\Box$  raction (XRD) experiments were carried out on an X-ray di  $\Box$  ractometer (Rigaku D/Max 2500 v/PC) with a graphite monochrometer and Cu  $K\alpha$  radiation ( $\lambda = 0.15418$  nm), with the voltage of 40 kV and current of 40 mA. X-ray absorption near-edge structure (XANES) spectra and extended X-ray absorption fine structure (EXAFS) spectra at Mn *K*-edge, Cu *K*-edge were obtained at BL14W of SSRF with an electron beam energy of 3.5 GeV and a ring current of 200-300 mA. The soft-X-ray absorption spectra at the Cu *L*-edge were obtained in total electron yield (TEY) mode at BL08U1A of the SSRF. Transmission electron microscopy (TEM) images and high resolution TEM (HRTEM) images were obtained using a JEOL JEM-2100F transmission electron microscope (JEOL Company, Tokyo, Japan). X-ray photoelectron spectroscopic (XPS) data were collected on an ESCALAB 250

multifunctional X-ray photoelectron spectroscopy instrument (Thermo Fisher) with a monochromatic Al-*K*a X-ray source (hu = 1486.6 eV). The experiments of temperature-programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR) and temperature-programmed desorption of O<sub>2</sub> (O<sub>2</sub>-TPD) were performed on an AutoChem II 2920 chemical adsorption instrument (Micromeritics, USA) with a thermal conductivity detector (TCD). In each measurement, the sample was pretreated at 300 °C for 2 h to remove the substances physically adsorbed on surface. Then the sample was reduced by increased the temperature linearly from 50 °C to 800 °C at a heating rate of 10 °C/min in a 10 vol% H<sub>2</sub>/Ar atmosphere. For O<sub>2</sub>-TPD experiments, after the sample adsorb O<sub>2</sub> excessively under the atmosphere of 10 vol% O<sub>2</sub>/He, the temperature was increased from 50 °C to 800 °C at a heating rate of sand contents of catalysts were obtained from X-ray Fluorescence Spectrometer (XRF) on a Bruker-AXS S4 Explorer. The specific surface areas of catalysts were measured by N<sub>2</sub> adsorption at -196 °C using an ASAP 2460 (USA, Micromeritics) automated gas sorption system.

### 1.3. Catalytic Evaluation.

CO oxidation was carried out in a fixed-bed quartz reactor. Prior to each test, 200 mg powder catalysts were pressed into blocks, crushed into particles and sieved to 40-60 mesh. The reaction conditions without H<sub>2</sub>O were set as follows: the total flow rate was 50 mL/min, including 1.0 vol% CO, 21.0 vol% O<sub>2</sub> and N<sub>2</sub> as balance gas. When water vapor was present, due to the limitations of the experimental gas distribution system, the total flow rate was still 50 mL/min, including 0.7 vol% CO, 13.9 vol% O<sub>2</sub>, water vapor 5.0 vol% and N<sub>2</sub> as balance gas. The reaction temperature increased from below room temperature to about 200 °C with a heating rate of 1 °C/min. For testing under water vapor, the saturated water vapor was obtained by passing a part of N<sub>2</sub> through a reservoir containing deionized water at 54 °C. Then the saturated water vapor was mixed with remaining gas components before entering the reactor. Moreover, the concentrations of CO and CO<sub>2</sub> were monitored by an on-line Agilent 7890B gas chromatograph equipped with the TCD and FID detectors. The X<sub>CO</sub> was calculated as:

$$X_{CO} = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100\%$$

where  $CO_{in}$  and  $CO_{out}$  are the inlet concentration and outlet concentration of CO, respectively.

**Figures and Tables** 



Fig. S1. TEM and HTEM images of  $\alpha$ -MnO<sub>2</sub> (a, b, c). c: an enlargement of the selected area in (b).



Fig. S2. TEM and HTEM images of  $Cu_1/MnO_2$  (a, b, c).



**Fig. S3.** Cu  $L_3$ -edge soft-X-ray absorption spectra of CuO and Cu<sub>1</sub>/MnO<sub>2</sub>.



Fig. S4. Mn 2p XPS data of  $\alpha$ -MnO<sub>2</sub> and Cu<sub>1</sub>/MnO<sub>2</sub>.



Fig. S5. O 1s XPS spectra of  $\alpha$ -MnO<sub>2</sub> and Cu<sub>1</sub>/MnO<sub>2</sub>.



**Fig. S6.** *R*-space EXAFS spectra ( $\Delta k = 2-10.396 \text{ Å}^{-1}$ ) and inverse FT EXAFS spectra ( $\Delta r = 1.0-5.0 \text{ Å}$ ) at the Cu *K*-edge of Cu<sub>1</sub>/MnO<sub>2</sub>, CuO, and Cu<sub>2</sub>O with the  $k^2$  weight.



**Fig. S7.** *R*-space EXAFS spectra ( $\Delta k = 2-10.396 \text{ Å}^{-1}$ ) and inverse FT EXAFS spectra ( $\Delta r = 1.0-5.0 \text{ Å}$ ) at the Mn *K*-edge of  $\alpha$ -MnO<sub>2</sub> with the  $k^2$  weight.



**Fig. S8.** (a) XANES spectra and (b) pre-edge absorption spectra of  $Cu_1/MnO_2$ , CuO,  $Cu_2O$ , and Cu foil at Cu *K*-edge.



**Fig. S9.** (a) XANES spectra of  $\alpha$ -MnO<sub>2</sub> at the Mn *K*-edge.



Fig. S10. The local structure models of Cu in  $Cu_2O$ , CuO, and  $Cu_1/MnO_2$ .



**Fig. S11.** (a)  $X_{CO}$  and (b) *R* based on the unit content of Cu over Cu<sub>1</sub>/MnO<sub>2</sub> and CuO/MnO<sub>2</sub> series catalysts at 22 °C. Reaction condition: CO = 1%, O<sub>2</sub> = 21%, N<sub>2</sub> balance, flow rate = 50 mL/min, 200 mg catalyst with sizes of 40~60 mesh.



Fig. S12. VB-XPS data of  $\alpha$ -MnO<sub>2</sub> and Cu<sub>1</sub>/MnO<sub>2</sub>.



**Fig. S13.** H<sub>2</sub>-TPR profiles of  $\alpha$ -MnO<sub>2</sub> and Cu<sub>1</sub>/MnO<sub>2</sub>. 3% refers to the percentage of surface active oxygen (which can participate on CO oxidation) in total lattice oxygen.



Fig. S14. O<sub>2</sub>-TPD results of  $\alpha$ -MnO<sub>2</sub> and Cu<sub>1</sub>/MnO<sub>2</sub>.



**Fig. S15.** Mn  $L_3$ -edge soft-X-ray absorption spectra of Cu<sub>1</sub>/MnO<sub>2</sub> before and after CO oxidation.



Fig. S16. H<sub>2</sub>O resistance of  $\alpha$ -MnO<sub>2</sub> and Cu<sub>1</sub>/MnO<sub>2</sub>. Reaction condition: 90 °C, CO = 0.7%, O<sub>2</sub> = 13.9%, H<sub>2</sub>O = 5.0%, N<sub>2</sub> balanced, flow rate = 50 mL/min, catalyst 0.2 g, 40-60 mesh.

Samples	Elements (%)			Formula	-S (m <sup>2</sup> c <sup>-1</sup> )	
	Mn	Cu	K		$S_{\text{BET}}$ (III <sup>2</sup> g <sup>2</sup> )	
$\alpha$ -MnO <sub>2</sub>	54.10	-	1.95	K <sub>0.05</sub> MnO <sub>2</sub>	141	
Cu <sub>1</sub> /MnO <sub>2</sub>	57.40	3.79	1.21	K <sub>0.03</sub> Cu <sub>0.06</sub> MnO <sub>2</sub>	133	

 Table S1. The composition and surface areas of catalysts.

Samples	Shell	CN <sup>[b]</sup>	$R^{[c]}/\text{\AA}$	$\sigma^{2[d]}$ / Å <sup>2</sup>	$\Delta E_0^{[e]} / eV$	R-factor
Cu <sub>1</sub> /MnO <sub>2</sub>	Cu-O	6	1.88(3)	0.011(6)	-2.4	0.012
CuO	Cu-O	4	1.94(7)	0.007(5)	5.3	0.003
	Cu-O	2	2.78(6)	0.033(3)	1.0	0.003
	Cu-Cu	4	2.90 (3)	0.001(5)	8.0	0.003
	Cu-Cu	6	3.05(4)	0.042(9)	0.5	0.003
Cu <sub>2</sub> O	Cu-O	4	1.82(2)	0.003(2)	2.6	0.008
	Cu-Cu	8	2.97(6)	0.021(2)	9.0	0.008
	Cu-O	12	3.53(0)	0.047(4)	7.6	0.008
	Cu-Cu	8	3.59(4)	0.035(9)	7.0	0.008

**Table S2.** EXAFS parameters at the Cu *K*-edge of Cu<sub>1</sub>/MnO<sub>2</sub>, CuO, and Cu<sub>2</sub>O with the  $k^2$  weight.<sup>[a]</sup>

[a] *R*-space fit,  $\Delta k = 2-10.396 \text{ Å}^{-1}$ ,  $\Delta r = 1-5 \text{ Å}$ ;

[b] CN, coordination number;

[c] *R*, distance between absorber and backscatter atoms;

[d]  $\sigma^2$ , Debye-Waller factor;

[e]  $\Delta E_0$ , energy shift.

Samples	Shell	CN <sup>[b]</sup>	$R^{[c]}/\text{\AA}$	$\sigma^{2[d]}$ / Å <sup>2</sup>	$\Delta E_0^{[e]} / eV$	R-factor
α-MnO <sub>2</sub>	Mn-O	6	1.90(5)	0.005(7)	2.1	0.00087
	Mn-Mn	4	2.84(7)	0.007(6)	-5.0	0.00087
	Mn-O	6	3.38(6)	0.164(3)	5.2	0.00087
	Mn-Mn	4	3.45(4)	0.003(9)	-4.9	0.00087

**Table S3.** EXAFS parameters at the Mn *K*-edge of  $\alpha$ -MnO<sub>2</sub> with the  $k^2$  weight.<sup>[a]</sup>

[a] *R*-space fit,  $\Delta k = 2-10.396 \text{ Å}^{-1}$ ,  $\Delta r = 1-5 \text{ Å}$ ;

[b] CN, coordination number;

[c] *R*, distance between absorber and backscatter atoms;

[d]  $\sigma^2$ , Debye-Waller factor;

[e]  $\Delta E_0$ , energy shift.