

Electronic Supplementary Information

Intergrowth Effect of CuO- γ -Al₂O₃ Mixed Oxides

Bin Li,^{*a} Guangzhou Jin,^b Junbin Gao,^b Rusong Zhao,^b Lihui Dong,^{*a} and Yanjun Gong^c

^a School of Chemistry and Chemical Engineering, Guangxi Key Laboratory Petrochemical Resource Processing and Process Intensification Technology, Guangxi University, Nanning 530004, China

E-mail: binli@gxu.edu.cn

^b School of Chemistry and Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China

^c School of Chemistry and Chemical Engineering, China University of Petroleum, Beijing 102249, China

Experimental Section

Preparation of the samples

All of the samples were prepared by IACP method.^[1,2] In a typical synthesis, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (A.R. aladdin) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (A.R. aladdin) were dissolved in deionized water, both at 2.00 molL^{-1} . Mixed solutions with different molar ratio of Cu/Al (100/0, 90/10, 80/20, 70/30, 60/40, and 0/100) were prepared by mixing the above solutions. Citric acid (A.R. aladdin) was added to the solution such that the molar ratio of citric acid to total amount of metal ions was 2:1. After the citric acid was dissolved, the solution was stirred overnight. Carbon black (Cabot VXC-72, overall surface area of $254 \text{ m}^2\text{g}^{-1}$) was added to soak up the solution. The mixture was dried at 373 K, ground into a fine powder, decomposed at 533 K, and calcined at 973 K under air flow for 3 h. The products were black powder. Samples expressed as $\text{Cu}_m\text{Al}_n\text{O}$, which m:n for the Cu:Al atomic ratio.

Characterization

Powder X-ray diffraction data was collected at room temperature on a Rigaku D/max-rA diffractometer with Cu $\text{K}\alpha$ radiation and graphite monochromator. The measurement conditions were 40 KV and 120 mA. Step-scans were taken over the range of 2θ from 25° to 80° in steps of 0.02° and the intensities data for each was collected for 2 s for phase identification. The lattice parameters were refined by Full-proful 2000.^[3,4]

^{27}Al ^{63}Cu ^{65}Cu magic angle spinning nuclear magnetic resonance experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer equipped with a Chemagnetic double-resonance 4-mm probe. The samples were packed into a ZrO_2 NMR rotor (4 mm o.d.) with a Kel-F endcap. The resonance frequency was 104.26 MHz for ^{27}Al , the excitation pulse length was adjusted to $\pi/12$, the pulse duration was 0.5 s for ^{27}Al single-pulse experiments. The ^{27}Al chemical shift was referenced to a 0.1 molL^{-1} $\text{Al}(\text{NO}_3)_3$ solution. The MAS spinning speed was 11 kHz.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versaprobe system, using monochromatic Al $\text{K}\alpha$ radiation (1486.6 eV). All binding

energies (BE) were referenced to the C 1s peak at 285.0 eV.

The TPR analysis of samples was tested by a FINESORB-3010 temperature-programmed chemisorption analyzer. The 0.1 g samples (between 40-60 mesh) was charged into the U type quartz reactor, was pretreated at 700 °C for 2 h, and was cooled to room temperature. H₂/Ar(5%v) was used to purge the samples until the baseline was stable. The TPR analysis started at 120 °C and ended at 700 °C. The heating rate was 2 °Cmin⁻¹. The TPR signal was detected by a thermal conductivity detector.

The measurement of CO oxidation was carried out on a fixed quartz bed micro-reactor. The powder samples were pressed into tablet under 2 MPa and then crashed into small pieces for meshing. The 20.0±0.1 mg samples (between 40-60 mesh) were mixed with 2 g quartz (between 40-60 mesh) and the mixture was charged into the U type quartz reactor (6.0 mm i.d) with a sieve-plate. The bed temperature was controlled in the range ±0.5 K. The mixture gas was CO 6.0% (v/v) and O₂ 3.6% with He as balance. The hourly space velocity was 20000 h⁻¹. When temperature reached what we required, the mixture gas was introduced into the reactor. After 1 h, the response of left CO signal was recorded used GC-7890T gas chromatograph (Shanghai Tianmei Instrument Co. Ltd., China). Sampling was repeated five times and the results were averaged. The conversion of CO oxidation was calculated by taking the average value and using the following formula:

$$\text{CO conversion \%} = (1-A/A_0) \times 100\%$$

A was the area of left CO after reaction (μV·s); A₀ was the area of CO of blank analysis (μV·s); T₉₀ was the temperature when the conversion of CO was 90%.

Results and discussion

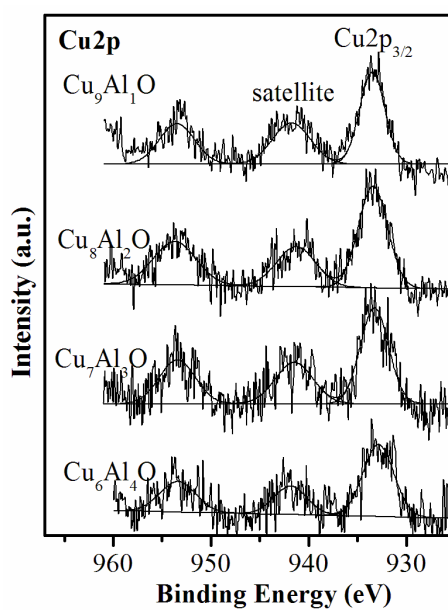


Figure S1 Cu 2p XPS spectra of Cu-Al-O samples

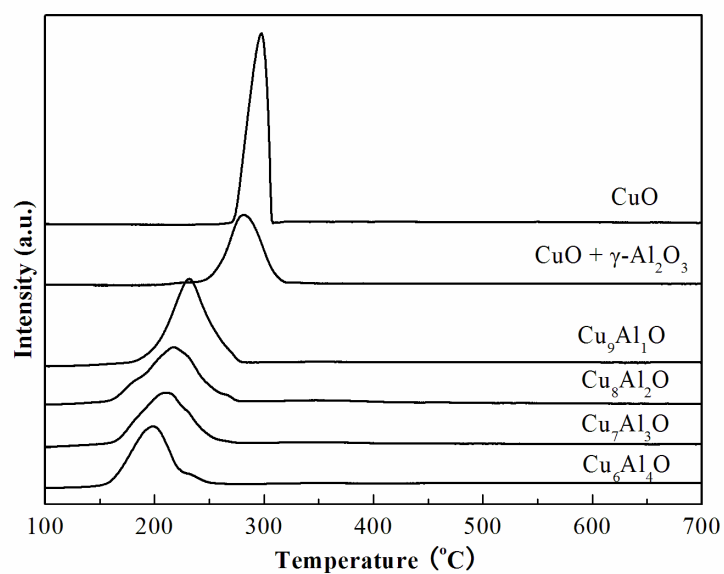


Figure S2 TPR profiles of Cu-Al-O samples and the mechanically mixed CuO + γ -Al₂O₃ sample.

Table S1 Structural parameters of CuO in Cu-Al-O samples

Sample	Lattice parameter				Lattice volume (Å ³)
	a (Å)	b (Å)	c (Å)	β (°)	
CuO	4.6865 (14)	3.4250 (5)	5.1324 (10)	99.4266 (127)	81.27 (0.02)
Cu ₉ Al ₁ O	4.6875 (7)	3.4248 (3)	5.1305 (5)	99.5051 (67)	81.23 (0.01)
Cu ₈ Al ₂ O	4.6941 (18)	3.4284 (6)	5.1353 (13)	99.5311 (63)	81.50 (0.03)
Cu ₇ Al ₃ O	4.6979 (25)	3.4297 (8)	5.1369 (17)	99.5416 (221)	81.62 (0.04)

Cu₆Al₄O 4.6956 (27) 3.4289 (9) 5.1349 (18) 99.5286 (237) 81.54 (0.04)

Table S2 Crystallographic parameters corrected by Rietveld for the Cu-Al-O

Item	Value				
Sample	CuO	Cu ₉ Al ₁ O	Cu ₈ Al ₂ O	Cu ₇ Al ₃ O	Cu ₆ Al ₄ O ^[b]
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	C 2/C (No.15)	C 2/C (No.15)	C 2/C (No.15)	C 2/C (No.15)	C 2/C (No.15)
a/nm	0.46817 (1) ^[a]	0.46826 (1)	0.46833 (1)	0.46838 (1)	0.46840 (1)
b/nm	0.34227 (1)	0.34237 (1)	0.34238 (1)	0.34240 (1)	0.34240 (1)
c/nm	0.51292 (1)	0.51294 (1)	0.51298 (1)	0.51296 (1)	0.51316 (1)
β/degree	99.4434 (6)	99.4310 (5)	99.4708 (5)	99.4678 (5)	99.4642 (6)
Wavelength(Cu-Kα)					
λ(Kα1)/nm	0.15406	0.15406	0.15406	0.15406	0.15406
Wavelength(Cu-Kα)					
λ(Kα2)/nm	0.15443	0.15443	0.15443	0.15443	0.15443
I(Kα2)/I(Kα1)	0.5	0.5	0.5	0.5	0.5
Range of 2θ (°)	30-78	30-78	30-78	30-78	30-78
Step width of 2θ (°)	0.01	0.01	0.01	0.01	0.01
Number of points	4801	4801	4801	4801	4801
Number of restraints	0	0	0	0	0
Number of structural variables	13	13	13	13	13
Peak profile	Split pseudo-voigt	Split pseudo-voigt	Split pseudo-voigt	Split pseudo-voigt	Split pseudo-voigt
	Linear	Linear	Linear	Linear	Linear
Background correction	interpolation of background points	interpolation of background points	interpolation of background points	interpolation of background points	interpolation of background points
R _F	0.033	0.033	0.029	0.032	0.037
R _{Bragg}	0.027	0.029	0.025	0.030	0.028
R _P	0.097	0.078	0.088	0.081	0.086
R _{WP}	0.083	0.072	0.077	0.073	0.075
R _{exp}	0.056	0.056	0.057	0.054	0.054

^a The estimated standard deviation (ESD) of the least significant figure is given in parentheses. R_F—structure deviation factor, R_{Bragg}—Bragg deviation factor, R_P—pattern deviation factor, R_{WP}—weighted pattern deviation factor, R_{exp}—expected deviation factor. ^b Rietveld refinement for two phases.

Table S3 Structural parameters of CuO crystalline in CuO the and Cu-Al-O

Sample	Atom	Wyckoff. Position	x ^a	y ^a	z ^a	Population parameter	U×100
CuO	Cu	4c	0.2500	0.0000	0.2500	0.5000	0.6
	O	4e	0.0000	0.4260 (1) ^b	0.2500	0.5000	2.8
Cu ₉ Al ₁ O	Cu	4c	0.2500	0.0000	0.2500	0.5000	0.4
	O	4e	0.0000	0.4265 (1)	0.2500	0.5000	1.8
Cu ₈ Al ₂ O	Cu	4c	0.2500	0.0000	0.2500	0.5000	0.4
	O	4e	0.0000	0.4260 (1)	0.2500	0.5000	1.8
Cu ₇ Al ₃ O	Cu	4c	0.2500	0.0000	0.2500	0.5000	0.2
	O	4e	0.0000	0.4286 (1)	0.2500	0.5000	0.8
Cu ₆ Al ₄ O	Cu	4c	0.2500	0.0000	0.2500	0.5000	0.6
	O	4e	0.0000	0.4324 (1)	0.2500	0.5000	1.6

^a x, y, z: fractional coordinate; Population parameters: defined as atom numbers of atoms per unit cell; The thermal parameters are U/nm². ^b The ESD of the least significant figure is given in the parentheses.

Table S4 Bond lengths of Cu ions in the Cu-Al-O

Sample	Atom	Bond lengths (nm)
CuO	Cu-O (1) ^a	0.1967 (1) ^b
	Cu-O (2)	0.1937 (1)
Cu ₉ Al ₁ O	Cu - O (1)	0.1968 (1)
	Cu-O (2)	0.1936 (1)
Cu ₈ Al ₂ O	Cu-O (1)	0.1969 (1)
	Cu-O (2)	0.1936 (1)
Cu ₇ Al ₃ O	Cu-O (1)	0.1971 (1)
	Cu-O (2)	0.1932 (1)
Cu ₆ Al ₄ O	Cu-O (1)	0.1975 (1)
	Cu-O (2)	0.1925 (1)

^a The serial number of the atoms. ^b The ESD of the least significant figure is given in the parentheses.

References:

1 N. Li, X. M. Yan, W. J. Zhang, B. X. Lin, *J. Power. Sources* **1998**, *74*, 255-258.

- 2 N. Li, X. Xu, D. Luo, Y. S. Wu, S. J. Li, B. X. Lin, *J. Power. Sources* **2004**, *126*, 229-235.
- 3 T. Roisne, J. R. Carvajal, *Mater. Sci. Forum. European Power Diffraction Conference (EPTIC 7)*, **2001**, *378-381*, 118-123.
- 4 M. G. Fan, B. Li, F. Y. Zhang, J. L. Fang, W. L. Li, J. M. Xing, Z. L. Liu, *Chinese J. Catal.* **2009**, *30*, 1041-1048.