

## Supplementary Information

### **A-site defective $\text{La}_{2-x}\text{CuO}_4$ perovskite-type oxide catalysts for efficient oxidation of cyclohexylbenzene**

Yanlin Xiao<sup>#</sup>, Lingyu Zhong<sup>#</sup>, Guoli Fan, Feng Li \*

*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

\*Corresponding authors: Email: lifeng@mail.buct.edu.cn (F. Li).

<sup>#</sup> Y. Xiao and L. Zhong contributed equally to this work.

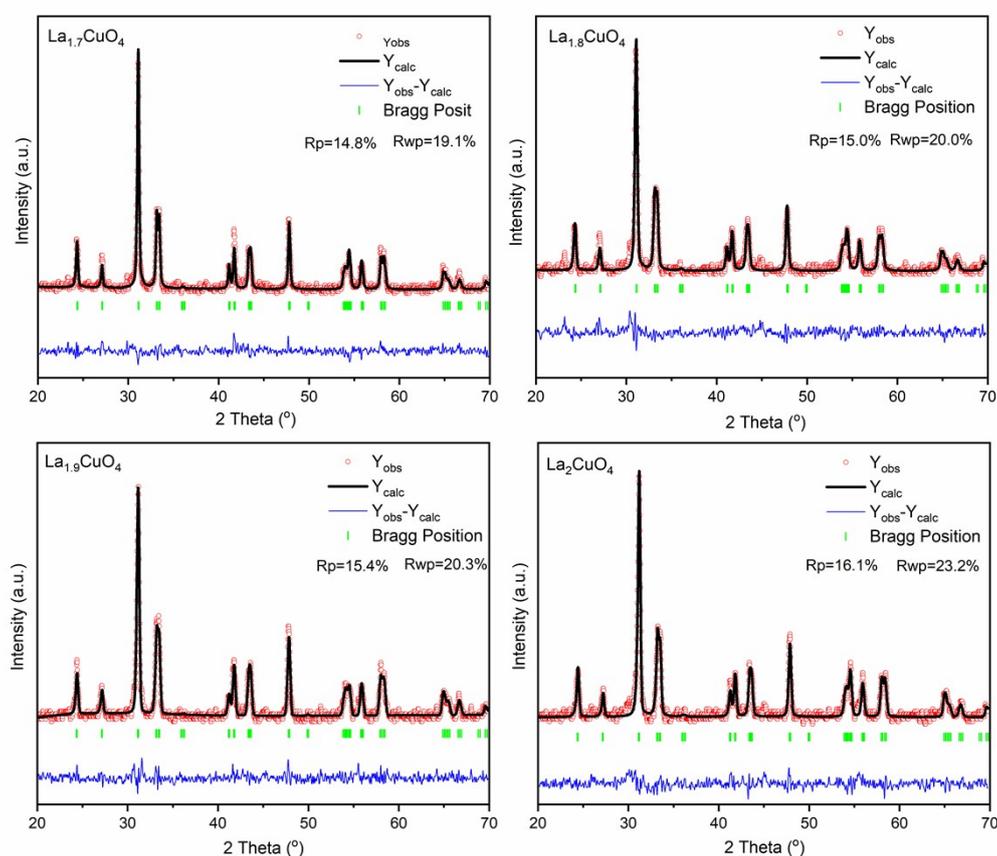
## Sample characterizations

X-ray diffraction patterns (XRD) of samples were obtained using a Shimadzu XRD-6000 diffractometer using the Cu K $\alpha$  radiation. Metal contents in samples were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES) using nitrohydrochloric acid to dissolve samples. Low temperature nitrogen adsorption–desorption experiments were conducted using a Micromeritics ASAP 2020 sorptometer apparatus. Before measurements, all samples were purged at 250 °C under a vacuum for 1 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and pore size analysis was performed by BJH method based on desorption branches of the nitrogen sorption isotherms. The morphology and microstructure of all samples were analyzed by scanning electron microscopy (SEM, Zeiss Supra 55). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected on JEOL 2100 transmission electron microscope. Photoluminescence (PL) emission experiments were conducted using Shimadzu RF-6000 fluorescence spectrophotometer with excitation wavelength 255 nm, Electron paramagnetic resonance (EPR) spectra was attained on a Bruker ESP300E spectrometer at room temperature. X-ray photoelectron spectra (XPS) and X-ray-induced Auger electron spectra (XAES) were collected on Thermo VG ESCALAB250 X-ray photoelectron spectrometer using the Al K $\alpha$  radiation (1486.6 eV photons). All of the binding energies were corrected by the C 1s binding energy of 284.6 eV. CHB temperature-programmed desorption (CHB-TPD) were performed on Micromeritics AutoChem II 2920. Before characterization, the sample (100 mg) was immersed into a dichloromethane solution containing CHB for two days. Afterwards, the sample was pretreated under Ar flow at 25 °C for 1 h and heated from the 50 °C at a 10 °C min<sup>-1</sup> rate. Temperature-programmed desorption of O<sub>2</sub> (O<sub>2</sub>-TPD) and temperature-programmed decomposition (TPDE) experiments were conducted on Micromeritics AutoChem II 2920. For O<sub>2</sub>-TPD, the sample (100 mg) was pretreated in an Ar flow at 500 °C for 2 h and cooled to 50 °C in an O<sub>2</sub> atmosphere for 1 h, and then physically adsorbed gases were removed in the pure He atmosphere for 1 h. The signal was collected from 50 to 600 °C at 10 °C·min<sup>-1</sup> with O<sub>2</sub> desorption. For TPDE, the sample (100 mg) was degassed under Ar flow at 300 °C for 2 h. Afterward, the temperature was raised from 50 to 600 °C under Ar flow at a ramping rate of 10°C min<sup>-1</sup>. In addition, O<sub>2</sub>-TPD experiments using mass spectrometer detector (UK HIDEN QIC-20) also were carried out

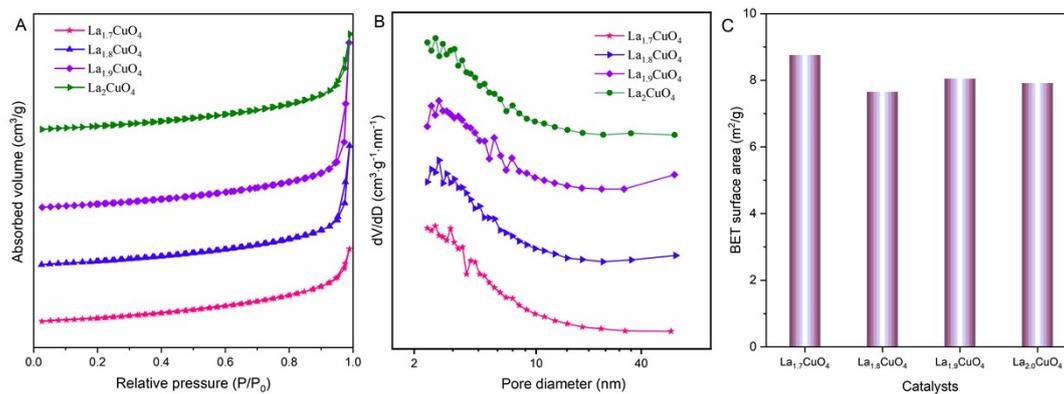
under the identical procedure to that for O<sub>2</sub>-TPD experiments using TCD detector.

*In-situ* diffuse reflectance infrared Fourier transform (DRIFT) spectra of pre-adsorbed CHB over samples were recorded using a BRUKER TENSOR II spectrometer equipped with an MCT narrow-band detector. First, 50 mg self-supporting sample wafer was soaked in a dichloromethane solution containing CHB for two days and then dried at 25 °C under vacuum for 12h. Afterwards, the wafer was purged with an Ar gas flow of 50 ml·min<sup>-1</sup> at 50 °C for 4 h, and then series of DRIFT spectra of CHB pre-adsorbed were collected under O<sub>2</sub>/N<sub>2</sub> mixture gas (v/v,5:95) at different temperatures.

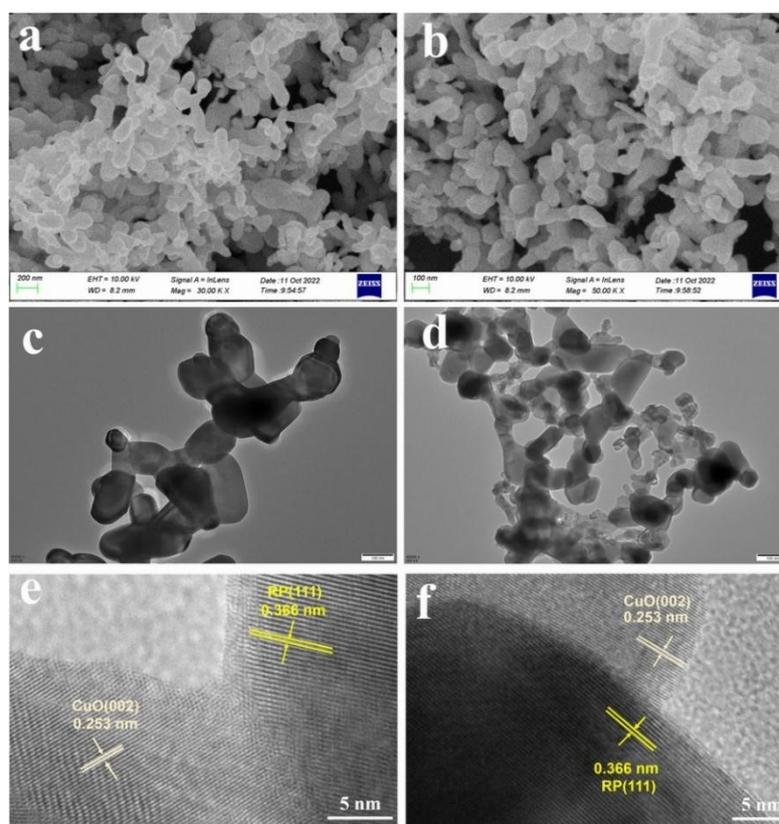
## Figures and Tables



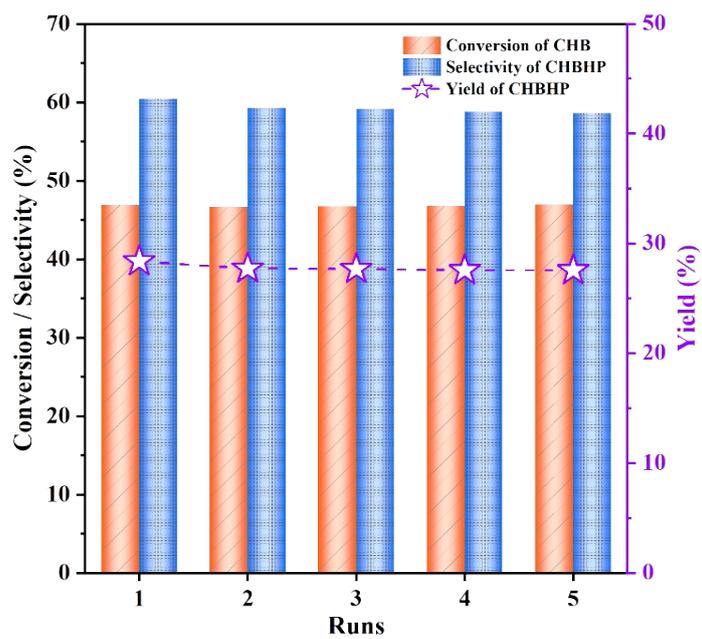
**Fig. S1.** Rietveld refinement of La<sub>1-x</sub>CuO<sub>4</sub> samples. The figure shows the experimental (red points) and refined pattern (continuous black line) and the difference curve (lower blue curve). The green ticks indicate the Bragg reflections.



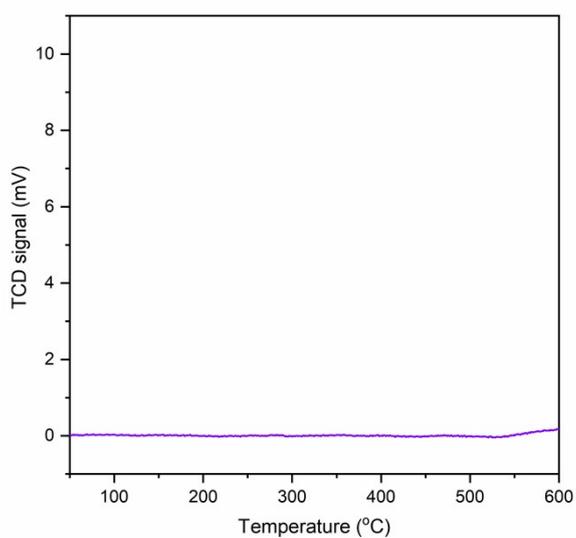
**Fig.S2** N<sub>2</sub> adsorption-desorption isotherms (A), pore size distribution (B), and BET specific surface areas (C) of La<sub>2-x</sub>CuO<sub>4</sub> perovskite samples.



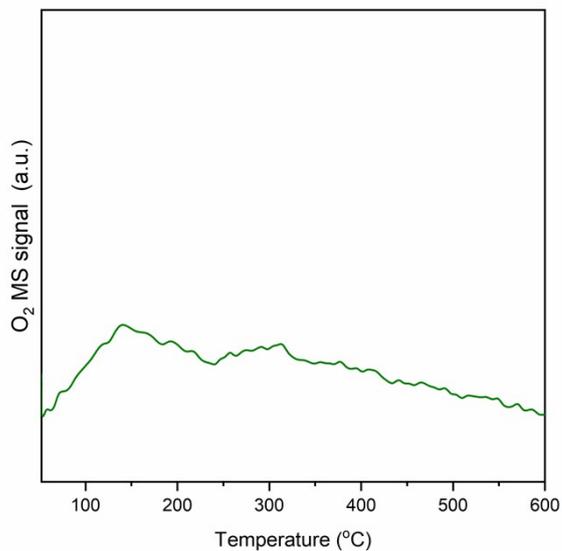
**Fig. S3** SEM, TEM and HRTEM images of La<sub>1.7</sub>CuO<sub>4</sub> (a,c,e) and La<sub>1.8</sub>CuO<sub>4</sub> (b,d,f) samples.



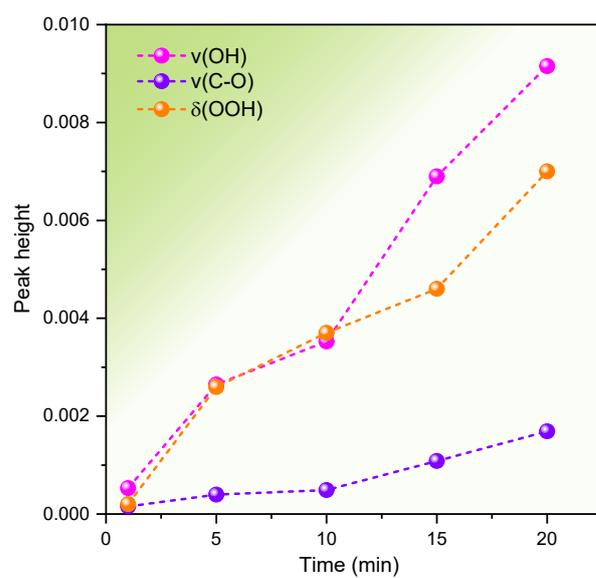
**Fig. S4** The reusability of La<sub>1.9</sub>CuO<sub>4</sub> catalyst. Reaction conditions: CHB, 50 mL, catalyst, 100 mg; 120 °C; 12h.



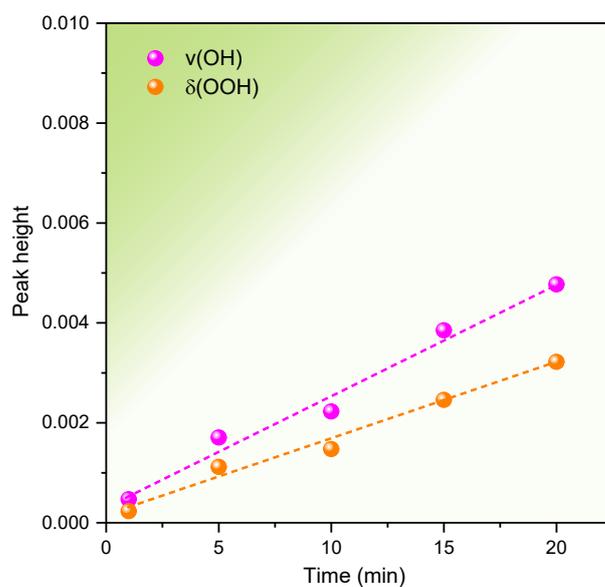
**Fig.S5** TPDE profile of representative La<sub>1.9</sub>CuO<sub>4</sub> sample.



**Fig.S6** MS signal of O<sub>2</sub> for O<sub>2</sub>-TPD profile on the La<sub>1.9</sub>CuO<sub>4</sub> sample.



**Fig.S7** The change in the peak intensities of ν(OH), ν(C-O), and δ(OOH) bands for *in-situ* time-evolved DRIFT spectra of pre-adsorbed CHB versus the exposure time under O<sub>2</sub>/N<sub>2</sub> flow (5:95, v/v) over the La<sub>1.9</sub>CuO<sub>4</sub> catalyst at 120 °C.



**Fig.S8** The change in the peak intensities of  $\nu(\text{OH})$  and  $\delta(\text{OOH})$  bands for *in-situ* time-evolved DRIFT spectra of pre-adsorbed CHB versus the exposure time under Ar flow over the  $\text{La}_{1.9}\text{CuO}_4$  catalyst at 120 °C.

**Table S1** Unit cell parameters for  $\text{La}_{2-x}\text{CuO}_4$  samples

Catalysts	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)
$\text{La}_{1.7}\text{CuO}_4$	0.5360	0.5404	1.3157
$\text{La}_{1.8}\text{CuO}_4$	0.5353	0.5395	1.3143
$\text{La}_{1.9}\text{CuO}_4$	0.5355	0.5400	1.3143
$\text{La}_{2.0}\text{CuO}_4$	0.5354	0.5401	1.3137
$\text{La}_{2.0}\text{CuO}_4^{\text{a}}$	0.5355 <sup>a</sup>	0.5401 <sup>a</sup>	1.3149 <sup>a</sup>

<sup>a</sup>: obtained from JCPDS No. 38-0709.