Modulation of active metal species in MOF-derived catalysts for efficient NO reduction by CO

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Experimental section

Synthesis of Cu MOF-74

By the reported method[1], Cu-MOF-74 samples were synthesized by solvent-thermal approach. In a typical experimental procedure, a mixture of 2,5-dihydroxyterephthalic acid (H_2DHTP) and copper nitrate trihydrate (2.2 g and 5.9 g, respectively) was added into a solution comprising N, N-dimethylformamide (DMF) and isopropanol (250 mL) in a 20:1 (v/v) ratio. The suspension underwent agitation for approximately 15 minutes until achieving a homogenous solution. Subsequently, the uniform solution was transferred into five 100-milliliter capacity Teflon-lined stainless steel autoclaves. The autoclaves were sealed, and the mixtures were subjected to hydrothermal treatment at 80°C for 18 hours. After naturally cooling the autoclaves to room temperature, red microcrystals were collected via vacuum filtration and subjected to repeated DMF washing. The crystals were then immersed in 100 mL of methanol for 3 days, with fresh solvent renewal every 12 hours. Finally, the preliminary product was obtained through vacuum filtration and stored in a drying chamber. This catalyst sample is designated as Cu-MOF-74.

Catalyst Characterization

In the investigation of the crystal structure of the Cu-MOF-74 sample, a variety of analytical techniques and instruments were employed: X-ray Diffraction (XRD): The analysis was conducted on a Bruker D8 Advance X-ray

diffractometer employing Cu Kα X-ray radiation (k = 0.15406 nm), 40 kV and 40 mA, 2θ scanning range of 0–80°, and a scanning rate of 5°/min. The samples were characterized by field emission scanning electron microscopy (SEM) and field transmission electron microscopy (TEM) at 1.0 kV, the instruments were Hitachi S-4800 and FEI Talos F200X, respectively. Nitrogen Adsorption-Desorption Isotherms: Nitrogen adsorption-desorption isotherms were obtained at a low temperature of 77 K. ASAP 2420 adsorption-desorption instrument was utilized for this purpose. Surface Area and Pore Volume Calculations: Surface area, micropore volume, and mesopore volume data were derived using the Brunauer−Emmett−Teller (BET), Horvath−Kawazoe (HK), and Barrett−Joyner−Halenda (BJH) equations. Thermal Stability Analysis: The thermal stability of the samples was determined by employing a Mettler DSC/TGA 851 thermal analyzer (TG). Additionally, thermal stability was further assessed using a Balzer PFEIFFER Thermo Star mass spectrometer. X-ray Photoelectron Spectroscopy (XPS): X-ray photoelectron spectroscopy (XPS) was conducted utilizing a thermo Scientific K-Alpha X-ray photoelectron spectrometer with an Al Kα radiation source. The binding energy (BE) of the C 1s peak was calibrated to 284.8 eV for XPS analysis. Temperature-programmed reduction (TPR) or Temperature Programmed Desorption (TPD): Temperature-programmed experiments were carried out employing H_2 or O_2 as probe molecules. The AutoChem II 2920 adsorption testing equipment from Micromeritics was employed. The catalyst samples

underwent pretreatment at 200 °C for 30 min in a helium flow (50 mL/min) and were then cooled to 100°C in the same flow. Subsequently, the samples were exposed to a mixture of 1% H_2 (or O_2) in helium at 40 mL/min for 1 hour. Before commencing TPR (or TPD) experiments, the catalyst samples were flushed with a helium flow (30 mL/min) for 1 hour to eliminate physically adsorbed H_2 (or O_2).H_2 (or O_2)-TPR (or TPD) curves were recorded linearly, and the samples were heated at a rate of 10 °C/min from 25 °C to 800 °C/(600°C) in a helium flow.
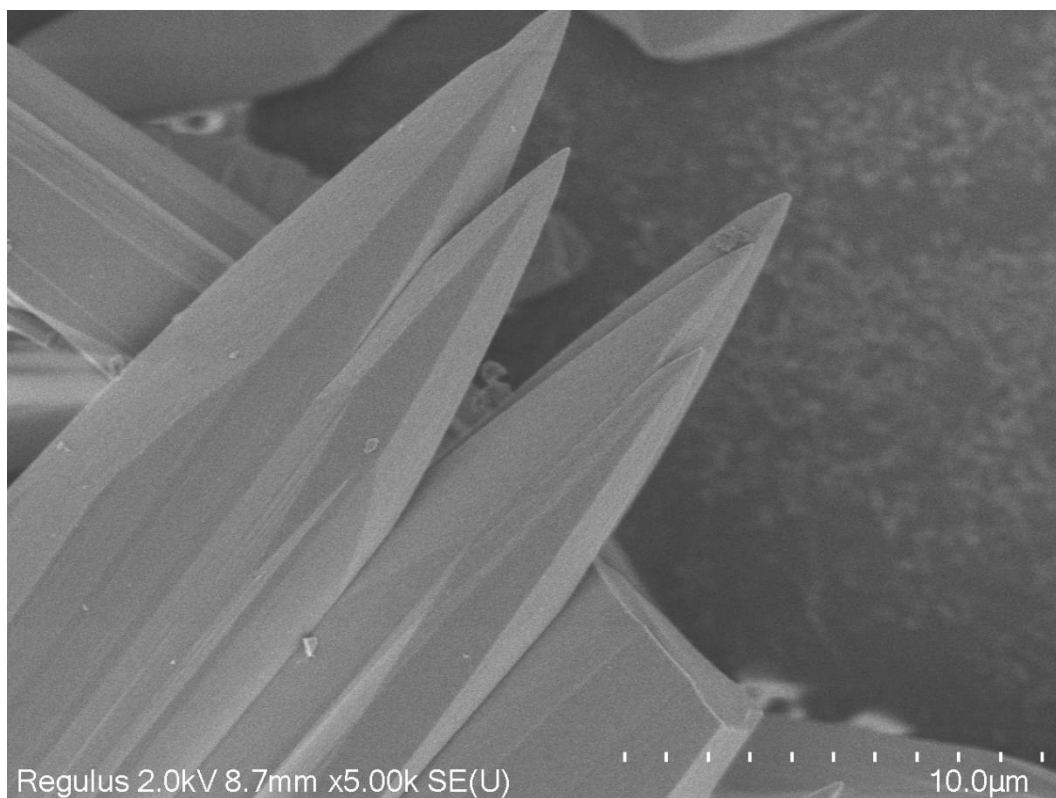
Fig.S1: The SEM image of Cu-MOF-74
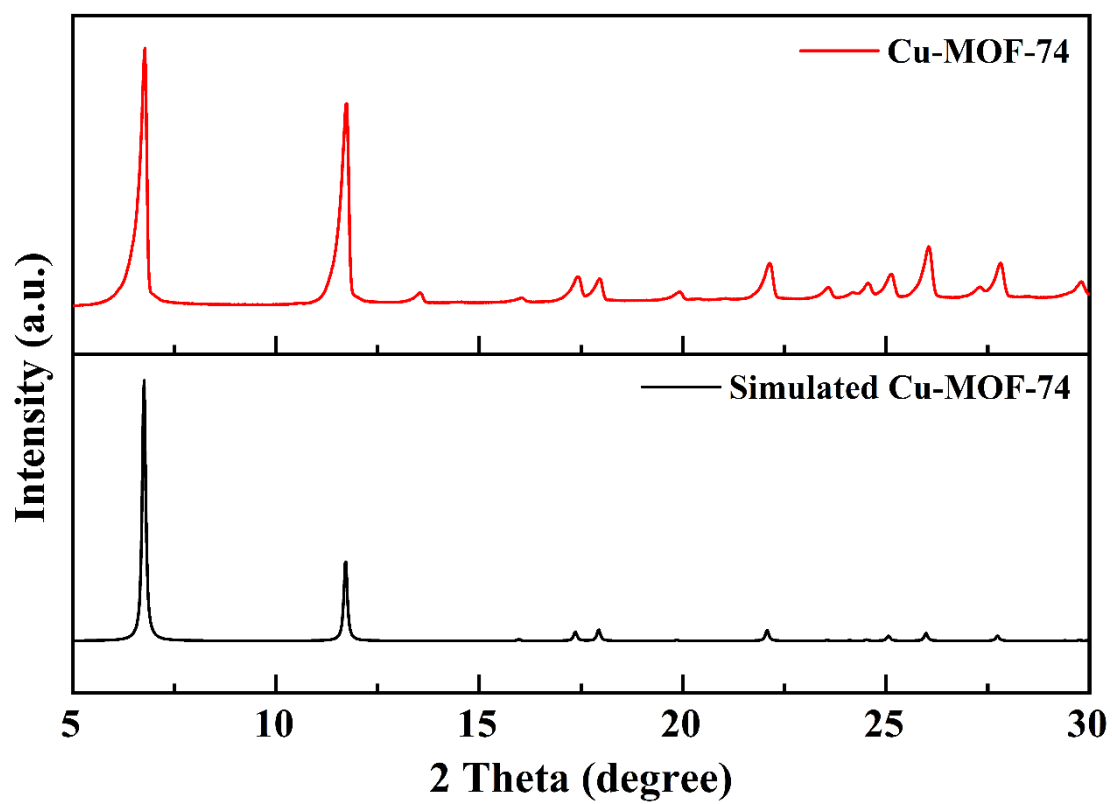
Fig.S2: The XRD patterns of Cu-MOF-74.
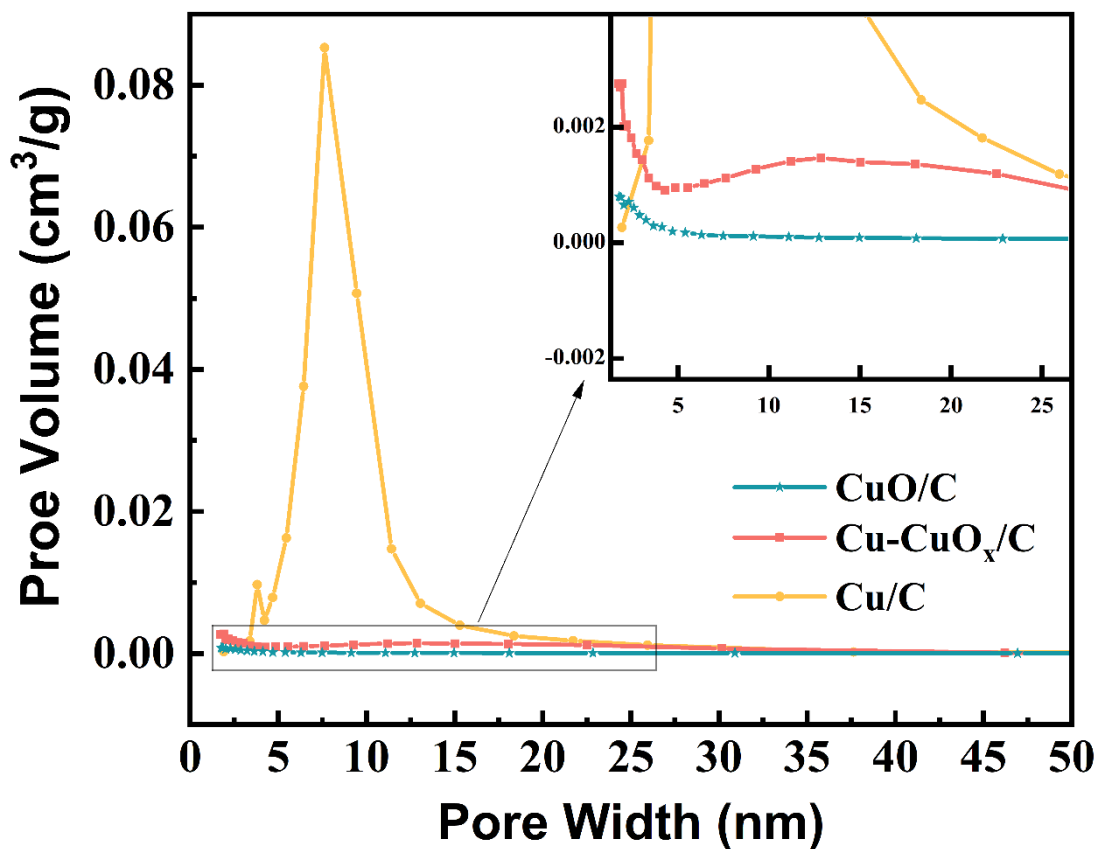
Fig.S3: The BET (Brunauer–Emmett–Teller) isotherms for CuO/C, Cu-CuOx/C, and Cu/C.

Table.S1: The BET (Brunauer–Emmett–Teller) physical properties of CuO/C, Cu-CuOx/C, and Cu/C catalysts.

Samples	BET surface area (m²/g)	Pore volume (cm³/g)	Pore size (nm)
CuO/C	3.15 m²/g	0.01 cm³/g	12.53 nm
Cu-CuOx/C	22.34 m²/g	0.05 cm³/g	9.14 nm
Cu/C	235.56 m²/g	0.42 cm³/g	7.20 nm
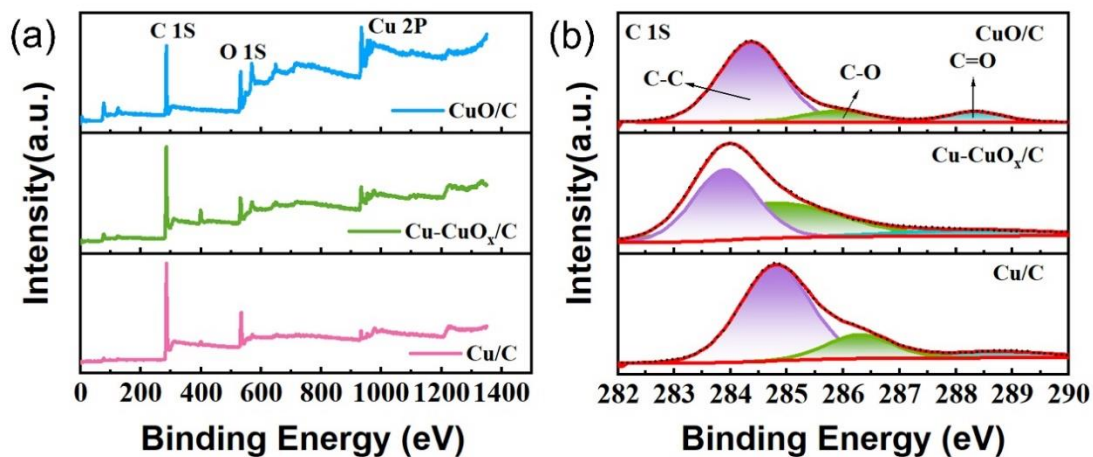
Fig.S4: (a) The XPS full spectrum analysis of CuO/C, Cu-CuO$_x$/C, Cu/C sample. (b) The C 1s spectrogram of CuO/C, Cu-CuO$_x$/C, and Cu/C (The purple, green, and blue regions represent C-C, C-O, and C=O, respectively).
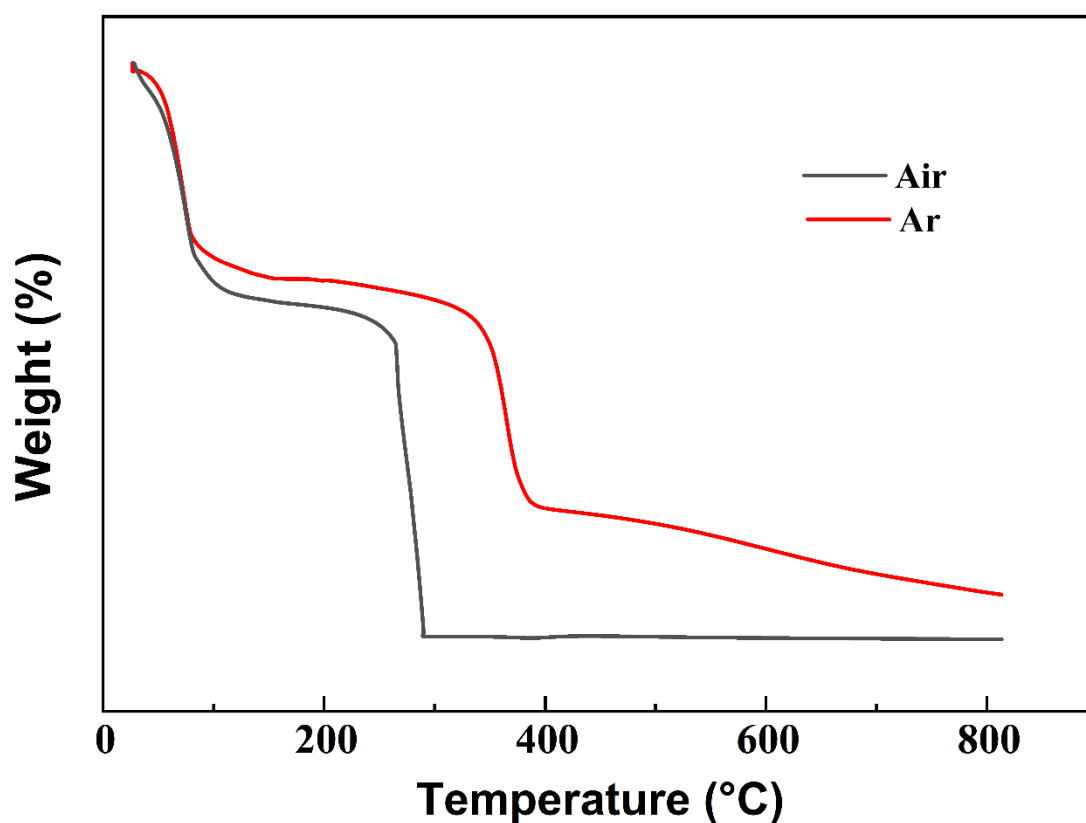
Fig.S5: Cu-MOF-74 sample TG curves under argon and in air. Additionally, the TG experiments indirectly verified Cu-MOF-74's relative stability in argon.
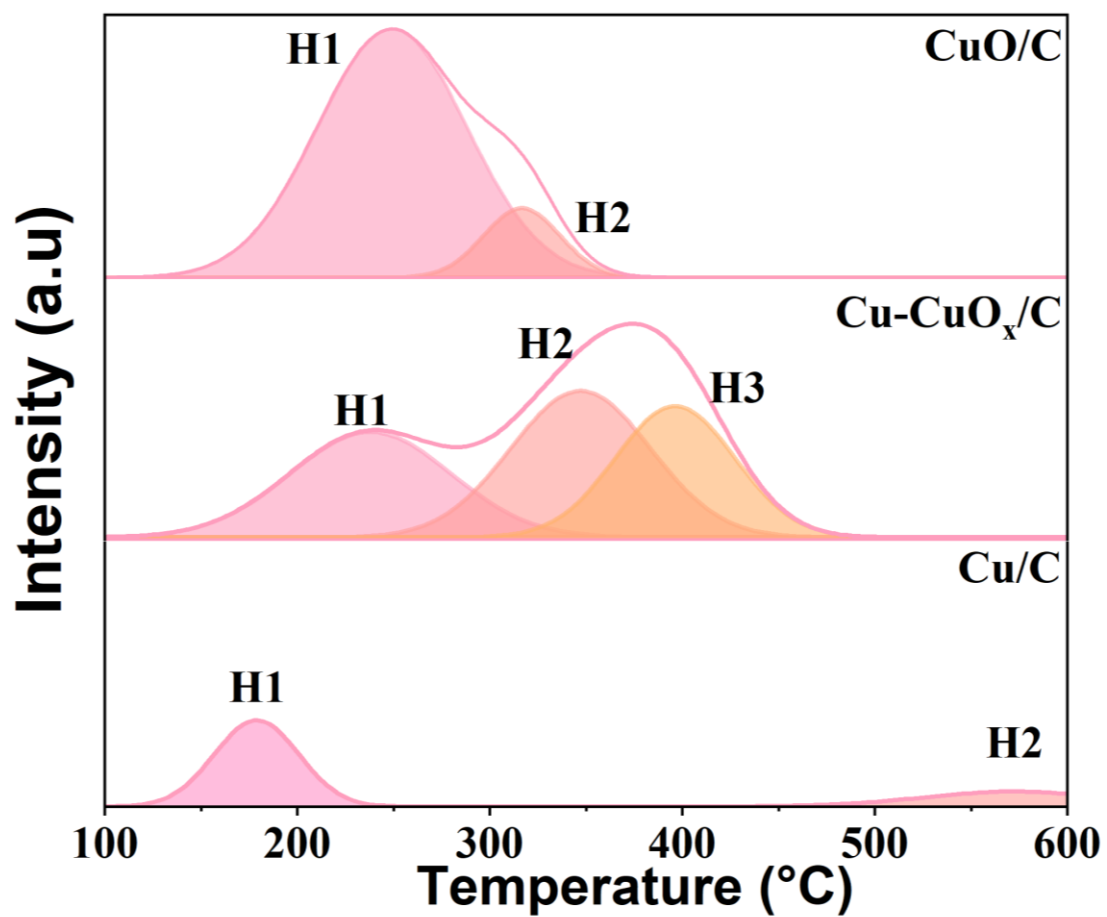
Fig.S6: The characterization spectrum of H_2-TPR images of CuO/C, Cu-CuO$_x$/C, Cu/C samples (H1, H2, and H3 represent different stages of hydrogen adsorption).
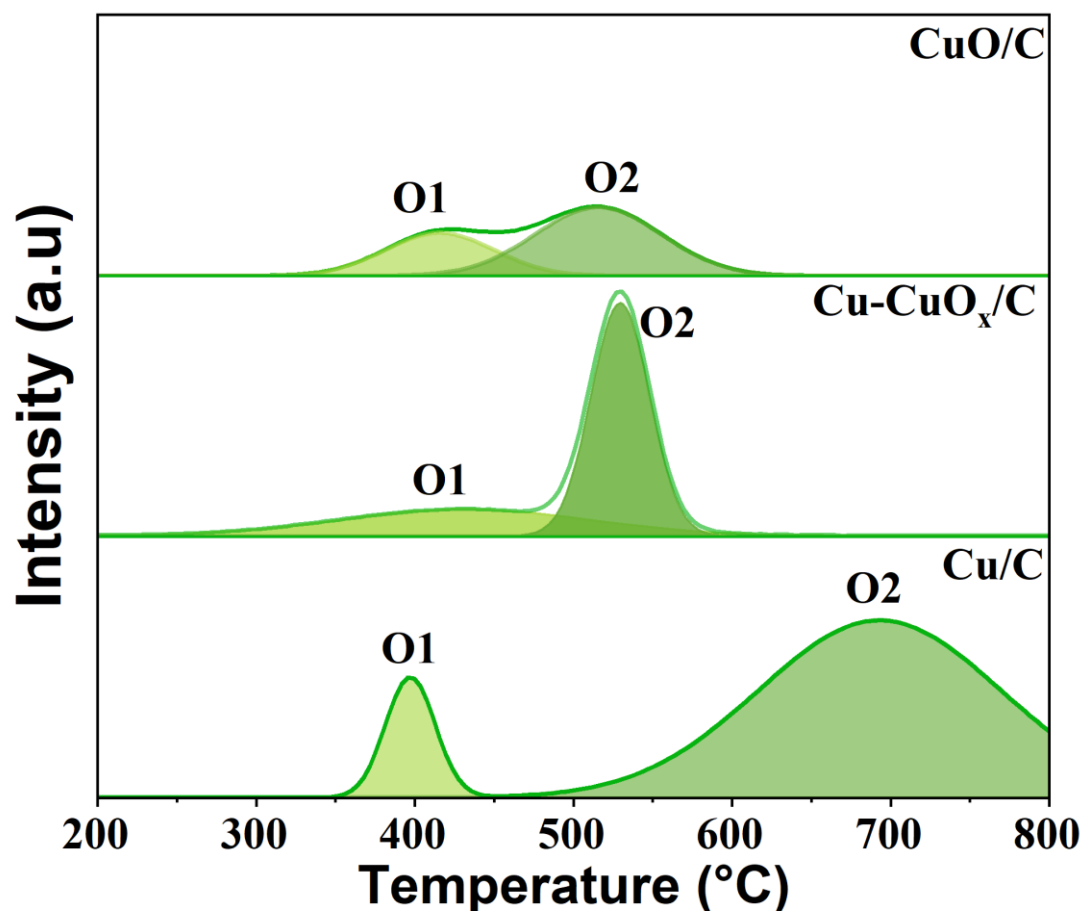
Fig.S7: The characterization spectrum of O₂-TPD images of CuO/C, Cu-CuOₓ/C, Cu/C samples (O1 and O2 represent different stages of oxygen adsorption).
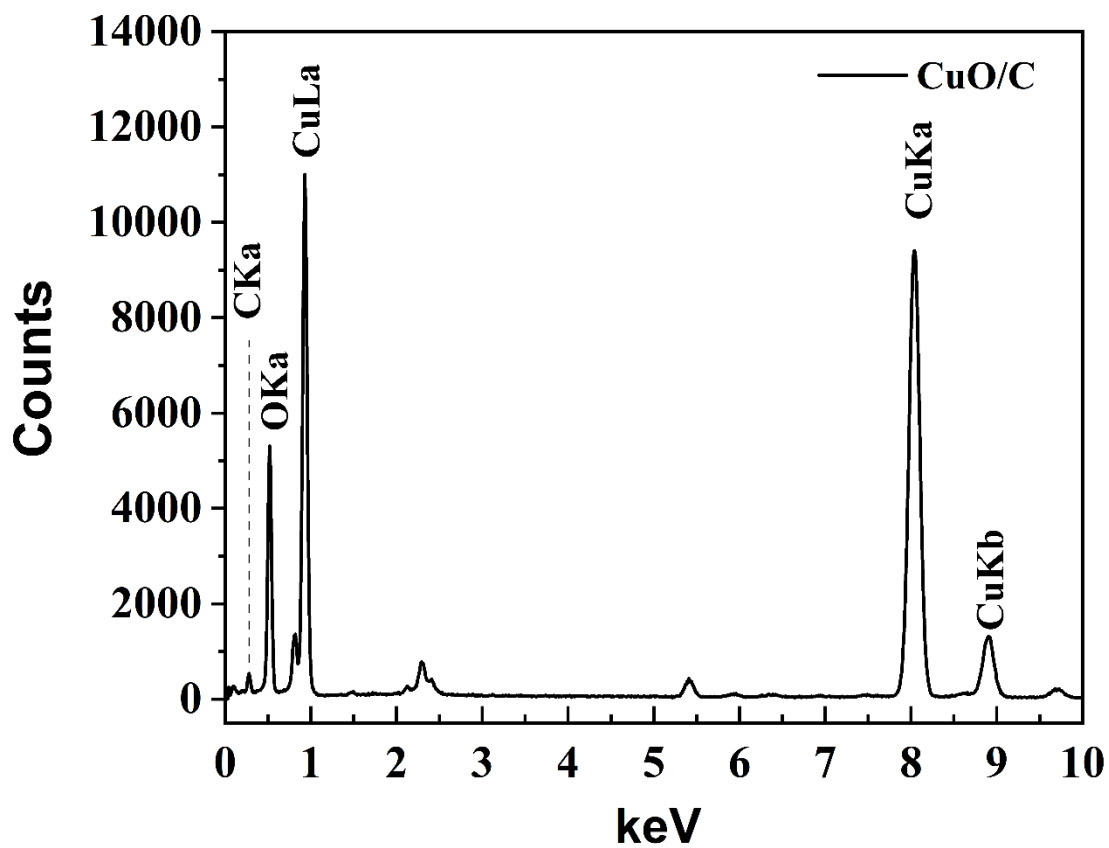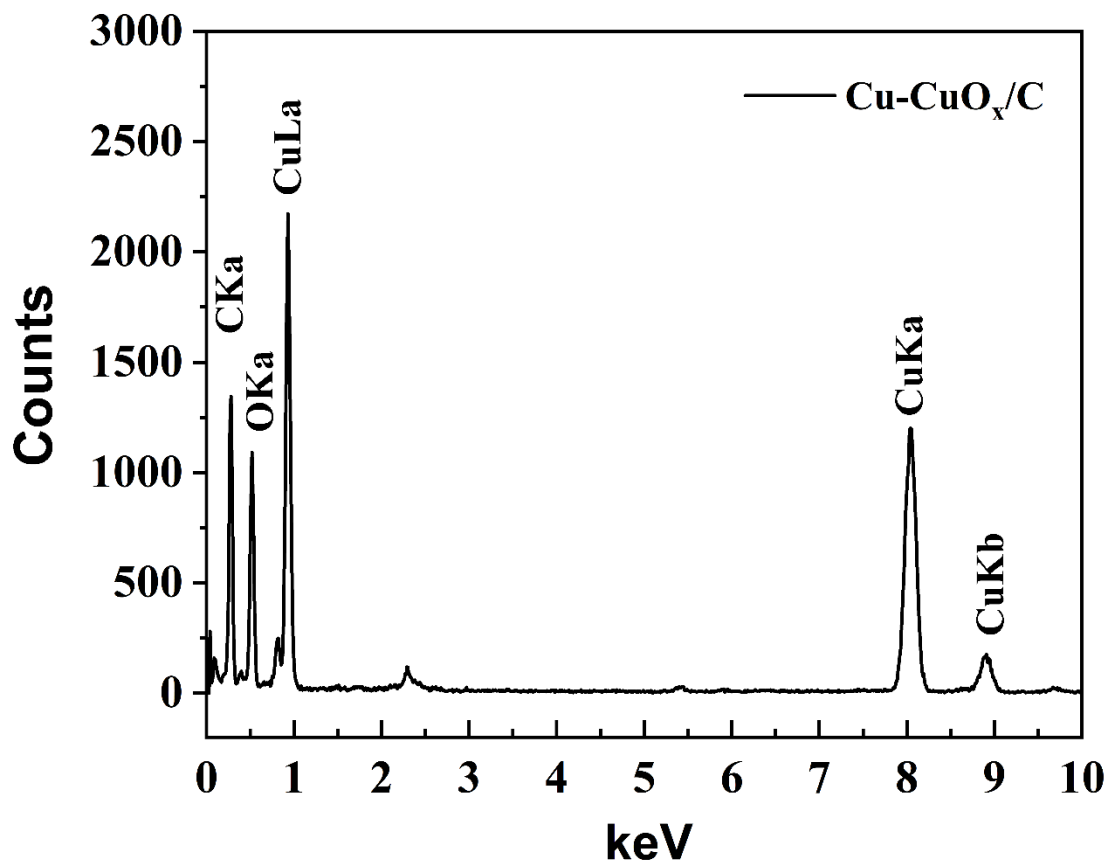
Fig.S8: EDS images of CuO/C sample.

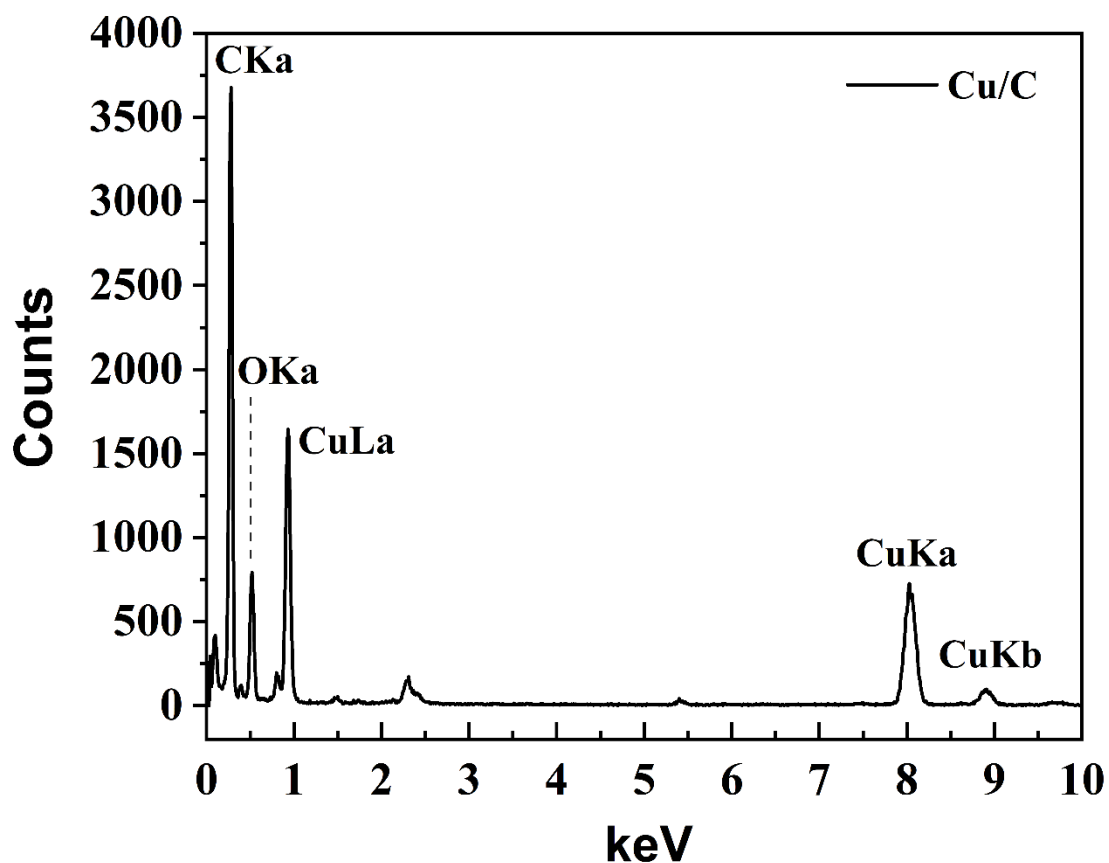**Fig.S9: EDS images of Cu-CuO$_x$/C sample.**

Fig.S10: EDS images of Cu /C sample and the positions of CKa, OKa, CuLa, CuKa, and CuKb are labeled in the figure.

Table S2. EDS spectra of Cu/C, Cu-CuO$_x$/C and CuO/C with C, O, Cu and atomic percentages.

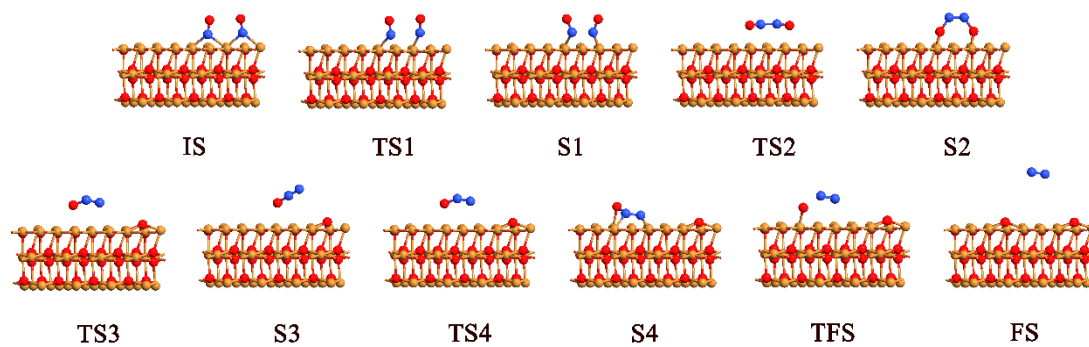| sample	C atom%	O atom%	Cu atom%
Cu/C	85.52	7.45	7.03
Cu-CuOx/C	57.93	21.94	20.13
CuO/C	5.68	40.53	53.79

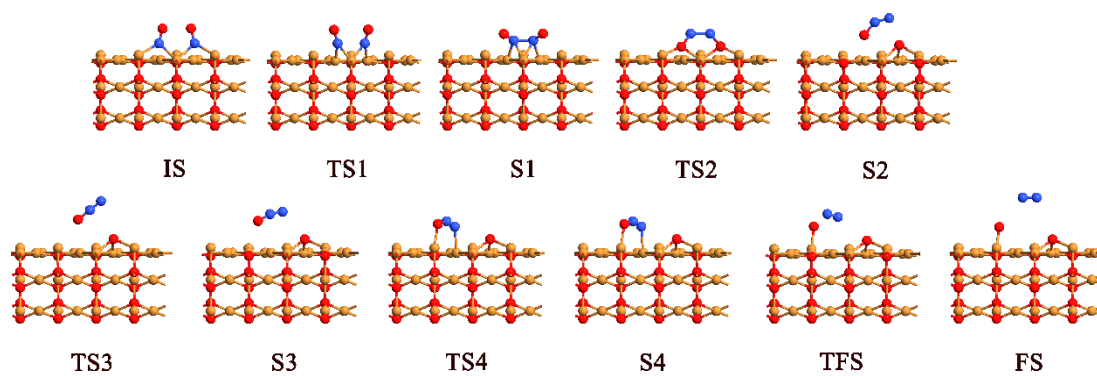**Fig.S11: Potential reaction pathways for DFT simulations of CuO/C.**

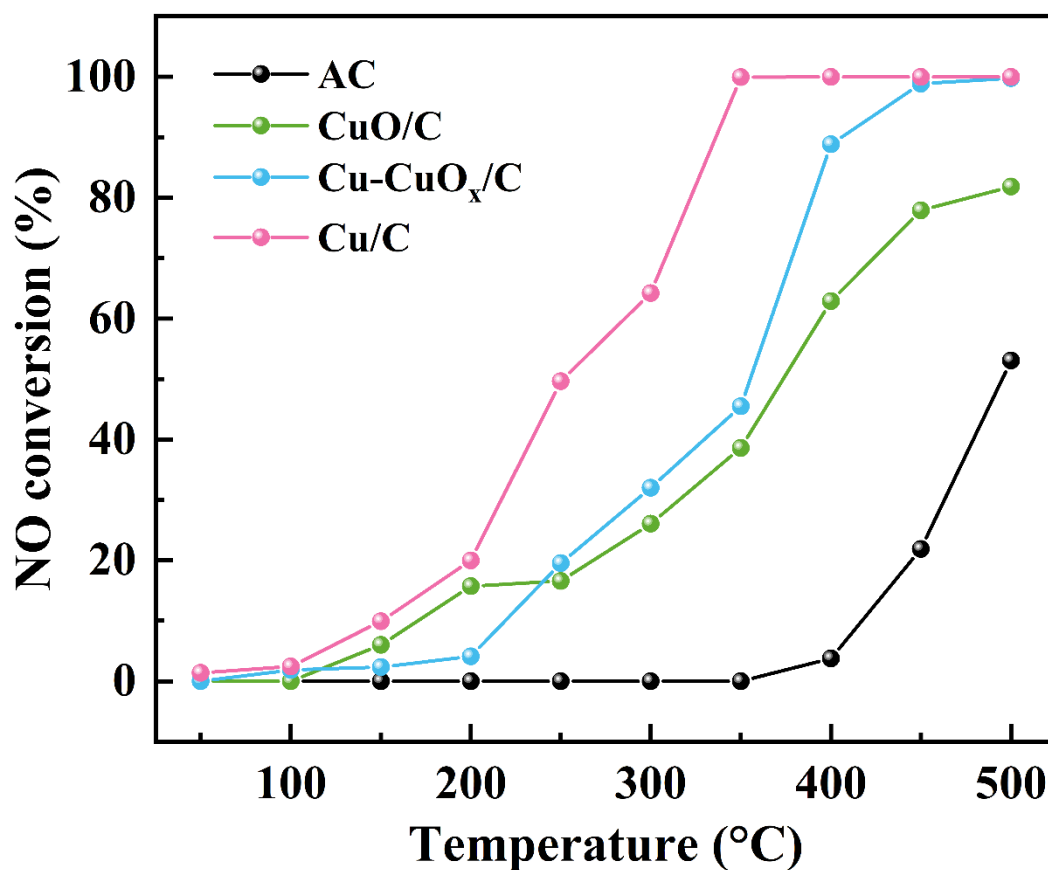**Fig.S12: Potential reaction pathways for DFT simulations of Cu$_2$O/C.**

Fig.S13. NO conversions in CO-SCR of AC, CuO/C, Cu-CuOx and Cu/C catalysts.

References

1. Jiang, H.; Zhou, J.; Wang, C.; Li, Y.; Chen, Y.; Zhang, M., Effect of Cosolvent and Temperature on the Structures and Properties of Cu-MOF-74 in Low-temperature NH_3-SCR. *Industrial & Engineering Chemistry Research* **2017,** *56* (13), 3542-3550.