

Supporting Information

**Dynamics of the Cu/CeO₂ Catalyst during Methanol
Steam Reforming**

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Experimental details

Catalyst preparation

The supported Cu/CeO₂ catalysts were synthesized following a deposition-precipitation method. Briefly, CeO₂ (Sigma-Aldrich, 99.999%, 2.0 g) was suspended in 100 mL of deionized water. A calculated amount of Cu(NO₃)₂·3H₂O (Aladdin, 99.999%, 0.1930 g for 3 wt.% Cu/CeO₂, 2.6743 g for 30 wt.% Cu/CeO₂) was dissolved into 100 mL deionized water and mixed with the CeO₂ suspension. The precipitating agent prepared by dissolving Na₂CO₃ (Aladdin, 99.999%, 0.2458 g for 3 wt.% Cu/CeO₂, 3.0000 g for 30 wt.% Cu/CeO₂) in 50 mL deionized water was added dropwise into the mixture under vigorous mechanical stirring (700-900 rpm). Afterwards, the precipitate was collected by centrifugation, washed thoroughly with deionized water, dried overnight at 60 °C, and finally calcined at 400 °C for 3 h in static air.

Catalyst characterization

STEM measurement was carried out on a ThermoFisher Talos F200X. For HAADF-STEM characterization, a convergence semi-angle of 11 mrad was used, and the inner- and outer collection angles were 59 and 200 mrad, respectively. Energy-dispersive X-ray spectroscopy (EDS) was measured using 4 in-column Super-X detectors.

H₂-TPR was carried out using the Tianjin Xianquan TP-5080B chemisorption instrument. 50 mg sample was loaded into a quartz tube, pretreated with N₂ (Air Liquid, 99.999%, 30 mL/min) at 300 °C for 30 min, and then cooled down to room temperature.

Afterwards, the inlet gas was switched to 10% H_2/N_2 (Air Liquid, 30 mL/min), and the temperature was ramped up to 300 °C at a heating rate of 10 °C/min with the consumption of H_2 monitored by an online TCD. The H_2 -TPR-treated catalyst was further exposed to N_2O (Air Liquid, 99.999%, 30 mL/min) at 50 °C for 30 min. The inlet gas was then switched to 10% H_2/N_2 (30 mL/min), and the temperature was ramped up to 300 °C at a heating rate of 10 °C/min, with the consumption of H_2 again monitored by the online TCD.

The BET-specific surface area and BJH pore size distribution of the samples were obtained from N_2 adsorption-desorption conducted on Micromeritics ASAP 2460 apparatus at -196 °C. The samples were outgassed under vacuum at 200 °C for 3 h before N_2 adsorption.

Quasi *in situ* XPS spectra were collected with a Thermo ESCALAB 250Xi spectrometer equipped with a monochromatic Al K α radiation source (1486.6 eV, pass energy 20.0 eV). The sample was placed in a reaction chamber connected to the XPS equipment and exposed to 60% H_2/N_2 (Air Liquid, 30 mL/min) at 300 °C for 1 h. Afterwards, the pretreated sample was directly transferred into the analysis chamber without exposure to air. Binding energies of all elements were calibrated using the C 1s peak at 284.8 eV as a reference.

Pulsed N_2O chemisorption was performed in an in-house build setup (Fig. S8) to measure the exposed metallic copper sites of the Cu/CeO₂ catalysts. 50 mg of catalyst was loaded into a quartz tube. The sample was treated under various conditions (described in

the main text) and then cooled to 50 °C in He. Subsequently, pulses of N₂O from a sample loop (92 μL) were introduced to the He stream by a six-way valve every 5 min. N₂O and N₂ were analyzed using online gas chromatography (Ruimin GC 2060, Shanghai) equipped with a 13x column and a TCD.

In situ FT-IR spectrometer (PerkinElmer Frontier) equipped with a low void-volume cell (DR-A01, Jiaying Puxiang Tech. Ltd., Fig. S9) was used for *in situ* DRIFTS analysis. Spectra were collected with a spectral resolution of 4 cm⁻¹, and each spectrum was the average of 64 scans. Approximately 10 mg catalyst powder was placed into the low void-volume *in situ* reaction cell. The sample was treated under various conditions (described in the main text), flushed with Ar (Air Liquid, 99.999%, 30 mL/min) for 30 min, and cooled down to room temperature. Next, the inlet gas was switched to a 0.05%CO/He (Air Liquid, 30 mL/min) mixture for 30 min, and the spectra were collected within the range of 4000-800 cm⁻¹. For *in situ* DRIFTS measurement during MSR, the catalyst was first reduced by 60%H₂/N₂ (30 mL/min) at 300 °C, then cooled down to 200 °C, and then exposed to a flow of Ar (30 mL/min) passing through a bubbler containing aqueous methanol solution to introduce vapor/methanol mixture at a ratio of 1.3 for 1 h, the inlet gas was subsequently switched to 60%H₂/N₂ (30 mL/min) or Ar (30 mL/min) for 30 min.

Activity Measurements

The catalytic activity of Cu/CeO₂ for MSR was tested in a fixed-bed plug flow reactor

equipped with online gas chromatography at atmospheric pressure, the catalyst (100 mg, 60-80 mesh) was placed into a quartz tube and fixed between two quartz wool plugs. The catalyst was reduced with 60% H_2/N_2 at 300°C for 1 h prior to the catalytic activity measurements and then cooled down to 200°C. The mixture of water and methanol with a molar ratio of 1.3:1 was preheated to 170°C and fed to the reactor by a syringe pump at a flow rate of 20 $\mu\text{L}/\text{min}$. The gas chromatograph (Ruimin GC 2060, Shanghai) was equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD was used to quantify H_2 , and the FID to quantify CO, CO_2 , and CH_4 . Methanol conversion (X_{MeOH}) and CO_2 selectivity(S_{CO_2}) over catalysts were calculated according to equations (1) and (2).

$$X_{\text{MeOH}} (\%) = (F_{\text{CO, out}} + F_{\text{CO}_2, \text{out}}) / F_{\text{MeOH, in}} \times 100\% \quad (1)$$

$$S_{CO_2} (\%) = F_{\text{CO}_2, \text{out}} / (F_{\text{CO, out}} + F_{\text{CO}_2, \text{out}}) \times 100\% \quad (2)$$

Where $F_{\text{CO, out}}$ and $F_{\text{CO}_2, \text{out}}$ are the molar flow rates of CO and CO_2 feed out, respectively, $F_{\text{MeOH, in}}$ is the molar flow rates of methanol feed in.

The value of turnover frequency (TOF) was calculated as follows:

$$\text{TOF} (\text{h}^{-1}) = (F_{\text{MeOH}} \times X_{\text{MeOH}}) / (W_{\text{cat}} \times N_{\text{sites}}) \quad (3)$$

Where W_{cat} is the weight of the loaded catalyst, N_{site} is the number of surface Cu sites in gram.

Supplementary Figures

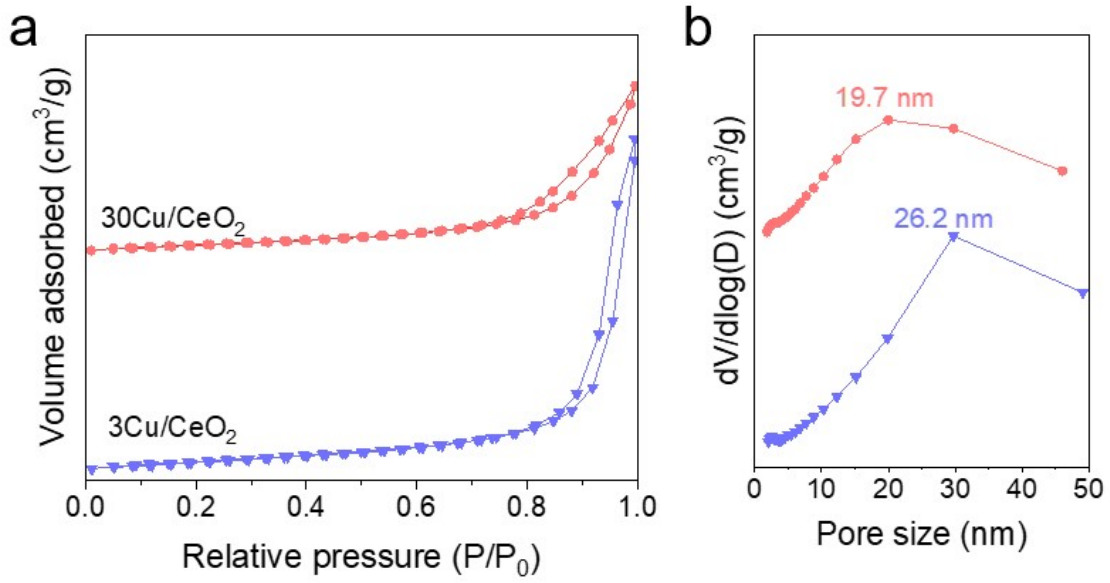


Fig. S1 (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distribution of prepared Cu/CeO₂ catalysts.

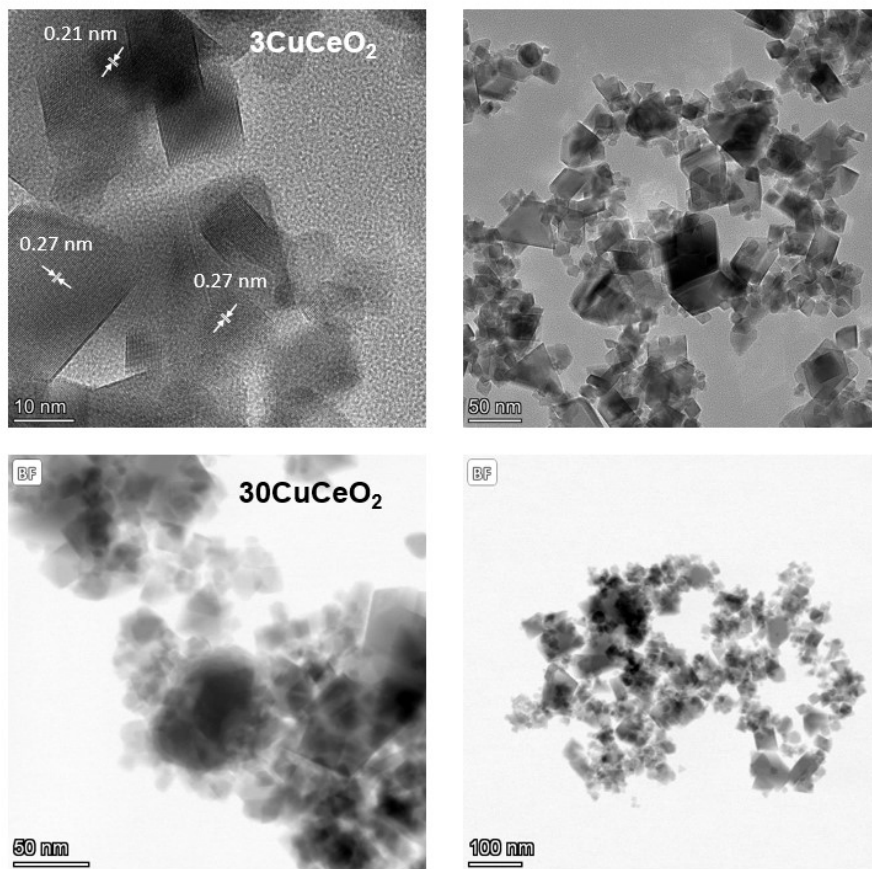


Fig. S2 HR-TEM images of reduced 3%Cu/CeO₂ and 30%Cu/CeO₂.

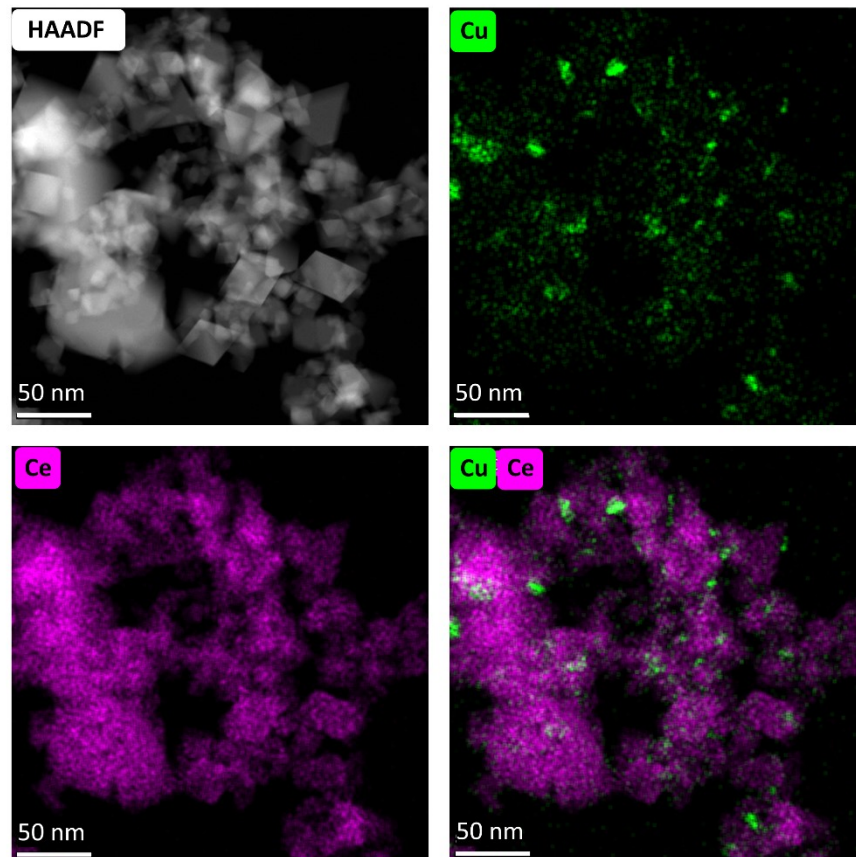


Fig. S3 HAADF-STEM image of reduced 3%Cu/CeO₂ with the corresponding elemental maps of Cu and Ce.

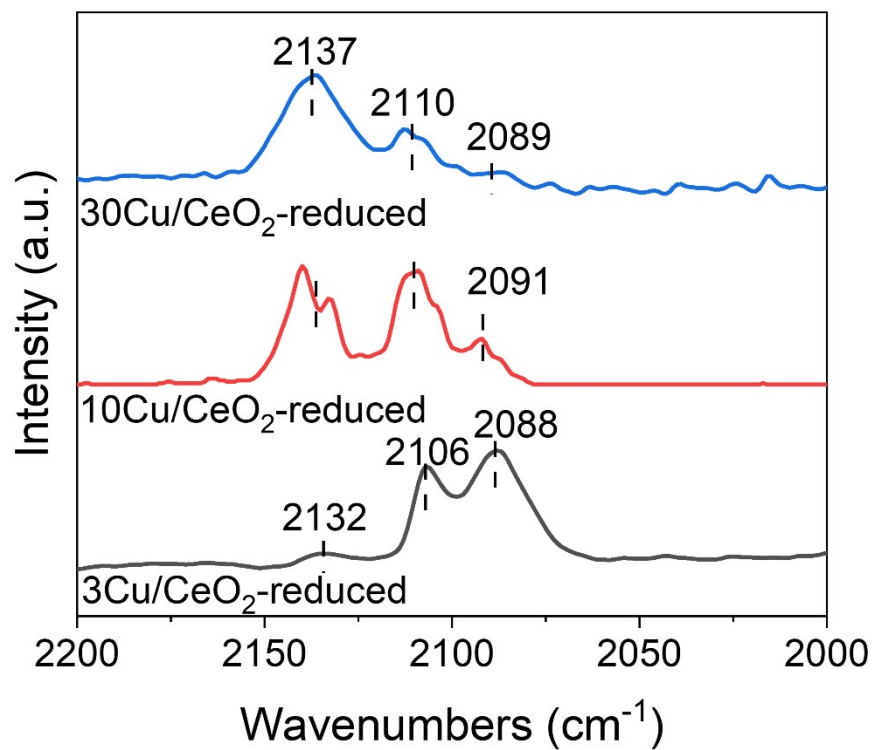


Fig. S4 *In situ* CO-DRIFTS of the reduced 3%Cu/CeO₂, 10%Cu/CeO₂, and 30%Cu/CeO₂ catalysts.

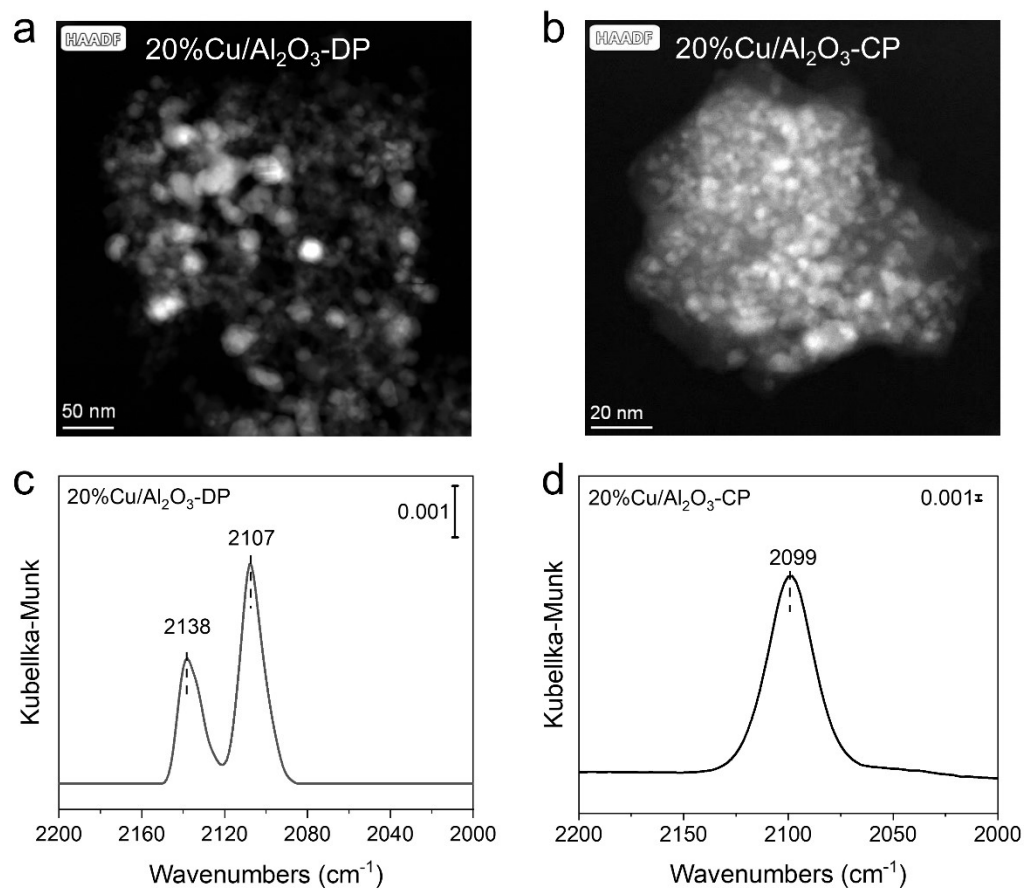


Fig. S5 HAADF-STEM images of the 20%Cu/Al₂O₃ catalysts prepared by (a) deposition-precipitation method and (b) co-precipitation method. *In situ* CO-DRIFTS of the H₂-reduced 20%Cu/Al₂O₃ catalysts prepared by (c) deposition-precipitation method and (d) co-precipitation method.

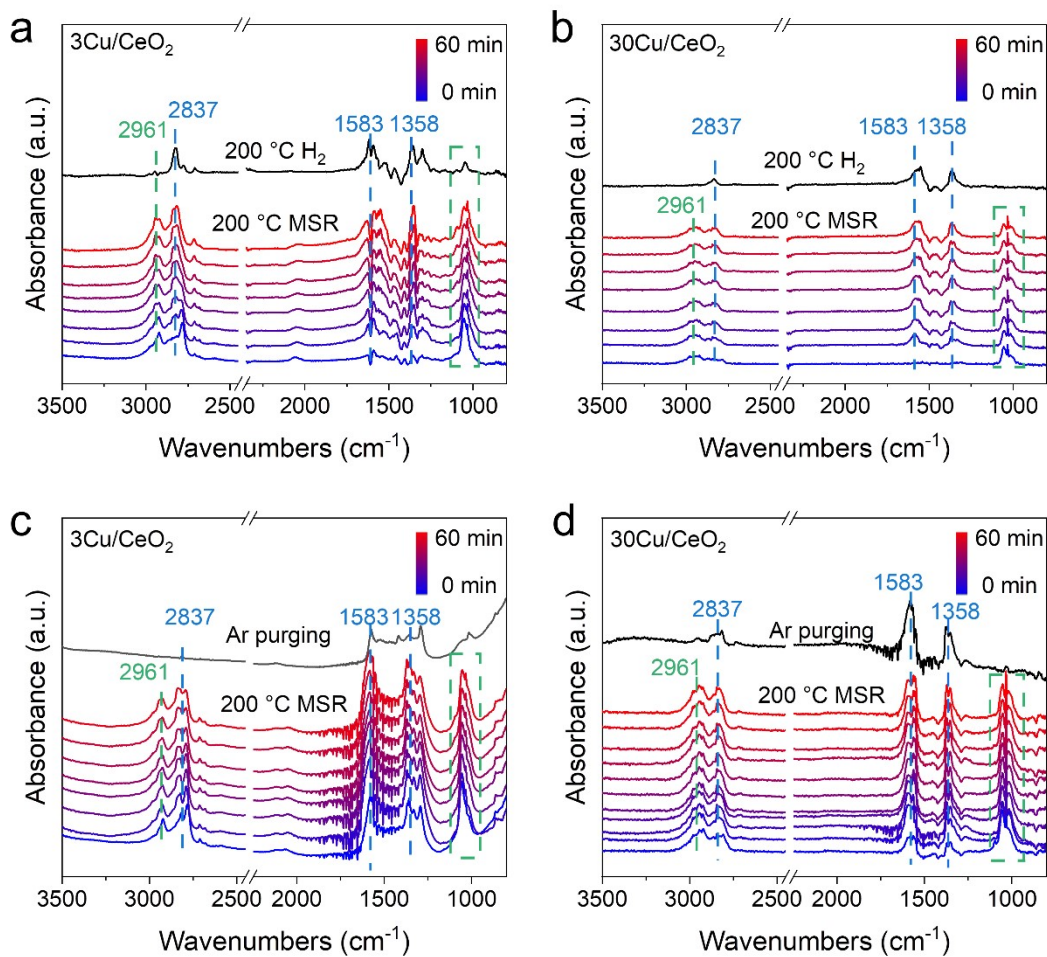


Fig. S6 *In situ* DRIFTS of (a) 3%Cu/CeO₂ and (b) 30%Cu/CeO₂ in the MSR→H₂ sequence. *In situ* DRIFTS of (c) 3%Cu/CeO₂ and (d) 30%Cu/CeO₂ in the MSR→Ar sequence.

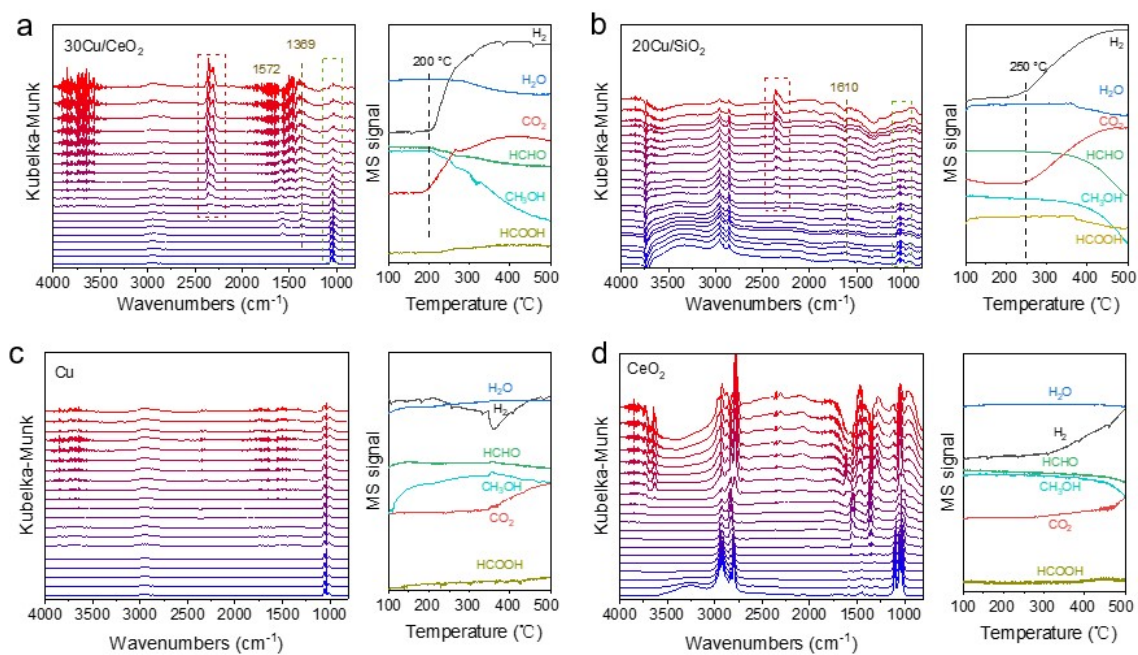


Fig. S7 Operando TPSR-DRIFTS of (a) reduced 30%Cu/CeO₂, (b) reduced 20%Cu/SiO₂, (c) unsupported Cu, and (d) CeO₂ support.

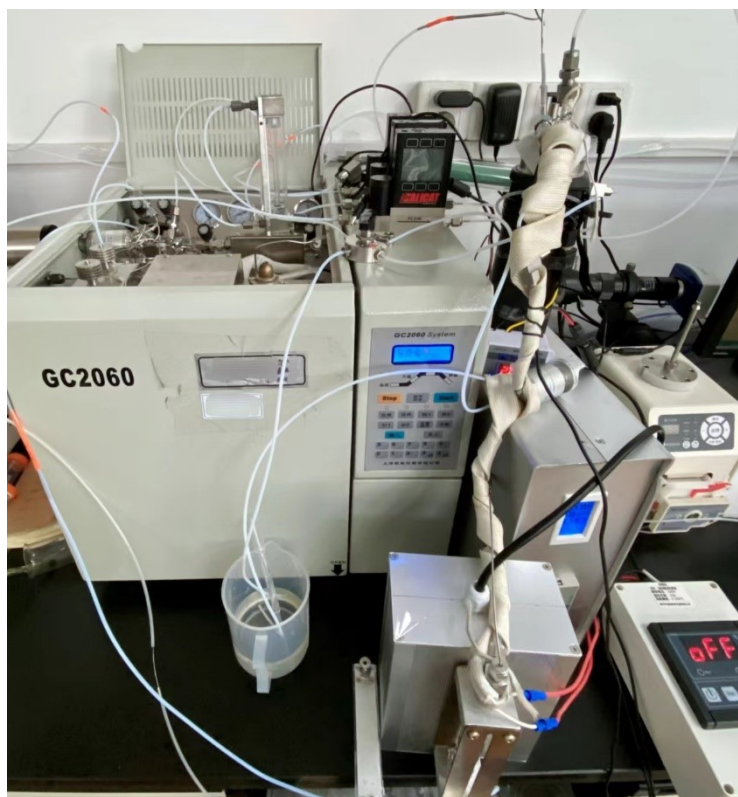


Fig. S8 Home-built experimental setup for the pulsed N₂O chemisorption.

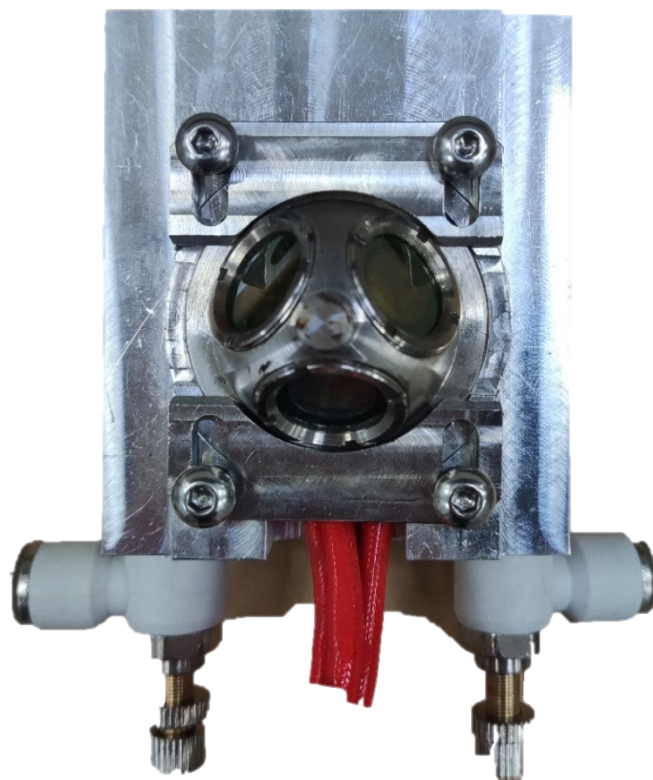


Fig. S9 Low void-volume cell for *in situ* FT-IR spectrometer.