

Electronic Supplementary Information

Tuning Interfaces between Cu and Oxide via Atomic Layer Deposition Method for CO₂ Hydrogenation to Methanol

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1. Experimental

1.1. Materials

Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 98.0-103%) was purchased from Sigma-Aldrich, Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%) and Zinc oxide (ZnO , 99.8%) were purchased from Aladdin. Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99%), Sodium Hydroxide (NaOH , AR) and Diethylzinc solution ($(\text{C}_2\text{H}_5)_2\text{Zn}$, 1.0 M in Hexane) were obtained from Sinopharm and Macklin, respectively.

1.2. Catalysts preparation

Synthesis of CeO_2 nanorods: The CeO_2 nanorods were synthesized by hydrothermal method as reported previously.¹ Typically, 3.472 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL deionized water and 38.4 g NaOH was dissolved in 140 mL deionized water, respectively. After the dissolution completed, the cerium nitrate solution was pumped dropwise slowly into the sodium hydroxide under vigorous stirring. After being stirred for another 30 min, the obtained slurry was transferred into 250 mL stainless steel autoclave with a Teflon liner, followed the temperature was kept at 100 °C for 24 h. After that, the precipitation was washed with deionized water to pH = 7, followed by drying in an oven at 80 °C overnight. Finally, the samples were calcined in a muffle furnace at 400 °C for 4 h.

Synthesis of Cu/CeO_2 catalyst: 10 wt.% Cu/CeO_2 catalyst was prepared by incipient wetness impregnation. The required quantity of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in the exact amount of deionized water and added in a dropwise manner,

according to the absorption capacity of the CeO₂ nanorods. The obtained paste was then dried overnight at 80 °C and calcined at 400 °C for 4 h in a muffle furnace.

ZnO deposition by ALD: Based on the synthesis of Cu/CeO₂ catalyst, ZnO was deposited by homemade ALD reactor (closed chamber-type) with ultrahigh purity N₂ as a carrier gas. ZnO deposition was executed at 150 °C, using diethylzinc and deionized water as precursors. For each ALD cycle, the pulses, exposure, and purge times for (C₂H₅)₂Zn were 0.02 s, 8 s, 25 s, and those for deionized water were 0.1 s, 8 s, 30 s, respectively. Cu/xc-ZnO/CeO₂ catalysts were prepared by depositing ZnO with various numbers of cycles on the CeO₂ nanorods (x = 5, 10, 20), followed by impregnating Cu. Similarly, xc-ZnO/Cu/xc-ZnO/CeO₂ catalysts were prepared by further deposition ZnO on Cu/xc-ZnO/CeO₂. xc-ZnO/Cu/CeO₂ catalysts were obtained by depositing ZnO on the Cu/CeO₂ for comparison. In total, four catalysts were synthesized: Cu/10c-ZnO/CeO₂, Cu/20c-ZnO/CeO₂, 5c-ZnO/Cu/5c-ZnO/CeO₂ and 10c-ZnO/Cu/CeO₂.

Synthesis of other catalysts: Cu/10c-ZnO/CeO₂ show the highest CH₃OH production, so in this work we focus on catalysts promoted by 10 cycles of ALD-ZnO. The catalysts with same composition of metal element content were prepared as follows. Cu/ZnO/CeO₂-co catalyst was prepared by co-precipitation method according to the procedure described elsewhere.² Cu/ZnO/CeO₂-IWI and Cu/ZnO catalysts were prepared by incipient wetness impregnation method as above the synthesis method of Cu/CeO₂. All the catalysts were dried overnight and calcined in air for 4 h at 400 °C. Meanwhile, commercial Cu/ZnO/Al₂O₃ was also synthesized by co-precipitation

method, in which molar ratio of Cu/Zn/Al was 6: 3: 1. Typically, a certain amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 50 mL deionized water. After the dissolution completed, the solution was pumped dropwise (1 mL min^{-1}) into the beaker containing 50 mL of deionized water at $65 \text{ }^\circ\text{C}$. $1.5 \text{ M Na}_2\text{CO}_3$ solution simultaneously was pumped dropwise, in order to keep the $\text{pH} = 7$. Then the obtained precipitates were aged at $65 \text{ }^\circ\text{C}$ for 2 h. After that, the precipitation was washed with deionized water, followed by drying in an oven at $80 \text{ }^\circ\text{C}$ overnight. Finally, the samples were calcined in a muffle furnace at $350 \text{ }^\circ\text{C}$ for 4 h.

1.3 Catalysts characterization

Crystallographic characterization of all catalysts were identified using XRD (Rigaku SmartLab SE diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 25 mA. The intensity data were recorded from 10° to 90° for 2θ Bragg angle at a scanning rate of $5^\circ/\text{min}$.

The N_2 adsorption/desorption isotherms were measured on an ASAP 2020 (Micrometrics) instrument at $-196 \text{ }^\circ\text{C}$. Prior to analysis, about 150 mg of catalyst sample was pretreated under vacuum at $300 \text{ }^\circ\text{C}$ for 6 h to remove moisture.

Elemental composition of the catalysts was determined on a iCAP 7000 series ICP-OES (Thermo Fisher Scientific, USA).

The reduction behavior of Cu-Zn-Ce oxide catalysts was investigated by temperature-programmed reduction (H_2 -TPR) on Micromeritics AutoChem II 2920 instrument. Before analysis, approximately 100 mg catalyst was loaded in a quartz U-tube reactor and purged with Ar at $300 \text{ }^\circ\text{C}$ for 30 min, followed by cooling to $50 \text{ }^\circ\text{C}$.

Then the gas stream was switched to 30 mL·min⁻¹ of 10% H₂/Ar, and the temperature was raised at 10 °C/min to 400 °C. The H₂ consumption during temperature ramp was recorded by a thermal conductivity detector (TCD).

CO₂ temperature-programmed desorption (CO₂-TPD) was conducted with similar processes. 100 mg catalyst was firstly pretreated in 10% H₂/Ar at 300 °C for 2 h and then cooled in He to 50 °C. At 50 °C, the catalyst was exposed to 10% CO₂/Ar for 30 min, followed by He purging for 60 min. Afterward, the temperature was slowly increased to 750 °C and recorded the TCD signal at the same time.

Scanning electron microscopy (SEM) was recorded on a Helios G4 CX to study the morphology of the catalysts. Transmission electron microscopy (TEM) images and HAADF-STEM images were acquired on a FEI Talos F200S G2 microscope at 200 kV (FEI, USA).

Semi-in situ XPS measurements were carried out on Thermo Scientific Escalab 250Xi spectrometer which was equipped with an Al K α X-ray source (E = 1486.6 eV) with a pass energy of 20 eV, providing an energy resolution of 0.05 eV. The catalyst was introduced into a preparation chamber, reduced in pure H₂ at 300 °C for 3 h and then down to room temperature for further testing. The binding energies were calibrated by environmental C 1s at 284.8 eV.

In-situ DRIFT spectra were performed in a FT-IR spectrometer (Bruker Vertex 70) with MCT detector and Harrick cell for observation at 250 °C as well as high pressure (3 MPa) environment. Typically, the catalyst was reduced in H₂ atmosphere at 300 °C for 3 h and purged with Ar for 30 min at 250 °C, followed by the background spectrum

collection at a resolution of 4 cm^{-1} for 32 scans. Subsequently, the catalysts were passed in CO_2/H_2 (1: 3) at 3 MPa. The corresponding dynamic changes were recorded with absorb time.

1.4 Catalysts performance

CO_2 hydrogenation was performed in a fixed bed reactor with 8 mm inner diameter. In a typical test, 0.5 g catalysts (40-60 mesh) diluted with 2.0 g quartz sand (40-60 mesh) were pretreated in 30 mL/min pure H_2 at $300 \text{ }^\circ\text{C}$ for 3 h. After the reactor was cooled down to $250 \text{ }^\circ\text{C}$, a reaction gas ($\text{CO}_2: \text{H}_2: \text{Ar} = 24: 72: 4$) was introduced continuously to a pressure of 3.0 MPa. The contents of CH_4 , CO , CO_2 were detected by an online gas chromatograph (Shimazu, TCD, GC-2014) with a carbon molecular sieves column. The contents of CH_3OH , CH_4 were analyzed by an online gas chromatograph (Shimazu, FID, GC-2014) with a capillary column. The CO_2 conversion (X_{CO_2}), product selectivity (S_i), and space-time yield of methanol ($\text{STY}_{\text{Methanol}}$) were calculated as following:

$$X_{\text{CO}_2} (\%) = \frac{f_{\text{CO}_2,\text{in}}/f_{\text{Ar},\text{in}} - f_{\text{CO}_2,\text{out}}/f_{\text{Ar},\text{out}}}{f_{\text{CO}_2,\text{in}}/f_{\text{Ar},\text{in}}} \times 100\% \quad (1)$$

$$S_i (\%) = \frac{R_{i,m} \cdot f_i}{\sum_i R_{i,m} \cdot f_i} \times 100\% \quad (2)$$

$$\text{STY}_{\text{Methanol}} (\text{mol} \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}) = \frac{F_{\text{CO}_2,\text{in}} \cdot X_{\text{CO}_2} \cdot S_{\text{Methanol}}}{W_{\text{cat}}} \quad (3)$$

Where $R_{i,m}$ and f_i are the peak area of product i and the carbon molar response of product i , respectively; $F_{\text{CO}_2,\text{in}}$ (mol/h) represents molar flow rate of CO_2 ; W_{cat} is catalyst weight.

2. Supplementary tables and figures

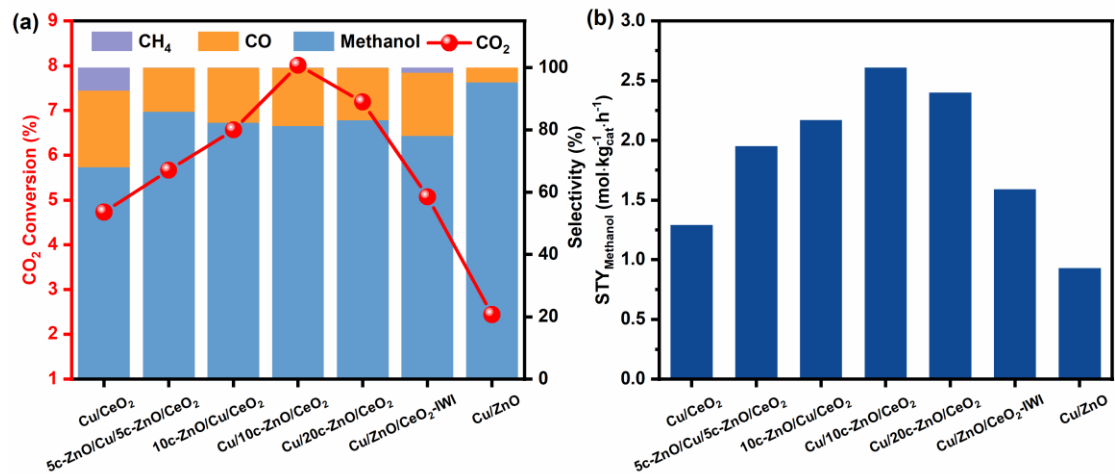


Fig. S1 Catalytic performance of CO₂ hydrogenation over different Cu-based catalysts. (a) CO₂ conversion and product selectivity; (b) The space time yield (STY) of CH₃OH. Reaction condition: 0.5 g catalysts, 3.0 MPa, 250 °C, CO₂: H₂: Ar = 24: 72: 4, 30 mL/min.

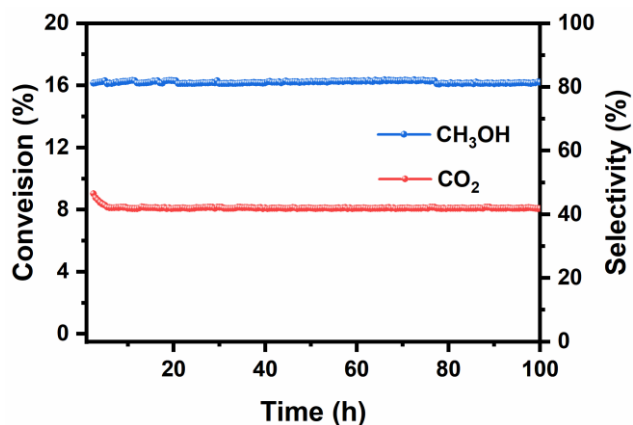


Fig. S2 The CO₂ conversion and CH₃OH selectivity with time for Cu/10c-ZnO/CeO₂. Reaction condition: 0.5 g catalysts, 3.0 MPa, 250 °C, CO₂: H₂: Ar = 24: 72: 4, 30 mL/min.

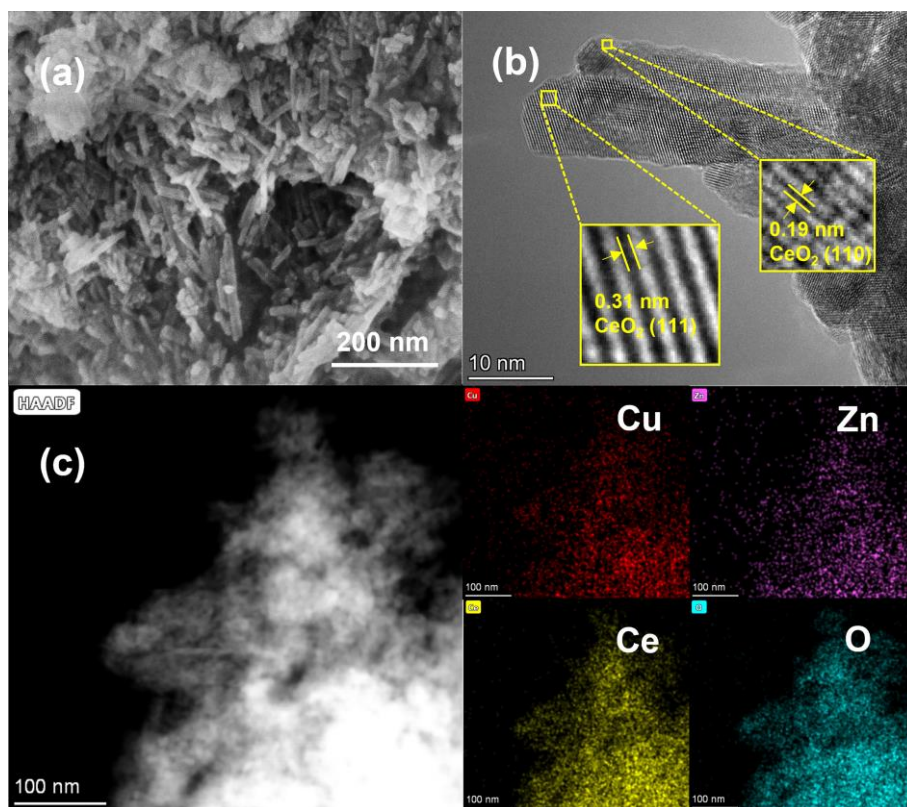


Fig. S3 SEM and TEM analysis of spent Cu/10c-ZnO/CeO₂ catalyst. (a) SEM image; (b) HR-TEM image; (c) HAADF-STEM image and corresponding element mapping of Cu, Zn, Ce and O.

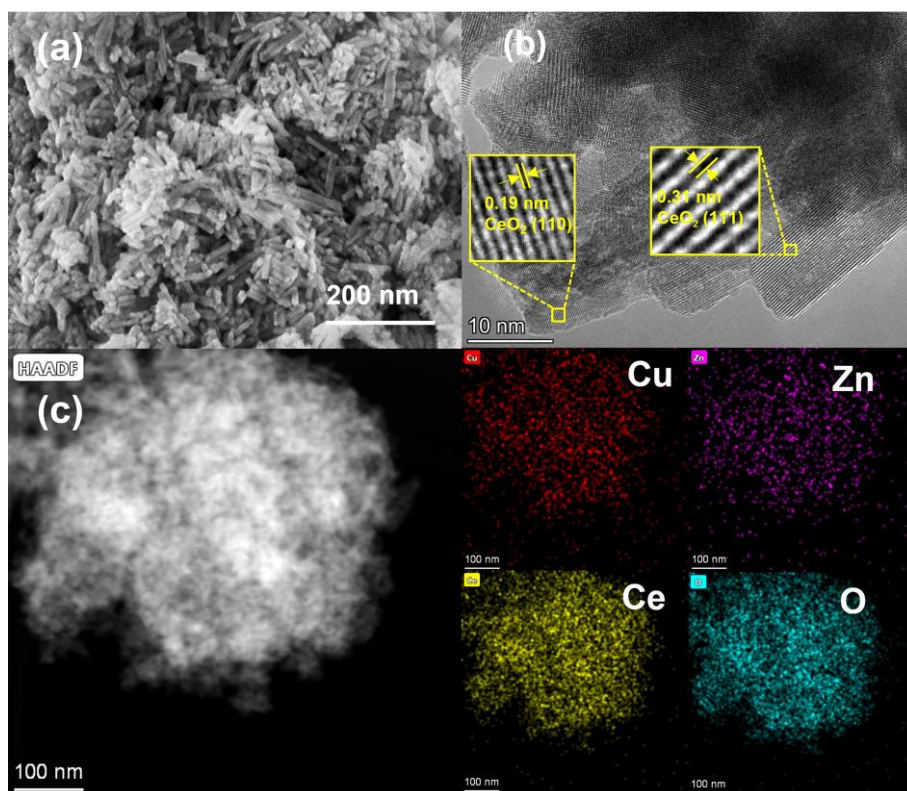


Fig. S4 SEM and TEM analysis of 10c-ZnO/Cu/CeO₂ catalyst. (a) SEM image; (b) HR-TEM image;

(c) HAADF-STEM image and corresponding element mapping of Cu, Zn, Ce and O.

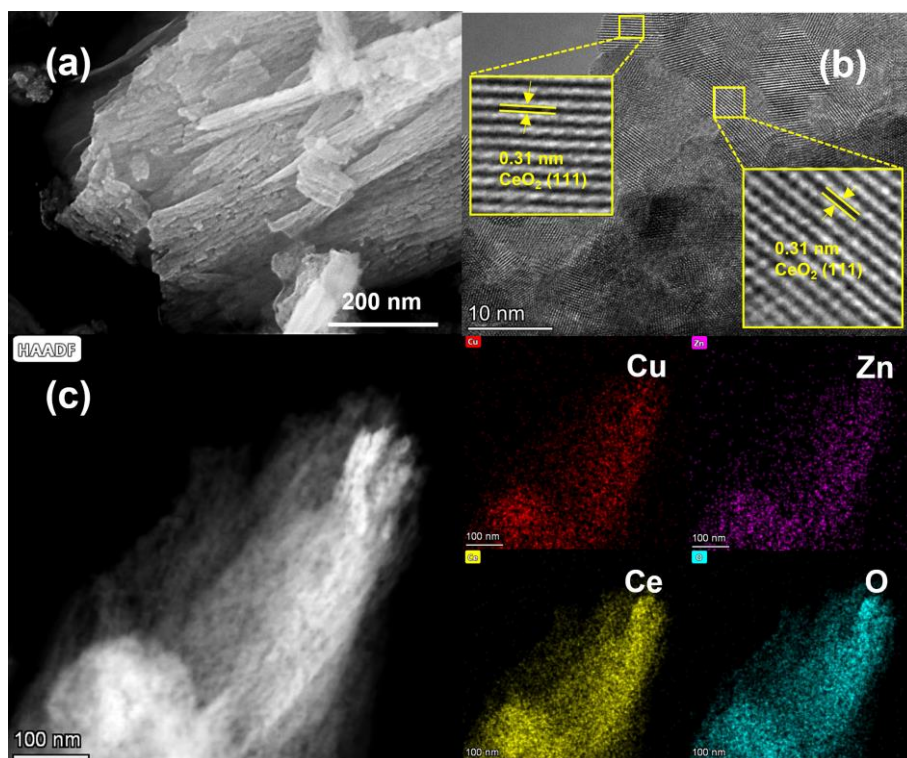


Fig. S5 SEM and TEM analysis of Cu/ZnO/CeO₂-co catalyst. (a) SEM image; (b) HR-TEM image; (c) HAADF-STEM image and corresponding element mapping of Cu, Zn, Ce and O.

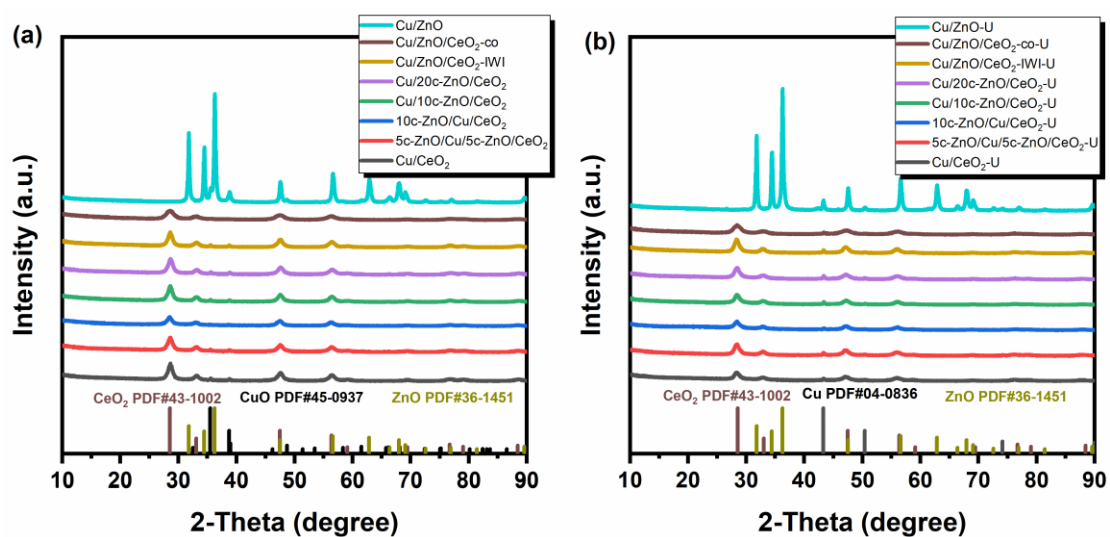


Fig. S6 XRD patterns of different Cu-based catalysts. (a) fresh; (b) used.

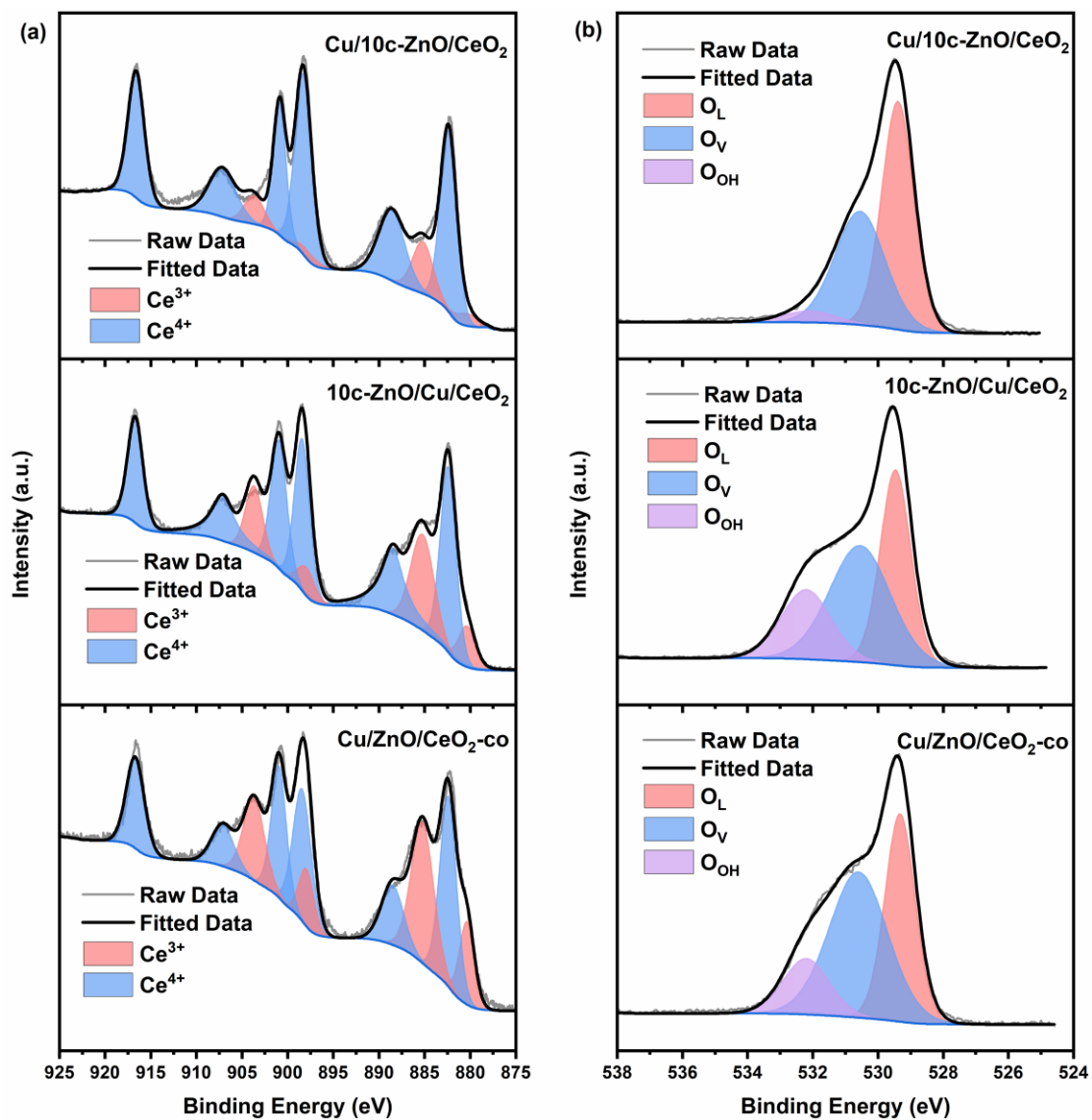


Fig. S7 Semi-in situ XPS spectra of (a) Ce 3d; (b) O 1s over Cu/10c-ZnO/CeO₂, 10c-ZnO/Cu/CeO₂ and Cu/ZnO/CeO₂-co catalysts.

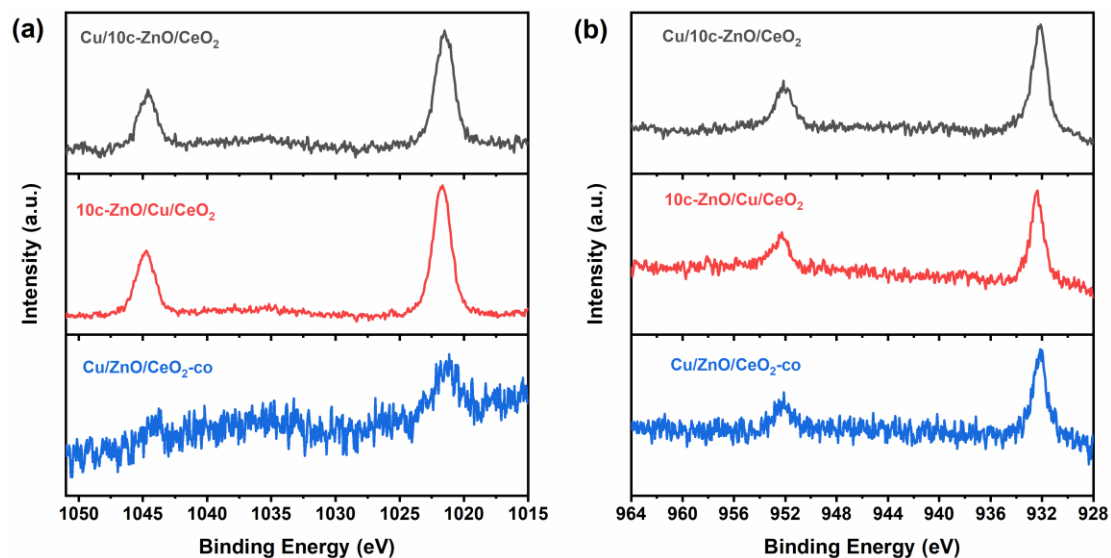


Fig. S8 Semi-in situ XPS spectra of (a) Zn 2p and (b) Cu 2p over Cu/10c-ZnO/CeO₂, 10c-ZnO/Cu/CeO₂ and Cu/ZnO/CeO₂-co catalysts.

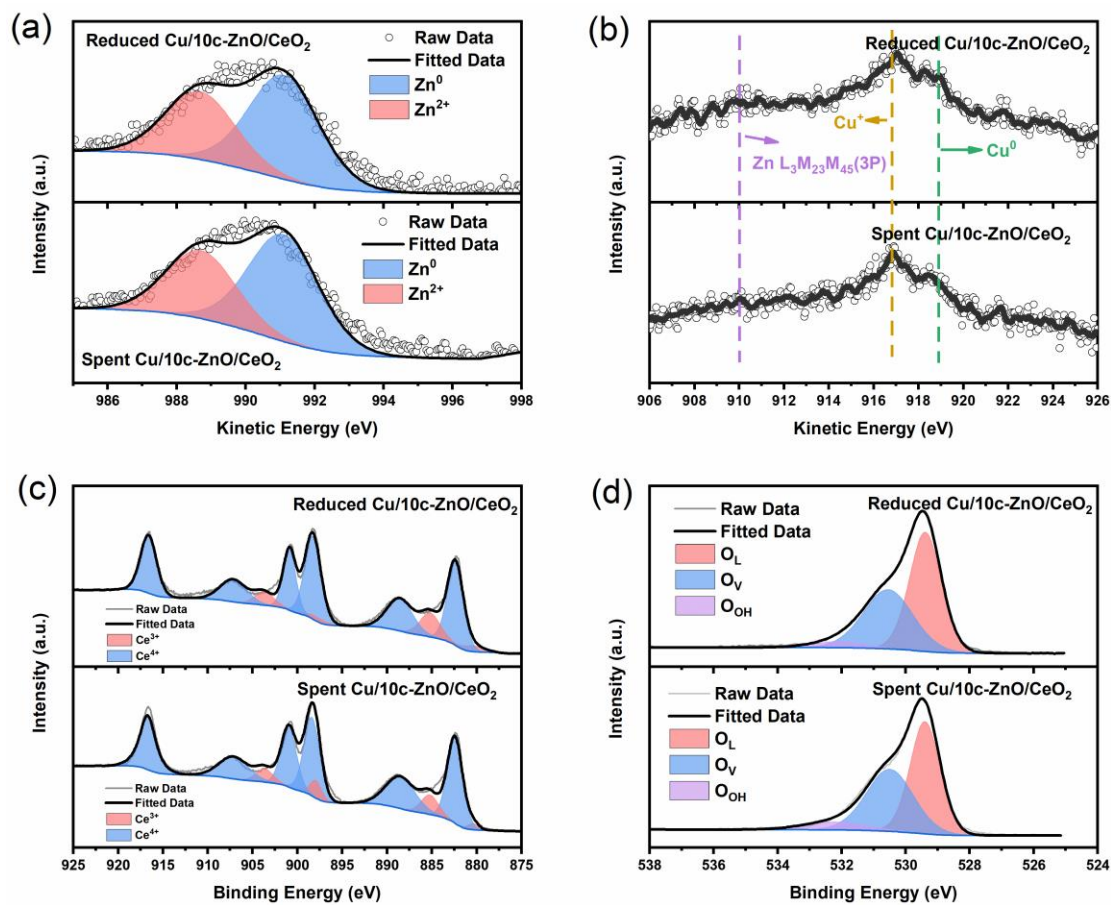


Fig. S9 Semi-in situ XPS spectra of Cu/10c-ZnO/CeO₂ catalyst and XPS spectra of spent Cu/10c-ZnO/CeO₂ catalyst. (a) Zn LMM; (b) Cu LMM; (c) Ce 3d; (d) O 1s.

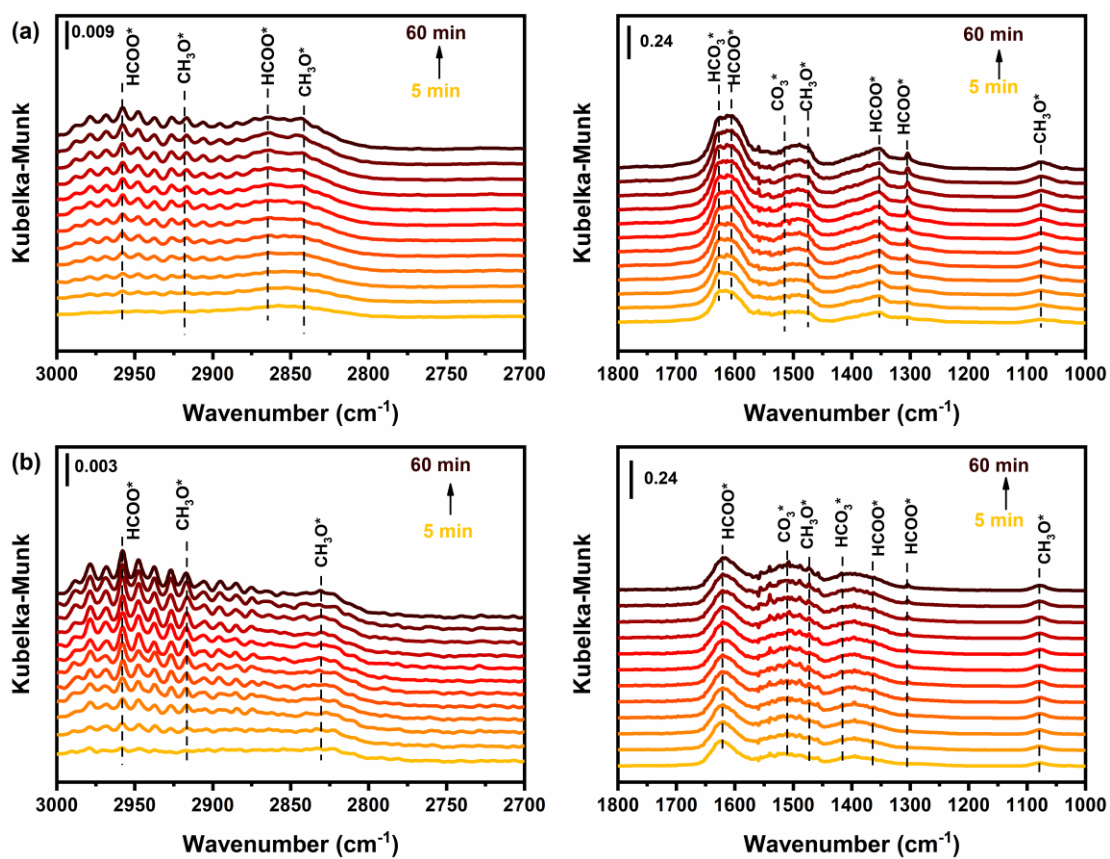


Fig. S10 In-situ DRIFT spectra of CO₂ hydrogenation over different Cu-based catalysts. (a) 10c-ZnO/Cu/CeO₂; (b) Cu/ZnO/CeO₂-co. Conditions: 3.0 MPa, 250 °C.

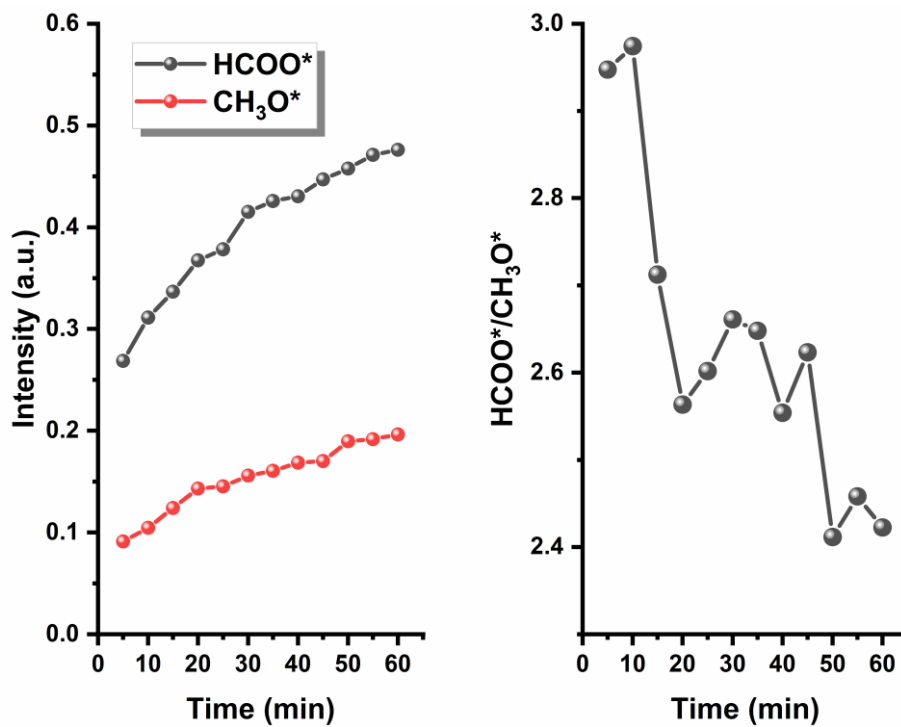


Fig. S11 The time-dependent curves of HCOO* and CH₃O* active intermediates on Cu/10c-

ZnO/CeO₂ catalyst.

Table S1 The Cu and Zn loadings of Cu-Zn-Ce oxide catalysts.

Catalyst	Cu loading ^a (wt.%)	Zn loading ^a (wt.%)
Cu/10c-ZnO/CeO ₂	9.74	0.66
10c-ZnO/Cu/CeO ₂	9.78	0.66
Cu/ZnO/CeO ₂ -co	9.87	0.63

^aMeasured by ICP-OES.

Table S2 Comparison of different Cu-baesd catalysts for CO₂ hydrogenation to methanol.

Catalysts	Cu loading (wt.%)	Temperature/Pressure (°C/MPa)	WHSV (mL g _{cat} ⁻¹ h ⁻¹)	CO ₂ Conversion (%)	CH ₃ OH Selectivity (%)	STY (mol _{MeOH} kg _{cat} ⁻¹ h ⁻¹)	STY (mmol _{MeOH} g _{Cu} ⁻¹ h ⁻¹)	Ref.
4CZA-AE	4	220/3.0	9000 ^a	12.3	97.2	9.9	247.7	3
ZnO/Cu/Al ₂ O ₃ -PCVD	5	250/3.0	31200	1.2	65.5	2.79	55.8	4
33Cu/ZnFe-0.5	33	260/4.5	21600	9.4	71.6	15.9	48.3	5
Cu/CeW _{0.25} O _x	10	250/3.5	7500	13	87	12.3	123.1	6
Cu/ZnO@UiO-66	5.86	250/4.0	18000 ^a	3.0	87.5	3.0	51.8	7
Cu/ZnO/Al ₂ O ₃	50.13	250/4.0	12000 ^a	9.72	47.2	3.6	7.2	7
Cu/10c-ZnO/CeO ₂	10	250/3.0	3600	8.1	79.9	2.6	26	this work
Cu/10c-ZnO/CeO ₂	10	250/3.0	18000	3.3	86.1	5.7	57	this work

WHSV = mass flow rate/catalyst mass, mL g_{cat}⁻¹ h⁻¹

^a GHSV = volume flow rate/bed volume, h⁻¹

STY (mmol g_{Cu}⁻¹ h⁻¹): the methanol production is referred to in terms of grams of copper

Table S3 Semi-in situ XPS quantitative results of Cu-based catalysts.

Catalyst	Zn ⁰ /Zn (at/at)	O _v /O (at/at)	Ce ³⁺ /Ce (at/at)	Atomic%			
				Cu	Zn	Ce	O
Cu/10c-ZnO/CeO ₂	60.6	41.9	14.1	4.7	2.6	23.9	68.8
10c-ZnO/Cu/CeO ₂	48.2	42.9	26.5	3.5	3.9	19.0	73.6
Cu/ZnO/CeO ₂ -co	25.4	49.1	37.8	2.8	1.1	20.8	75.3
Spent Cu/10c-ZnO/CeO ₂	61.3	43.3	12.2	4.6	2.8	24.4	68.2

Table S4 The amount of CO₂ desorption of Cu-Zn-Ce oxide catalysts.

Catalyst	Region α	Region β
	CO ₂ desorption (mmol g ⁻¹)	CO ₂ desorption (mmol g ⁻¹)
Cu/10c-ZnO/CeO ₂	20.3	12.5
10c-ZnO/Cu/CeO ₂	11.2	46.8
Cu/ZnO/CeO ₂ -co	10.3	53.7

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