Supplementary Information

ZrO_2-Promoted Highly Dispersed Cu-ZnO Catalysts for CO_2 Hydrogenation to Methanol Under Mild Conditions

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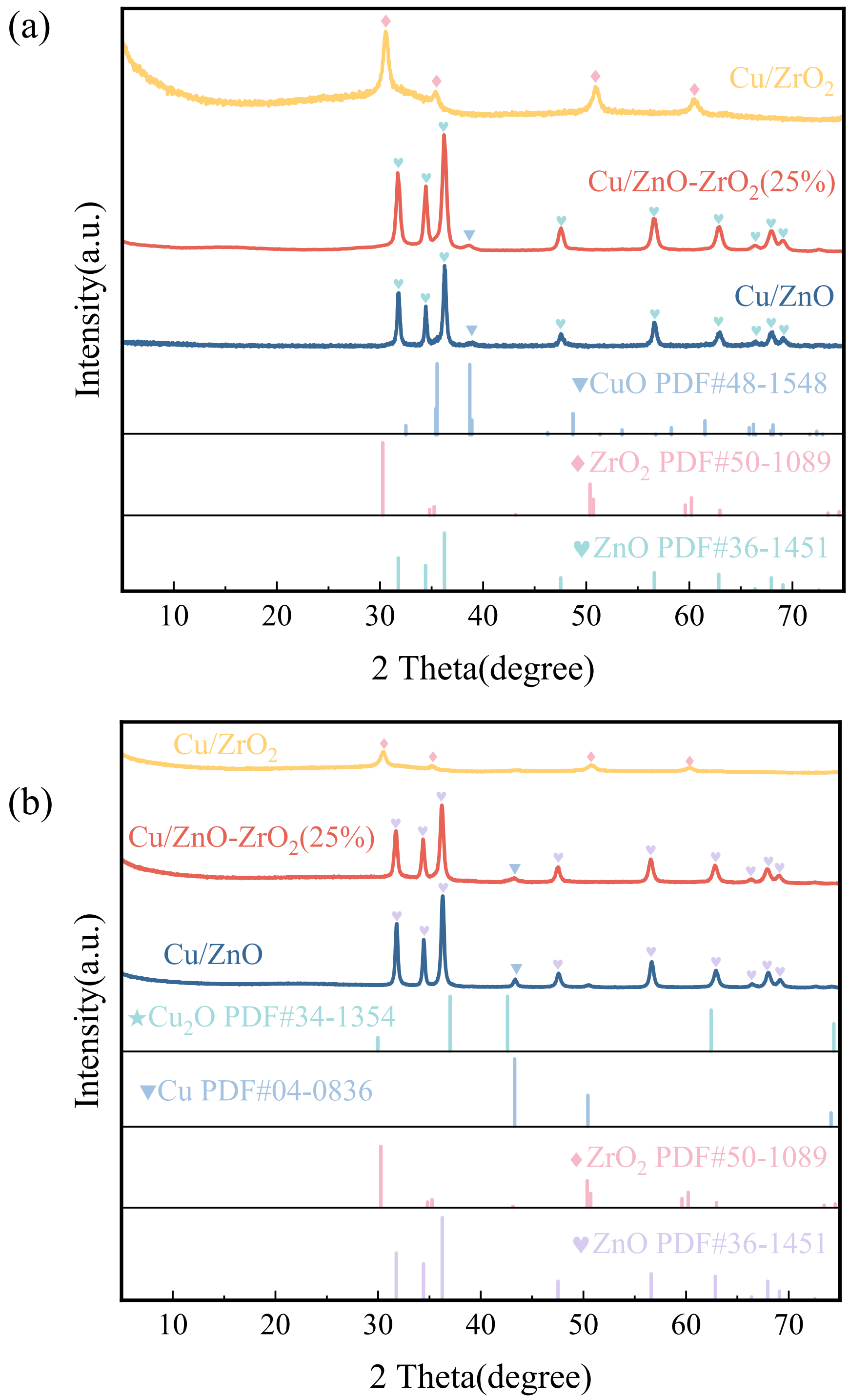

Fig. S1 (a) XRD patterns of calcined Cu/ZnO-x%ZrO_2 catalysts without formamide；(b) XRD patterns of reduced Cu/ZnO-x%ZrO_2 catalysts without formamide.

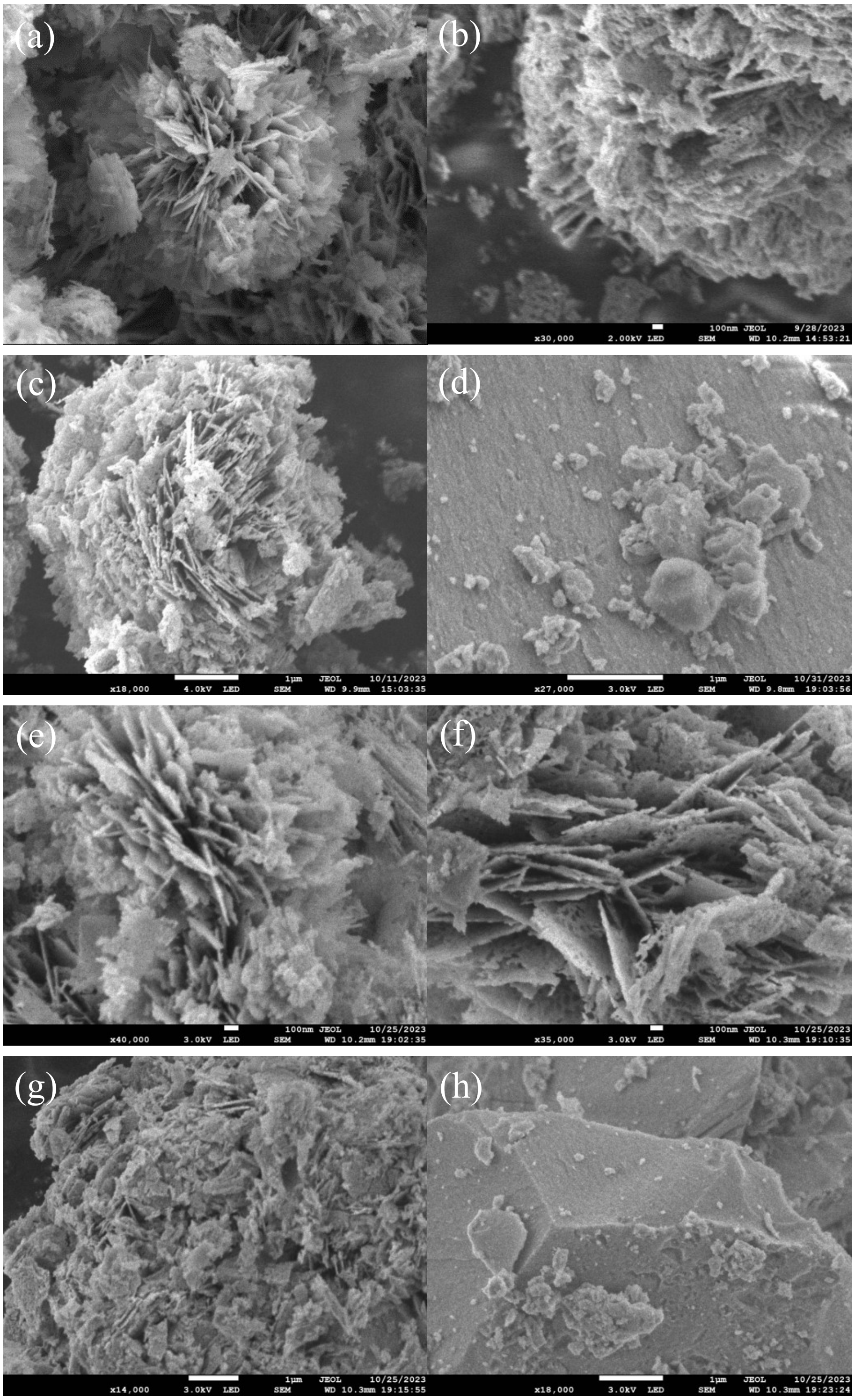

Fig. S2 (a-d) SEM images of calcined Cu/ZnO-x%ZrO_2 catalysts (x=0,25,40,100); (e-h) SEM images of reduced Cu/ZnO-x%ZrO_2 catalysts (x=0,25,40,100).

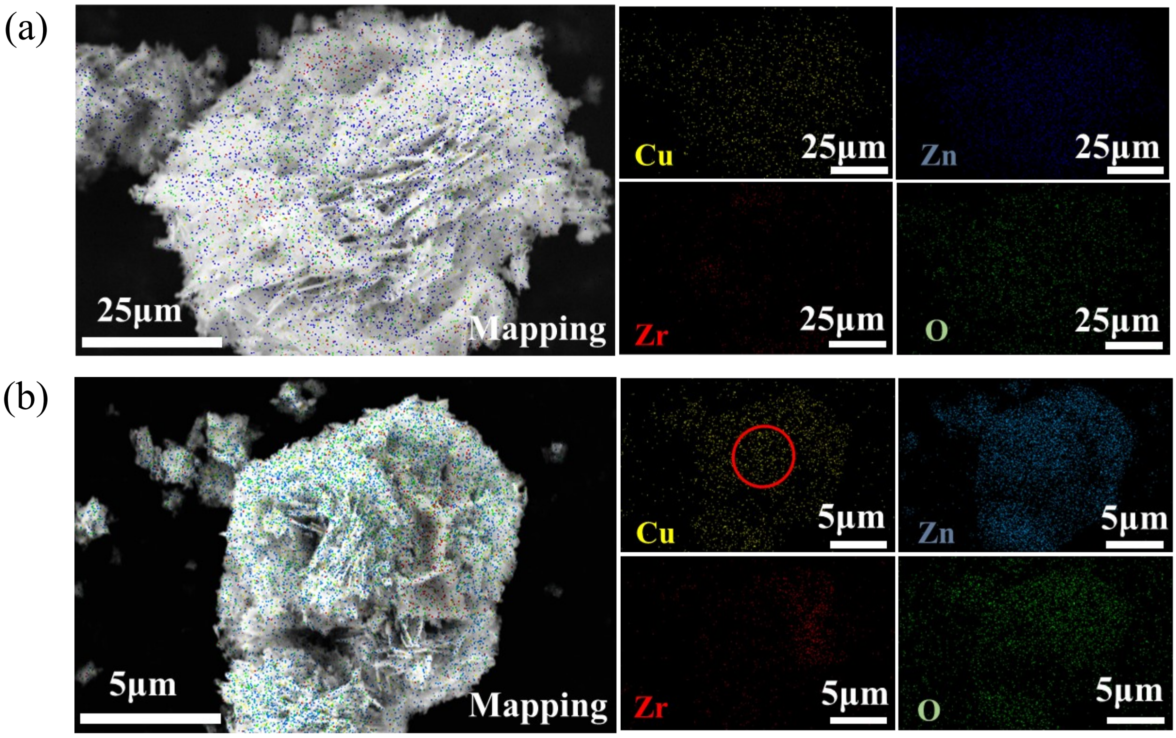

Fig. S3 SEM-Mapping images of calcined catalysts: (a) Cu/ZnO-25%ZrO_2; (b) Cu/ZnO-40%ZrO_2.

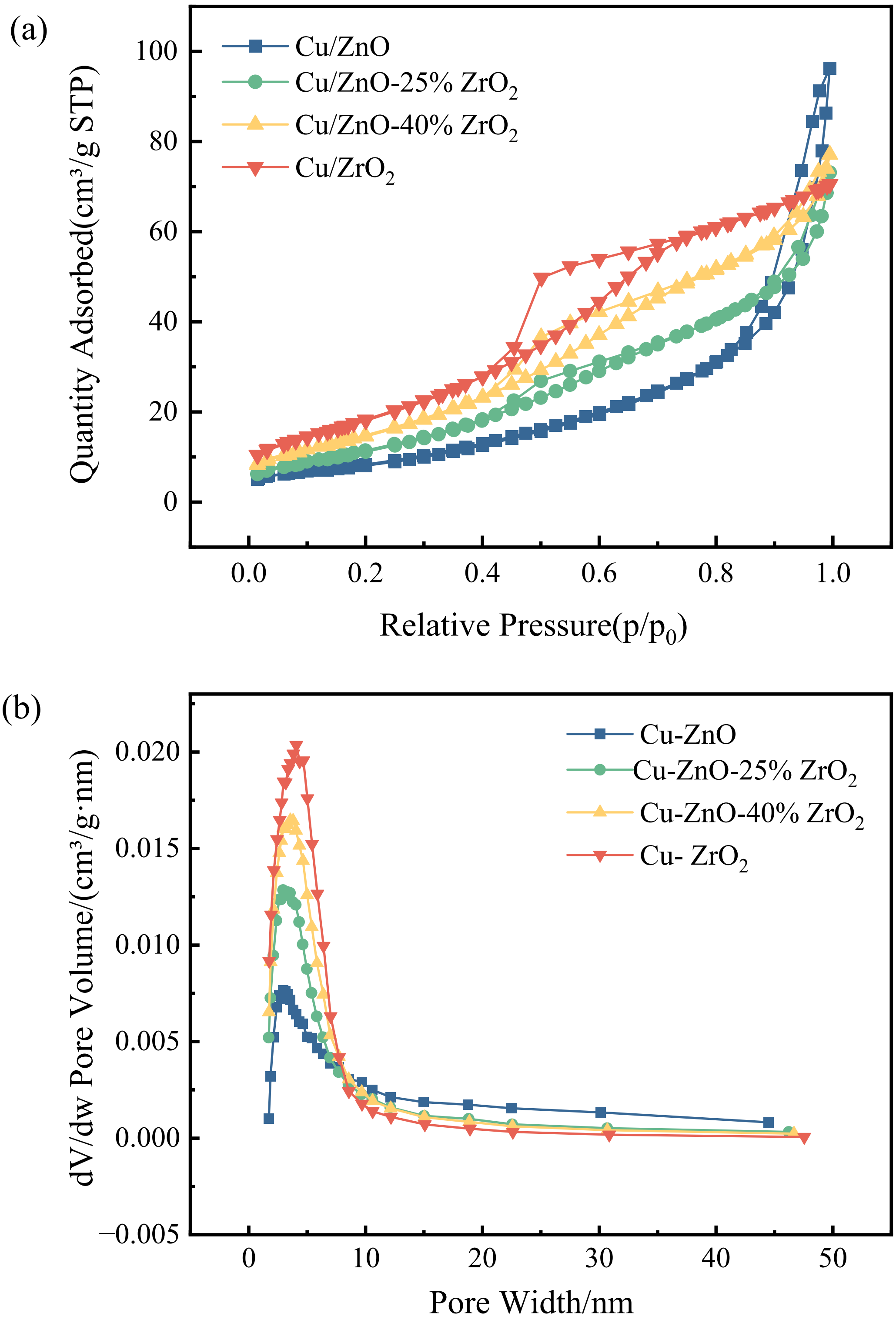

Fig. S4 The isotherm of N_2 adsorption-desorption and pore size distribution of Cu/ZnO-x%ZrO_2 catalysts.

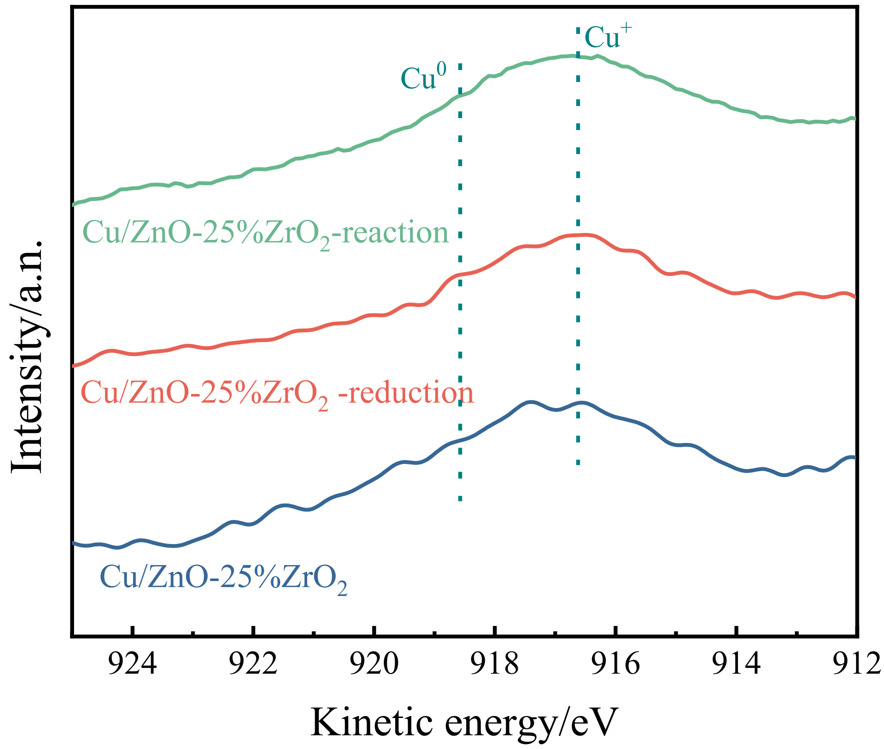

Fig. S5 Auger electron spectra (AES) of Cu of the Cu/ZnO-25%ZrO_2, Cu/ZnO-25%ZrO_2 -reduction and Cu/ZnO-25%ZrO_2-reaction.

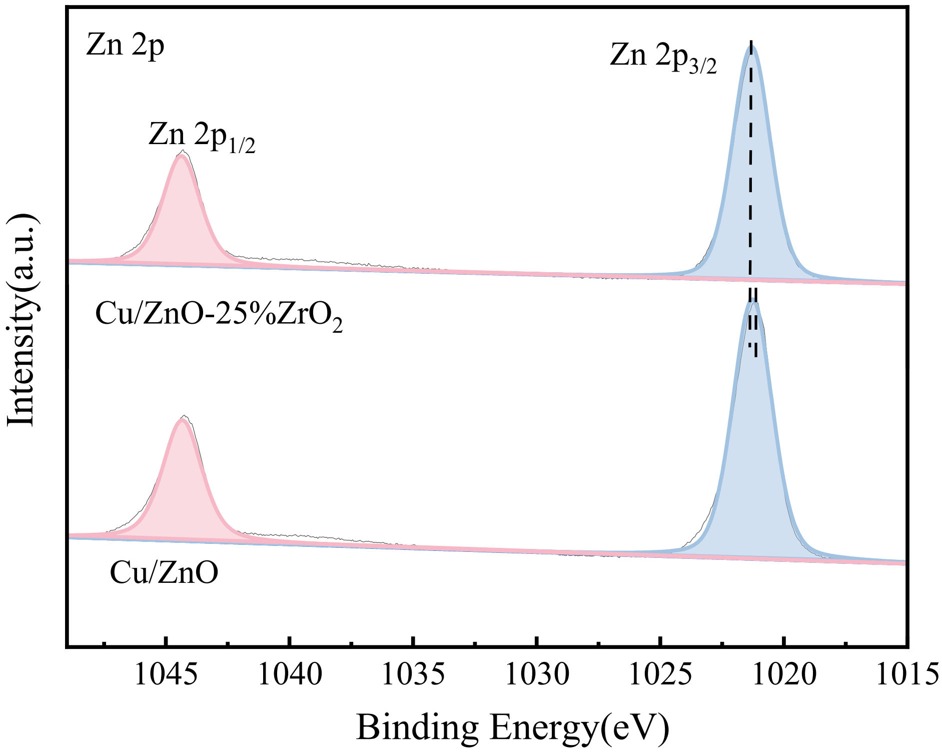

Fig. S6 Zn 2p XPS spectra for reduced Cu/ZnO-x%ZrO_2 catalysts.

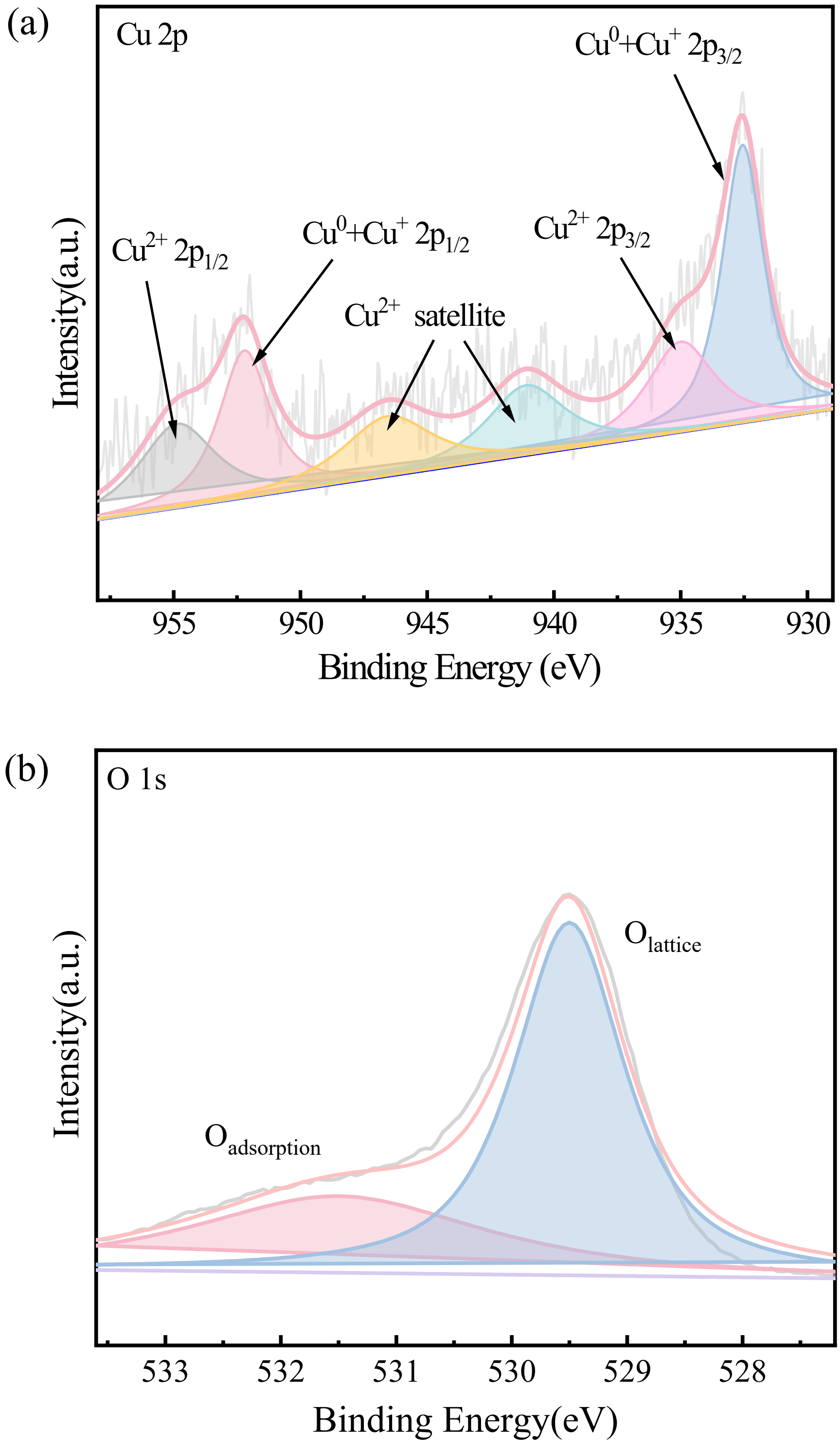

Fig. S7 Cu 2p XPS spectra and O 1s XPS spectra of Cu/ZnO-25%ZrO_2 catalysts after the reaction.

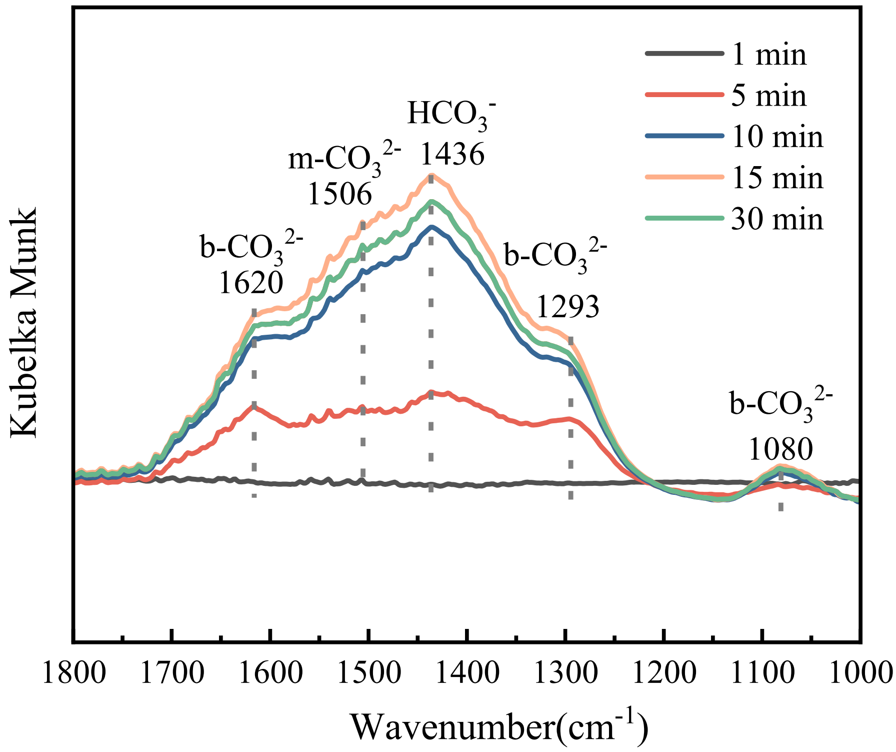

Fig. S8 CO_2 adsorption spectra of Cu/ZnO-25%ZrO_2 catalysts.

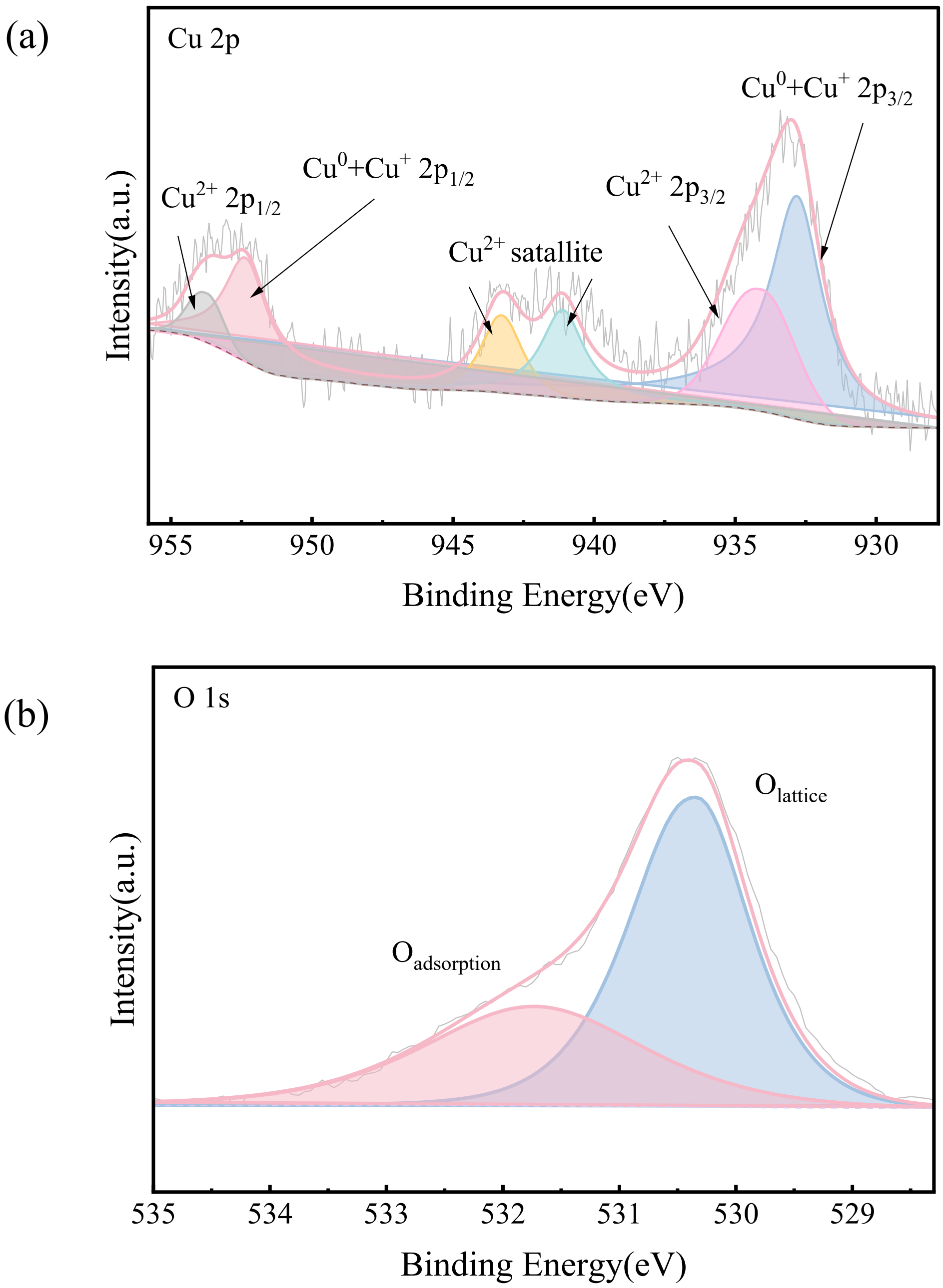

Fig. S9 Cu 2p XPS spectra and O 1s XPS spectra of reduced Cu/ZnO-40%ZrO_2 catalysts.

Table S1 Physicochemical properties of the $Cu/ZnO\text{-}x\%ZrO_2$ catalysts.

Catalysts	Metal Composition (wt%)			S_{BET} ($m^2 \cdot g^{-1}$)	D_{Cu} (%)
	Cu	Zr	Zn		
Cu/ZnO	7.98	0	73.71	32.03	16.91
$Cu/ZnO\text{-}25\%ZrO_2$	7.95	16.37	48.82	47.58	28.72
$Cu/ZnO\text{-}25\%ZrO_2$ without adding FA	7.96	16.42	48.57	47.41	19.26
$Cu/ZnO\text{-}40\%ZrO_2$	7.97	29.32	36.18	59.16	23.83
Cu/ZrO_2	7.98	75.07	0	72.33	20.25

Table S2 O 1s XPS analysis data of Cu/ZnO-x%ZrO_2 catalysts.

Catalysts	Peak area of $O_{lattice}$	Peak area of $O_{adsorption}$	$O_{adsorption}$/ (O_{lattic}+$O_{adsorption}$) (%)
Cu/ZnO	7862.18	2832.93	26.49
Cu/ZnO-25%ZrO_2 (Before reaction)	6081.60	3736.64	38.05
Cu/ZnO-25%ZrO_2 (After reaction)	5925.03	3591.07	37.82
Cu/ZnO-40%ZrO_2	7391.73	2953.32	28.55
Cu/ZrO_2	8441.87	2148.98	20.29

Table S3 Cu 2p XPS analysis data of $Cu/ZnO-x\%ZrO_2$ catalysts.

Catalysts	Peak area of Cu^0+Cu^+	Peak area of Cu^{2+}	Cu^0+Cu^+/ $(Cu^0+Cu^++Cu^{2+})$(%)
Cu/ZnO	2752.31	1343.76	67.19
$Cu/ZnO-25\%ZrO_2$ (Before reaction)	2647.60	984.66	72.89
$Cu/ZnO-25\%ZrO_2$ (After reaction)	3566.35	1490.50	70.53
$Cu/ZnO-40\%ZrO_2$	3060.39	1374.50	69.00
Cu/ZrO_2	1092.61	931.63	53.98

Table S4 H_2-TPR analysis data of Cu/ZnO-x%ZrO_2 catalysts.

Catalyst	Reduction T（℃）	Hydrogen consumed（mmol·g_{cat}^{-1}）	Reduction T（℃）	Hydrogen consumed（mmol·g_{cat}^{-1}）
Cu/ZnO	157	0.186	200	0.434
Cu/ZnO-25%ZrO_2	153	0.268	193	0.442
Cu/ZnO-40%ZrO_2	164	0.136	192	0.534
Cu/ZrO_2	/	/	176	0.471

Table S5 Catalyst for hydrogenation of CO_2 to CH_3OH, where T, P, S_{MeOH}, and STY are denoted to be temperature, pressure, methanol selectivity, and space time yield of CH_3OH, respectively.

Catalyst	T(K)	P(bar)	X_{CO2}(%)	S_{MeOH}(%)	STY ($g_{MeOH} \cdot g_{cat} \cdot h^{-1}$)	Ref.
Cu/ZnO-25%ZrO_2	473	30	6.7	85.0	0.586	/
Cu@ZIF-8	523	50	10.2	98.0	0.27	[1]
Cu/ZnO@UIO-66	523	40	7.33	86.1	0.320	[2]
Pd-ZnO@ZIF-8	563	45	3.5	78.0	0.594	[3]
CuIn-350	513	/	8.6	87.0	0.192	[4]
CuIn@SiO_2	553	30	9.8	78.1	0.515	[5]
CuNi-rGO	498	40	7.87	98.7	/	[6]
Cu-ZnOMOF⊂Al_2O_3	513	30	9.1	86.9	0.407	[7]

Notes and references

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