Supplementary Information for

Deactivation Mechanisms of Cu-Zn-Al_2O_3 in CO_2 Hydrogenation Induced by SO_2 Exposure

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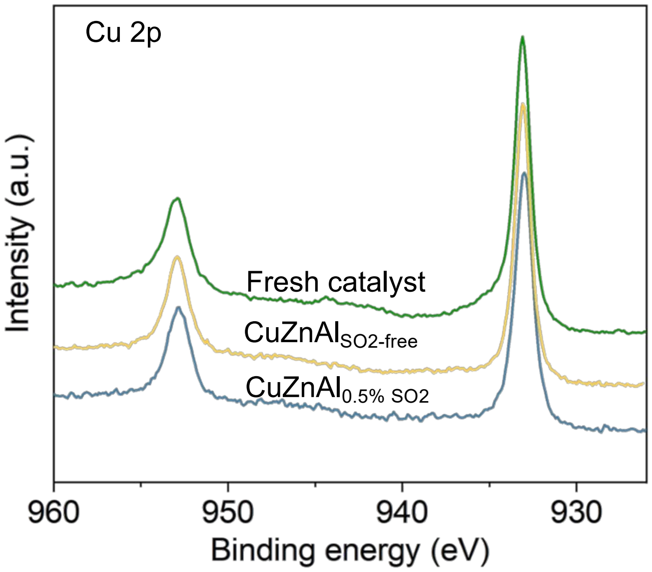

Fig. S1. XPS spectra of Cu 2p of fresh and used Cu-ZnO-Al_2O_3 catalysts.

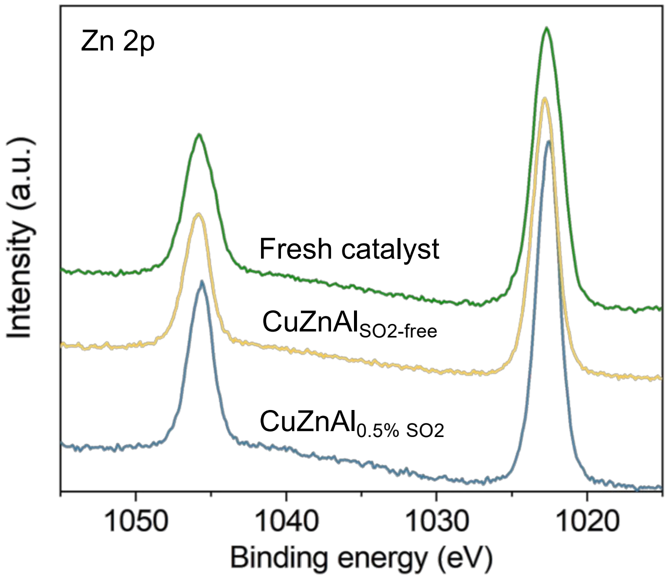

Fig. S2. XPS spectra of Zn 2p of fresh and used Cu-ZnO-Al_2O_3 catalysts.

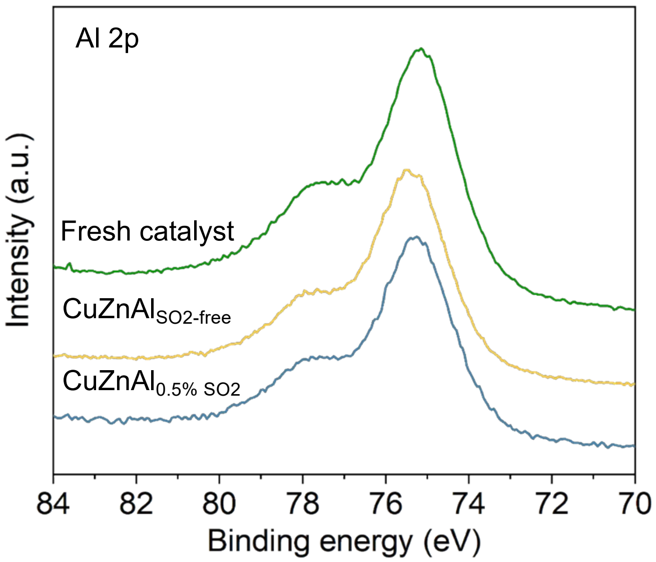

Fig. S3. XPS spectra of Al 2p of fresh and used Cu-ZnO-Al_2O_3 catalysts.

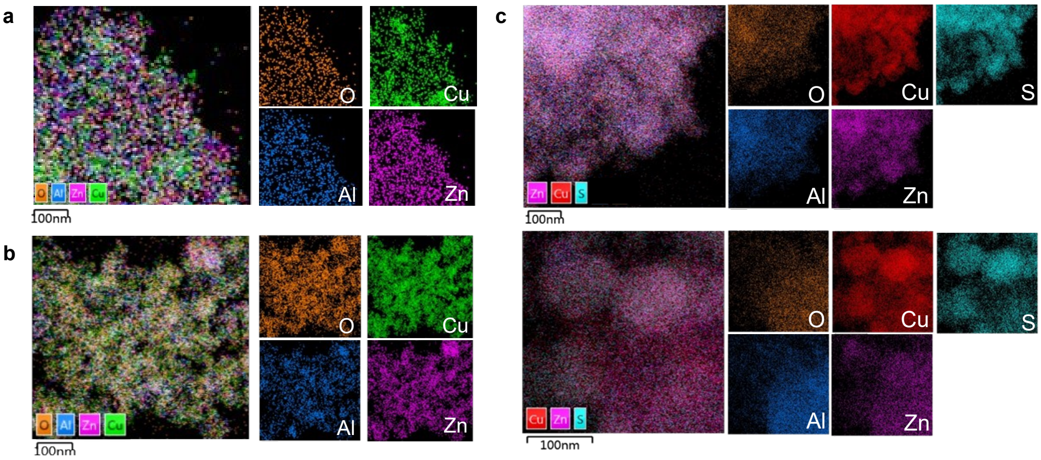

Fig. S4. STEM analysis and EDX mapping of Cu-ZnO-Al_2O_3.

(a) Fresh catalyst. (b) The used catalyst exposed to $H_2/CO_2/N_2$ (1:1:1) for 400 min at 500 °C. (c) The used catalyst exposed to $H_2/CO_2/N_2$ (1:1:1) with 0.5% SO_2 for 400 min at 500 °C.

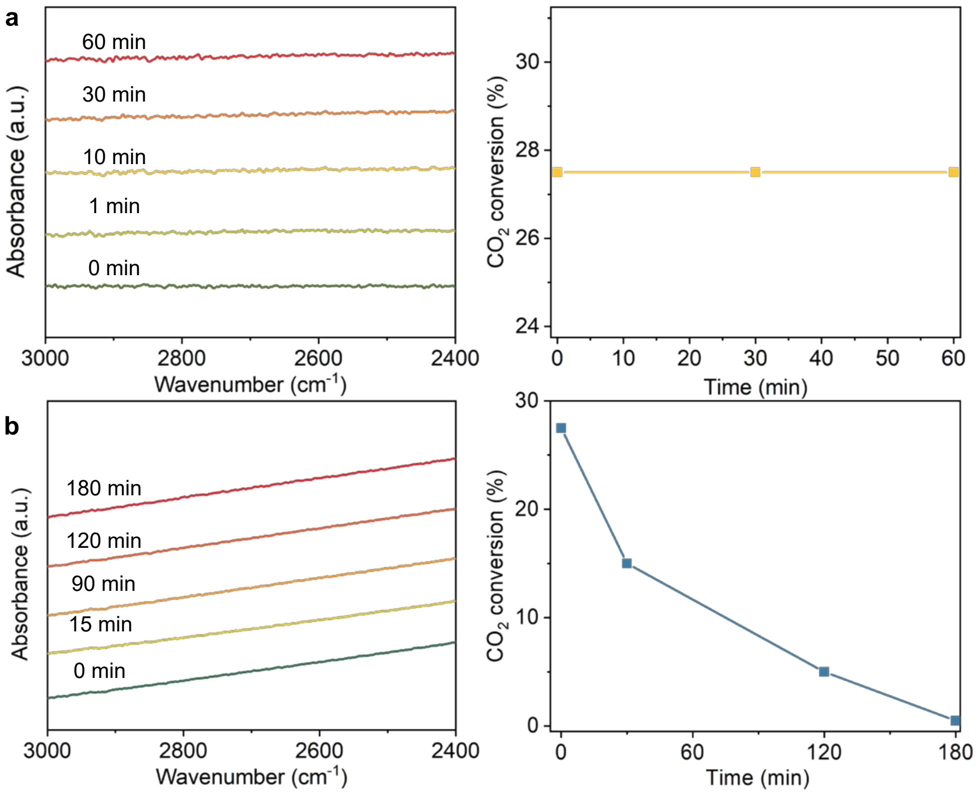

Fig. S5. Evolution of the surface functional groups over Cu-ZnO-Al_2O_3 with TOS.

The catalyst was first exposed to (a) $CO_2/H_2/N_2$ (1:1:1) for 60 min, followed by (b) switching the gas flow to $CO_2/H_2/N_2$ (1:1:1) with 0.5% SO_2. CO_2 conversion during the TOS of 180 min detected by gas analyzer. No CH_4 formation was detected. Reaction conditions: 500 °C, 1 bar, gas flow rate of 30 mL min^{-1}.

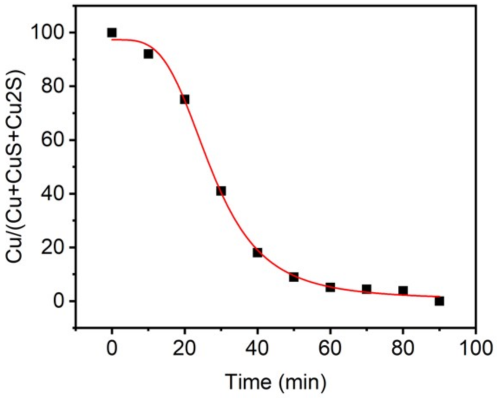

Fig. S6 Experimental data and fit of metallic Cu phase disappearance kinetics

The normalized phase fraction evolution of Cu (derived from XRD peak area) was fitted using a power-law logistic function:

$$X(t) = 0.64 + 96.68/(1 + (\frac{t}{27.3})^{3.8}$$

where:

X_0=0.64 represents the residual Cu fraction at equilibrium (unreacted Cu or background signal),

A=96.68 is the maximum amplitude of the reaction (total convertible Cu),

τ=27.3 min is the characteristic time for 50% conversion,

n=3.8 is the growth exponent reflecting the reaction mechanism.

Model validation demonstrates excellent agreement with experimental XRD trends (R^2=0.978). The kinetic analysis of copper sulfidation reveals a diffusion-controlled nucleation-growth mechanism, characterized by a time constant τ=27.3 min, indicating that 50% of Cu converts to CuS/Cu_2S within ~27 min. The growth exponent n=3.8 aligns with 3D diffusion-limited Avrami-like kinetics (theoretical n=3−4), supporting a three-stage mechanism.

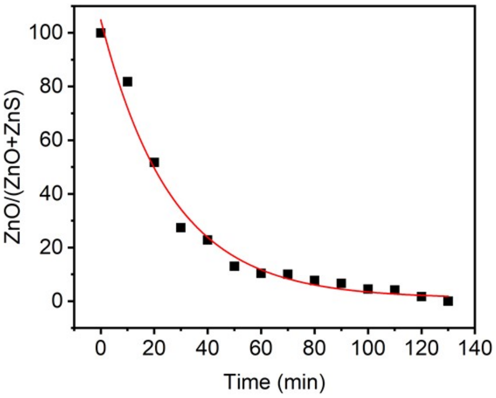

Fig. S7 Experimental data and fit of ZnO phase disappearance kinetics

The normalized residual ZnO fraction X(t), derived from XRD peak area integration, was fitted using a single-exponential decay model with a baseline offset:

$$X(t) = 103.8e^{-\frac{t}{26.3}} + 1.08$$

where:

A=103.8 represents the initial ZnO content,

τ=26.3 min is the characteristic time constant,

B=1.08 accounts for residual unreacted ZnO or instrumental background.

Model validation confirms the single-exponential decay model's superiority (R^2=0.983). The sulfidation kinetics of ZnO follows a first-order process with a rate constant k=0.038 min^{-1} and a half-life $t_{1/2}$≈18.2 min, indicating rapid consumption of 50% ZnO within 18 min. A small residual fraction (~1%, B=1.08) persists due to kinetic limitations, likely from ZnS passivation layers blocking further sulfur diffusion. Mechanistically, the reaction proceeds via two distinct phases:

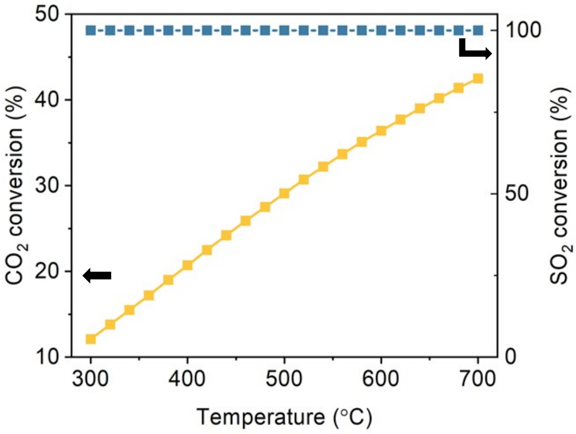

Fig. S8. Thermodynamic equilibrium calculation. (500°C, 0.5% SO_2, H_2/CO_2=1:1), SO_2 is converted to H_2S.

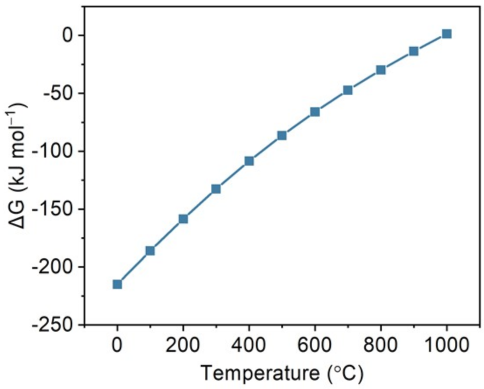

Fig. S9. Gibbs free energies of the reaction: SO_2 (g) + $3H_2$ (g) → H_2S (g) + $2H_2O$ (g).

Table S1. XPS fitting parameters of Cu LMM for fresh and used catalysts.

Material	State	Cu LMM B.E. (eV)	FWHM (eV)	[a]L/G Mix (%)	Amount (%)
Fresh catalyst	Cu^+	570.3		30	0
	Cu^0	568.4	1.5	30	100
$CuZnAl_{SO2\text{-}free}$	Cu^+	570.3	1.3	30	18
	Cu^0	568.4	1.4	30	82
$CuZnAl_{0.5\%\ SO2}$	Cu^+	570.3	1.8	30	58
	Cu^0	568.4	1.7	30	42

[a] L/G: Lorentzian/Gaussian line shape.

Table S2. XPS fitting parameters of Zn LMM for fresh and used catalysts.

Material	State	Zn LMM (eV)	FWHM (eV)	[a]L/G Mix (%)	Amount (%)
Fresh catalyst	$Zn^{\delta+}$	496.0	3.5	30	37
	Zn^{2+}	499.5	3.5	30	63
$CuZnAl_{SO2\text{-}free}$	$Zn^{\delta+}$	496.0	3.4	30	37
	Zn^{2+}	499.5	3.5	30	63
$CuZnAl_{0.5\%\ SO2}$	$Zn^{\delta+}$	496.0	3.5	30	33
	Zn^{2+}	499.5	3.5	30	67

[a] L/G: Lorentzian/Gaussian line shape.

Table S3. ICP-OES results of the fresh and used Cu/ZnO/Al_2O_3 catalysts.

	Cu (mg g^{-1})	Zn (mg g^{-1})	Al (mg g^{-1})	Cu loading (wt.%)	ZnO loading (wt.%)	Al_2O_3 loading (wt.%)	S (mg g^{-1})
Before reaction	461.9	182.4	49.1	59.1	29.0	11.9	-
$CuZnAl_{SO2\text{-}free}$	468.3	175.2	50.2	59.8	28.2	11.9	-
$CuZnAl_{0.5\%\ SO2}$	471.2	178.3	49.5	-	-	-	335.3

Note S1:

Theoretical sulfur content for complete conversion of Cu → Cu_2S and ZnO → ZnS was calculated as follows:

1. Mass balance:
    1) Initial Cu: 591 mg/g^{-1} → Moles of Cu = 591 mg / 63.55 g mol^{-1} = 9.30 mmol g^{-1}
    2) Initial ZnO: 290 mg g^{-1} → Moles of Zn = (290 mg × 65.38/81.38) / 65.38 g mol^{-1} = 3.56 mmol g^{-1}
2. Sulfur stoichiometry:
    1) Cu_2S requires 4.65 mmol S g^{-1} (9.30 mmol Cu × 1 mol S / 2 mol Cu).
    2) ZnS requires 3.56 mmol S g^{-1}.
    3) Total S = 4.65 + 3.56 = 8.21 mmol S g^{-1} → 263 mg S g^{-1} (26.3 wt%).

If Cu was fully converted to CuS, theoretical sulfur content for complete conversion of Cu → CuS and ZnO → ZnS was calculated as follows:

3. Sulfur stoichiometry:
    4) CuS requires 9.30 mmol S g^{-1} (9.30 mmol Cu × 1 mol S / 1 mol Cu).
    5) ZnS requires 3.56 mmol S g^{-1}.
    6) Total S = 9.30 + 3.56 = 12.86 mmol S g^{-1} → 412.3 mg S g^{-1} (41.2 wt%).