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Efficient CO_2 catalytic hydrogenation over CuO_x-ZnO/ Silicalite-1 with stable Cu^+ species

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Table S1. Reaction performance of the catalysts at different temperature.

Catalyst	T (°C)	Conversion (%)	Selectivity (%)				CO_2 Reaction Rate/(mmol/g/h)
			CO	CH_4	C_{2+}	CH_3OH	
10CuO-2ZnO/S-1	200	0.8	93.0	7.0	0.0	0.00	0.17
	250	7.5	88.0	2.6	0.0	9.4	1.87
	300	17.9	94.0	3.3	0.4	2.4	4.48
10CuO/S-1	200	--	--	--	--	--	--
	250	2.5	93.1	6.9	0.0	0.00	0.62
	300	10.6	91.1	8.7	0.0	0.2	2.65
2ZnO/S-1	200	--	--	--	--	--	--
	250	1.1	87.6	12.4	0.0	0.00	0.27
	300	5.4	84.5	14.2	1.3	0.00	1.35
10ZnO/S-1	250	1.7	91.4	8.6	0.0	0.00	0.42
	300	6.6	89.7	10.3	0.0	0.00	1.65
S-1	250	0.8	96.7	3.3	0.0	0.00	0.19
	300	5.3	89.5	10.5	0.0	0.00	1.34

Reaction conditions: Pressure 3 MPa, Gas flow rate 90 mL/min 10%CO_2/30%H_2/60%N_2, 0.9 g catalyst，WHSV=6000 mL/g_{cat}/h.

Table S2. Physicochemical properties of different catalysts.

Catalyst	Cu(wt.%)[a]	Zn(wt.%)[a]	S_{BET}(m^2/g)	D_{Cu}(%)[b]
S-1	--	--	420	--
2ZnO/S-1	--	1.7	391	--
10CuO/S-1	8.6	--	372	10.4
10CuO-2ZnO/S-1	8.6	1.4	340	10.8
Used-10CuO-2ZnO/S-1	7.6	0.9	323	--

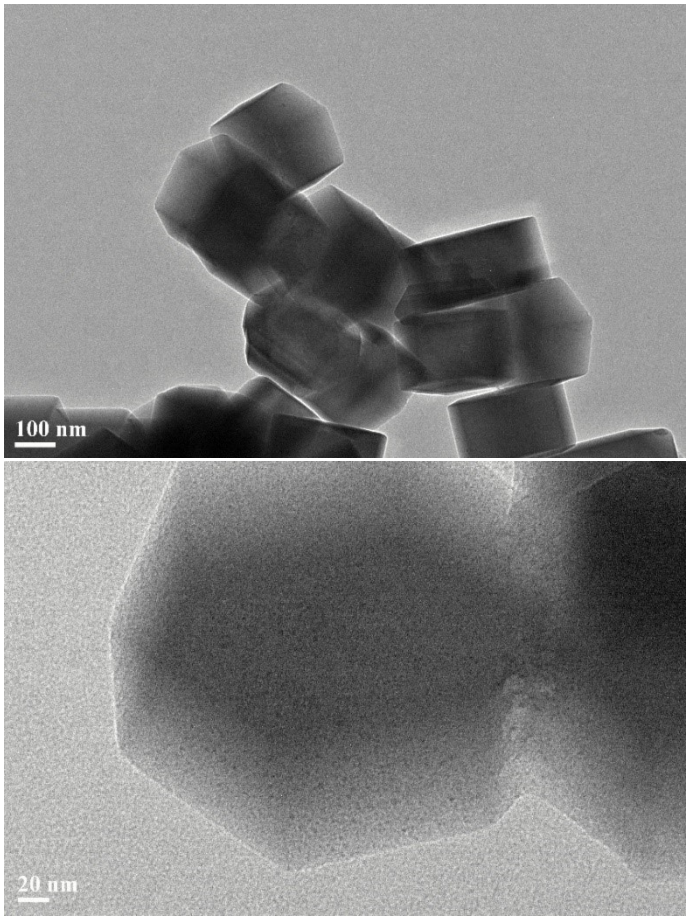
[a] Obtained from ICP-OES analysis.

[b] Through N_2O chemisorption experiments, calculated method referred to reference[1].

Table S3. Catalytic performance of the Cu-based/S-1 and $10Cu^0/SiO_2$ catalysts.

Catalyst	T (°C)	Conversion (%)	Selectivity (%)				Reaction Rate (mmol/g/h)
			CO/CO_2	CH_4	C_{2+}	CH_3OH	
10CuO-2ZnO/S-1[a]	250	8.2	0.0	30.7	69.3	0	4.69
10CuO/S-1[a]	250	8.9	0.0	28.8	71.2	0	5.28
$10Cu^0/SiO_2$[b]	250	1.4	67.8	21.9	1.2	9.1	0.36

Reaction conditions: [a] Pressure 3MPa, Gas flow rate 30 mL/min 10%CO_2/30%H_2/60%N_2, 0.3 g catalyst，WHSV=6000 mL/g_{cat}/h. [b] Pressure 3MPa, Gas flow rate 30 mL/min 24%CO/72%H_2/4%N_2, 0.3 g catalyst，WHSV=6000 mL/g_{cat}/h.



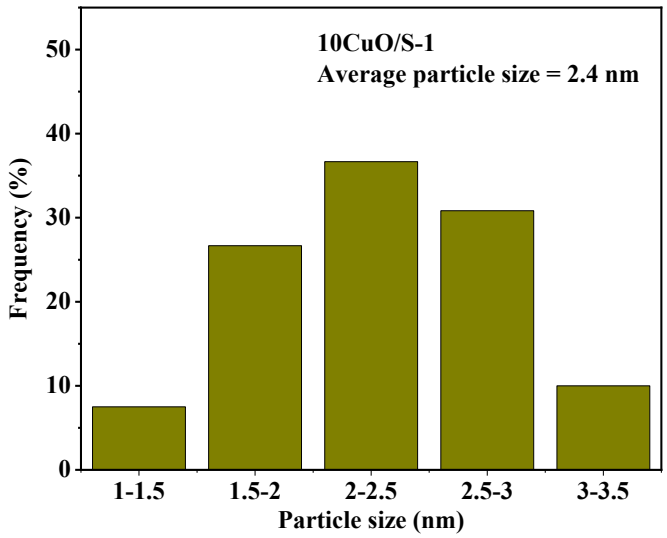


Figure S1. TEM image of the 10CuO/S-1.

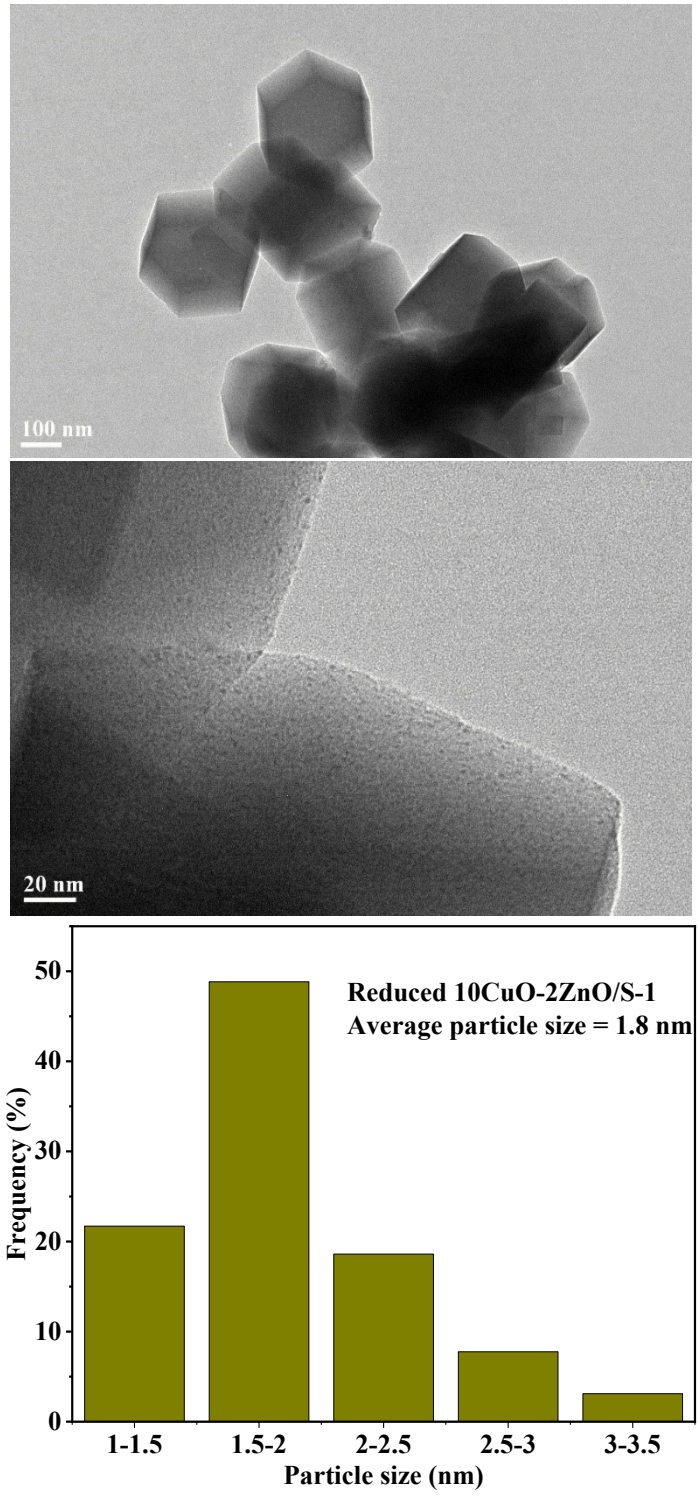


Figure S2. TEM image of the 10CuO-2ZnO/S-1.

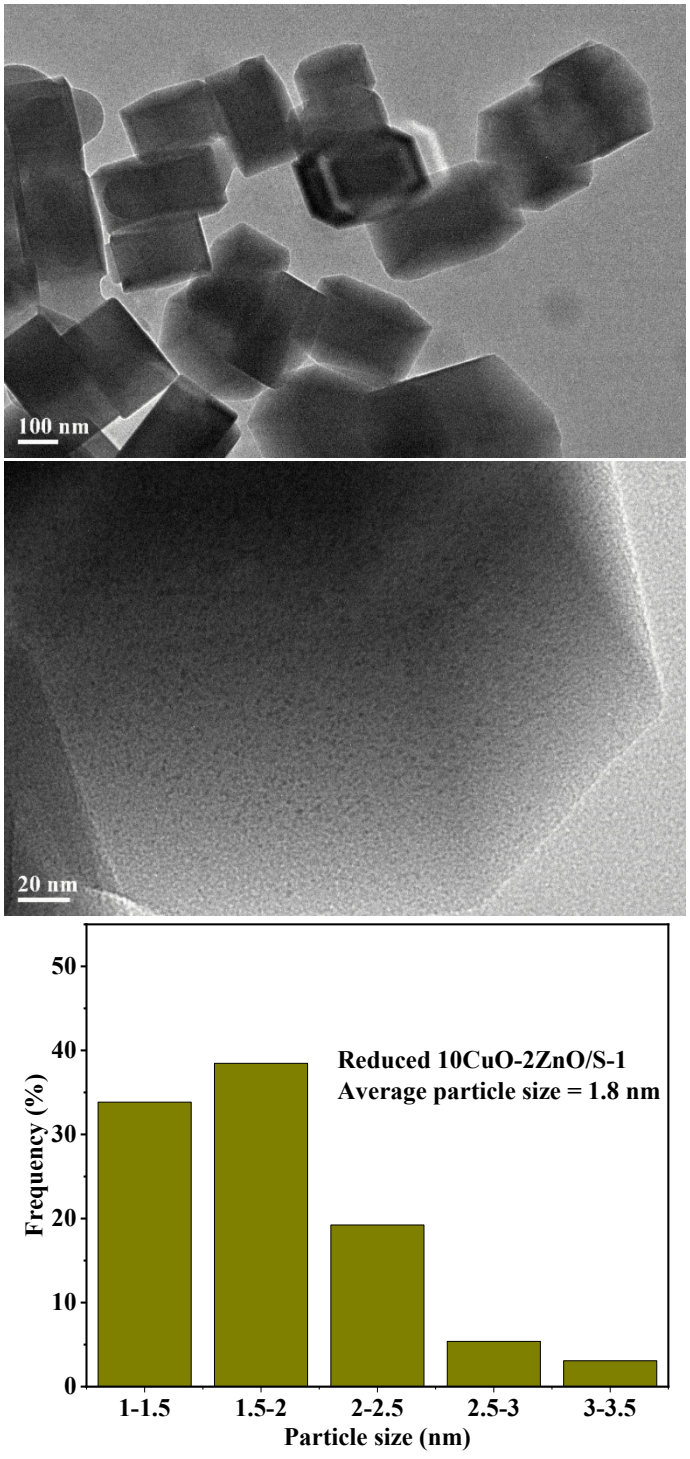


Figure S3. TEM image of the reduced 10CuO-2ZnO/S-1.

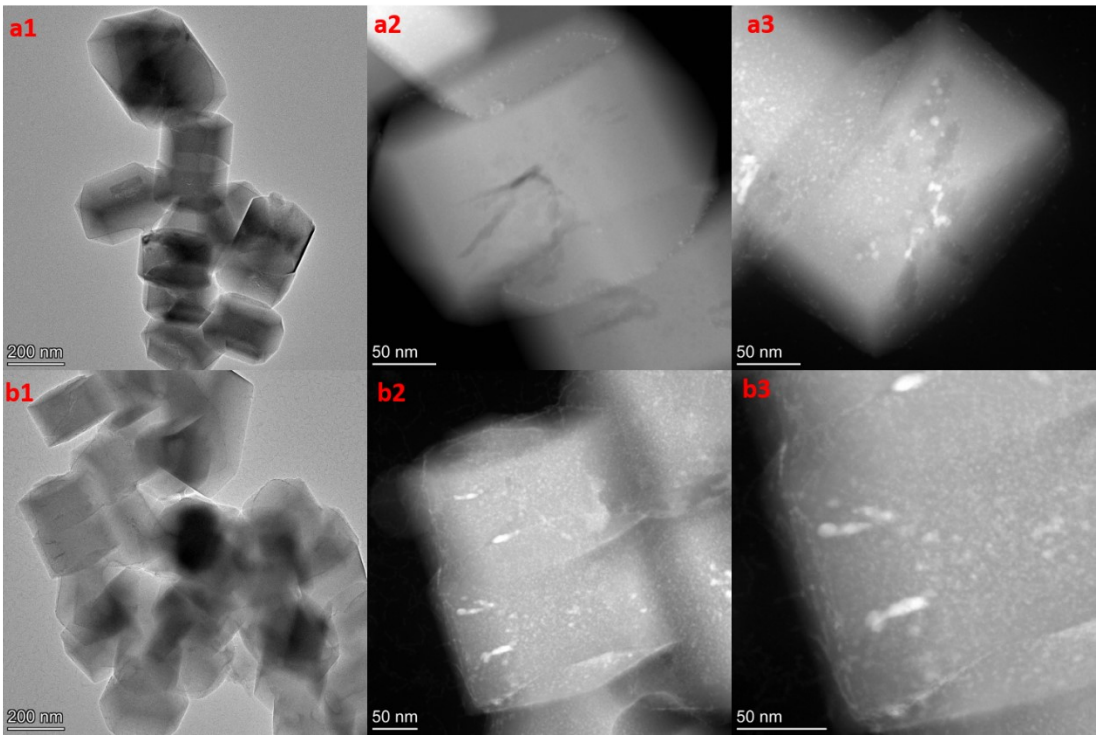


Figure S4. HAADF-STEM image of the (a1-a3) 10CuO/S-1 and (b1-b3) 10CuO-2ZnO/S-1.

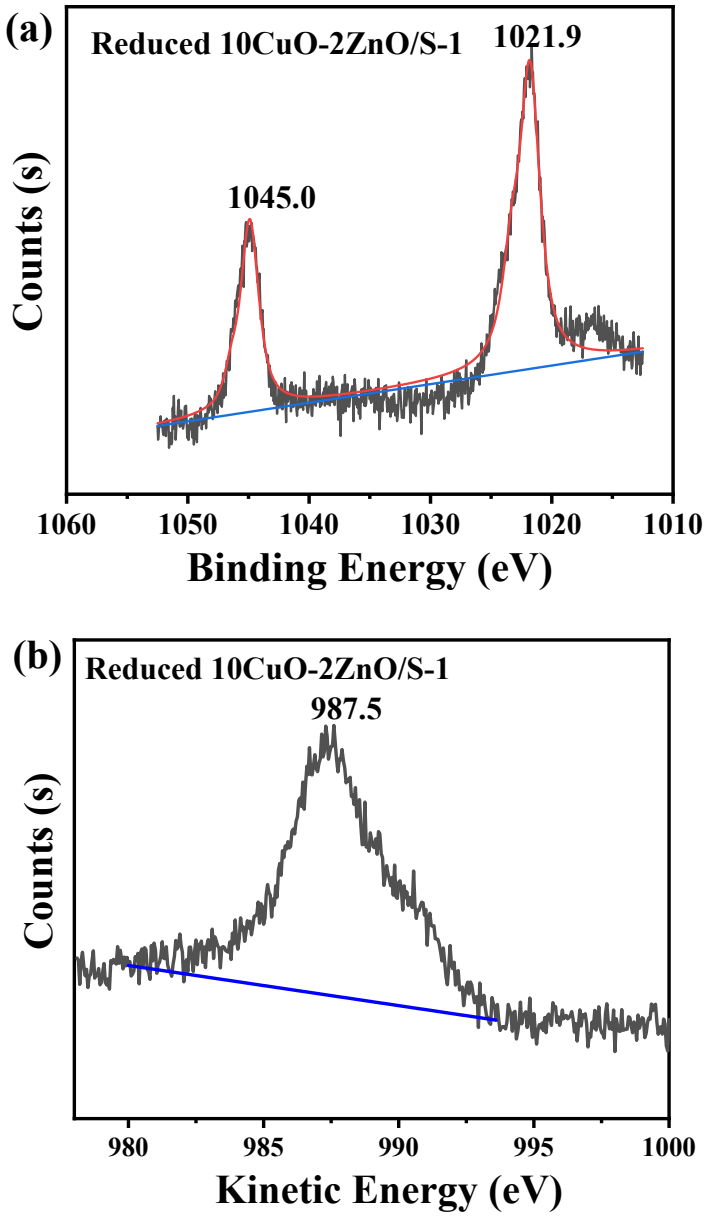


Figure S5. X-ray photoelectron spectra of (a) Zn; (b) Zn L3M45M45 of reduced 10CuO-2ZnO/S-1.

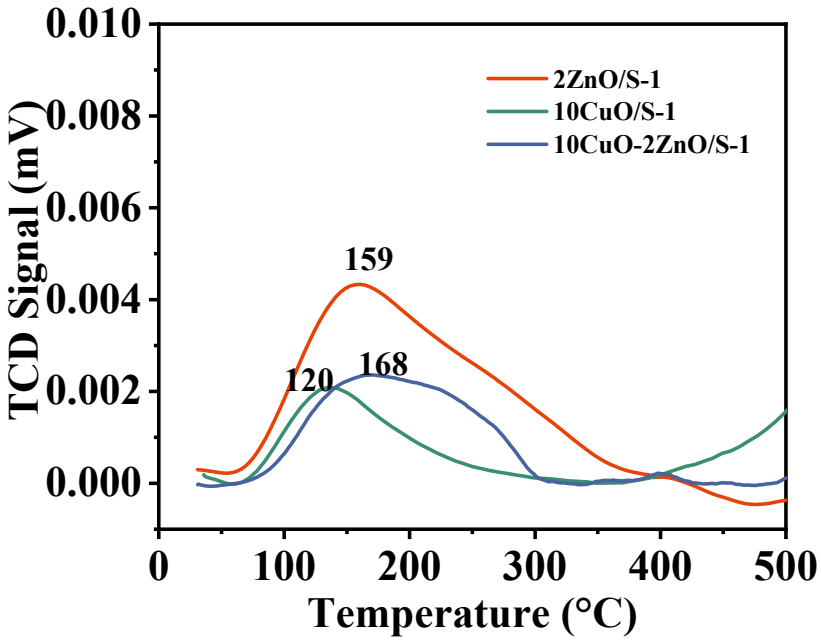


Figure S6. H_2-TPD of 2ZnO/S-1, 10CuO/S-1 and 10CuO-2ZnO/S-1.

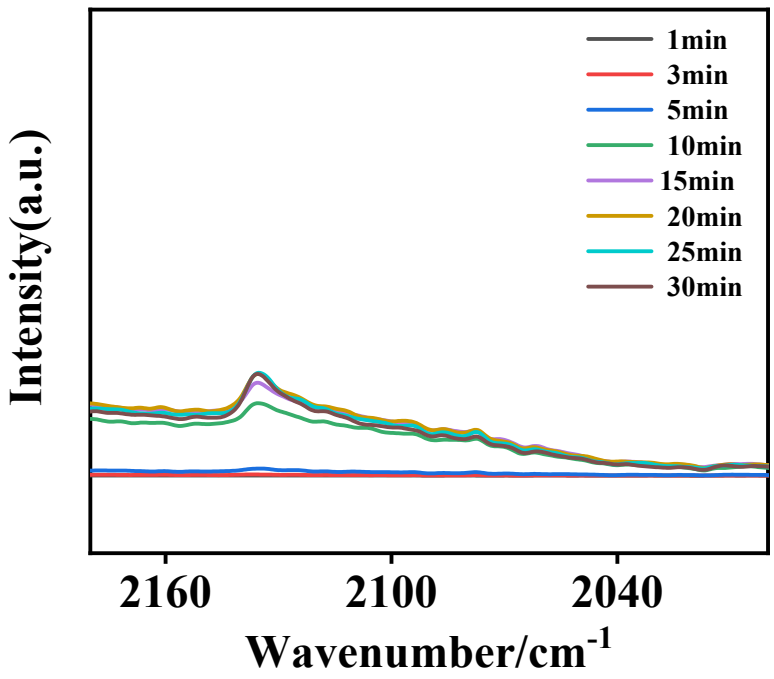


Figure S7. In-situ CO_2+H_2 DRIFT spectra at CO region of 10CuO-2ZnO/S-1 at 35 °C.

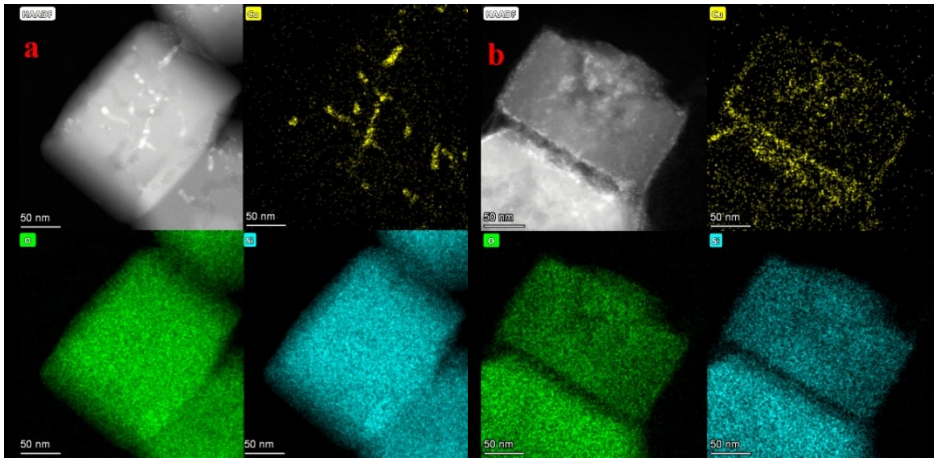


Figure S8. HAADF-STEM image and corresponding EDX elemental mapping spectra of the (a) 10CuO/S-1; (b) 10CuO-2ZnO/S-1 after reaction for 100 h.

References：

1. Chinchen, G. C.; Hay, C. M.; Vandervell, H. D.; Waugh, K. C., The measurement of copper surface areas by reactive frontal chromatography. *J. Catal.* **1987,** *103* (1), 79-86.