Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Dependence of copper particles size and interface on the methanol and CO formation in CO_2 hydrogenation over Cu@ZnO catalysts

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1. Supplementary figures:

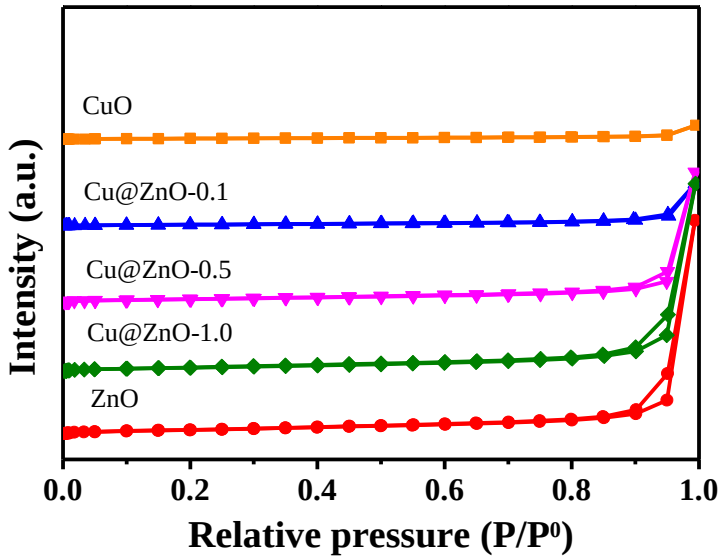

Fig. S1 The N_2 adsorption-desorption isotherms of CuO@ZnO catalysts.

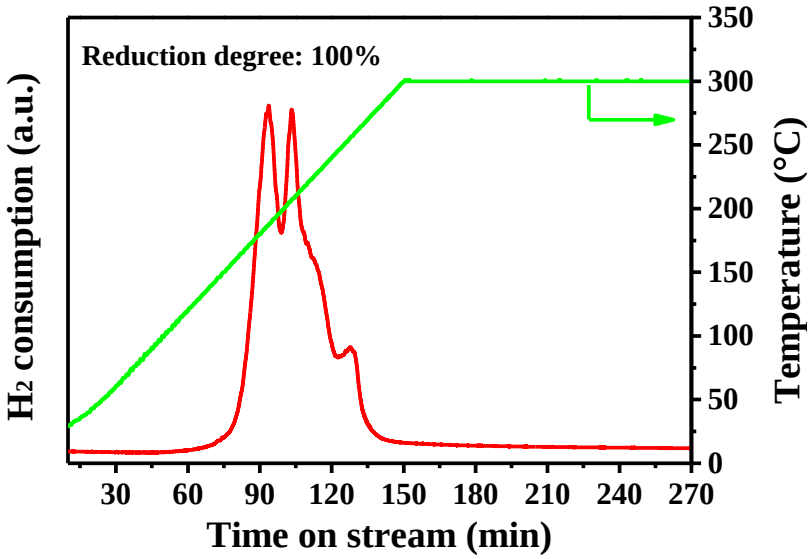

Fig. S2 H_2-TPR profiles of pure CuO under the real reduction conditions of 300 ℃, 2 h and a rate of 2 ℃ min^{-1}.

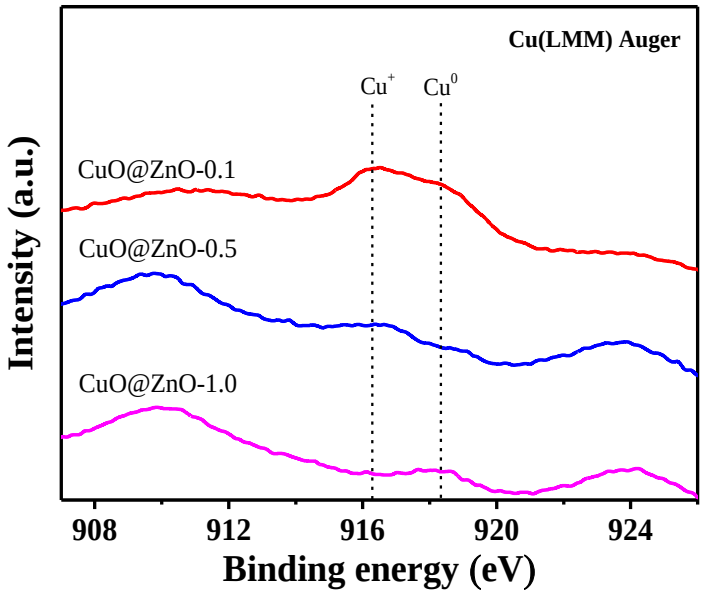

Fig. S3 Cu LMM Auger spectra of the reduced CuO@ZnO catalysts

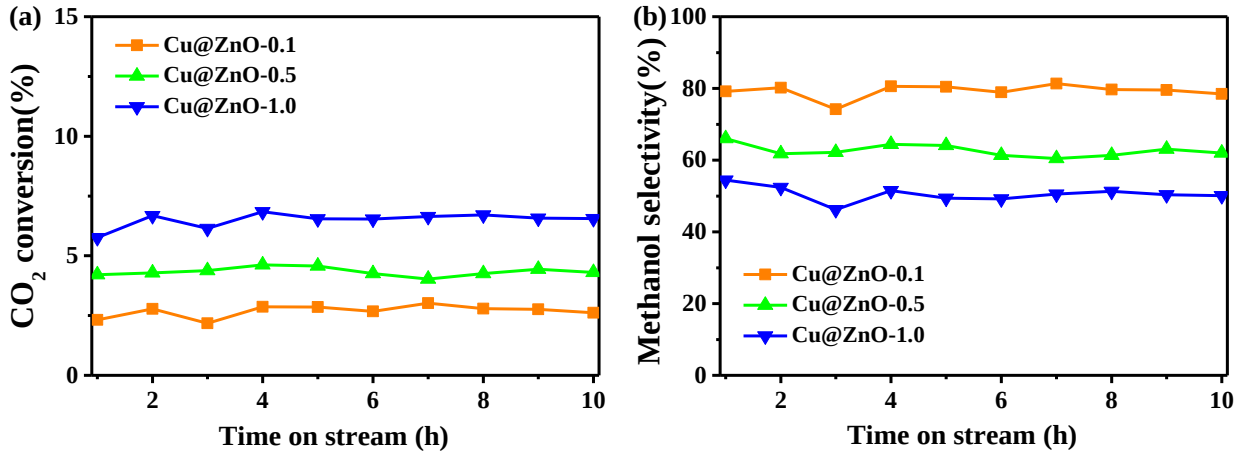

Fig. S4 Time on stream of evolution of CO_2 conversion (a) and product selectivity (b) over various Cu@ZnO catalysts. Reaction conditions: catalyst = 0.3 g, H_2/CO_2 = 3, GHSV = 12000 mL g_{cat}^{-1} h^{-1}, 3 MPa, 10 h, 240 ℃.

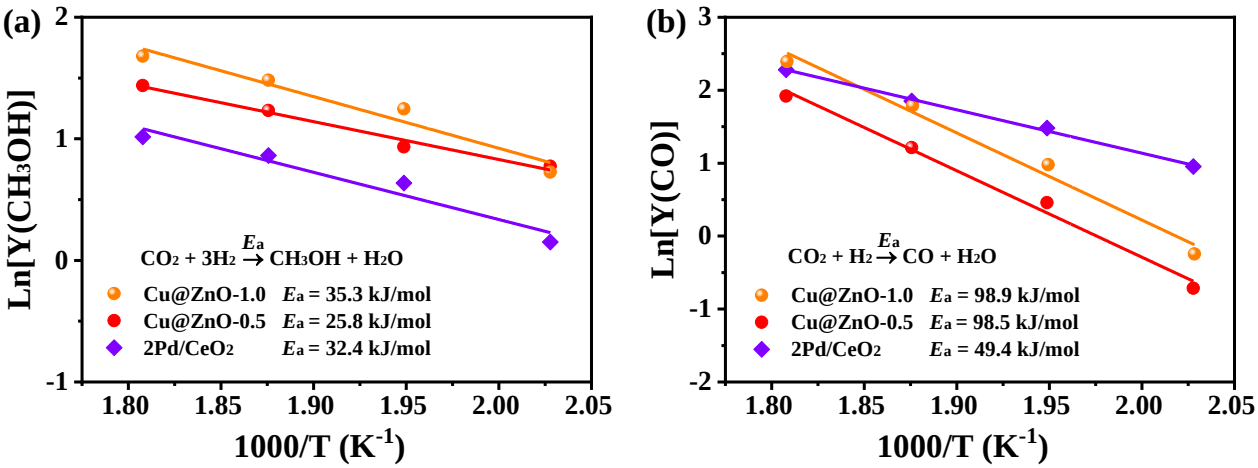

Fig. S5 Arrhenius plots for (a) methanol synthesis, and (b) RWGS reaction between 220 and 280 ℃ for the calculations of apparent activation energy (E_a) for Cu@ZnO and Pd/CeO_2 catalysts.

2. Supplementary tables:

Table S1 The compositions of Cu@ZnO catalysts measured by ICP.

Catalyst	Cu (wt. %)	Zn (wt. %)	Zn/Cu
Cu@ZnO-0.1	69.7	8.1	0.11
Cu@ZnO-0.5	46.8	26.8	0.56
Cu@ZnO-1.0	35.4	35.9	1.11

Table S2 Summary of the Cu-ZnO based catalysts for the hydrogenation of CO_2 to methanol

Catalyst	Preparation	H_2/CO ratio	T_R (℃)	P_R (MPa)	Space velocity[a]	Conv. (%)	Sel. (%)	CH_3OH rate (mg g_{cat}^{-1} h^{-1})	Reference
Cu@ZnO-1.0	Deposition precipitation	3:1	240	3.0	(W) 36000	3.7	72.6	335.7	This work
Cu-ZnO	Oxalate coprecipitation	3:1	240	3.0	(W) 2400	16.1	36.5	44.3	1
Cu(1)ZnO	Wet impregnation	9:1	180	0.7	(W) 4000	--	--	1.1	2
Cu(8)ZnO	Wet impregnation	9:1	180	0.7	(W) 4000	--	--	2.8	2
Cu(15)ZnO	Wet impregnation	9:1	180	0.7	(W) 4000	--	--	3.4	2
Cu-ZnO	Carbonate coprecipitation	3:1	240	3.0	(W) 12096	10.6	54.1	240	3
Cu-ZnO-rod	Stepwise precipitation	3:1	240	3.0	(W) 12096	8.0	61.8	210	3
Cu-ZnO-filament	Stepwise precipitation	3:1	240	3.0	(W) 12096	16.5	78.2	550	3
5%Cu/plate ZnO	Impregnation	3:1	280	3.0	(W) 3600	9.8	43.4	50.9	4
Cu-ZnO	Coprecipitation	9:1	167	0.1	(W)12000	--	56.6	8.8	5
Cu-ZnO	Coprecipitation	3:1	250	3.0	(G)18000	4.0	--	64.0	6
CuZn@ZnO_x	Surface modification precipitation	3:1	250	3.0	(G)18000	0.3	--	19.2	7
Cu@ZnO_x	Surface modification precipitation	3:1	250	3.0	(G)18000	2.3	--	147.2	7
Cu-ZnO	Coprecipitation	3:1	250	3.0	(G)18000	10.7	--	51.2	7

[a] (W) = volume flow rate/catalyst mass, mL g_{cat}^{-1} h^{-1}, (G) = volume flow rate/bed volume, h^{-1}

References

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