Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Revealing the promoting effect of Zn on Ni-based CO_2 hydrogenation catalysts

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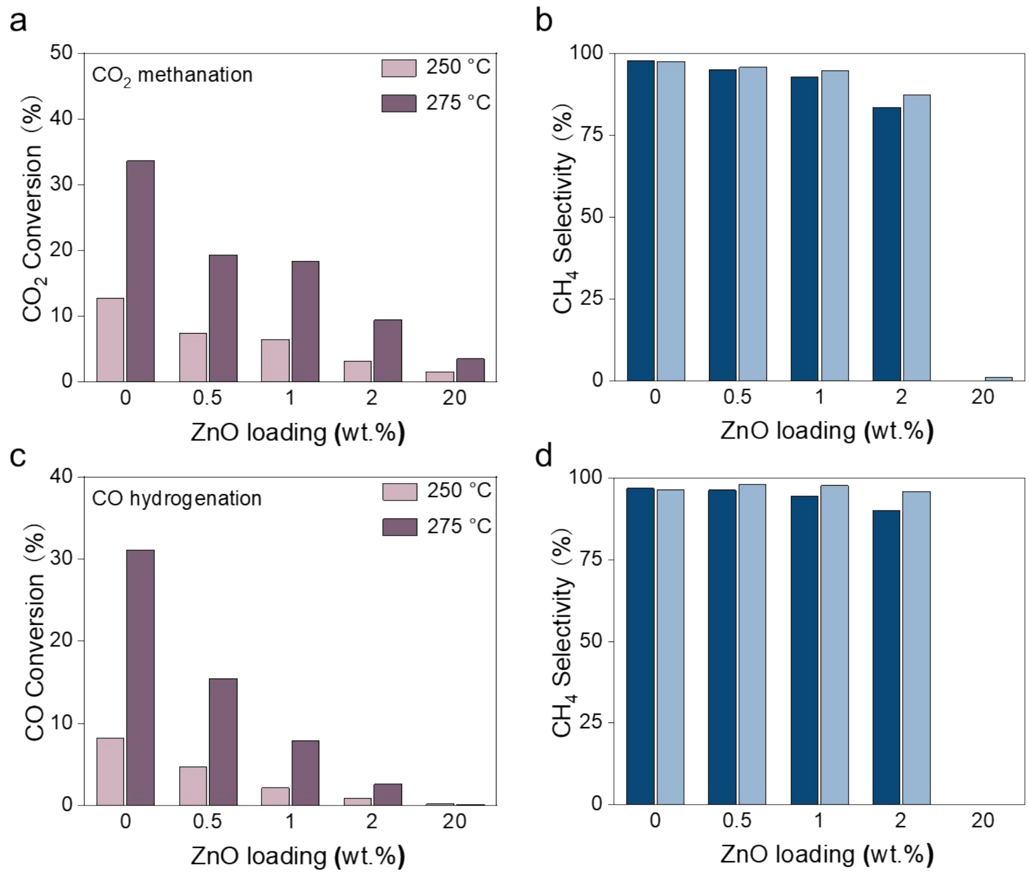

Fig. S1 Catalytic performance of CO_2 and CO hydrogenation over $NiZn/Al_2O_3$ catalysts

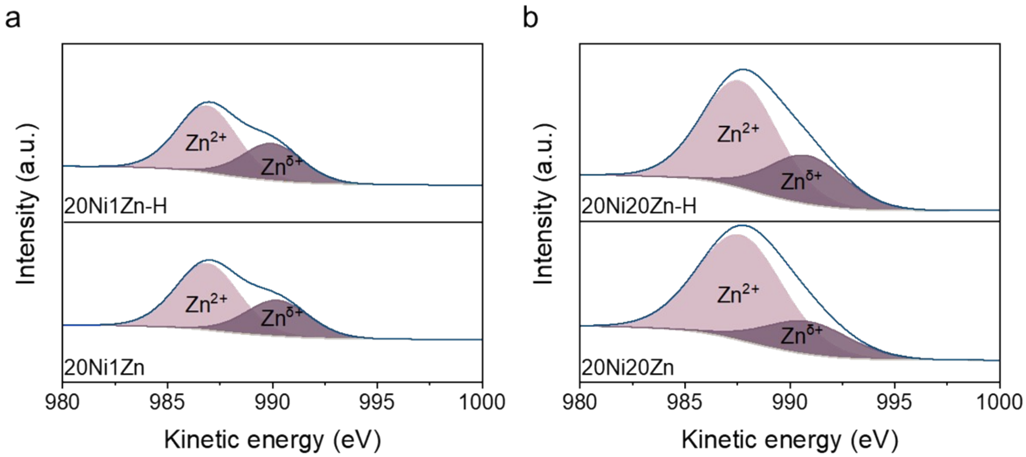

Fig. S2 XPS spectra of Zn LMM for c) as-prepared and d) reduced catalysts

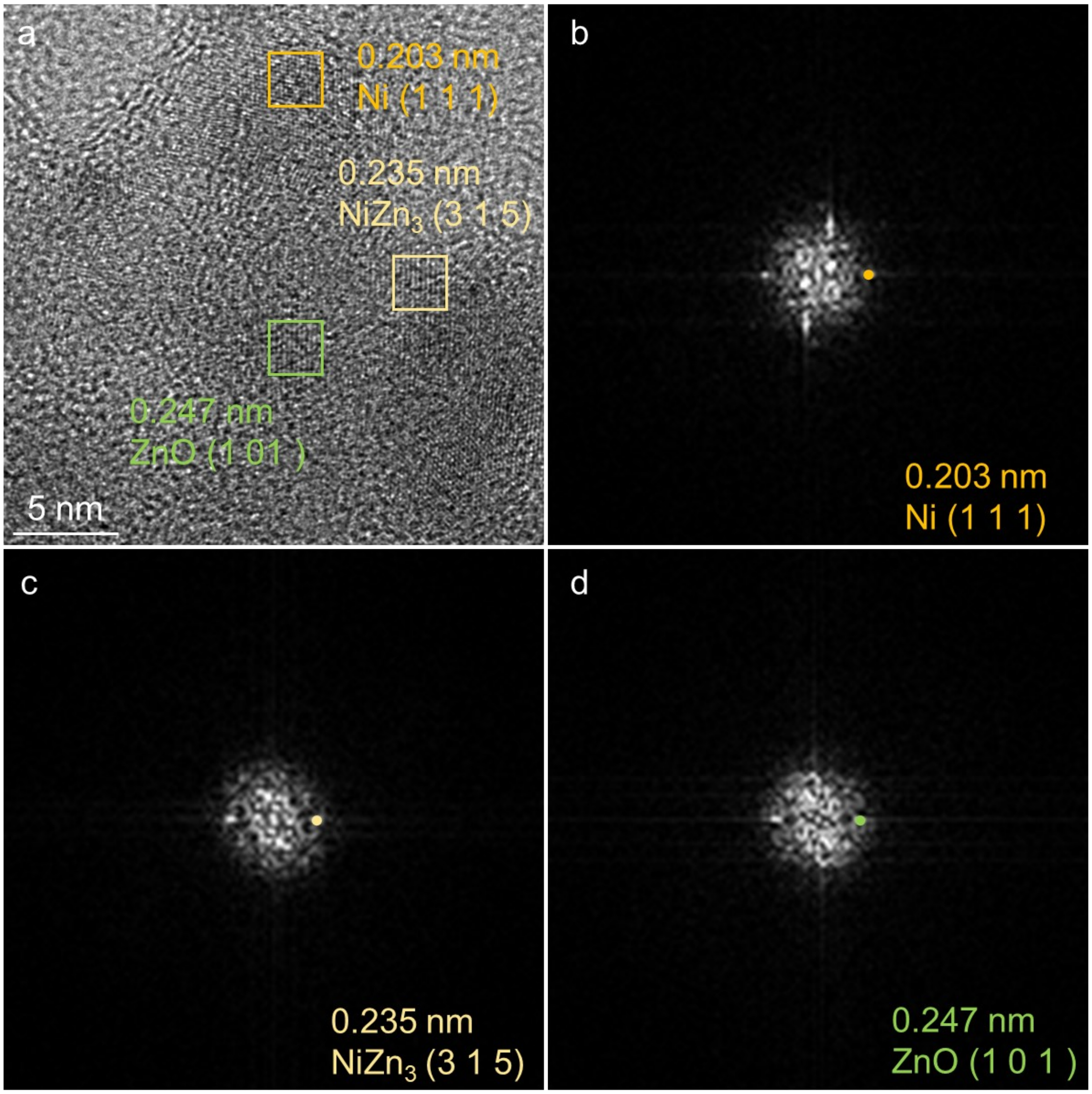

Fig. S3 The FFT images of 20Ni1Zn-H

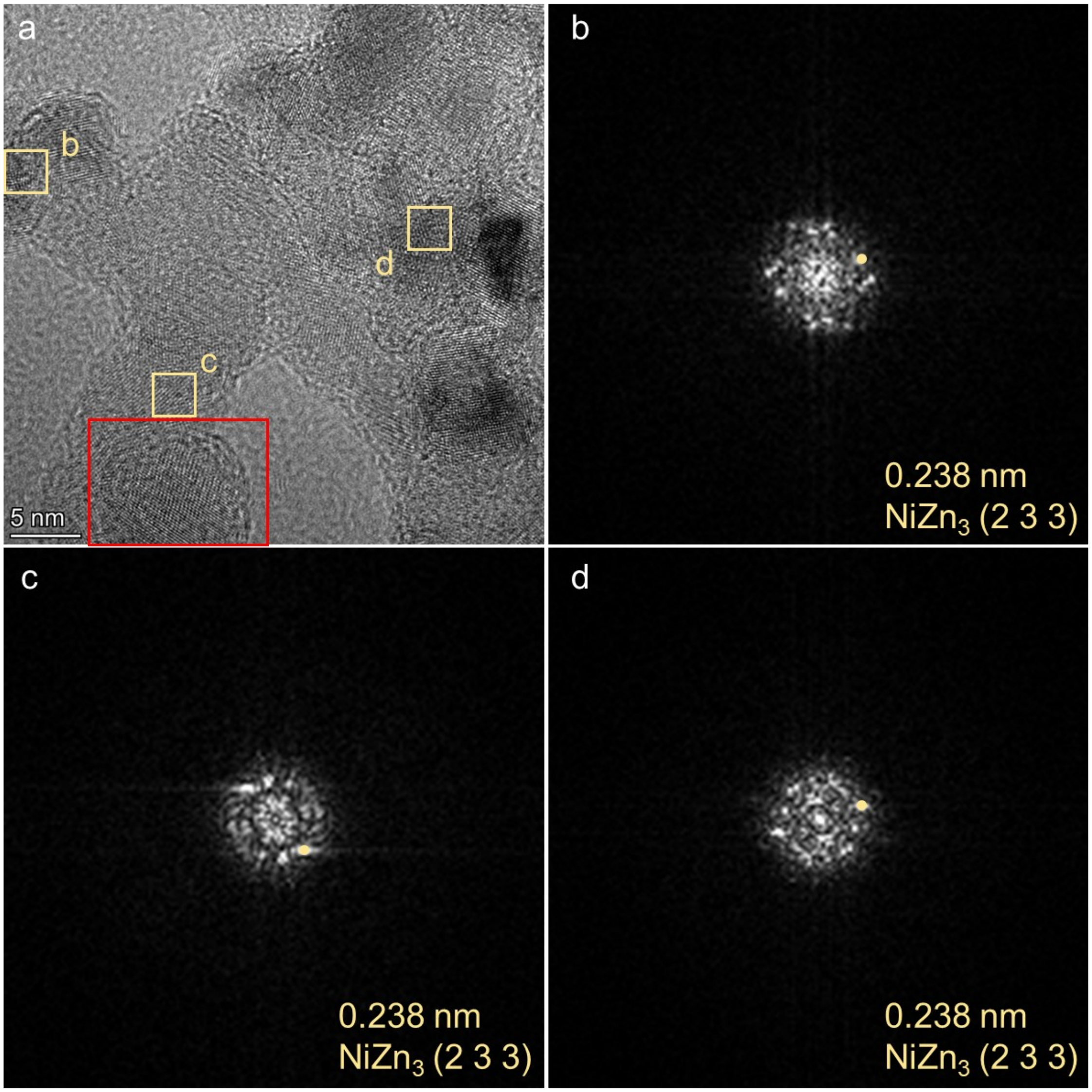

Fig. S4 The FFT images of 20Ni20Zn-H

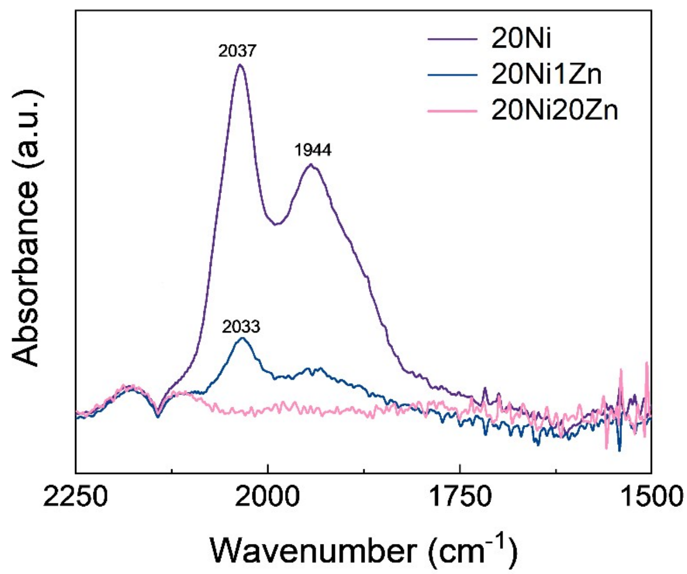

Fig. S5 CO-DRIFTS spectra of NiZn/Al_2O_3 catalysts

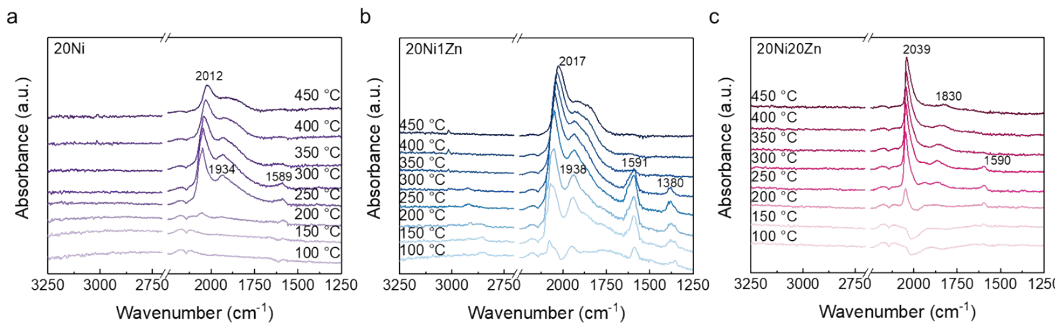

Fig. S6 *In situ* DRIFTS spectra of NiZn/Al_2O_3 catalysts during CO hydrogenation

In order to prove that the particle size effect was not the main reason for the selective regulation of $NiZn/Al_2O_3$ catalysts, we first prepared Ni/Al_2O_3 with 20 wt.% by the same method. Then we loaded the catalyst with different amounts of Zn, to ensure that Ni nanoparticles have nearly the same size. The results of the activity test in Fig. S4 show a similar pattern.

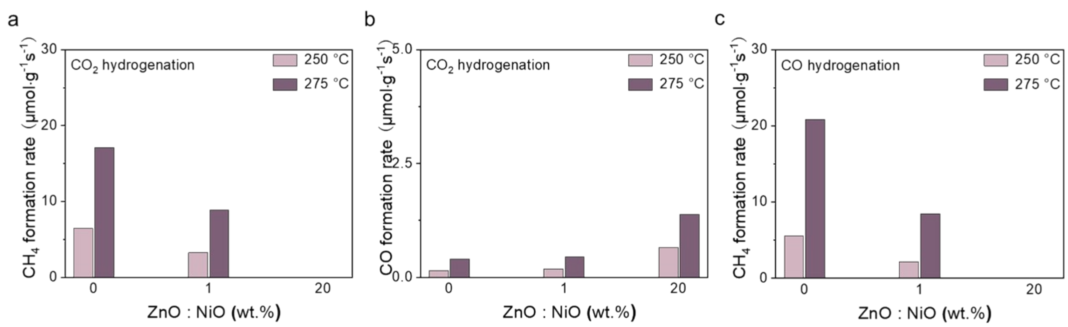

Fig. S7 Catalytic performance of CO_2/CO hydrogenation over ZnO-Ni/Al_2O_3 Catalysts

Table S1. Comparison of CO_2 conversion and CO selectivity for the catalysts

Catalyst	H_2:CO_2 ratio	Temperature (°C)	CO_2 conversion (%)	CO selectivity (%)	Ref.
20Ni20Zn	4:1	350/400	14.4/26.8	95.5/83.4	This work
CuO_x/CeO_2	1:1	400	9	100	1
Pd/SiO_2	4:1	450	40.8	89.6	2
Fe_3O_4	1:1	480	12.5	> 99	3
Fe film	4:1	300	2.2	~80	4
Fe@graphite@C	1:1	550	30.2	>99	5
MoO_2/FAU	1:1	500	14.3	99	6

Table S2. Dispersion and turnover frequency of $NiZn/Al_2O_3$ catalysts

Catalyst	Dispersion (%)	TOF (s^{-1})	
		CO_2 hydrogenation	CO hydrogenation
20Ni	14.27	$15.59\times10^{--3}$	14.89×10^{-3}
20Ni1Zn	8.15	14.79×10^{-3}	6.84×10^{-3}
20Ni20Zn	5.93	3.80×10^{-3}	0.75×10^{-3}

Table S3. Surface chemical states of as-prepared/reduced catalysts based on XPS analysis

Catalyst	$Zn^{\delta+}/(Zn^{\delta+}+Zn^{2+})$ (%) [a]	$Zn^{\delta+}/(Zn^{\delta+}+Zn^{2+})$ (%) [b]	$Ni^0/(Ni^0+Ni^{\delta+})$ (%) [b]
20Ni	/	/	71.78
20Ni1Zn	35.13	35.81	63.85
20Ni20Zn	23.78	31.54	57.12

[a] as-prepared

[b] reduced

References

1 M. Ronda-Lloret, S. Rico-Francés, A. Sepúlveda-Escribano and E. V. Ramos-Fernandez, *Appl. Catal. A Gen.*, 2018, **562**, 28–36.

2 J. N. Park and E. W. McFarland, *J. Catal.*, 2009, **266**, 92–97.

3 Chou, Loiland and Lobo, *Catalysts*, 2019, **9**, 773.

4 H. Kierzkowska-Pawlak, M. Ryba, M. Fronczak, R. Kapica, J. Sielski, M. Sitarz, P. Zając, K. Łyszczarz and J. Tyczkowski, *Catalysts*, 2021, **11**, 883.

5 X. Zhao, Z. Wu, J. Fu, J. Guo and S. Kang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 57100–57106.

6 A. Okemoto, M. R. Harada, T. Ishizaka, N. Hiyoshi and K. Sato, *Appl. Catal. A Gen.*, 2020, **592**, 117415.