

Electronic supplementary information

Synergistic Effect of K and Zn on Fe-based Catalysts for Efficient CO₂ Hydrogenation

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Supplementary Figures and Tables

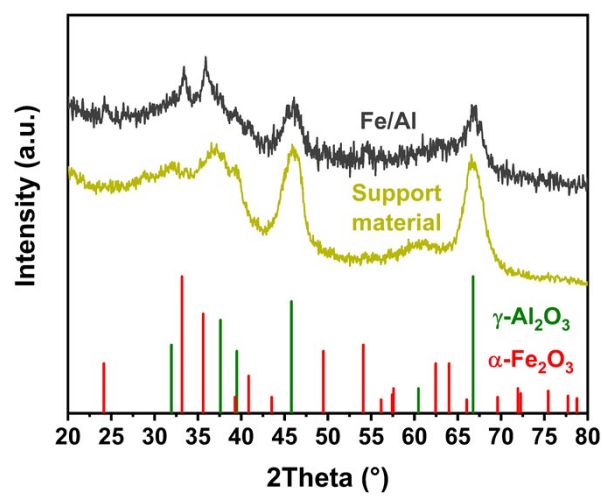


Fig. S1 XRD patterns of $\gamma\text{-Al}_2\text{O}_3$ support material and calcined sample Fe/Al.

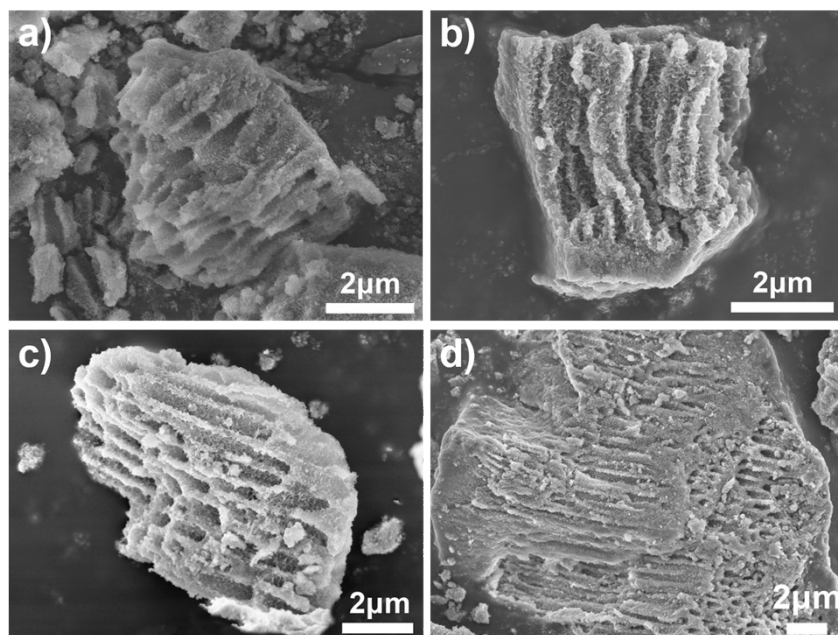


Fig. S2 SEM images of (a) calcined support γ -Al₂O₃, (b) Fe/Al, (c) 10K-Fe/Al, and (d) 10Zn-Fe/Al material.

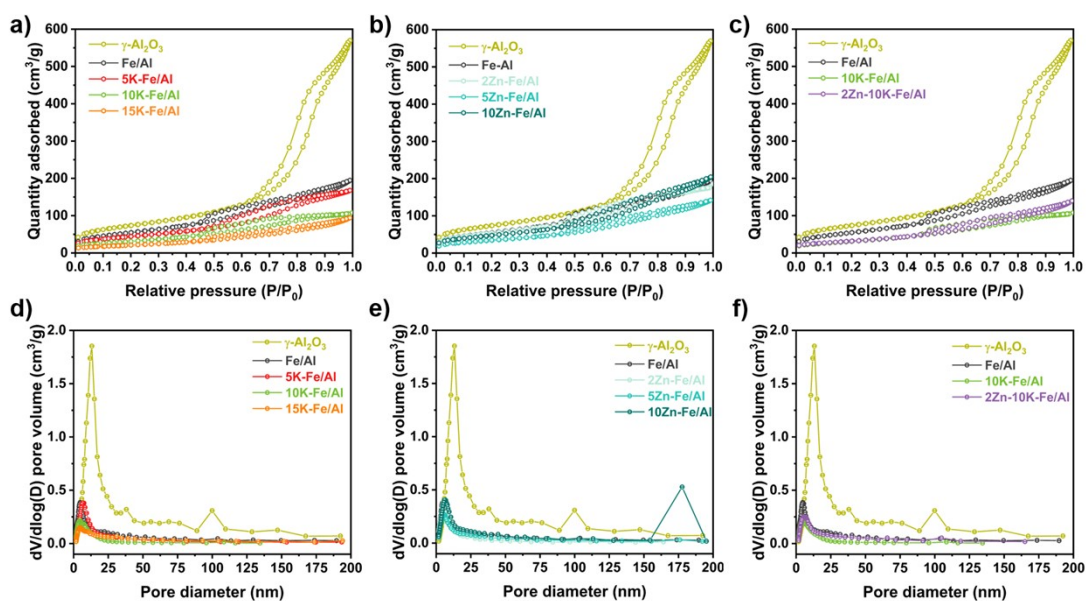


Fig. S3 (a–c) N₂ adsorption–desorption isotherms and (d–f) pore diameter distribution curves of calcined samples modified with different amounts of K, calcined samples modified with different amounts of Zn, and calcined samples modified with K and Zn.

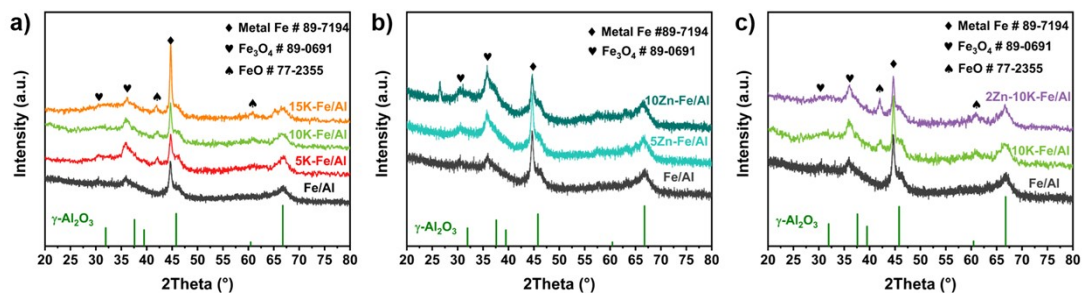


Fig. S4 XRD patterns of reduced samples modified with (a) different amounts of K, (b) different amounts of Zn, and (c) K and Zn.

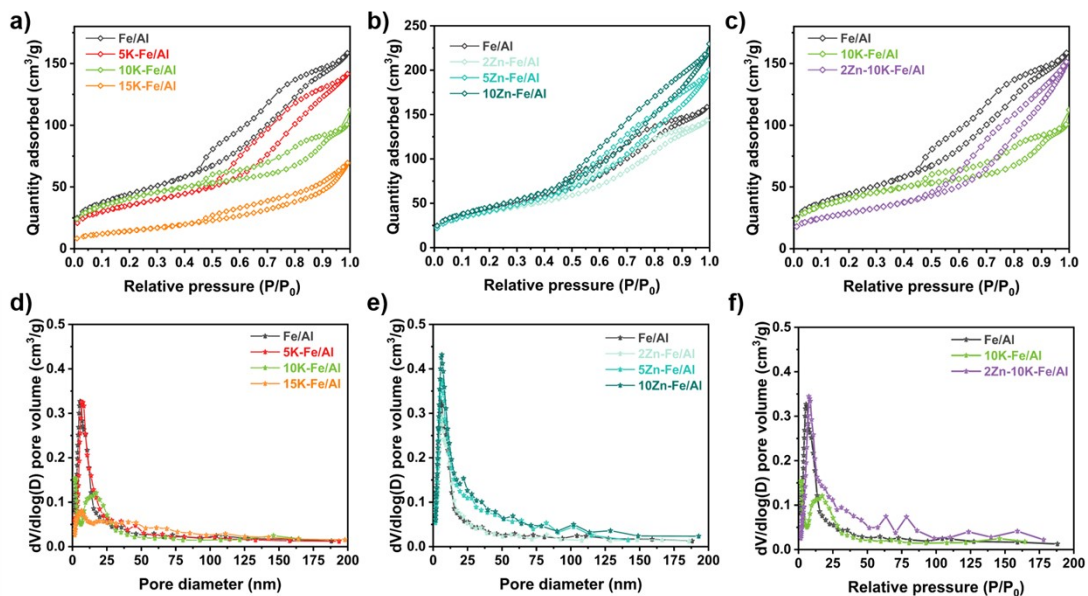


Fig. S5 (a–c) N_2 adsorption–desorption isotherms and (d–f) pore diameter distribution curves of reduced samples modified with different amounts of K, reduced samples modified with different amounts of Zn, and reduced samples modified with K and Zn.

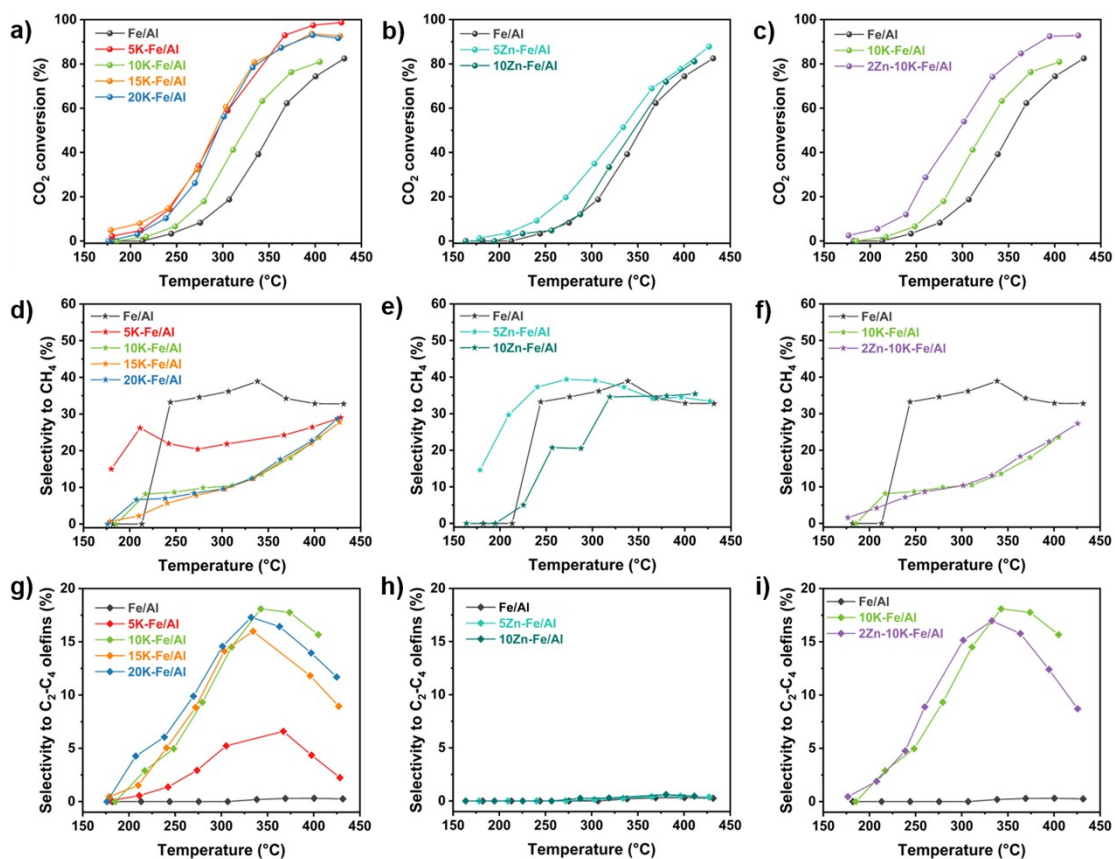


Fig. S6 (a–c) CO₂ conversion, (d–f) selectivity to CH₄, (–) selectivity to C₂–C₄ olefins of catalysts modified with different amounts of K, Zn, or K and Zn as a function of reaction temperature.

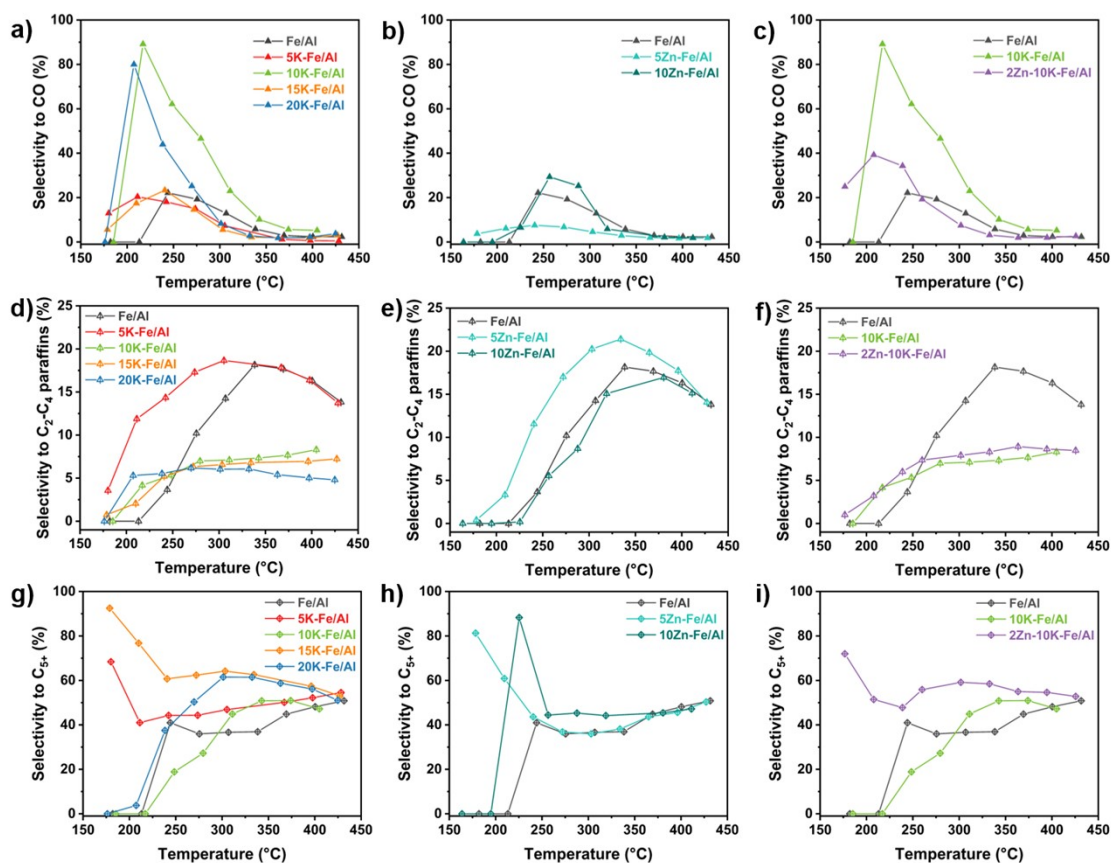


Fig. S7 Selectivity to (a–c) CO, (d–f) C₂-C₄ paraffins, (g–h) C₅₊ hydrocarbons of catalysts modified with different amounts of K, Zn or K and Zn as a function of reaction temperature.

Table S1 Textural data from N₂ adsorption-desorption tests.

As-prepared sample	S _{BET} (m ² /g)	V _{tol} (cm ³ /g)	D _{meso} (nm)	Reduced sample	S _{BET} (m ² /g)	V _{tol} (cm ³ /g)	D _{meso} (nm)
γ-Al ₂ O ₃	261	0.88	12.9	-	-	-	-
Fe/Al	202	0.29	4.8	Fe/Al	160	0.23	4.8
5K-Fe/Al	159	0.25	7.0	5K-Fe/Al	123	0.21	7.2
10K-Fe/Al	117	0.17	4.4	10K-Fe/Al	142	0.13	17.2
15K-Fe/Al	78	0.15	4.5	15K-Fe/Al	54	0.11	6.9
2Zn-Fe/Al	199	0.26	5.1	2Zn-Fe/Al	144	0.21	6.4
5Zn-Fe/Al	126	0.21	5.5	5Zn-Fe/Al	153	0.30	5.9
10Zn-Fe/Al	172	0.31	6.3	10Zn-Fe/Al	171	0.35	6.3
2Zn-10K-Fe/Al	117	0.22	5.9	2Zn-10K-Fe/Al	103	0.23	7.6

Reduction condition: 0.2 MPa, 450°C for 4 h in pure H₂ with a flow of 25 mL/min

Table S2 Calculated Metal Fe particle size of samples reduced at 450°C for 4 h by the Debye-Scherrer equation

Reduced samples	Fe/Al	5K- Fe/Al	10K- Fe/Al	15K- Fe/Al	2Zn- Fe/Al	5Zn- Fe/Al	10Zn- Fe/Al	2Zn-10K- Fe/Al
Fe particle diameter (nm)	18	18	28	35	16	22	23	24

Table S3 Catalytic performance of catalysts

Sample	conversion		Selectivity				
	CO ₂	CO	CH ₄	C ₂ ⁼ -C ₄ ⁼	C ₂ ⁻ -C ₄ ⁻	C ₂ -C ₄	C ₅₊
Fe/Al	42	6	39	0	18	18	37
5K-Fe/Al	78	4	23	6	18	24	49
10K-Fe/Al	63	11	13	18	7	25	51
15K-Fe/Al	82	2	13	16	7	23	62
20K-Fe/Al	81	3	13	17	6	23	61
5Zn-Fe/Al	55	3	37	0	21	21	39
10Zn-Fe/Al	47	5	35	0	16	16	44
2Zn-10K-Fe/Al	77	3	14	17	8	25	58

Reaction condition: 340°C, 3.0 MPa, and 6360 mL/g/h with reactant gas H₂/CO₂ = 3/1.