

Table S1. Catalytic performance of CO₂ hydrogenation over different catalysts

Catalysts	GHSV (mLh ⁻¹ g _{cat} ⁻¹)	T(°C)	P(Mpa)	CO ₂ Conv (%)	CO sel (%)	Hydrocarbon selectivity (%)		
						CH ₄	C ₂₋₄	C ₅₊
Na-Fe ₃ O ₄ / HZSM-5 ¹	4000	320	3.0	34.0	14.0	8.0	18.0	74.0
In ₂ O ₃ / HZSM-5 ²	9000	340	3.0	19.0	48.0	1.0	27.6	71.4
FeNa(1.18) ³	2000	320	3.0	40.5	13.5	15.8	54.1	30.1
Fe-MOF- derived ⁴	3600	400	3.0	46.1	17.5	32.3	26.9	40.8
10K13Fe ₂ Co 100ZrO ₂ ⁵	7200	400	3.0	42.3	21.9	25.7	34.0	18.4
Na-Fe ₃ O ₄ ⁶	4000	320	3.0	34.0	14.0	12.0	48.0	40.0
FeK/Al ₂ O ₃ ⁷	1800	400	3.0	53.5	17.0	20.0	37.0	26.0
5Mn-Na/Fe ⁸	2040	320	3.0	39.3	9.0	8.9	31.2	59.9
K- ZnFe ₂ O ₄ ⁹	12000	320	2.0	47.1	8.7	14.8	39.1	46.1
FeAlOx-5 ¹⁰	4000	330	3.5	36.8	7.2	12.1	30.1	57.8
Our work	12000	320	3.0	57.75	9.06	8.13	18.13	73.8

Table S2. Catalyst components (Same K content in each catalyst)

Catalyst	Distribution of element (%)						
	K		Fe	Co	Ni	Cu	Zn
	a*	b*					
Fe-Fe	0.805	0.805	63.5				
Co-Fe	0.696	0.816	40.4	18.4			
Ni-Fe	0.342	0.885	33.4		15.0		
Cu-Fe	0.0438	0.812	35.2			16.3	
Zn-Fe	0.0242	0.833	32.0				15.2

a: K content before K supplementation

b: K content after K supplementation

Note: The data in this table were measured by ICP

Table S3 Comparison of performances of the catalyst (Reaction condition: T: 320 °C, P: 3 MPa, H₂/CO₂/N₂: 18/6/6, GHSV: 12000 mL.g⁻¹ cat. h⁻¹, TOS: 8 h, same K content).

Catalyst	CO ₂ conversion	S _C ₀	FTY ^a (μmol _{CO₂} ·g ⁻¹ ·Fe·s ⁻¹)	STY ^b (mmol·g ⁻¹ ·Fe·h ⁻¹)	Selectivity (C-%, CO-free)				O/P ^c
					CH ₄	C=2-4	CO 2-4	C ₅₊	
Fe-Fe	34.67	26.53	11.94	20.29	17.59	41.09	6.66	34.68	6.17
Co-Fe	46.03	15.48	28.66	36.12	23.54	40.05	6.84	29.59	5.86
Ni-Fe	36.63	28.28	23.41	9.18	65.36	15.53	11.31	7.81	1.37
Cu-Fe	32.93	38.96	17.10	2.59	25.77	40.23	8.29	25.74	4.85
Zn-Fe	50.67	12.04	41.45	105.44	11.64	22.28	3.94	62.15	5.65

a: FTY: Iron time yield to hydrocarbons

b: STY: The space time yield (STY) from C₅₊ hydrocarbons

c: Olefin to paraffin ratio of C₂-C₄ hydrocarbons

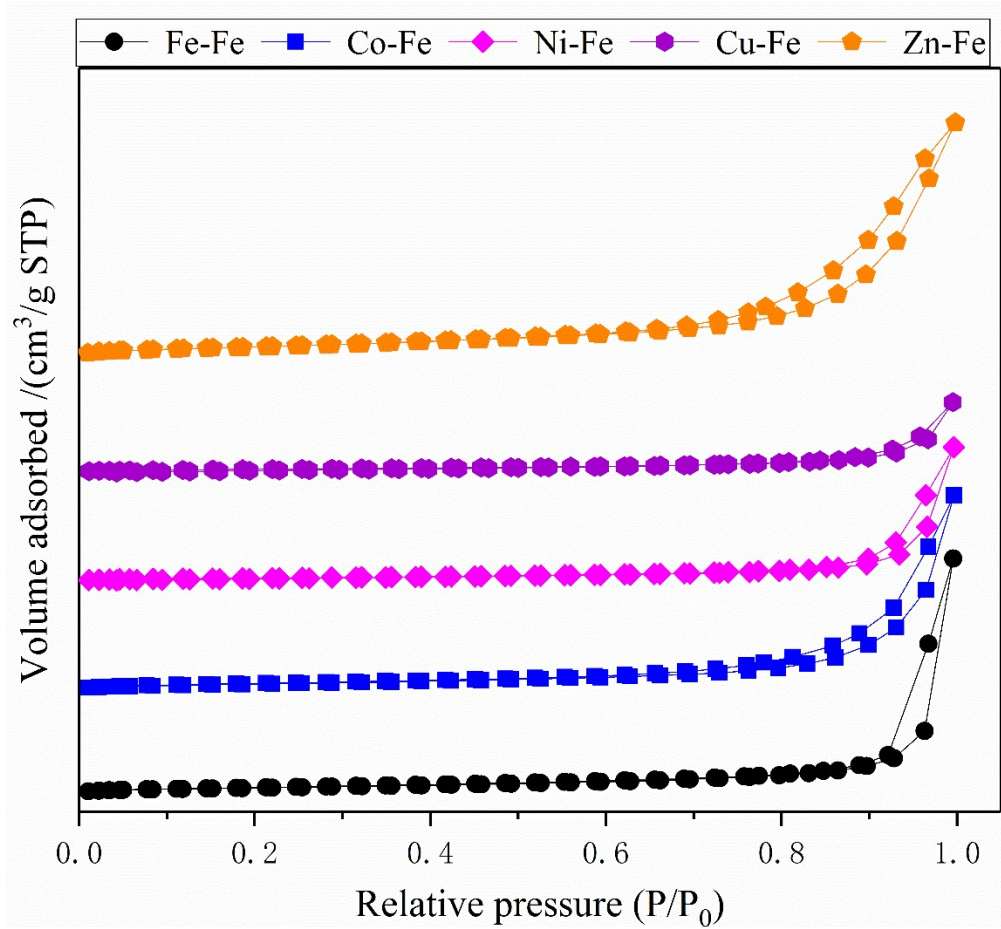


Fig S1. N₂ adsorption-desorption isotherms of different iron-based catalysts.

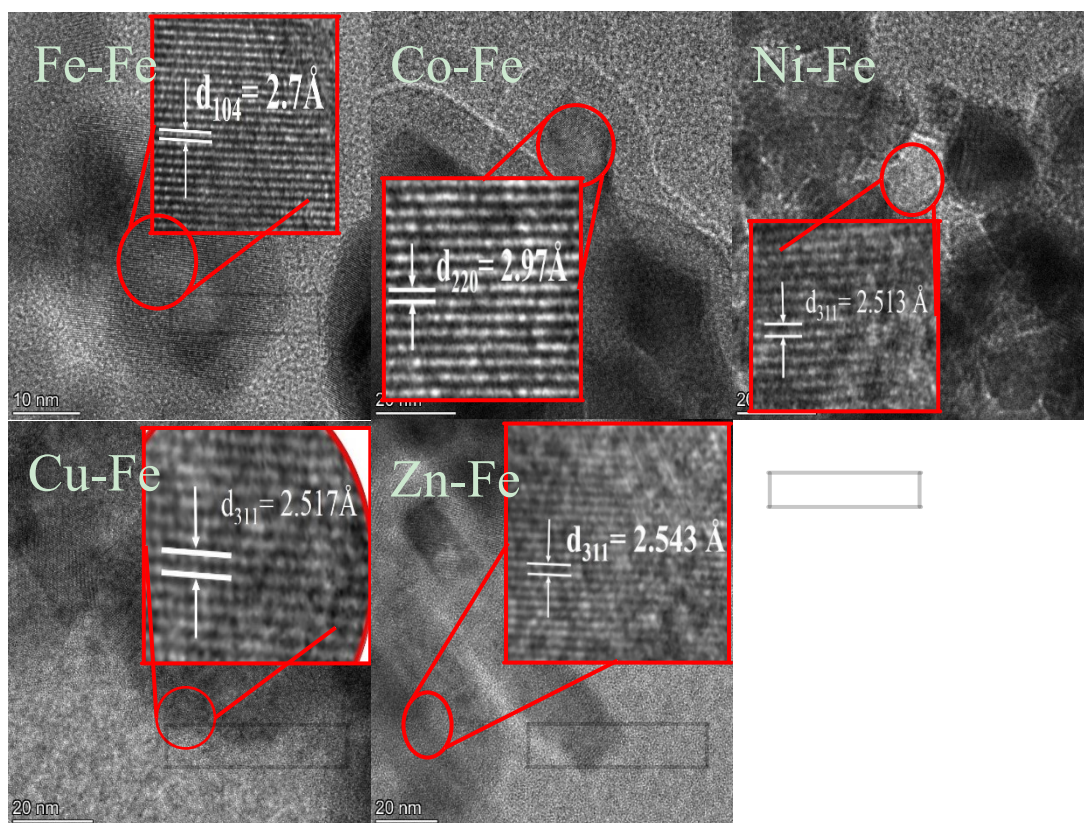


Fig S2 HR-TEM of fresh samples.

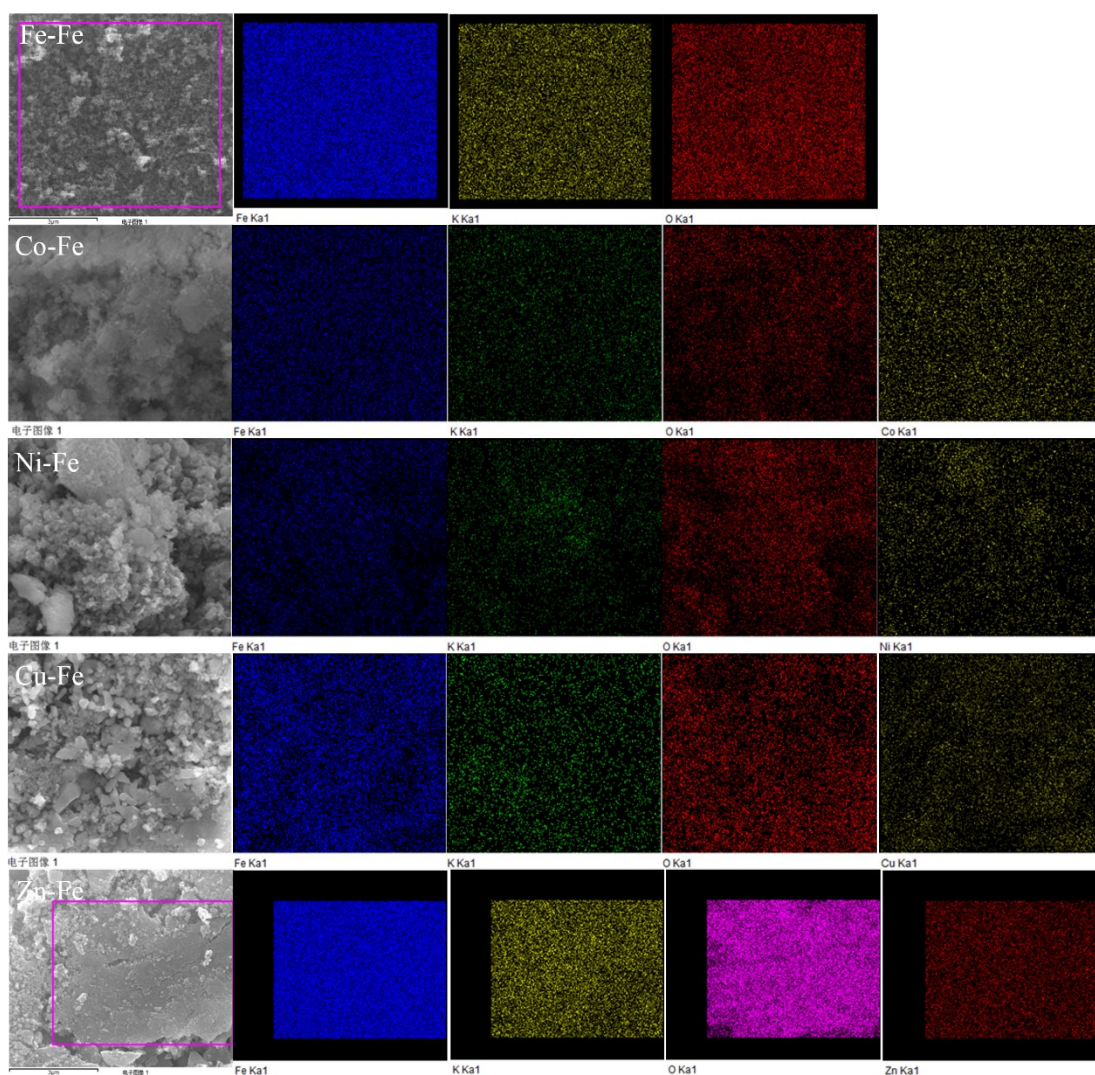


Fig S3 Special SEM images and corresponding element composition mapping of different spinel-like catalysts.

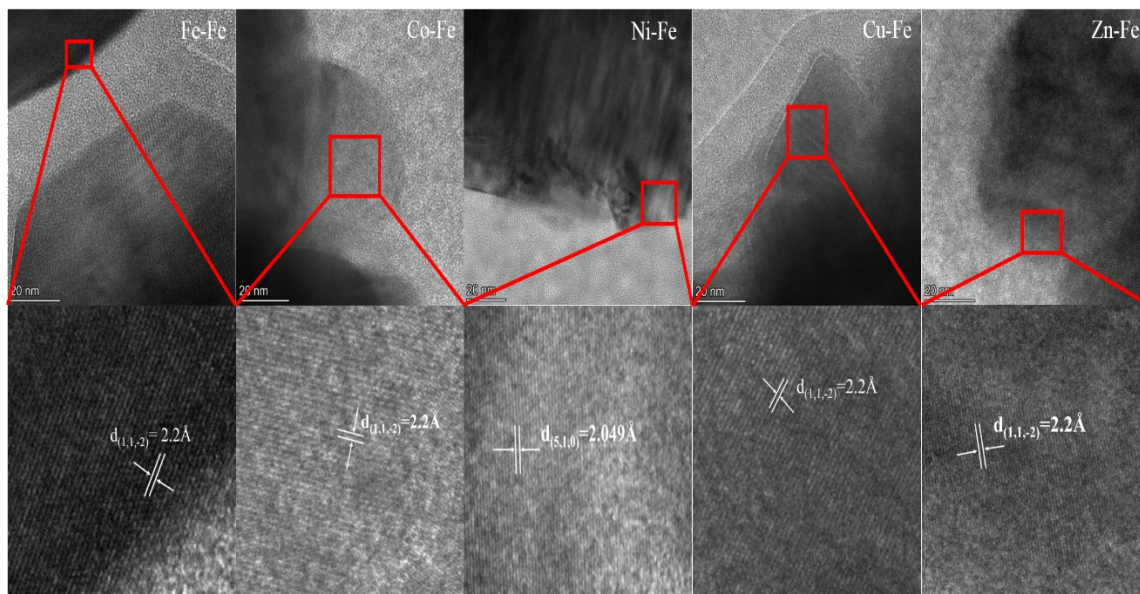


Fig S4 HR-TEM of spent catalysts.

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