

Supporting information

Catalysts preparation

The Ga modified and unmodified delafossite-CuFeO₂ were prepared by hydrothermal synthesis. Briefly, 8.08 g of Fe(NO₃)₃·9H₂O and 4.8 g of Cu(NO₃)₂·3H₂O were dissolved with 160 mL deionized water, followed by the addition of 0.4 mol sodium hydroxide and stirring for 30 min. Then 2.0 mL of propionaldehyde was added as reduction agent for Cu²⁺ to Cu⁺. Finally, the mixture was transferred to 200-mL autoclave and maintained at 180 °C for 24 h. The product was separated by centrifugation, washed by deionized water and ethanol for several times, and dried then under vacuum at 80 °C for 12 h. The obtained sample is denoted as CuFeO₂. These Ga modified CuFeO₂ samples were prepared by using the same method with desired amounts of GaCl₃ into the synthesis solution. The Ga modified CuFeO₂ was denoted as xGa-CuFeO₂ (x=0.15, 0.25, 0.50, 1.0). The Fe₂O₃ was prepared by co-precipitation. In brief, a Fe(NO₃)₃ solution was used in precipitation with NH₄OH solution as precipitator at pH≈8.0 and 70 °C. The obtained precipitate was washed, filtered, dried at 120 °C over-night and calcined at 450 °C for 4 h.

Characterizations

The Bruker D8 Advance powder X-ray diffractometer (German) equips with Cu-Kα irradiation (40 kV, 40 mA) was used to record the X-ray diffraction (XRD) patterns. The element contents of catalysts were determined by X-ray Fluorescence Spectrometer (XRF, Shimadzu XRF-1800). The SEM images were obtained by using Tecnai G2 F20 (FEI, USA). The Mössbauer spectroscopy (MES) analysis was conducted on a MR-351 constant acceleration Mössbauer spectrometer (FAST, Germany). The X-ray photoelectron spectrometer (AXIS ULTRA) from Kratos Analytical Ltd was applied to record the X-ray photoelectron spectroscopy (XPS). The CO₂ temperature-programmed desorption (CO₂-TPD) was carried out on AutoChem 2920 (Micrometrics, USA). The sample was initially reduced in 10 vol.%H₂/Ar at 400 °C for 2 h, and then purified by Ar gas, cooled to 50 °C and saturated with CO₂. Afterwards, the sample was purged with He and heated to 700 °C at the rate of 10 °C /min in He. The pulse experiments

were also carried out on AutoChem 2920 (Micrometrics, USA) connected with a mass spectrometer (HPR-20, HIDEN). About 200 mg spent 0.25Ga-CuFeO₂ or CuFeO₂ samples were fed into the U-type quartz tube and cleaned with an Ar flow at 320 °C for 2 h, then the gas was switched to a 10%H₂/Ar flow. Afterwards, 250 μL of C₂H₄ gas was pulsed into the 10%H₂/Ar flow every 5 min, the effluents of C₂H₆ and C₂H₄ were detected by a mass spectrometer.

Catalytic tests

The catalytic performance was tested in a fixed-bed reactor. Typically, about 0.5 g sample was fed into the reactor. Prior to CO₂ hydrogenation reaction, the catalyst was reduced by a 100 mL/min H₂ gas flow at 400 °C for 2 h. After activation, the reaction tests were conducted in a reaction gas of 10%N₂/67.5%H₂/22.5%CO₂ at 320 °C, 5400 mL·gcat⁻¹·h⁻¹ (The N₂ was excluded when calculated the space-velocity), and 1.0 MPa. The gas reaction products were analyzed by an on-line gas chromatograph (Agilent GC 6820) equipped with a TCD and FID detector. The quantitative analysis of gas products was calculated by the internal standard method with N₂, while CH₄ was used as a reference bridge between TCD and FID. The heavy hydrocarbons in oil phase were captured by an ice trap and analyzed by another gas chromatograph (Agilent GC 6820) equipped with a FID detector and a HP-5 column, while the oxygenates in the water phase were also analyzed by GC connected with DB-FFAP capillary column. The total selectivity of oxygenates calculated based on the molar carbon basis is less than 2%. The selectivity of hydrocarbons was calculated based on the molar carbon basis and CO-free. The carbon balances of the reaction data were calculated, which were all higher than 95%.

The CO₂ conversion is calculated by:

$$\text{CO}_2 \text{ conversion} = \frac{\text{CO}_2 \text{ in} - \text{CO}_2 \text{ out}}{\text{CO}_2 \text{ in}} \times 100\%$$

The CO selectivity is calculated by:

$$\text{CO selectivity} = \frac{\text{CO out}}{\text{CO}_2 \text{ in} - \text{CO}_2 \text{ out}} \times 100\%$$

The hydrocarbon selectivity is calculated by:

$$C_iH_m \text{ selectivity} = \frac{i \times C_iH_m \text{ out}}{CO_2 \text{ in} - CO_2 \text{ out} - CO \text{ out}} \times 100\%$$

$CO_2 \text{ in}$, $CO_2 \text{ out}$ and $CO \text{ out}$: the mole number of CO_2 or CO , $C_iH_m \text{ out}$: the mole number of the hydrocarbon with i carbons at the outflow.

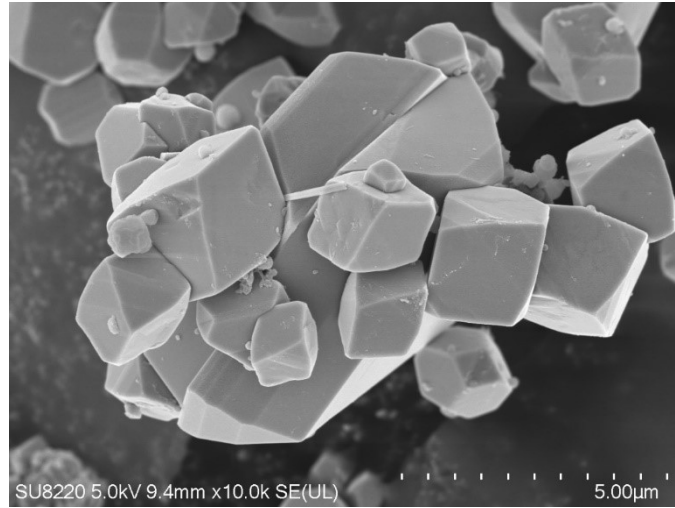


Fig. S1 SEM image of CuFeO₂

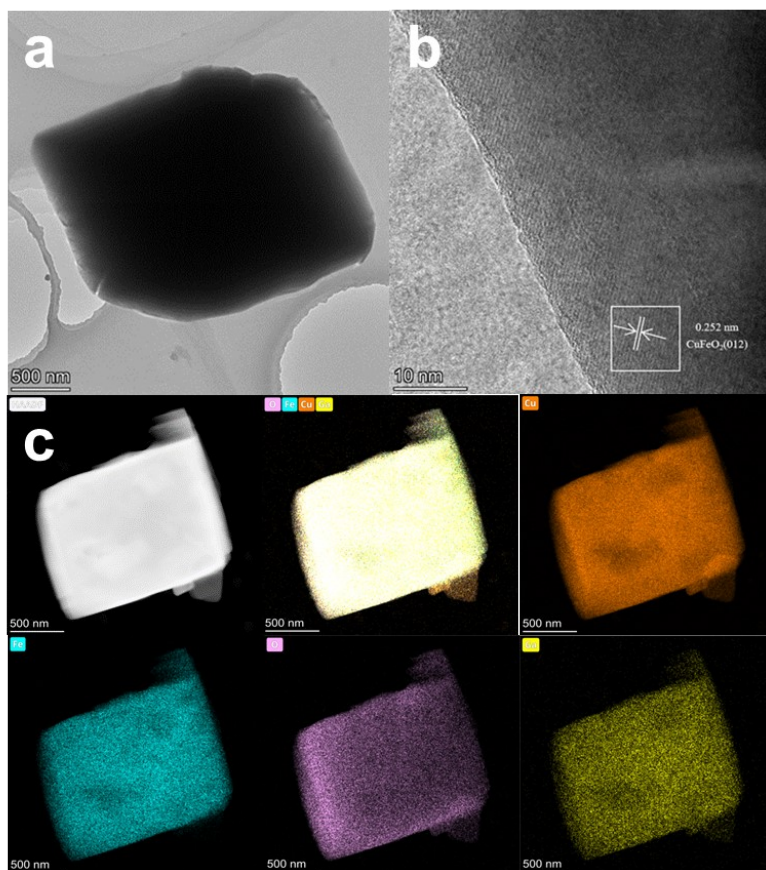


Fig. S2 The TEM, HRTEM and EDS element mapping of 0.25Ga-CuFeO₂.

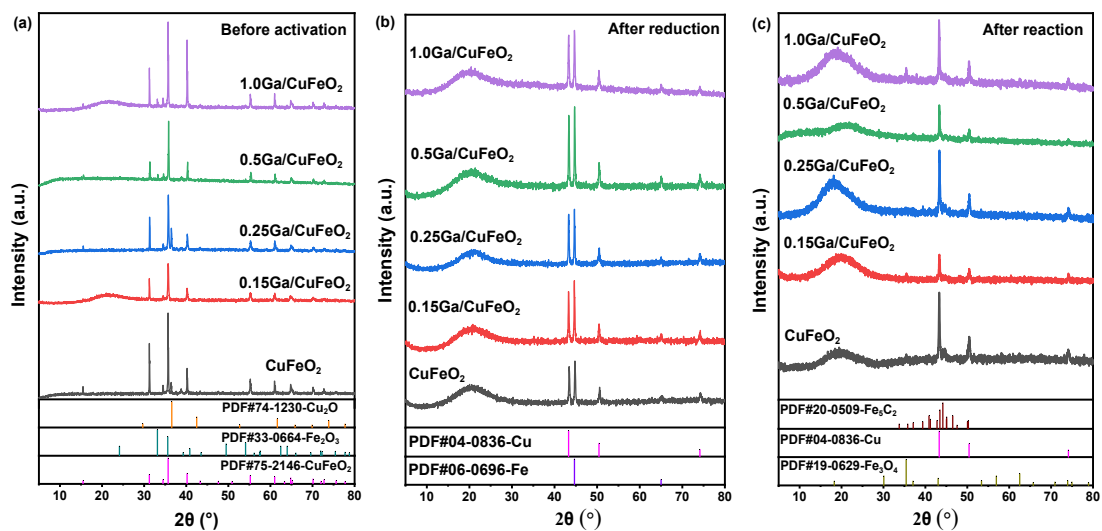


Fig. S3 XRD patterns of the fresh (a), reduced (b) and spent (c) catalysts.

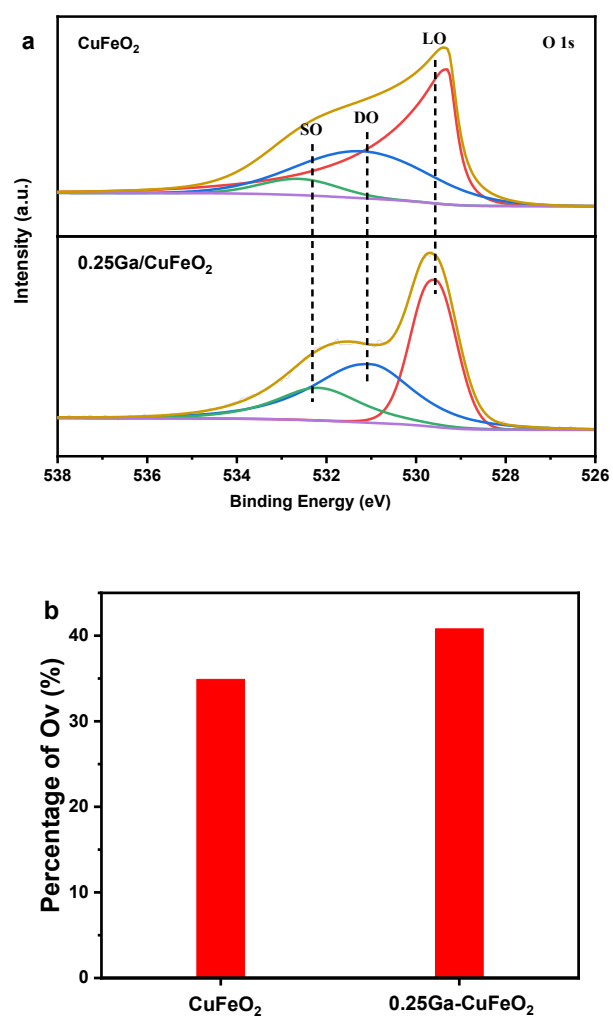


Fig. S4 The O1s spectra (a) and Ov (b) percentage of CuFeO₂ and 0.25Ga-CuFeO₂.

Table S1 The Mössbauer parameters of spent CuFeO₂ and 0.25Ga-CuFeO₂ catalysts.

Catalysts	IS (mm/s)	QS (mm/s)	Area (%)	Assignment
Spent CuFeO ₂	0.40	-0.02	23.39	Fe ₃ O ₄ (A)
	0.70	-0.67	13.14	Fe ₃ O ₄ (B)
	0.38	0.11	12.20	Fe ₅ C ₂ (A)
	0.32	0.02	26.19	Fe ₅ C ₂ (B)
	0.38	-0.02	13.15	Fe ₅ C ₂ (C)
	0.40	0.18	8.06	Fe ₃ C (A)
	0.30	-0.04	3.86	Fe ₃ C (B)
Spent 0.25Ga-CuFeO ₂	0.76	2.0	4.98	Fe ₃ O ₄ (A)
	0.13	2.0	5.65	Fe ₃ O ₄ (B)
	0.24	0.11	39.31	Fe ₅ C ₂ (A)
	0.18	0.02	37.34	Fe ₅ C ₂ (B)
	0.00	0.54	12.72	Fe ₅ C ₂ (C)

Table S2. The elements relative content of fresh catalysts determined by XRF

Sample	Cu(wt%)	Fe(wt%)	Ga(wt%)
1.0Ga/CuFeO ₂	53.28	45.75	0.97
0.5Ga/CuFeO ₂	55.40	44.12	0.48
0.25Ga/CuFeO ₂	58.06	41.72	0.22
0.15Ga/CuFeO ₂	55.61	44.13	0.16
CuFeO ₂	55.42	44.58	0.00

Table S3 The product yield and space time yield (STY) of various catalysts

Catalysts	C ₅₊ ^o Yield [mol %]	FTY(C ₅₊ ^o) ^a
Fe ₂ O ₃	1.8	1.2
CuFeO ₂	16.3	18.2
0.15Ga/CuFeO ₂	18.5	22.4
0.25Ga/CuFeO ₂	19.6	25.1
0.5Ga/CuFeO ₂	13.9	15.3
1.0Ga/CuFeO ₂	10.5	10.7

^ammol CH₄·g⁻¹Fe·h⁻¹

Table S4 Catalytic performance of various catalysts^[a]

Catalysts	Conv.[%]	CO sel.[%]	Selectivity [mol%] ^[b]				O/P ^[c]
			CH ₄	C ₂₋₄ ^O	C ₂₋₄ ^P	C ₅₊	
CuFeO ₂	43.1	15.6	14.5	24.5	4.0	57.0	6.2
0.25Ga/CuFeO ₂	41.5	11.7	10.2	20.3	2.9	66.6	7.1
0.15In/CuFeO ₂	8.0	12.7	19.2	32.8	4.9	43.1	6.0
0.25Al/CuFeO ₂	28.7	16.0	13.2	24.2	4.3	58.4	5.7

[a]Reaction conditions: H₂/CO₂=3, 5400 h⁻¹, 1 MPa, 320 °C. Activation conditions: 100 mL/min H₂, 400°C, 2 h. The data was collected at 24 h.

[b]The selectivity of hydrocarbons was calculated based on excluded CO.

[c]The ratio of olefin to paraffin in the C₂₋₄ range hydrocarbons.