

Supplementary Information

Bifunctional CoFe/HZSM-5 Catalysts Orient CO₂

Hydrogenation to Liquid Hydrocarbons

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1. Experimental section

1.1. Catalyst preparation

CoFe bimetallic catalysts were prepared by co-precipitation method as in our previous report.¹ Typically, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 75 mL distilled water under continuous stirring. The aqueous sodium hydroxide solution was then added dropwise to the metal salt solution at a uniform rate under water bath conditions with stirring at 60 °C until the pH was adjusted to 10. After precipitation, continuous stirring was maintained at 60 °C for 1 h. Then, the reaction mixture was quickly transferred to a Teflon-lined autoclave and placed in an oven at 150 °C for 24 h. The resulting solid phase products were obtained by centrifugation and washing. Finally, the product obtained was calcined at 400 °C in a muffle furnace for 3 h after drying overnight in an oven at 80 °C. Finally, the product was grinding, pelletization, and sieving (mesh size 20-40) for subsequent use. The Na content in the CoFe catalyst was determined to be 1.0% by inductively coupled plasma optical emission spectrometer (ICP-OES).

The ZSM-5 zeolites were synthesized using a hydrothermal method, with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 40 serving as a representative example. For a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 40, the typical synthesis involved dissolving 20.447 g tetraethyl orthosilicate (TEOS), 4.34 g 25% tetra propylammonium hydroxide (TPAOH) in 13.92 g distilled water. The solution was stirred for 30 minutes before 0.402 g of NaAlO_2 was added and stirred for an additional 3 hours. The mixture was then transferred to a Teflon-lined autoclave and placed in an oven at 120 °C for 12 h, then raised to 170 °C for 48 h. After filtration and washing, the resulting products were dried at 100 °C overnight and then calcined in a muffle furnace at 550 °C for 6 hours. To obtain H-type ZSM-5, the calcined products were dispersed in 1M NH_4NO_3 solution, stirred at 80 °C for 6 hours, and then calcined again at 550 °C

for 6 hours. For ZSM-5 zeolites with other $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (80, 160, 320, 640), the general synthesis procedure remains similar; however, the quantities of TEOS and NaAlO_2 are adjusted to achieve the desired $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

The Fe catalyst was synthesized via a co-precipitation method.² Initially, 31.62 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 12.54 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed in 150 mL of distilled water to prepare a ferric salt solution. Subsequently, 5.1 mL of a 12.1 mol/L HCl solution was added. The mixture was heated to 60 °C under continuous stirring. A 1.5 mol/L NaOH solution (approximately 360 mL) was added dropwise to the stirred mixture over the course of about 1.5 hours. During this period, the pH of the solution was adjusted from acidic to around 10. After the completion of the NaOH addition, the mixture was further stirred at 60 °C for an additional hour, followed by cooling to room temperature. The precipitated product was separated using magnetic decantation and washed once with 800 mL of deionized water. Finally, the separated product was dried at 60 °C and subjected to grinding, pelletization, and sieving (mesh size 20–40) for subsequent use. ICP-OES analysis revealed that the Fe catalyst has a Na content of 0.9%.

1.2. Catalyst characterization

The phase composition and crystallinity of the sample were characterized using X-ray powder diffraction (XRD) method. The tests were conducted on a PANalytical Empyrean-100 X-ray diffractometer, with a Cu-K α radiation source (40 kV, 40 mA). The testing range for the sample was $2\theta = 5^\circ\text{--}90^\circ$.

X-ray fluorescence (XRF) on a PANalytical Zetium Epsilon 3 spectrometer was employed to establish the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the zeolites.

The inductively coupled plasma optical emission spectrometer (ICP-OES) on a PerkinElmer 7300

DV instrument was used for the analysis of Na promoter contents in the calcined catalysts.

Ammonia temperature-programmed desorption (NH₃-TPD) was performed on a BELCAT II chemisorption analyzer (MicrotracBEL, Corp.) to characterize the strength of acid sites in HZSM-5. After subjecting the samples to a 30-minute preconditioning at 600 °C in a helium atmosphere within a quartz reactor, they were cooled to 100 °C. A saturation step with ammonia was followed by a 30-minute purge using helium to eliminate physically and reversibly bound NH₃. Subsequently, a thermal desorption profile from 100 °C to 700 °C was generated at a 10 °C/min ramp rate under helium flow.

The textural properties of zeolites (pore volume, specific surface area, pore size distribution, etc.) are characterized using a N₂ adsorption-desorption test method. The samples were tested using QuantaChrome equipment. The adsorption properties of both the newly prepared and used catalysts were assessed at -196 °C. Prior to adsorption measurements, the samples were subject to a degassing process in two stages: initially for one hour at 90 °C and subsequently for six hours at 300 °C, both under a vacuum.

The microstructure of the sample was observed using a Thermo Scientific Apreo 2S scanning electron microscope (SEM).

Acidic site categorization on the zeolites was achieved through Py-IR spectroscopy. Measurements were performed on a Bruker tensor 27, vertex 80v FT-IR spectrometer, scanning a wavenumber range from 4000 to 400 cm⁻¹. Prepared samples were compressed into discs and situated in the sample holder. A 1-hour vacuum pre-treatment at 400 °C was performed before cooling the sample to ambient conditions. A baseline spectrum was acquired prior to saturating the sample with pyridine. Post-saturation, infrared scans were taken under 40 °C, following a vacuum purge at both

200 °C for 30 minutes. The net spectra were obtained by baseline subtraction. Concentrations of Brønsted and Lewis acid sites were computed using the formula provided by C. A. Emeis et al.³

1.3. Catalyst activity test

Catalytic performance test was conducted in a stainless steel fixed-bed reactor. In a typical experiment, 1g of the catalyst was put into the reactor. Next, it was reduced at 350 °C using pure H₂ for 8 hours. Following this, the catalytic performances were investigated under the conditions of GHSV = 4000 mL·g_{cat}⁻¹·h⁻¹, 320 °C, 3 MPa, H₂/CO₂/N₂ = 72/24/4 (vol%). The function of nitrogen was as an internal benchmark. During the reaction, the organic products were analysed in real-time using an Agilent 7890B instrument equipped with a flame ionisation detector (FID) and a PONA type capillary column. Concurrently, the reaction tail gas was directed through a cold trap to condense and separate the organic products. The cooled gaseous products, namely CO, CH₄, N₂, and CO₂, were subsequently analysed using a thermal conductivity detector (TCD, GC-2014AT, SHIMADZU) fitted with a TDX-01 column.

Herein, CO₂ conversion, CO selectivity and the hydrocarbon distribution (not counting CO product) were calculated as following Eqs. (1-3).

$$CO_2 \text{ conversion (\%)} = \frac{CO_{2 \text{ in}} - CO_{2 \text{ out}}}{CO_{2 \text{ in}}} \times 100\% \quad (1)$$

$$CO \text{ selectivity (\%)} = \frac{CO_{\text{out}}}{CO_{2 \text{ in}} - CO_{2 \text{ out}}} \times 100\% \quad (2)$$

$$C_i \text{ hydrocarbon selectivity (C - mol\%)} = \frac{\text{mol of } C_i \text{ hydrocarbon} \times i}{\sum_i \text{mol of } C_i \text{ hydrocarbon} \times i} \times 100\% \quad (3)$$

where the CO_{out} represents the mole of CO in the outlet, and CO_{2 in} and CO_{2 out} represent the moles of CO₂ in the inlet and outlet, respectively.

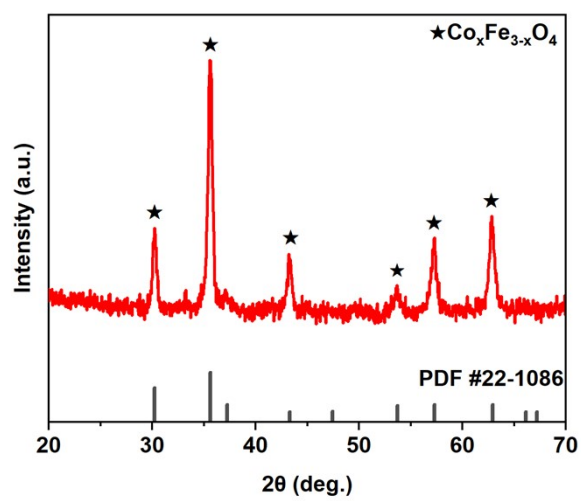


Fig. S1. XRD pattern of the fresh CoFe catalyst.

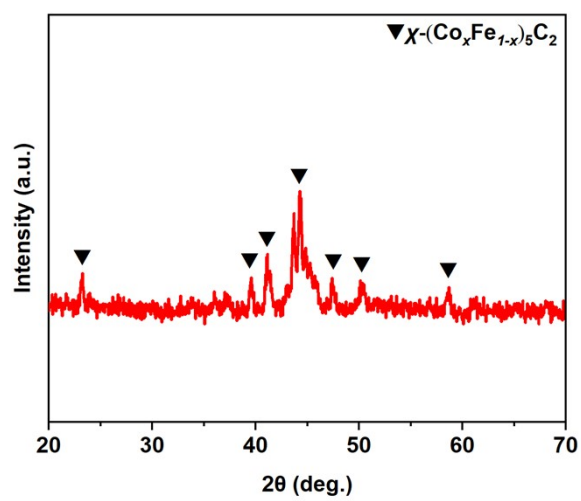


Fig. S2. XRD pattern of the spent CoFe catalyst.

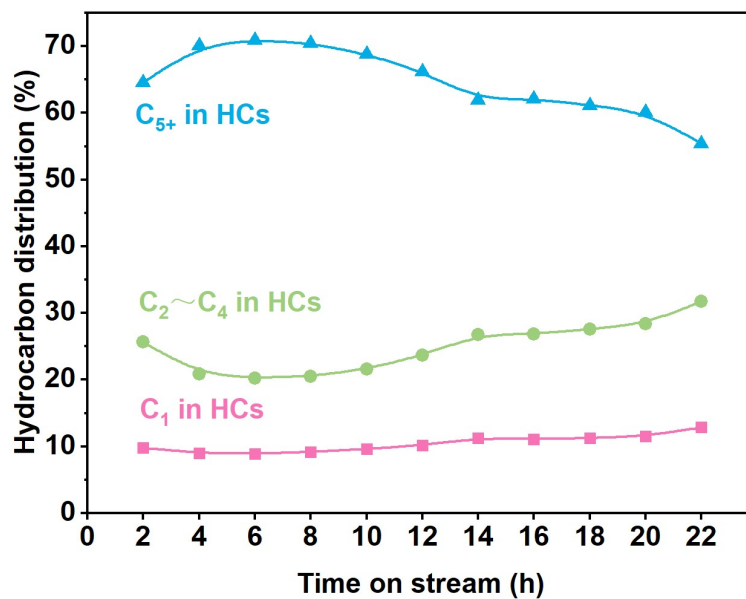


Fig. S3. The stability of the CoFe/HZ-5(20) catalyst in CO₂ hydrogenation.

Reaction conditions: 320 °C, 3.0 MPa, H₂/CO₂/N₂=72/24/4 (vol%), 4000 mL g_{cat.}⁻¹

h⁻¹.

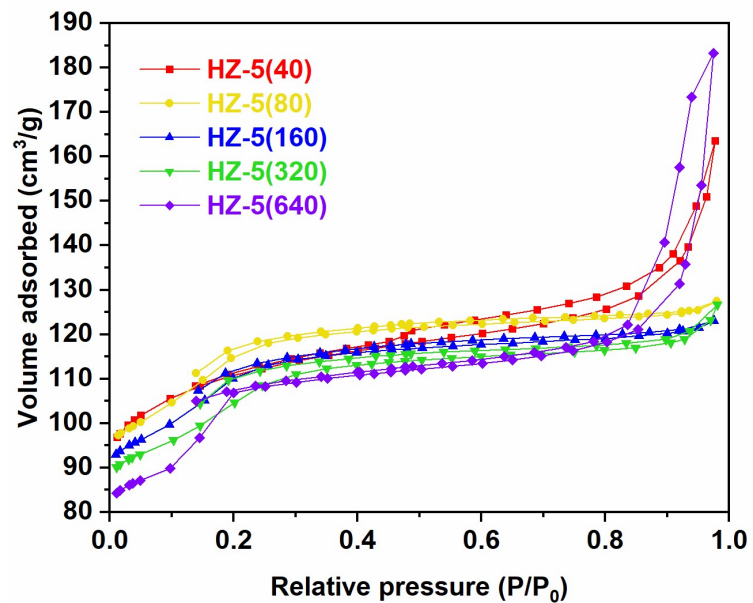


Fig. S4. N₂ adsorption-desorption isotherms of the HZSM-5 zeolites with different SiO₂/Al₂O₃ ratios.

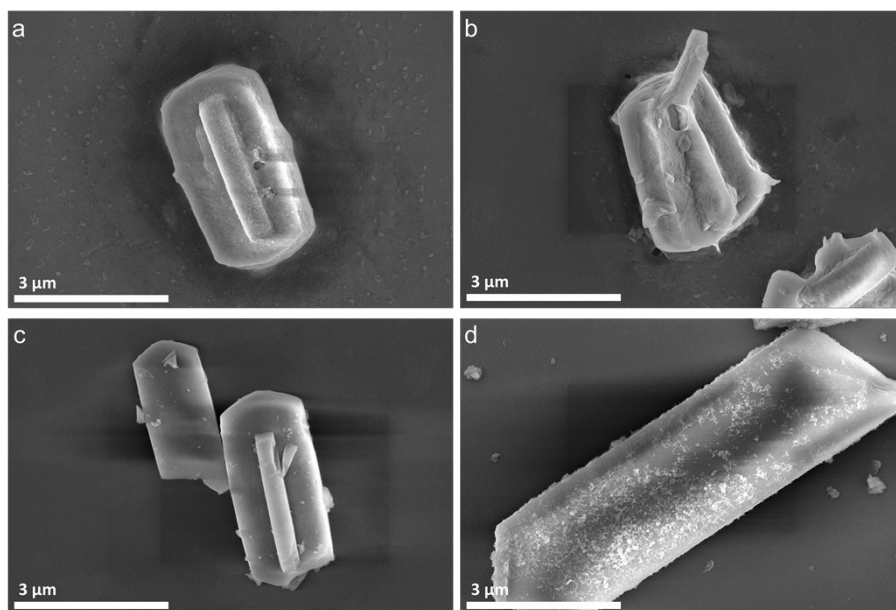


Fig. S5. SEM diagrams of (a) HZ-5(80), (b) HZ-5(160), (c) HZ-5(320), and (d) HZ-5(640).

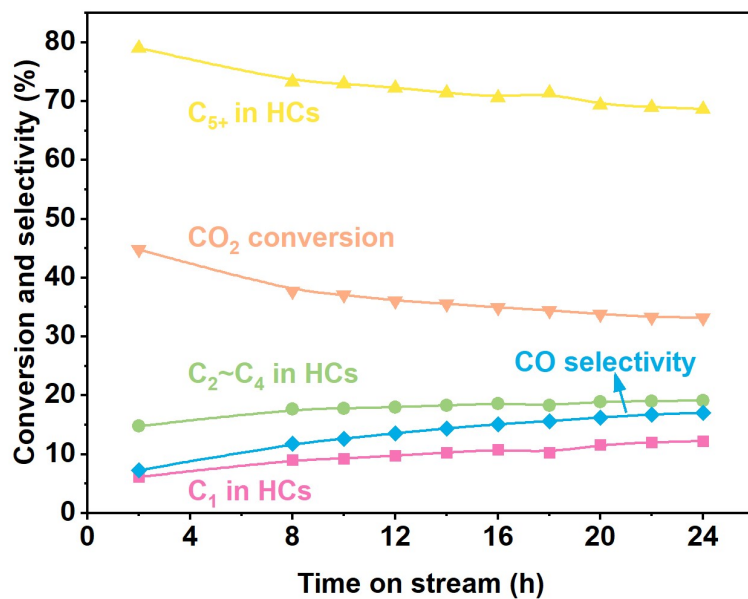


Fig. S6. The stability of the CoFe/HZ-5(40) catalyst in CO₂ hydrogenation.

Reaction conditions: 320 °C, 3.0 MPa, H₂/CO₂/N₂=72/24/4 (vol%), 4000 mL g_{cat.}⁻¹

h⁻¹.

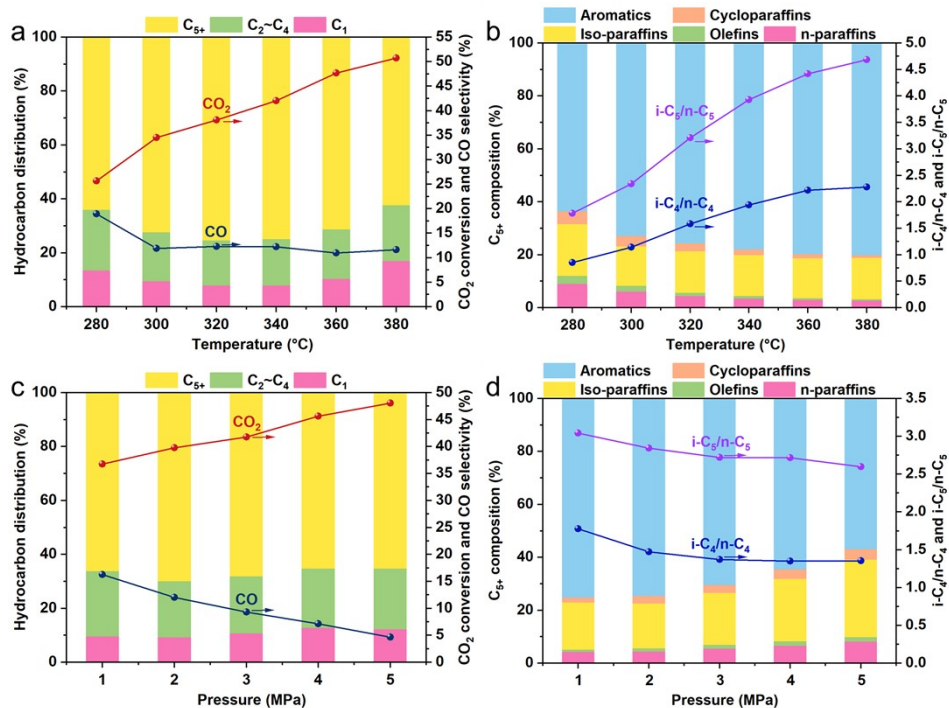


Fig. S7. Hydrocarbon distribution (a) and C_{5+} composition (b) of CO_2 hydrogenation over CoFe/HZ-5(40) at different reaction temperatures. Reaction conditions: 3.0 MPa, $H_2/CO_2/N_2=72/24/4$ (vol%), $4000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$, time on steam = 14 h. Hydrocarbon distribution (c) and C_{5+} composition (d) of CO_2 hydrogenation over CoFe/HZ-5(40) at different reaction pressures. Reaction conditions: 320 °C, $H_2/CO_2/N_2=72/24/4$ (vol%), $4000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$, time on steam = 14 h.

Table S1. Textural characteristics of CoFe and Fe.

Catalysts	S _{BET} ^a (m ² /g)	V _{pore} ^b (10 ⁻² cm ³ /g)	D _{pore} ^c (nm)
CoFe	44.22	0.19	11.60
Fe	32.34	0.04	16.84

^a S_{BET}: specific surface area calculated by BET method; ^b V_{pore}: t-Plot micropore pore volume; ^c

D_{pore}: Adsorption average pore diameter.

References

- 1 N. Liu, J. Wei, J. Xu, Y. Yu, J. Yu, Y. Han, K. Wang, J. I. Orege, Q. Ge and J. Sun, *Appl. Catal. B*, 2023, **328**, 122476.
- 2 J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu and J. Sun, *Nat. Commun.*, 2017, **8**, 15174.
- 3 C. A. Emeis, *J. Catal*, 1993, **141**, 347-354.