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Electronic Supplementary Information

High-Purity Hägg Carbide Supported by g-C3N4 for CO2 Hydrogenation to Liquid Fuel

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Preparation of g-C_3N_4 (CN) and hydrothermal support (HCN)

Firstly, CN was synthesized via thermal polymerization reaction. Typically, Usually, 4 g melamine is calcined at 550 °C and kept in a muffle furnace for 4 h. The resulting solid was subsequently gathered and grind it at room temperature. HCN was prepared via hydrothermal method. 0.75 g CN was ultrasonically dispersed in a mixture of 4 mL of HNO_3 and 56 mL of deionized water for 10 min, followed by mixing for 30 min. Afterward, the mixture was put into a 100 mL Teflon-lined autoclave and treated at 160 °C for 3 h. The residue was centrifuged with deionized water and ethanol and dried in vacuum at 60 °C for 12 h.

Synthesis of iron-based catalysts

Fe and 1% K were introduced into the support by a grinding method using ethanol. In terms of Fe_X/HCN(W)-M, X denotes the mass percent of iron element in whole catalyst during its preparation, HCN denotes using HCN as support, W denotes wet grinding, and M denotes microwave treating. Grinding and microwave-assisted heating strategies are two steps completed step by step. Ethanol can prevent material aggregation during the milling process, ensuring that the milled materials exhibit good dispersibility. Support and metal were firstly grinded, then the mixture was microwaved when it was dried at 80 °C for 10 h to remove ethanol and water absorbed from the air. The obtained catalyst was treated in a 700 W microwave oven with microwave heating for 30 seconds under the protection of N_2 atmosphere, marked as Fe_X/HCN(W)-M. In order to elevate the advantage of the grinding strategy, a series of reference catalyst were fabricated. When W was replaced by I, it means Fe and K were introduced in support by incipient wetness impregnation method, and it means grinding without solution when W is absent. Also, to elevate the strength of microwave-assisted synthesis, the grinding mixture was calcined at 550 °C within a N_2 atmosphere for 4 h when M was replaced by C, and operated without any treatment when M is absent. Thereinto, W stands for wetting grinding, M refers to microwave treatment, I stands for impregnation, and C refers to calcination.

Catalyst characterization

Powder XRD patterns of the catalysts were characterized by a Rigaku SmartLab 9 KW using Cu-Ka irradiation. Scans were recorded in the 2θ range of 5-80° with a step size of 0.36 °/s.

X-ray photoelectron spectroscopy (XPS) analysis was obtained using Thermo Fisher Scientific ESCALAB 250Xi multifunctional X-ray photoelectron spectroscope.

Transmission electron microscopy (TEM) for spent catalysts was obtained by JEM 2100. High-resolution Transmission electron microscopy (HRTEM) for spent catalyst was obtained by FEI-TALOS-F200X equipped with energy-dispersive X-ray spectroscopy (EDS) mapping (Super X instrument).

Scanning electron microscope（SEM）for fresh catalyst was obtained by Hitachi Regulus 8230. N_2 physisorption was performed on Micromeritics ASAP 2460.

The CO temperature-programmed desorption (CO-TPD), CO_2 temperature-programmed desorption (CO_2-TPD) and H_2-temperature programmed reduction (H_2-TPR) of the fresh catalysts were determined via Micromeritics AutoChem 2920. For TPD test, 50 mg of sample was first reduced at 400 °C in H_2 gas flow (30 mL/min) for 2 h. Then, the temperature was decreased to 50 °C in He gas flow (30 mL/min). 10 vol% CO_2/Ar or 5 vol% CO/Ar gas mixture was then introduced into the reactor for 1 h. Then He was introduced into the reactor to remove gas phase. The trace was recorded from 50 °C to 500 °C with a heating rate of 10 °C /min. For H_2-TPR test, Sample of 50 mg was first pretreated at 150 with He for 1 h. Then a 5 vol% $H_{2/}$Ar gas mixture (30 mL/min) was fed into the reactor when the temperature was cooled to 50 °C. Finally, the curves were recorded from 50 °C to 500 °C with a heating rate of 10 /min.

Fe K-edge X-ray absorption near-edge structure (XANES) spectra of catalysts were recorded at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility, China. After compressing the sample into a pellet, it was encapsulated on both sides with Kapton tape, resulting in a disc approximately 1 cm in diameter. The optical path and intensity were adjusted, the energy range was set, and the transmission spectrum of the sample was collected. The XANES were acquired using the Athena software, and the extended edge data were fitted with Artemis software to construct the wavelet transform spectrum.

Catalytic performance test

The catalytic performance of carbon dioxide was evaluated in a stainless steel fixed-bed reactor. Before the reaction, the prepared 0.25 g catalyst (20-40 mesh) was reduced in pure H_2 at 400 °C, 50 mL/min for 3 h, after which the temperature was reduced to 320 °C. Subsequently, CO_2/H_2/AR (24.5%/71.8%/3.7%) was introduced, gradually increasing to 2.0 MPa. The long-chain hydrocarbons were trapped by n-octane as solvent. For n-octane, the selectivity is calculated using the average selectivity of C_7 and C_9. Flame ionization detector (FID) was used to analyze the collected long-chain hydrocarbons by offline gas chromatography.

$$CO_2\ conversion\ (\%)\ = \frac{CO_{2\ inlet} - CO_{2\ outlet}}{CO_{2\ inlet}} \times 100\%\ (1)$$

$$CO\ \ selectivity\ (\%) = \frac{CO_{\ outlet}}{CO_{2\ inlet} - CO_{2\ outlet}} \times 100\%\ (2)$$

$$C_{ihydrocarbon\ selectivity}\ (C - mol\ \%) = \frac{Mole\ of\ Ci\ hydrocarbons}{Mole\ of\ total\ hydrocarbons} \times\ 100\%\ (3)$$

The C balance was calculated based on C number of each molecule, as shown in following equation:

$$C_{\ balanced}\ (\%)\ = \frac{n(C)_{gas} + n(c)_{liquid}}{n(c)_{charged}} \times 100\%\ (4)$$

In the equation, $n(C)_{charged}$ is the number of moles of C atoms in the CO_2 charged in to the reactor, $n(C)_{gas}$ is the number of moles of C atoms in the released gases, and $n(C)_{liquid}$ is the number of moles of C atoms of the liquid products and the CO_2 dissolved in the reaction solution after releasing the gases. The carbon balance data of all catalysts were between 90% and 95%.

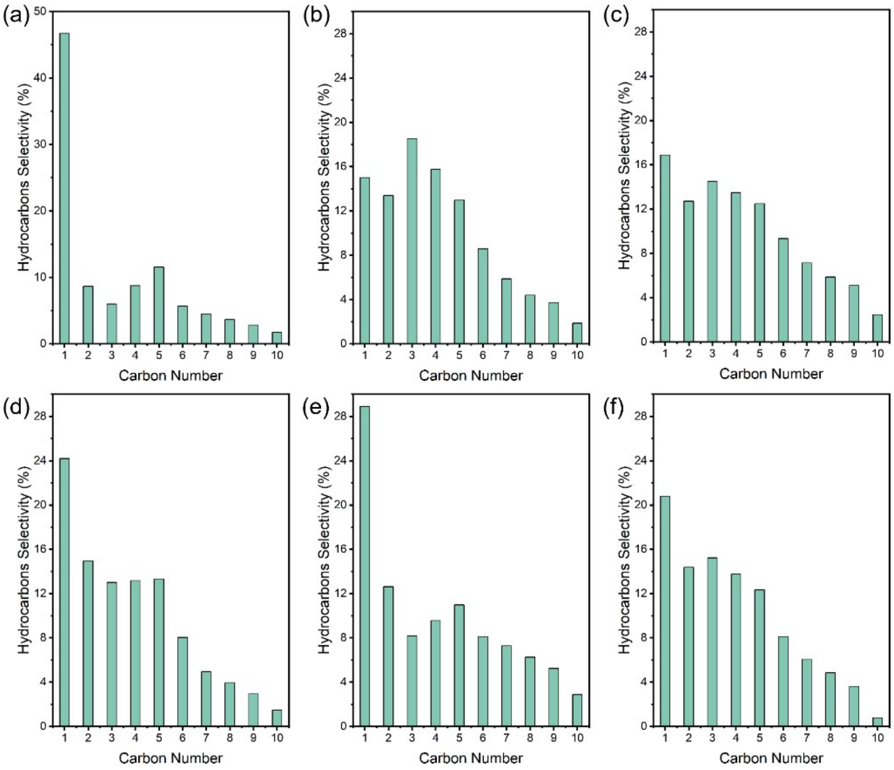

Fig. S1 Detailed product distribution over catalysts: (a) Fe_5/CN-M, (b) Fe_5/HCN-M, (c) Fe_5/HCN(W)-M, (d) Fe_5/HCN(W), (e) Fe_5/HCN(W)-C, (f) Fe_5/HCN(I)-C.

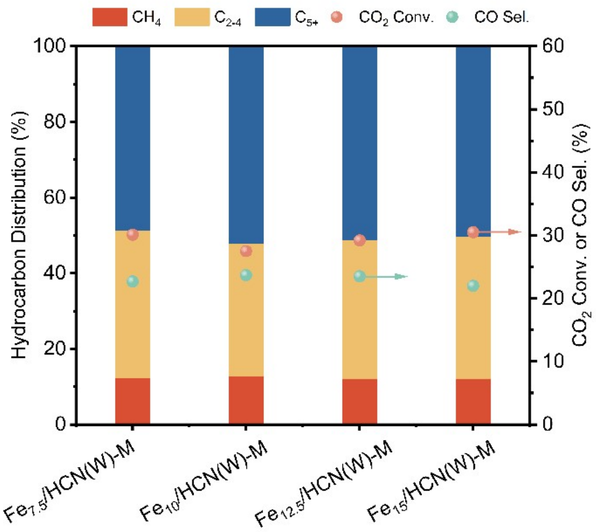

Fig. S2 Effects of Fe load conditions on CO_2 hydrogenation performance.

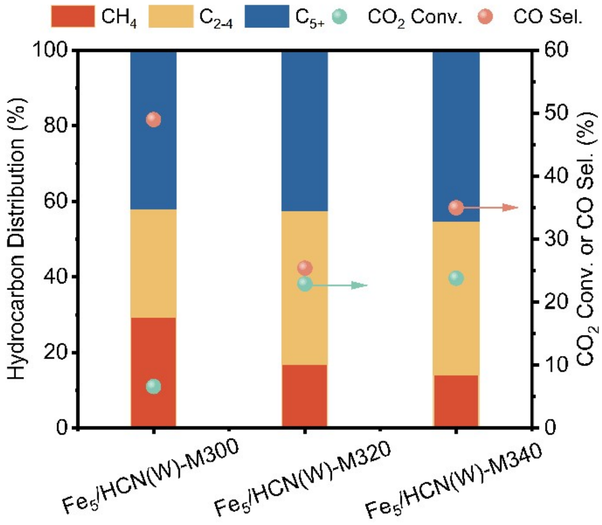

Fig. S3 Effects of temperature conditions on CO_2 hydrogenation performance. Fe_5/HCN(W)-M300, Fe_5/HCN(W)-M320, Fe_5/HCN(W)-M340 were reacted at 300 °C, 320 °C,340 °C temperatures separately.

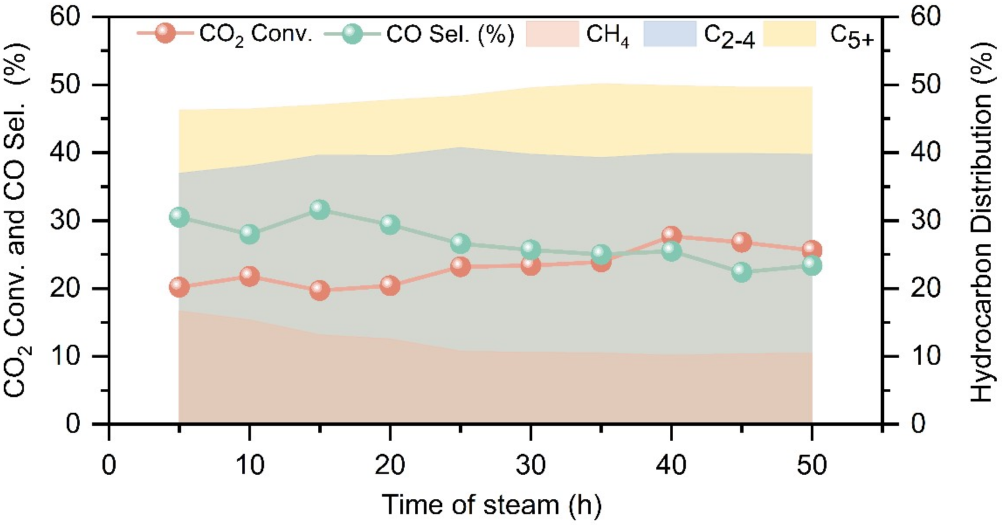

Fig. S4 Catalytic stability of Fe_5/HCN(W)-M. Reaction conditions: $H_2/CO_2/Ar = 72.2/24.3/3.5$, P = 2.0 MPa, 320 °C.

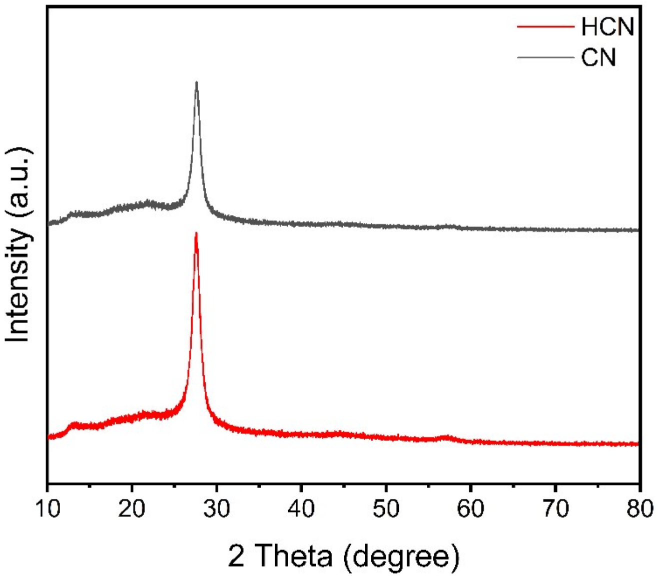

Fig. S5 XRD patterns of g-C_3N_4 (CN) and the hydrothermally treated support (HCN).

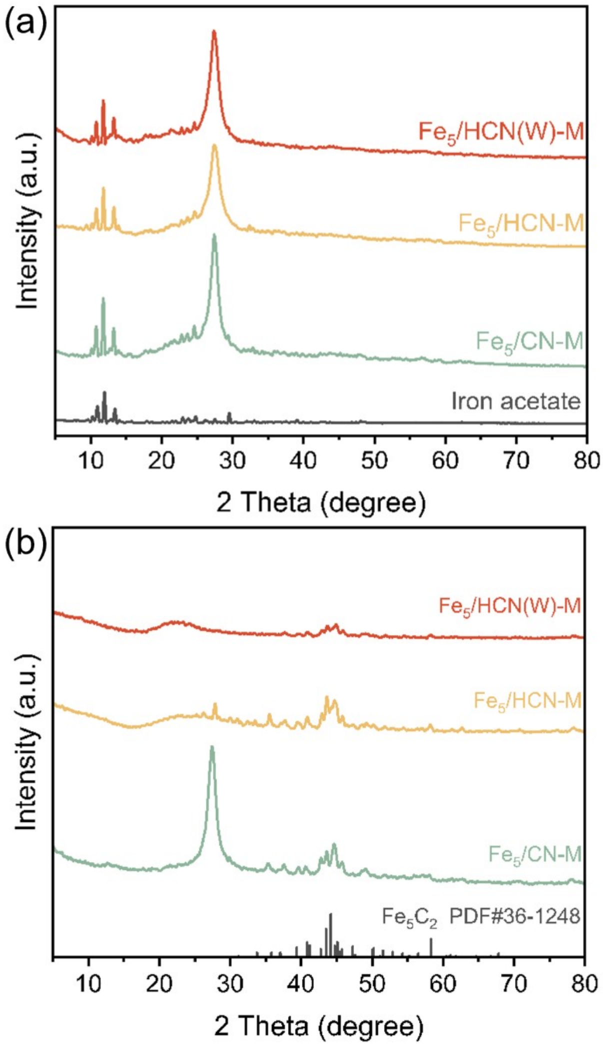

Fig. S6 XRD patterns of different microwave catalysts: (a) prepared catalysts, (b) spent catalysts.

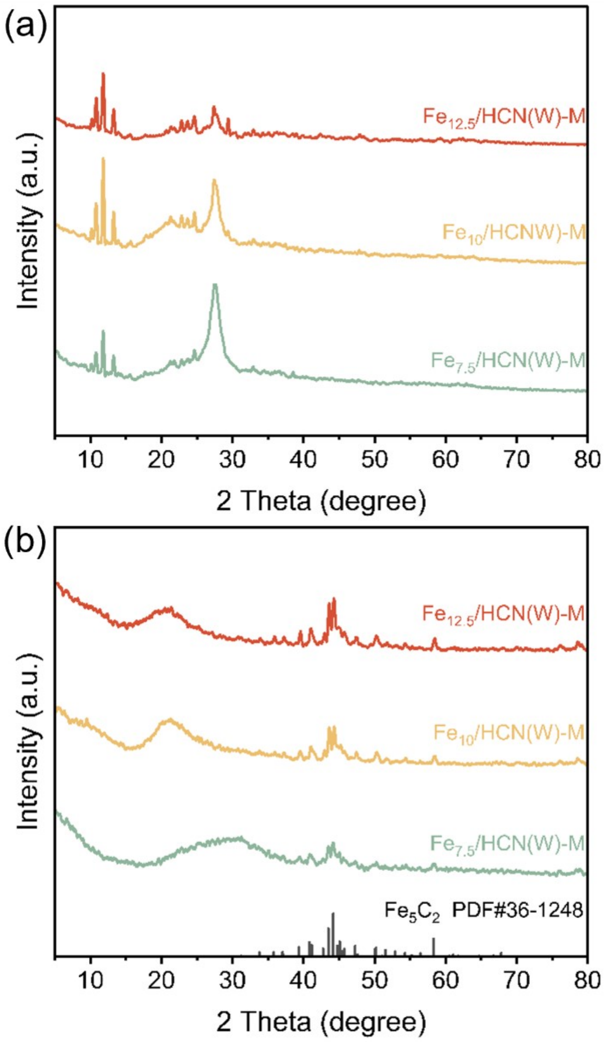

Fig. S7 XRD patterns of microwave catalysts with different Fe load: (a) as-prepared catalysts, (b) spent catalysts.

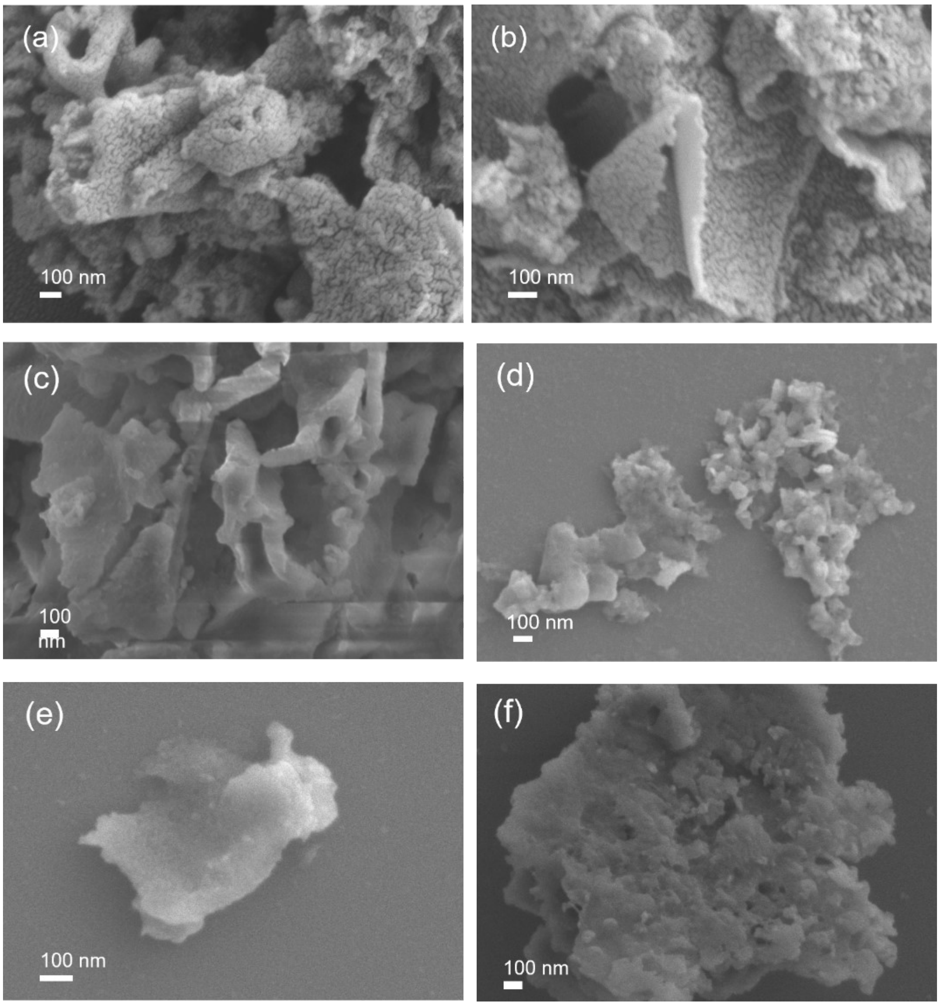

Fig. S8 SEM images of as-prepared catalysts: (a) CN, (b) HCN, (c) Fe$_5$/CN-M, (d) Fe$_5$/HCN-M, (e) Fe$_5$/HCN(W)-M, (f) Fe$_5$/HCN(W)-C.

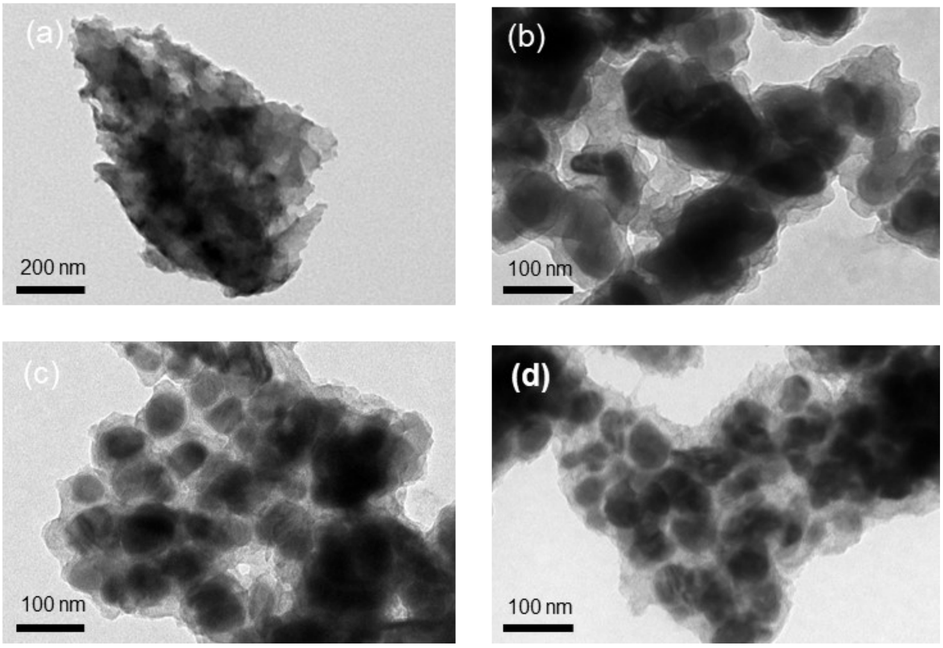

Fig. S9 TEM images of spent catalysts: (a) Fe$_5$/CN-M, (b) Fe$_5$/HCN-M, (c) Fe$_5$/HCN(W)-M, (d) Fe$_5$/HCN(W).

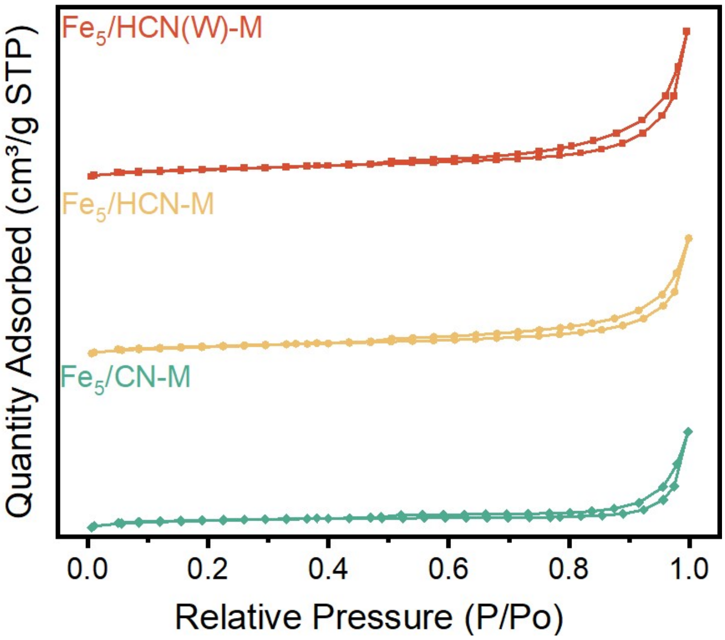

Fig. S10 BET curves of fresh Fe_5/CN-M, Fe_5/HCN-M, Fe_5/HCN(W)-M.

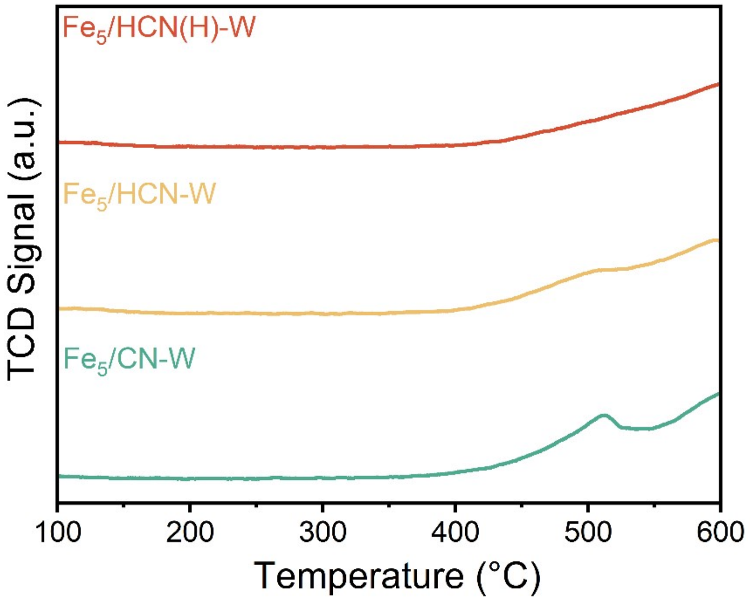

Fig. S11 CO_2-TPD curves of as-prepared Fe_5/CN-M, Fe_5/HCN-M, Fe_5/HCN(W)-M.

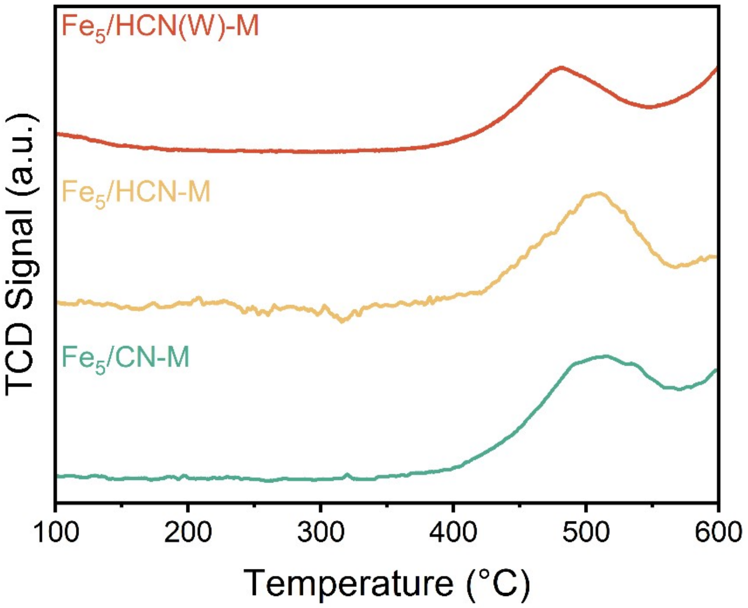

Fig. S12 CO-TPD curves of as-prepared Fe_5/CN-M, Fe_5/HCN-M, Fe_5/HCN(W)-M.

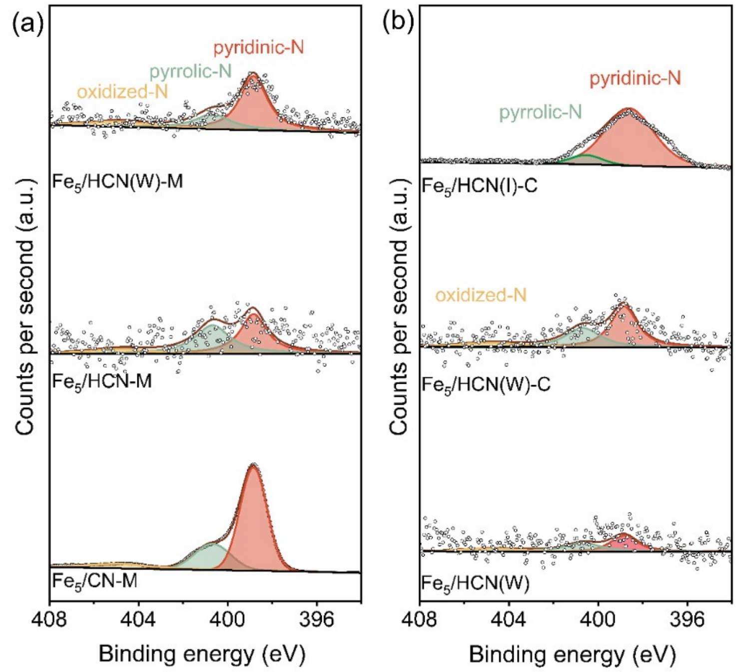

Fig. S13 N 1s XPS spectra of spent microwave catalysts: (a) microwave treatment catalysts, (b) contrast catalysts.

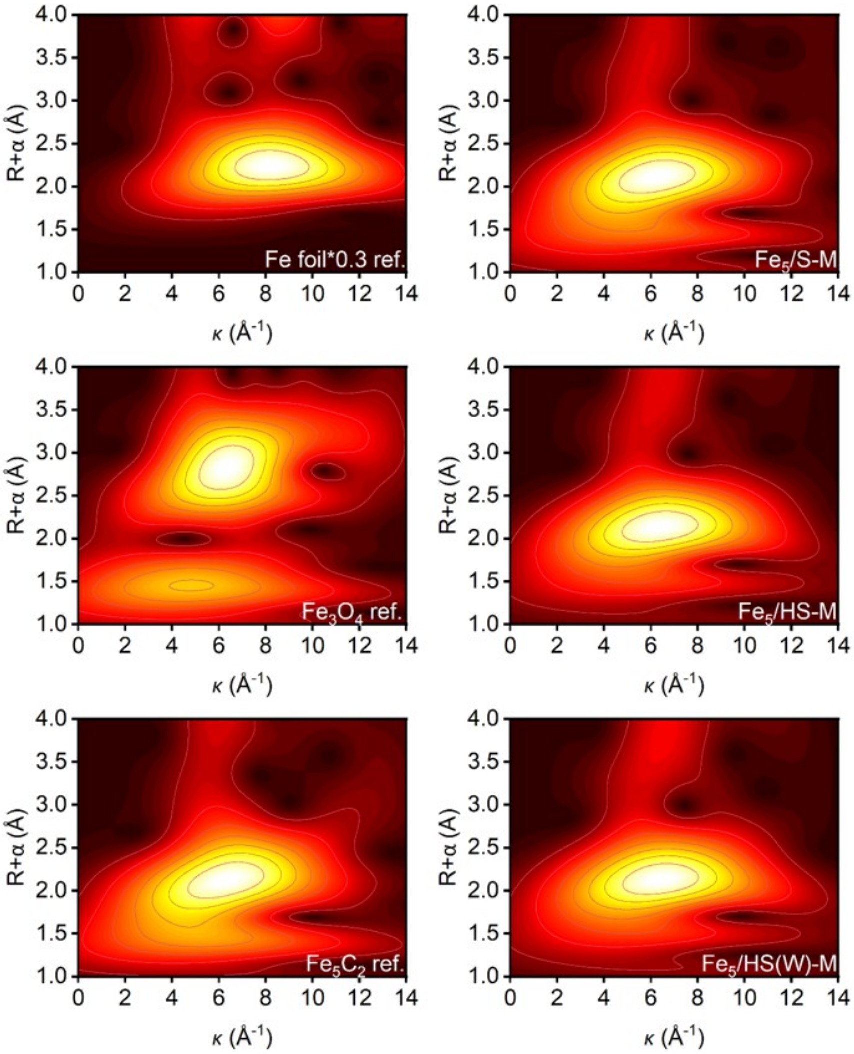

Fig. S14 Wavelet transform of the k^3-weighted EXAFS data of catalysts and reference samples (Fe foil, Fe_3O_4 and Fe_5C_2).

Table S1 CO_2 conversion and product selectivity from different catalysts.

Catalysts	P/MPa	T/°C	CO_2 Conv. /%	CO Sel. /%	HCs Sel. (mol-%)		
					CH_4	C_2-C_4	C_{5+}
Fe_5/CN-M	2.0	320	11.9	47.2	46.7	23.5	29.8
Fe_5/HCN-M	2.0	320	22.6	37.4	15.0	47.6	37.4
Fe_5/HCN(W)-M	2.0	300	6.6	49.0	17.3	41.4	41.3
Fe_5/HCN(W)-M	2.0	320	22.9	25.4	16.9	40.7	42.2
Fe_5/HCN(W)-M	2.0	340	23.8	35.0	14.0	40.8	45.2
Fe_5/HCN(W)-M (50 h)	2.0	320	25.7	22.4	10.5	39.8	49.7
Fe_5/HCN(W)	2.0	320	18.2	45.6	24.2	41.1	34.7
Fe_5/HCN(W)-C	2.0	320	22.9	37.5	28.9	30.4	40.7
Fe_5/HCN(I)-C	2.0	320	21.0	39.3	20.8	43.4	35.8
$Fe_{7.5}$/HCN(W)-M	2.0	320	30.1	22.7	12.4	39.0	48.6
Fe_{10}/HCN(W)-M	2.0	320	27.5	23.7	12.8	35.1	52.1
$Fe_{12.5}$/HCN(W)-M	2.0	320	29.2	23.5	12.1	36.7	51.2
Fe_{15}/HCN(W)-M	2.0	320	30.5	22.0	12.2	37.6	50.2

Table S2 XPS Elemental compositions of spent catalysts.

Samples	Fe /%	N /%	O /%
Fe_5/CN-M	3.3	43.6	9.3
Fe_5/HCN-M	3.5	0.8	31.5
Fe_5/HCN(W)-M	4.7	1.0	27.9
Fe_5/HCN(W)	5.7	0.6	35.0
Fe_5/HCN(W)-C	3.3	43.6	9.3