Enhancing the selectivity of C₂ hydrocarbons over Fe-

based catalyst by controlling nitrogen doping in

electrocatalytic CO₂ reduction

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Experimental Section

Methods

Materials. CO₂ (Beijing Beiwen Gas Chemical Industry Co., Ltd.,) had a purity of 99.999 % and used as received. Iron(II) sulfate hydrate (A. R. grade, Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na and ethylenediamine (EDA) were purchased from Innochem. Copper sulfate hydrate, Nickel sulfate and Cadmium sulfate were supplied by Aldrich. Acetonitrile (AcN, A. R. grade) and acetone (A. R. grade were provided by Sinopharm Chemical Reagent Co., Ltd, China. Toray Carbon Paper (CP, TGP-H-60, 19×19 cm) and Nafion N-117 membrane (0.180 mm thick, \geq 0.90 meg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Polytetrafluoroethylene (PTFE, 60 wt% aqueous solution) was provided by Sigma-Aldrich Co. LLC. 1-Butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF₆, purity > 99%) was obtained from the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

Preparation of p-N-Fe₂O₃. 300 mg of FeSO₄ (167 mg of NiSO₄ / 246.574 mg of CdSO₄), 93.5 mg of EDTA-2Na were added into 18 mL deionized water and stirred continuously at 30 °C. After 3 h, 62.62 mg CuSO₄ was added and stirred for 3 h. 1 mL EDA was added under stirring. The solution was stirred for 12 h. During the process, the reaction flask is sealed. The solid products (Fe(OH)₂, Y-Fe(OH)₂ and EDA-Fe(OH)₂) were collected by centrifugation, washed with water, ethanol and acetone for three times insuring to remove soluble copper complexes (2EDA-Cu) and iron complexes (2EDA-Fe. After vacuum drying at 60 °C for 10 h, the product was put into a tubular furnace and heated under N₂ atmosphere. The temperature was kept at 300°C for 3 h and 600 °C for 2 h, and the heating rate was 1 °C /min. The resulting catalyst was denoted as $p-N-Fe_2O_3$. More experimental procedures are provided in the Supporting Information.

Preparation of N-Fe₂O₃. 300 mg of FeSO₄, 93.5 mg of EDTA-2Na were added into 18 mL deionized water and stirred continuously at 30 °C. After 6 h, 1 mL EDA was added slowly under stirring. The solution was stirred for 12 h. The solution was stirred for 12 h. During the process, the reaction flask is sealed. The solid products (Fe(OH)₂ and EDA-Fe(OH)₂) were collected by centrifugation, washed with water, ethanol and acetone for three times insuring to remove soluble iron complexes (2EDA-Fe and Y-Fe. After vacuum drying at 60 °C for 10 h, the product was put into a tubular furnace and heated under N₂ atmosphere. The temperature was kept at 300 °C for 3 h and 600 °C for 2 h, and the heating rate was 1 °C /min. The resulting catalyst was named as N-Fe₂O₃.

Preparation of Fe-75, Fe-100, Fe-150 and Fe-300. 75mg, 100mg, 150mg and 300 mg of FeSO₄, 93.5 mg of EDTA-2Na were added into 18 mL deionized water and stirred continuously at 30 °C. After 3 h, 62.62 mg CuSO₄ was added and stirred for 3 h. 1 mL EDA was added under stirring. The solution was stirred for 12 h. During the process, the reaction flask is sealed. The solid products (Fe(OH)₂, Y-Fe(OH)₂ and EDA-Fe(OH)₂) were collected by centrifugation, washed with water, ethanol and acetone for three times insuring to remove soluble copper complexes (2EDA-Cu) and iron complexes (2EDA-Fe. After vacuum drying at 60 °C for 10 h, the precipitates were analyzed. The precipitates were named as Fe-100, Fe-150, Fe-300, respectively.

The precipitates were put into a tubular furnace and heated under N_2 atmosphere. The temperature was kept at 300 °C for 3 h and 600 °C for 2 h, and the heating rate was 1 °C /min.

Material characterizations. PXRD data were collected on the X-ray diffractometer (Model D/MAX2500, Rigaka with Cu-Kα radiation at a scan speed of 5 °/min. The morphologies of the products were characterized using SEM JEOL S-4800 and transmission electron microscope (TEM) (JEOL-2100F). The energy dispersive X-ray spectroscopy (STEM-EDX) elemental mapping analysis was obtained by JEOL-2100F. X-ray photoelectron spectroscopy (XPS) analysis was performed on the Thermo Scientific ESCALab 250Xi using a 200 W monochromated Al Kα radiation. Inorganic elements (Fe, Cu) in the catalysts were determined by ICP-AES method (VISTA-MPX). Organic elemental analysis was performed on the Thermo Flash Smart. Gas chromatography mass spectrometry (Shimadzu Ultra was used to confirm the origin of the products.

⁵⁷Fe Mössbauer spectroscopy. The ⁵⁷Fe Mössbauer spectra were recorded on an SEE Co W304 Mössbauer spectrometer at room temperature, using a ⁵⁷Co/Rh source in transmission geometry which was equipped with a helium cryostat (Advanced Research Systems, Inc., 4 K). The data were fitted by using the MossWinn 4.0 software. **XAS study.** The X-ray absorption fine structure spectra (Fe K-edge were collected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF. The storage rings of BSRF were operated at 2.5 GeV with an average current of 250 mA. Using Si (111) doublecrystal monochromator, the data collection was carried out in transmission mode using ionization chamber. All spectra were collected in ambient conditions. The raw data were energy-calibrated, background corrected, and normalized using Ifeffit software. For the Fe K-edge measurements, Fe foil was used as reference.

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k³-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k³-weighted $\chi(k)$ data of Fe K-edge were Fourier transformed to real (R) space using a hanning windows (d_k=1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

XES study. The XES data were obtained at beamline 4W1B of the Beijing synchrotron Radiation Facility, China. The storage ring ran 2.5 GeV electron with current of 250 mA. A polychromatic beam (pink beam) with an incident X-ray energy of 5 or 10-18 keV was used, and the photon flux was on the order of 10^{13} phs/s. The beam spot-size (FWHM) was focused down to 50 µm by a polycapillary half-lens. The K_β XES data were collected by means of a multiscriptal energy-dispersive spectrometer based on the von Hamos geometry. The spectrometer consisted of an array of 4 cylindrically bent Si crystal analyzers (500-mm radius) mounted in a horizontal geometry to minimize the scattering background. The dispersion axis was perpendicular to the axis of the incident beam. The crystal dimension in the dispersive and focusing directions was 50 mm and 100 mm, respectively. The analyzers diffracted and focused the emitted signal onto a position-sensitive detector. The 2D spectra were recorded using a Pilatus 100K detector with a pixel size of $172 \times 172 \ \mu m^2$. For the K_{β} line of Fe, Si (531) crystals were used. The XES raw data were processed by the standard procedures using the DAWN package.

Working electrode preparation. To prepare catalyst electrode, the synthesized catalysts were loaded on the carbon paper electrode by spraying catalyst ink. The catalyst ink was prepared by dispersing 5.0 mg of catalysts into a mixture solution of 1.0 mL acetone and 10 μ L Nafion (Alfa, 5 wt %) with sonication for 30 min. Carbon paper was used as the substrate electrode after mechanical polishing and complete cleaning with deionized water. The loaded amount of the catalyst on carbon support was 2 mg/cm².

Electrochemical study. An electrochemical workstation (CHI 6081E, Shanghai CH Instruments Co., China was used for all electrochemical experiments. [Bmim]PF₆/MeCN/H₂O (W/W/W= 30/65/5) was used as the cathode electrolyte. The LSV measurements were carried out in a typical H-type cell with three-electrode configuration composed of a working electrode, a platinum gauze auxiliary electrode and Ag/Ag⁺ reference electrode. Before each set of experiment, the electrolyte was bubbled with N₂ or CO₂ for at least 30 min to form saturated solution. The LSV measurement in gas-saturated electrolyte was conducted at a sweep rate of 0.001 V/s in the potential range of -1 to -2.6 V vs Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TBAP-MeCN).

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Product analysis. The gaseous product was collected and analyzed by gas chromatography (GC, HP 4890D, which was equipped with FID and TCD detectors using helium as the internal standard. ¹H NMR measurements were performed on a Bruker Avance III 400 HD spectrometer and no liquid product was detected. The current density and Faradaic efficiencies (FEs) of the products were calculated using the amounts of the products obtained from GC analysis.

From the GC peak areas and calibration curves of the TCD detector, the moles of a gaseous product can be obtained. After the quantification, the FE of each product was calculated as follows:

$$FE(\%) = \frac{n_{product} \times n_{electrons} \times F}{Q} \times 100\%$$

where F is the Faraday constant (96485 C mol⁻¹), $n_{product}$ is the product derived (mol) from GC (gaseous products), $n_{electrons}$ is the electron transfer number, and Q is the total charge passed during the CO₂ electrolysis.

Electrochemical impedance spectroscopy (EIS) measurements. The EIS measurements were recorded using CO₂-saturated electrolyte at open circuit potential with an amplitude of 5.0 mV (10^{-2} to 10^{5} Hz). The value for R_{ct} was obtained by fitting the EIS spectra using the Zview software (Version 3.1, Scribner Associates, USA, which gave a goodness of fit of > 95%.

Density functional theory calculation method. The spin-polarized density functional theory (DFT) calculations^{1,2} were carried out in the Vienna ab initio simulation package (VASP) based on the plane-wave basis sets with the projector augmented-wave method.^{3,4} The exchange-correlation potential was treated by using a generalized

approximation (GGA) with the Perdew-Burke-Ernzerhof gradient (PBE) parametrization.⁵ A supercell of Fe₂O₃(400) containing 2×2×1 unit cells was considered. Meanwhile, a vacuum region of about 15 Å was applied to avoid the interaction between adjacent images. The energy cutoff was set to be 450 eV. The structures were fully relaxed until the maximum force on each atom was less than 0.03 eV/Å, and the energy convergent standard was 10⁻⁵ eV. The different charge density can be defined as $\Delta \rho = \rho_{*CO} - \rho_{*} - \rho_{CO}$, where ρ_{*CO} , ρ_{*} , and ρ_{CO} are the electron densities of the N doped Fe₂O₃(400) with the adsorbed CO molecule, the isolated N doped Fe₂O₃(400), and isolated CO molecule, respectively. The adsorption energy E_{ads} per CO molecule is defined as, $E_{ads} = E_{*CO} - E_{*} - E_{CO}$, where E_{*CO} stands for the energy of the monolayer with the adsorbed O_2 molecule, E* is the energy of a clear monolayer, and E_{CO} is the energy of an CO molecule under vacuum. The KPOINTS file specifies a $2 \times 2 \times 1$ Monkhorst-Pack grid for the surface model.

Supplementary Figures



Fig. S1. IR spectrum of the precursors of catalysts. (a) $p-N-Fe_2O_3$. (b) $N-Fe_2O_3$ before calcination. (c) Standard sample was obtained by mixture of CuSO₄, FeSO₄, Y and EDA.



Fig. S2. (a) In situ Fe K-edge XANES spectra of the preparation process for $p-N-Fe_2O_3$. (b) Fourier-transformed EXAFS spectra in R-space of the preparation process for $p-N-Fe_2O_3$.



Fig. S3. (a) In situ Cu K-edge XANES spectra of the preparation process for $p-N-Fe_2O_3$. (b) Fourier-transformed EXAFS spectra in R-space of the preparation process for $p-N-Fe_2O_3$.



Fig. S4. The calculated mole fraction of different components in different catalysts based on the results of OEA.



Fig. S5. Schematic diagram of preparation process of N-Fe₂O₃ catalyst before calcination. Fe(II)-Y: $14.27 > Fe(II)-OH_2$: 9.77 > Fe(II)-EDA: 7.65.



Fig. S6. SEM images of p-N-Fe₂O₃ (a) and N-Fe₂O₃ (b).



Fig. S7. TEM images of N-Fe₂O₃.



Fig. S8. STEM image of N-Fe₂O₃ and the corresponding STEM-EDS elemental mapping images

of Fe, O and N of the region.



Fig. S9. (a) XPS survey spectrum of $p-N-Fe_2O_3$. (b) XPS spectra of in $p-N-Fe_2O_3$ Cu 2p. (c) The high-resolution O 1s spectra of $p-N-Fe_2O_3$ and $N-Fe_2O_3$. (d) The high-resolution N 1s spectra of $p-N-Fe_2O_3$ and $N-Fe_2O_3$.



Fig. S10. LSV curves in N₂ and CO₂ saturated electrolytes (a) p-N-Fe₂O₃. (b) N-Fe₂O₃.



Fig. S11. Comparison of the FE and current density of C_{2+} products with reported catalysts.



Fig. S12. Catalytic performances of p-N-Fe₂O₃ with different Fe amount in the preparation. (a)

100 mg of FeSO₄. (b) 150 mg of FeSO₄.



Fig. S13. Catalytic performances of N-Fe₂O₃.



Fig. S14. The results of isotope-labelled ¹³CO₂ experiments over p-N-Fe₂O₃.



Fig. S15. Catalytic performances of p-N-Fe₂O₃ in 0.1 M KHCO₃.



Fig. S16. (a) XRD patterns of p-N-Fe₂O₃ before and after reaction. (b) TEM and corresponding EDS mapping of p-N-Fe₂O₃ before and after reaction. (c) SEM and corresponding EDS mapping of p-N-Fe₂O₃ before and after reaction.



Fig. S17. The measured specific double layer capacitance and fitted results for $p\text{-}N\text{-}Fe_2O_3$ and

 $N-Fe_2O_3$.



Fig. S18. Nyquist plots using $p-N-Fe_2O_3$ and $N-Fe_2O_3$ as catalysts.



Fig. S19. Corresponding simulated circuit for Nyquist plots.



Fig. S20. The N-doping sites of p-N-Fe₂O₃ (a) and N-Fe₂O₃ (b).



Fig. S21. The desorption free energy of *CO intermediate over different catalysts.



Fig. S22. The corresponding differential charge density of (a) p-N-Fe₂O₃ and (b) N-Fe₂O₃ with different view.



Fig. S23. The PDOS (Projected density of states) of Fe atom in different catalysts.



Fig. S24. Characterizations of the catalyst prepared using Ni as substitutes for Cu. (a) TEM image. (b) HRTEM images. (c) HAADF image and the corresponding EDS elemental mapping images of Fe, O and N of the region. (d) XPS spectra in Fe 2p. (e) XPS spectra in Ni 2p. (f) Catalytic performances.



Fig. S25. Characterizations of the catalyst prepared using Ni as substitutes for Cu. (a) TEM image. (b) HRTEM images. (c) HAADF image and the corresponding EDS elemental mapping images of Fe, O and N of the region. (d) XPS spectra in Fe 2p. (e) XPS spectra in Cd 3d. (f) Catalytic performances.

Supplementary Tables

	FeSO ₄	CuSO ₄	EDTA-2Na	EDA
Number of moles	1.08 mmol	0.25 mmol	0.27 mmol	15 mmol
Molar ratios	4	1	1	60

Table S1. The molar ratios between EDTA-2Na, FeSO₄, CuSO₄, and EDA.

Table S2. EXAFS fitting parameters at the K-edge of Fe and Cu under different reaction time

Sample	path	N	R (Å)	σ² (Ų·10 ⁻³)	ΔE ₀ (eV)	R factor	range
Omin	Fe-O	7.5±1.1	2.09±0.01	12.7±2.8	-4.6±0.6	0.002	1-2
90min	Fe-O	7.2±1.0	2.10±0.01	11.9±2.9	-3.6±0.6	0.001	1-2
CuSO₄-0min	Fe-O	6.8±0.8	2.09±0.01	11.6±2.5	-3.2±0.5	0.001	1-2
CuSO₄-90min	Fe-O	6.7±0.9	2.10±0.01	12.2±2.7	-2.8±0.5	0.002	1-2
CuSO₄-180min	Fe-O	6.6±0.9	2.07±0.01	10.7±2.1	-5.3±0.5	0.001	1-2
CuSO₄-0min	Cu-O	4.0±0.6	1.93±0.01	6.3±2.8	-4.4+_0.7	0.001	1-2
CuSO₄-90min	Cu-O	4.5±0.6	1.93±0.01	5.5±2.0	-4.0+_0.7	0.002	1-2
CuSO₄-180min	Cu-O	3.4±0.3	1.93±0.01	2.5±1.4	-2.9+_0.5	0.002	1-2

during the synthesis process.*

^{*}N = Coordination numbers. R = Bond distance. σ^2 = Debye-Waller factors. ΔE_0 = The inner potential correction. R factor = fitting degree.

sample	Fe wt (%)	Cu wt (%)
p-N-Fe ₂ O ₃	92.47	ND
N-Fe ₂ O ₃	89.92	ND

Table S3. The results of ICP-OES of Fe and Cu for different catalysts.

ND= no detected.

Table S4. EXAFS fit parameters over different catalysts.*

sample	path	Ν	R (Å)	σ² (Ų·10 ⁻³)	ΔE0 (eV)	R	range
p-N-Fe ₂ O ₃	Fe-O	4.7±0.7	2.00±0.01	14.5±2.7	-1.2±0.6	0.001	1-2
$N-Fe_2O_3$	Fe-O	5.3±0.6	2.00±0.01	15.4±3.8	-1.2±0.9	0.001	1-2

^{*}In order to get value of S₀, we fixed the coordination numbers of the catalysts and Fe₂O₃, and got S₀ = 0.85. N = Coordination numbers. R = Bond distance. σ^2 = Debye-Waller factors. ΔE_0 = The inner potential correction. R factor is used to value the goodness of the fitting.

Sample	Component	IS (mm/s)	QS (mm/s)	H(T)	Γ(mm/s)	Area (%)
p-N-Fe ₂ O ₃	γ -Fe ₂ O ₃	0.22	0.01	49.63	0.5	39.7
	$FeO_{1-x}N_x$	0.54	-0.02	46.08	0.49	60.3
N-Fe ₂ O ₃	γ -Fe ₂ O ₃	0.23	0.03	49.21	0.47	33.6
	$FeO_{1-y}N_y$	0.54	0.01	45.63	0.46	53.9
	FeN ₄	0.81	0.63	_	0.58	12.5

Table S5. Mössbauer parameters derived from the fittings. Isomer shift (IS), quadrupolesplitting (QS), hyperfine field (H) and relative spectral area % of each component.

 Table S6.
 The results of OEA for different catalysts.

samples	C (wt %)	N (wt %)	O (wt %)
p-N-Fe ₂ O ₃	2.556	0.065	1.490
N-Fe ₂ O ₃	3.14	0.102	1.105

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