

**Electronic Supplementary Information (ESI) for:**

**Protein Powder Derived Nitrogen-Doped Carbon Supported  
Atomically Dispersed Iron Sites for Selective Oxidation of  
Ethylbenzene**

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## 1、 Experimental Section

### 1.1 Materials

Iron nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ≥98.5) was purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon black (99.9%) was purchased from Alfa Aesar. Protein powder was purchased from civilian market. Ethyl acetate (99.5%), ethylbenzene (99.5%), acetophenone (99.0%), 4-ethylanisole (98%), 4'-methoxyacetophenone (99.0%), 4- ethylnitrobenzene (99.0%), 4'-nitroacetophenone (99%), N-propylbenzene (99.5%), 2-ethylnaphthalene (99.0%), 2'-acetonaphthone (98%), diphenylmethane (99.0%), benzophenone (99.5%), decane (99.0%) were purchased from Shanghai Aladdin Biochemistry Technology Co., Ltd, China. Tert-butyl hydroperoxide (TBHP, 70% solution in water) was purchased from Energy Chemical Co., Ltd, China. Deionized water was obtained from the laboratory professional water purification system.

### 1.2 Synthesis of Fe<sub>1</sub>/NC, Fe<sub>n</sub>/NC and NC

For the synthesis of Fe<sub>1</sub>/NC. 145 mg Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 600 mg commercial protein powder and 2 g carbon black were mixed and put into a 100 ml agate ball milling jar, which contains ball milling beads of different sizes. Under the condition of 400 rpm, the mechanic ball milling was carried out for 24 h, and the forward and reverse rotation

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were alternated every 1.5 h, and the waiting time for stopping is 0. After the ball milling process, the obtained powder was put into a tube furnace and heated at 600 °C for 2 hours with a heating rate of 5 °C/min under nitrogen gas. The atomic dispersed Fe<sub>1</sub>/NC was obtained after natural cooling.

For the synthesis of Fe<sub>n</sub>/NC. 432 mg Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 600 mg commercial protein powder and 2 g carbon black were mixed and put into a 100 ml agate ball milling jar, which contains ball milling beads of different sizes. After the same mechanical ball milling process and calcination process as Fe<sub>1</sub>/NC, Fe<sub>n</sub>/NC was obtained after natural cooling.

For the synthesis of Fe/C. 145 mg Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 2 g carbon black were mixed and put into a 100 ml agate ball milling jar, which contains ball milling beads of different sizes. After the same mechanical balling milling and calcination process of Fe<sub>1</sub>/NC, Fe/C catalyst was obtained.

The synthesis of NC was the same as Fe<sub>1</sub>/NC but without adding Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. 300 mg commercial protein powder and 1 g carbon black were mixed and put into a 100 ml agate ball milling jar which contains ball milling beads of different sizes. After the same mechanical balling milling and calcination process, NC catalyst without Fe was obtained.

### 1.3 Characterizations

X-ray powder diffraction (XRD) measurements was carried out on a LIFM diffractometer with Cu K<sub>α</sub> radiation over a scanning range of 10°-80° (2θ) at a rage of 10° per minute. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALab250 XPS system with an Al K<sub>α</sub> source (1846.6 eV), then use surface pollution C 1s (284.8 eV) as standard for energy calibration. Transmission electron microscope (TEM), scanning transmission electron microscope (STEM) and energy dispersion spectrum (EDS) elemental analysis mapping images were obtained by a FEI Tecnai G2 F30 with 300 kV accelerating voltage. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) was carried out on a JEM-ARM200F transmission electron microscope operated at 200 kV.

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Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size were measured on a Micromeritic ASAP2020M analyzer at liquid nitrogen temperature with preevacuation at 200 °C for 6 h. Metal loading was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) which conducted on a PerkinElmer OPTIMA 8000DV. The content of non-metal elements in materials was determined by elemental analysis (EA) which performed on a Vario EL cube instrument. X-ray absorption spectroscopy measurements for the Fe K-edge were collected on the beamline BL07A1 in NSRRC, and were provided technical support by Ceshigo Research Service "www.ceshigo.com ". The radiation was monochromatized by a Si (111) double-crystal monochromator. XANES and EXAFS data reduction and analysis were processed by Athena software. The wavelets transform was produced by Matlab software.

#### 1.4 Catalyst testing

The synthesized catalyst was used in selective oxidation reactions of C-H bonds in aromatic compounds for performance evaluation. 20 mg catalyst, 0.25 mmol substrate, 1 mL TBHP (70 wt% in water) and 2 mL deionized water were put into a 10 mL glass reaction flask. The mixture was stirred for 48 h at 35 °C. After the reaction, 5 mL ethyl acetate was added for extraction. After filtration, the reaction products were qualitatively performed by GC-MS (GCMS-QP2010 Plus, Shimadzu), and then quantified by GC (GC-2010 Plus, Shimadzu) with decane as the internal standard. For the stability test, the catalysts were filtered, rinsed repeatedly with deionized water and ethanol, after dried at 60 °C overnight, then used in the next cycle experiment. The conversion rate of reactants was calculated by the Eq.1. The selectivity of phenyl ketone was calculated by the Eq.2. The activity was calculated by the Eq.3.

$$\text{Conversion} = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

$$\text{Selectivity} = \frac{C_2}{C_0 - C_1} \times 100\% \quad (2)$$

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$$\text{Activity} = \frac{\text{the amount of reactant (mmol)}}{\text{the amount of active metal (mmol)} \times \text{reaction time (h)}} \quad (3)$$

where  $C_0$  and  $C_1$  respectively represent the concentration of reactants before and after the reaction,  $C_2$  represent the concentration of phenyl ketone after the reaction.

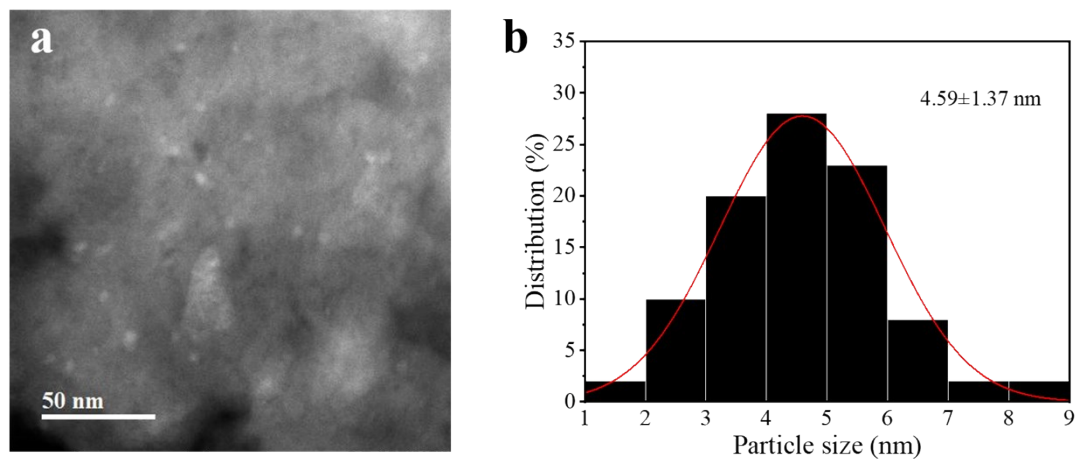


Fig. S1 (a) STEM image and the (b) nanoparticles' size distribution of Fe/C.

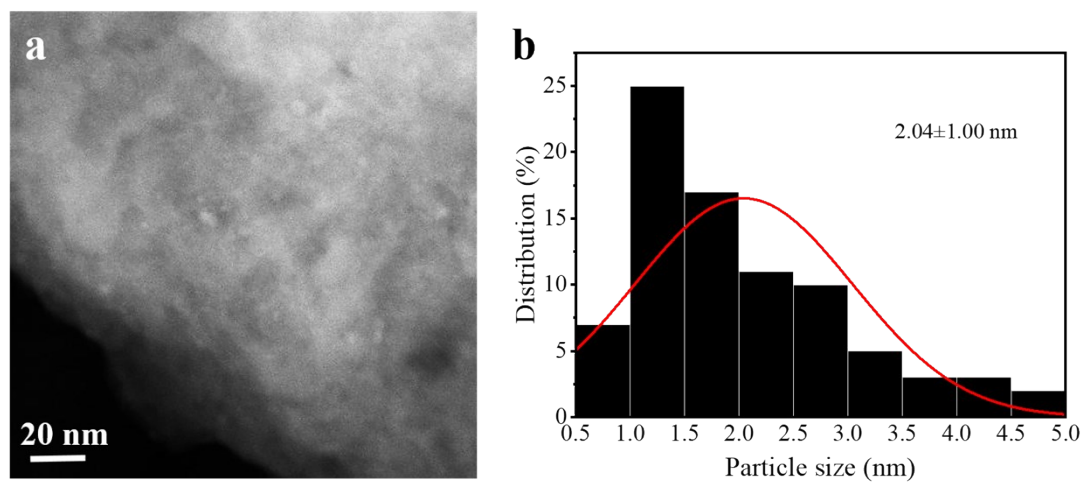


Fig. S2 (a) STEM image and the (b) nanoparticles' size distribution of Fe<sub>n</sub>/NC.

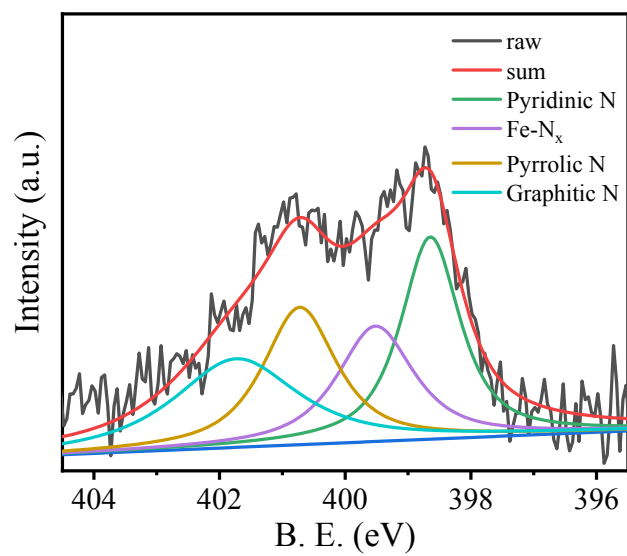


Fig. S3 XPS spectra of N1s for Fe<sub>1</sub>/NC.

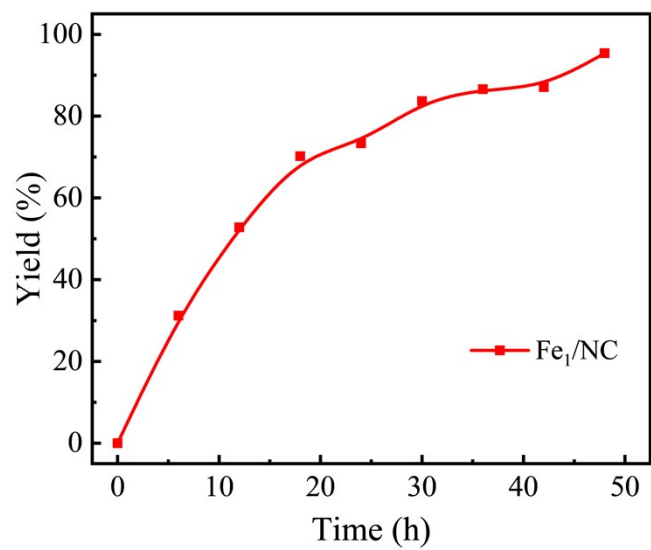


Fig. S4 Catalytic performance for selective oxidation of ethylbenzene to acetophenone by Fe<sub>1</sub>/NC.

**Table S1.** Fe loading of Fe<sub>1</sub>/NC, Fe<sub>n</sub>/NC, Fe/C and NC.

Samples	Fe loading (wt.%)
Fe <sub>1</sub> /NC	1.01
Fe <sub>n</sub> /NC	2.94
Fe/C	1.00
NC	-

**Table S2.** Structure parameters of EXAFS for Fe<sub>1</sub>/NC.

Sample	Scattering path	CN <sup>a</sup>	R (Å) <sup>b</sup>	σ <sup>2</sup> (×10 <sup>-3</sup> Å <sup>2</sup> ) <sup>c</sup>	E <sub>0</sub> (eV) <sup>d</sup>
Fe <sub>1</sub> /NC	Fe–N	4.0±1.0	1.98±0.05	0.05±0.03	-0.05±2.25

<sup>a</sup> CN is the coordination number; <sup>b</sup> R is bond distance; <sup>c</sup> σ<sup>2</sup> is Debye-waller factors; <sup>d</sup> E<sub>0</sub> is the inner potential correction. R-factor: 0.014.

**Table S3.** Recent heterogeneous catalysts used for selective oxidation of ethylbenzene.

Catalysts	loading (wt.%)	Oxidant	t (h)	T (°C)	Conv. of EB (%)	Select. of AP (%)	Ref.
Fe/SNC	0.70	TBHP	48	35	97	99	[1]
SACo@g-C <sub>3</sub> N <sub>4</sub>	3.17	peroxymonosulfate	15	60	97.5	95.6	[2]
Co SACs	23.58	air	24	120	46	97	[3]
Co/rGO	35.8	O <sub>2</sub>	2	120	84.1	96.2	[4]
Co@GCNs	22.57	O <sub>2</sub>	5	120	68.1	93.2	[5]
Cu/WO <sub>3</sub>	3.7	H <sub>2</sub> O <sub>2</sub>	12	90	86.5	100	[6]
Ni-MOF-5	14.8	O <sub>2</sub>	24	150	55.3	90.2	[7]
Au/SBA-15	3.86	TBHP	36	70	79	93	[8]

t is reaction time. T is reaction temperature. Conv. of EB means conversion of ethylbenzene. Select. of AP means selective of acetophenone.

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## Supplementary References

- 1 L. Huang, K. Wu, Q. He, C. Xiong, T. Gan, X. He and H. Ji, *AIChE J.*, 2021, **67**, e17197.
- 2 J. Li, S. Zhao, S.-Z. Yang, S. Wang, H. Sun, S. P. Jiang, B. Johannessen and S. Liu, *J. Mater. Chem. A*, 2021, **9**, 3029-3035.
- 3 Y. Xiong, W. Sun, Y. Han, P. Xin, X. Zheng, W. Yan, J. Dong, J. Zhang, D. Wang and Y. Li, *Nano Res.*, 2021, **14**, 2418.
- 4 L. Gao, W. Zhuge, X. Feng, W. Sun, X. Sun and G. Zheng, *New J. of Chem.*, 2019, **43**, 8189.
- 5 X. Lin, Z. Nie, L. Zhang, S. Mei, Y. Chen, B. Zhang, R. Zhu and Z. Liu, *Green Chem.*, 2017, **19**, 2164.
- 6 Acharyya SS., Mandal P., Bal R., *J. Adv. Catal. Sci. Techno.*, 2015, **2**, 31.
- 7 M. M. Peng, U. J. Jeon, M. Ganesh, A. Aziz, R. Vinodh, M. Palanichamy and H. T. Jang, *Bulletin of the Korean Chemical Society*, 2014, **35**, 3213.
- 8 A. V. Biradar and T. Asefa, *Applied Catalysis A: General*, 2012, **435-436**, 19-26.