

Electronic Supplementary Information For
Fe/Fe₃C Encapsulated in N-doped Carbon Tubes: A Recyclable
Catalyst for the Hydrogenation with High Selectivity

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S1. EXPERIMENTAL SECTION

1.1 Materials and characterization. All chemicals were from commercial and used without further purification: Iron(III) nitrate nonahydrate (98.5%), 4,4'-Biphenyldicarboxylic acid (98.9%), melamine (analytic reagent), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 85%). Powder X-ray diffraction patterns (PXRD) were carried out on Bruck D8. Field-emission microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer. The transmission electron microscopy (TEM), high-resolution TEM observation was acquired on JEOL-2011 with an electron acceleration energy of 200 kV. Aberration-corrected High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images was performed with a JEOL JEM-2010 LaB6 with a probe spherical aberration corrector. The content of Fe in the catalysts was determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). X-ray photoelectron spectroscopy (XPS) analysis was conducted on ESCALAB 250 Xi X-ray photoelectron spectrometer with Al $K\alpha$ radiation. XAFS measurement and data analysis: XAFS spectra at the Fe K-edge was collected at BL14W1 station in Beijing Synchrotron Radiation Facility (BSRF).

1.2 Synthesis of MIL-88d (Fe): Iron(III) nitrate hexahydrate (1.351 g) was dissolved in 5 mL of methanol, and 4'4-biphenyldicarboxylic acid (0.605 g) was dissolved in 20 mL of DMF. The above solutions were mixed together and stirring for 20 hours under 110 °C. The resulting yellow precipitates were harvested by centrifuging, washing with methanol, and finally being dried in vacuum at 40 °C overnight.

1.3 Preparation of Fe/Fe₃C@NⁿCT-T-x series. The catalysts Fe/Fe₃C@NⁿCT-T-x (n represent the ratio of melamine and MIL-88d, T represent pyrolysis temperature and x represent pyrolysis time; n=0, 2, 4, 6; T=800 °C, 900 °C, 1000 °C; x=1h, 2h, 3h), were synthesized via the mixture of MIL-88d and melamine in two-step process. First, MIL-88d was

solvothermally synthesized based upon $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 4,4'-biphenyldicarboxylic acid in DMF solution. Subsequently, the product was mixed with moderate amounts of melamine, and then the mixture were treated in sequential pyrolysis procedure in a Ar/H_2 atmosphere (Scheme 1). Catalysts optimization studies revealed a dependence on the three key variables: (1) the ratio of melamine and MIL-88d (Fe), (2) the pyrolysis temperature, and (3) the time of pyrolysis.

1.4 Catalytic Performance Evaluation

The reduction of nitrobenzene acetylene: Typically, the catalyst 3 mg was charged into a dried round bottom flask with 5 mL ethanol. Then 0.25 mmol nitrobenzene acetylene and 37.5 μL hydrazine hydrate (0.75 mmol) were added sequentially. Then the mixture was heated 40 $^\circ\text{C}$ with 18 h. The conversion and selectivity were detected by GC-MS with *n*-dodecane as standard.

The reduction of 1-bromo-4-nitrobenzene: Typically, the catalyst 3 mg was charged into a dried round bottom flask with 5 mL ethanol. Then 100 mg 1-bromo-4-nitrobenzene (1 mmol) and 2 mL hydrazine hydrate (40 mmol) were added sequentially. Then the mixture was heated 40 $^\circ\text{C}$ with 15 min. The conversion and selectivity were detected by GC-MS with *n*-dodecane as standard.

Recyclability investigation for $\text{Fe}/\text{Fe}_3\text{C}@N^6\text{CT-900-1}$ catalyst: After the reduction of 1-bromo-4-nitrobenzene for 15 min, the catalyst was separated out by an external magnet. Then the recovered catalyst was washed by ethanol for several times. After that, the catalyst was used by another reduction of fresh 1-bromo-4-nitrobenzene. This procedure was conducted five times to examine the recyclability of $\text{Fe}/\text{Fe}_3\text{C}@N^6\text{CT-900-1}$, and the selectivity and conversion were detected by GC-MS with *n*-dodecane as standard.

1.5 Computational methods. All spin-polarized electronic structure calculations were performed using the SIESTA package with Troullier-Martins norm conserving pseudopotentials.¹⁻³ The exchange-correlation functional utilized was at the

generalized gradient approximation (GGA) level with Perdew-Burke-Ernzerhof (PBE).⁴ A double- ξ plus polarization (DZP) basis set was employed and the orbital-confining cut off was determined from an energy shift of 0.01 eV. The van der Waals interactions were considered by vdw-DF functional proposed by Dion et al.⁵ A $p(4\times 4)$ supercell with a three-layer Fe (110) slab was used as the substrate and a one-layer consisting of C and N atoms as the shell on Fe (110). The model was displayed in Figure S1. The cut-off energy for the real space grid was 250 Ry and a $2\times 2\times 1$ Monkhorst-Pack k-point mesh was used. The vacuum region was ~ 12 Å to eliminate interactions between slabs.

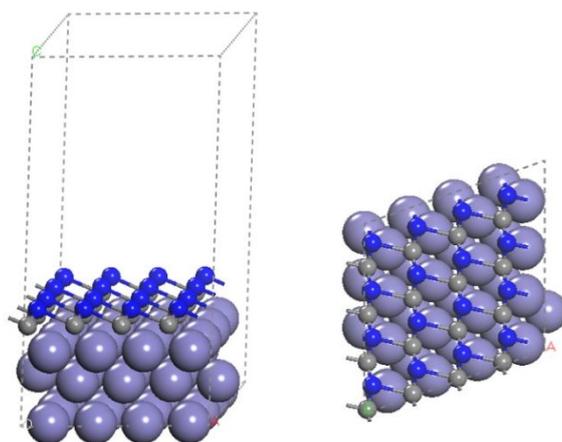


Figure S1. Top and side views of theoretical models for N, C covered Fe(110). Grey-blue: Fe; grey: C; blue: N.

1.6 The reduction of variety of nitro compounds: In a particular reaction, Fe-based catalysts (5~10mg) were put into a dried round bottom flask with 5 mL solvent. Sequentially, about 100 mg nitro compounds (0.5~1 mmol) and 2 mL hydrazine hydrate (40 mmol) were added. Then the mixture was heated 40 °C with 0.3 hour. The selectivity and conversion were detected by GC-MS with *n*-dodecane as standard.

1.7 The calculate method of TOF value on nitrobenzene:

Particle size: ac. 25 nm

Dispersity: $D=1/d=1/25=0.04$

Loading capacity: 18.26 %

Catalyst amount: 7.4 mg

Substrate amount: 0.5 mmol

Catalysis time: 50s

Conversion percent: 30%

TOF=N/(M*Time) N: The total conversion amount of substrates in 50s

M: The number of the iron/iron carbide atoms on the catalyst surface

$N=0.5*30\%/1000=0.00015$ mol

$M=0.0074*0.1826*0.04/56=0.00000096$

$TOF=0.00015/(0.00000096*50)=3.13s^{-1}=11268$ h⁻¹

S2. Characterization Section

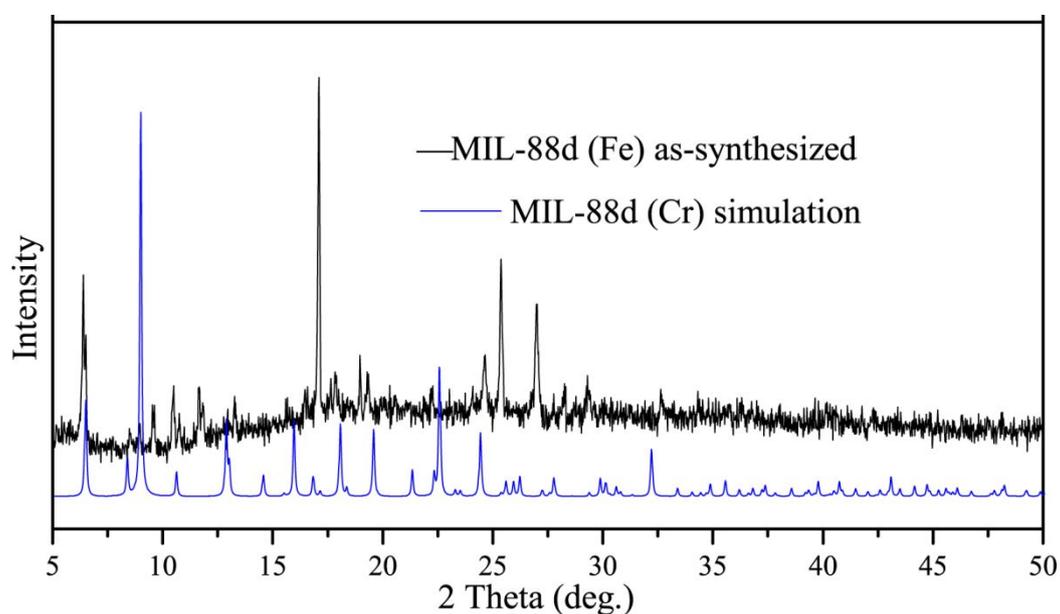


Figure. S2. The PXRD patterns of as-synthesized MIL-88d (Fe), in good agreement with the simulation.

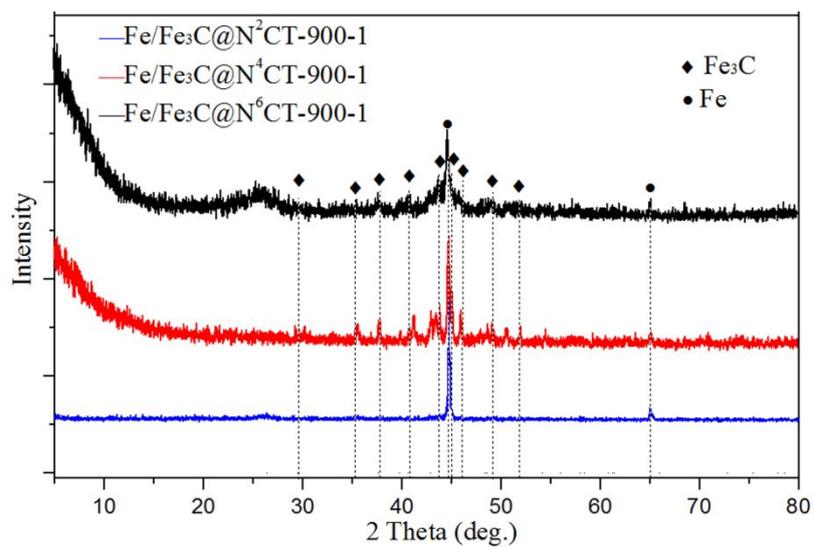


Figure. S3. The PXRD patterns of MOF-templated Fe-based nano particle encapsulated in N-doped porous carbon via pyrolysis of MIL-88d (Fe) in Ar/H₂ atmosphere for 1 h at 900 °C with different rate about melamine: 1:2; 1:4; 1:6.

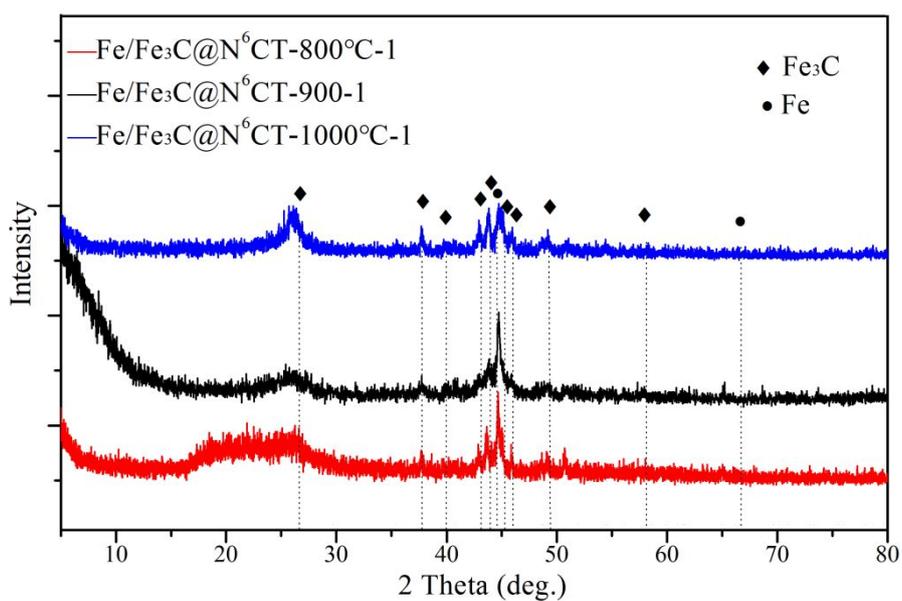


Figure. S4. The PXRD of Fe@N⁶CT-T-x with different pyrolysis temperatures.

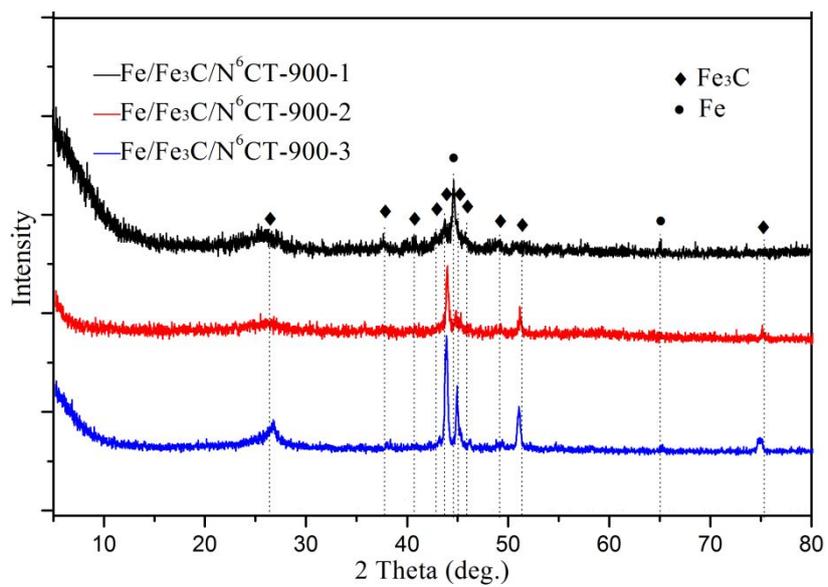


Figure. S5. The PXRD of Fe@N⁶CT-900-1 with different pyrolysis times: 1 h, 2 h, 3 h.

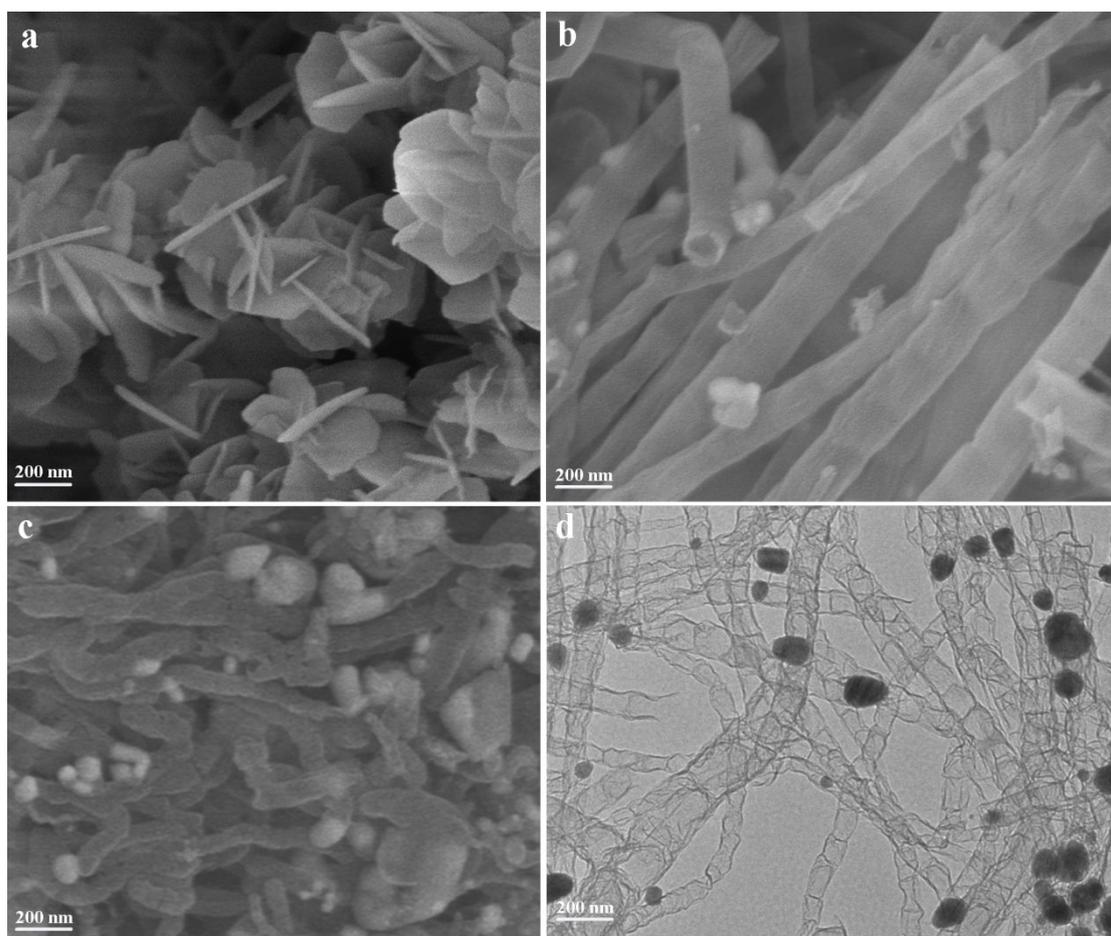


Figure. S6. (a) SEM of MIL-88d, (b) Fe/Fe₃C@N⁶CT-900-1, (c) Fe/Fe₃C@N²CT-900-1 and (d) TEM of Fe/Fe₃C@N⁶CT-900-1.

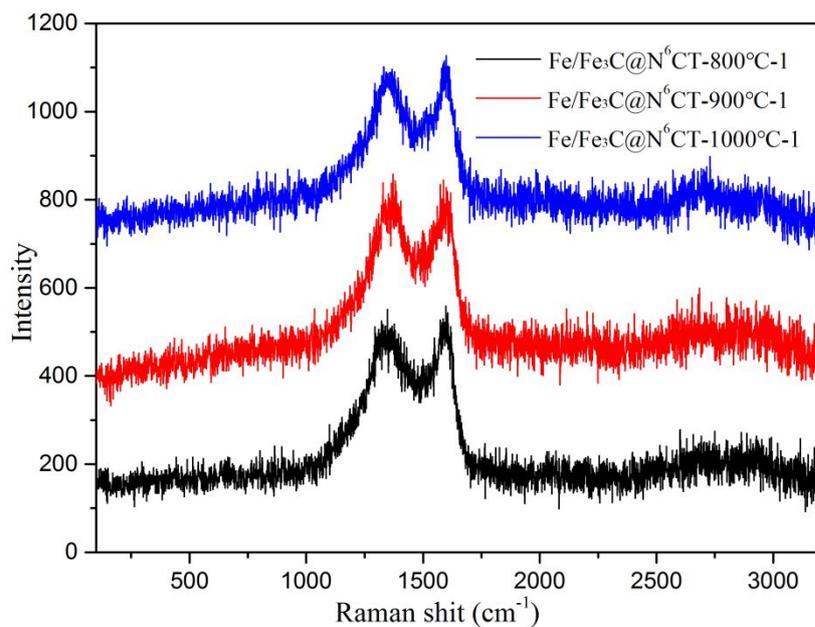


Figure. S7. Raman spectrum of Fe/Fe₃C@N⁶CT-800-1, Fe/ Fe₃C@N⁶CT-900-1 and Fe/ Fe₃C@N⁶CT-1000-1.

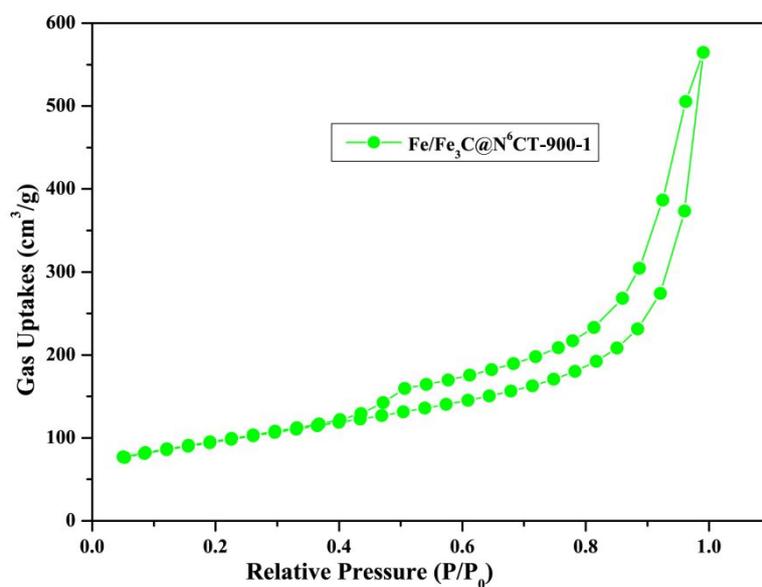


Figure S8. Nitrogen adsorption isotherms of Fe/Fe₃C@N⁶CT-900-1 with the BET is 330 m²/g.

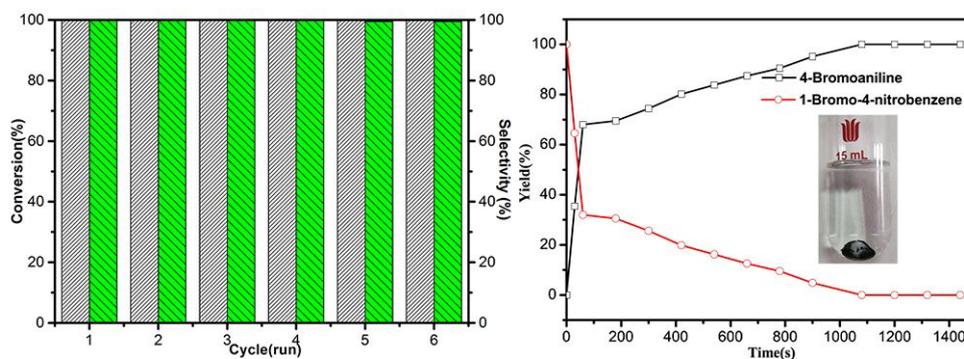


Figure. S9. Recyclability tests of $\text{Fe}/\text{Fe}_3\text{C}@N^6\text{CT-900-1}$; left: conversion of 1-bromo-4-nitrobenzen to 4-bromoaniline (inset, the facile separation of the catalyst via magnet).

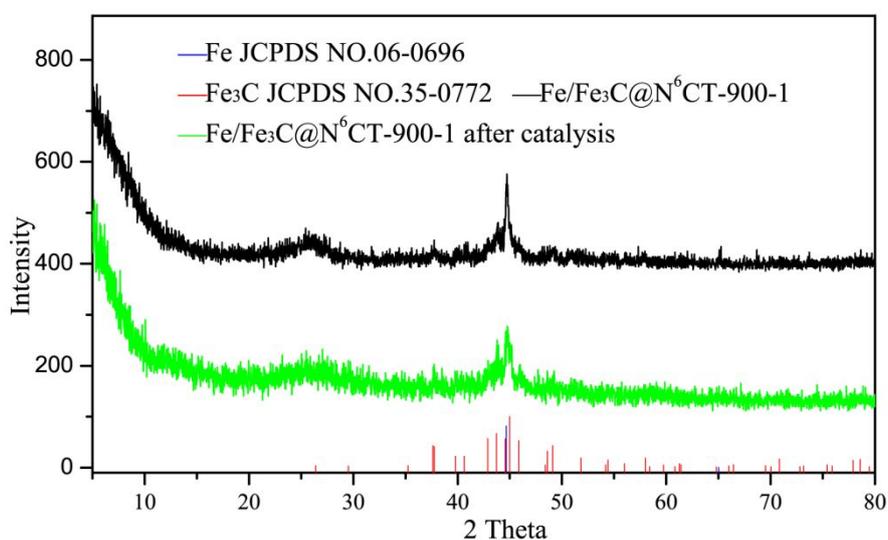


Figure. S10. The as synthesized PXRD of $\text{Fe}@N^6\text{CT-900-1}$ compared with the one after catalysis.

Table S1. ICP-AES and element analysis results for the contents of Fe in catalyst of $\text{Fe}/\text{Fe}_3\text{C}@N^x\text{CT-900-1}$ doped on Nitrogen-doped porous carbon.

$\text{Fe}/\text{Fe}_3\text{C}$ doped on Nitrogen-doped porous carbon	The content of Fe (%)
$\text{Fe}/\text{Fe}_3\text{C}@N^6\text{CT-900-1}$	18.26
$\text{Fe}/\text{Fe}_3\text{C}@N^5\text{CT-900-1}$	20.33
$\text{Fe}/\text{Fe}_3\text{C}@N^4\text{CT-900-1}$	26.24
$\text{Fe}/\text{Fe}_3\text{C}@N^3\text{CT-900-1}$	27.51
$\text{Fe}/\text{Fe}_3\text{C}@N^2\text{CT-900-1}$	31.22
$\text{Fe}/\text{Fe}_3\text{C}@N^1\text{CT-900-1}$	37.86
$\text{Fe}/\text{Fe}_3\text{C}@N^0\text{CT-900-1}$	46.02
$\text{Fe}/\text{Fe}_3\text{C}@N^6\text{CT-900-1}$ after reaction	16.37

Table S2. Performance of different hydrogen source in the hydrogenation of 1-bromo-4-nitrobenzene.

Catalyst	Hydrogen sources	Conv. (%)
Fe/Fe ₃ C@N ⁶ CT-900-1	Hydrazine hydrate	99
	NaBH ₄	<1
	i-PrOH	<1

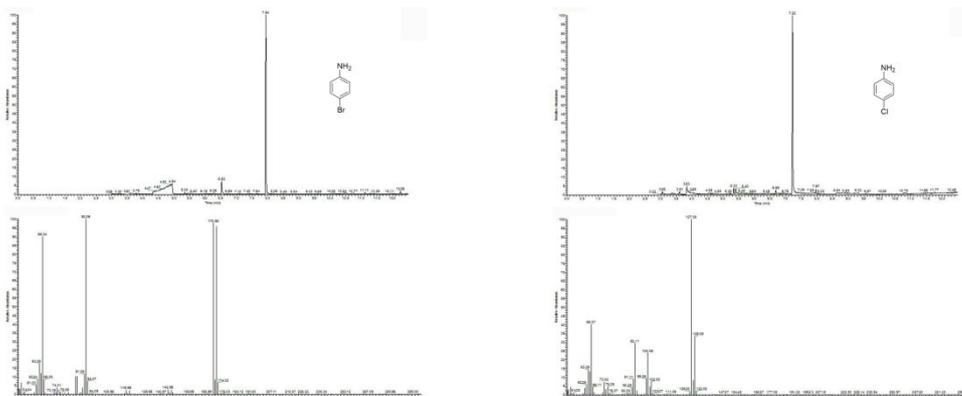
Table S3. Practical iron content in the catalysts.

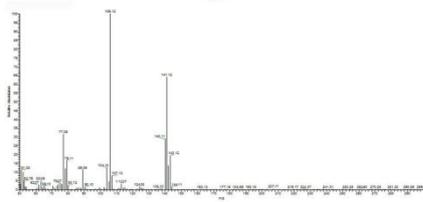
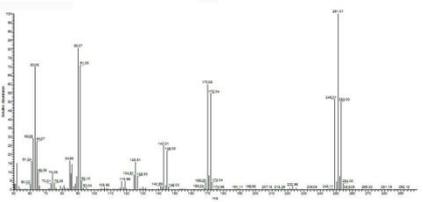
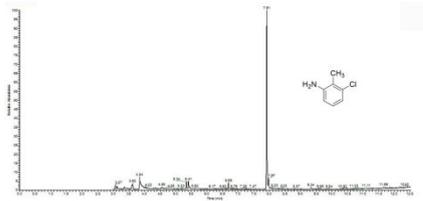
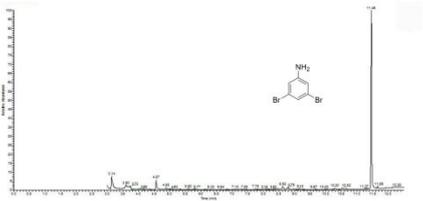
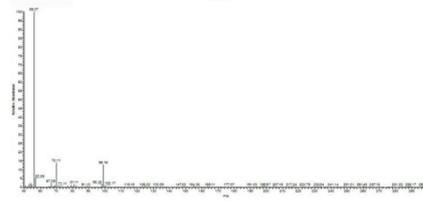
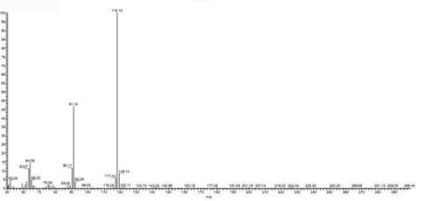
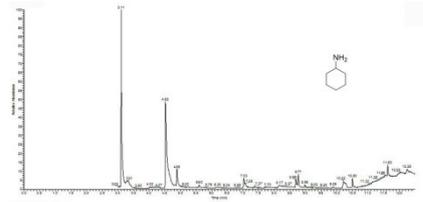
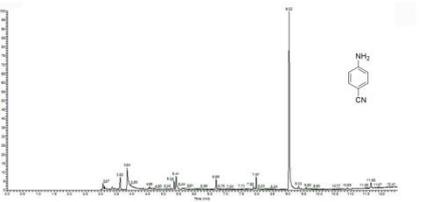
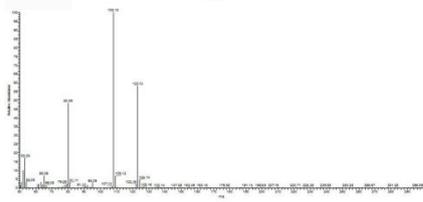
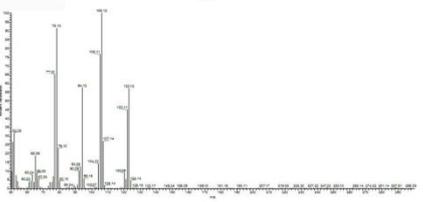
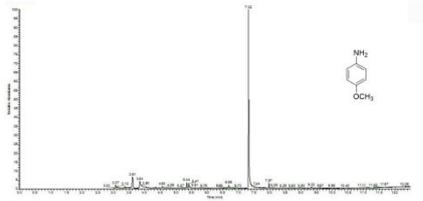
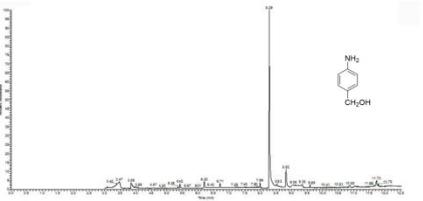
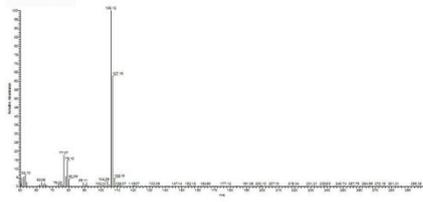
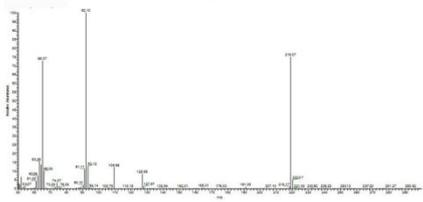
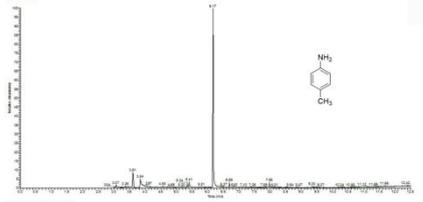
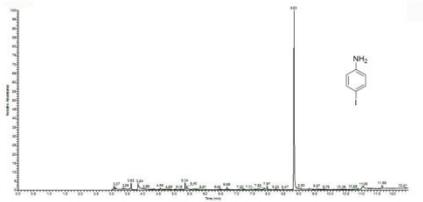
Catalyst	The content of Fe (%)	The rate of leaching for a recycle (%)
Fe/Fe ₃ C@N ⁶ CT-900-1 fresh	18.26	1.8
Fe/Fe ₃ C@N ⁶ CT-900-1 after recycle 6 times	16.37	

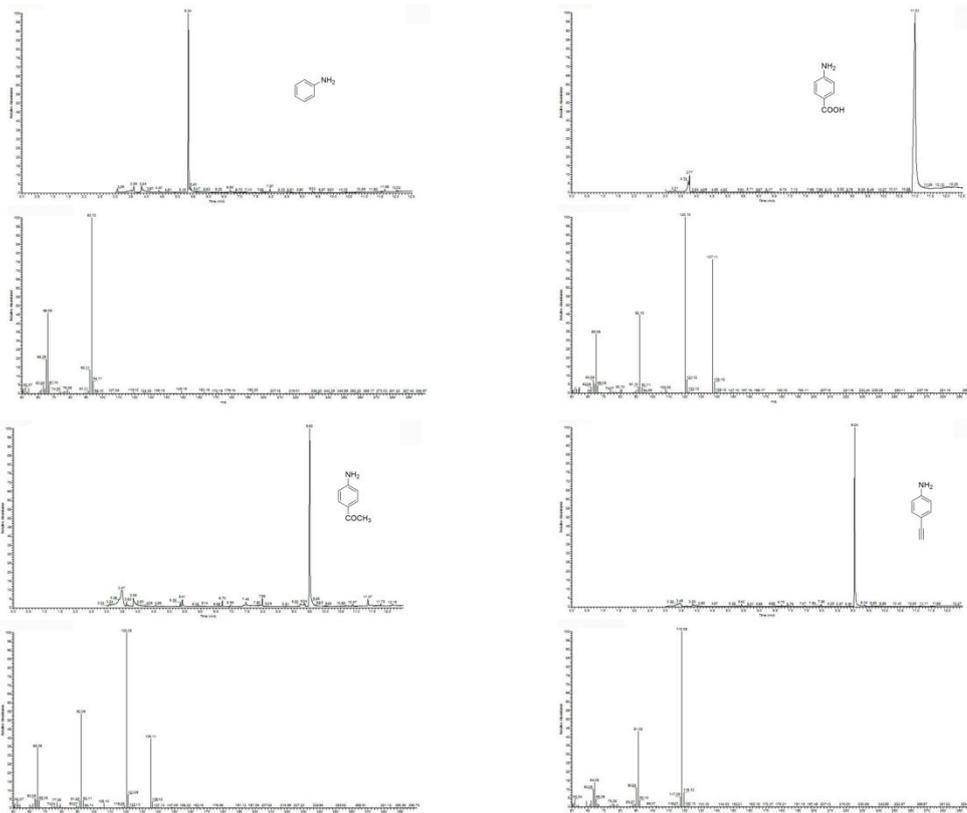
Table S4. Calculated reaction energies (ΔE , in eV) of the elementary steps in nitrobenzene reduction to aniline.

Reactions	ΔE
$C_6H_5NO_2 + * \rightarrow C_6H_5NO_2^*$	-1.79
$C_6H_5NO_2^* + H^* \rightarrow C_6H_5NOOH^*$	-0.45
$C_6H_5NOOH^* + H^* \rightarrow C_6H_5N(OH)_2^*$	0.44
$C_6H_5N(OH)_2^* + H^* \rightarrow C_6H_5NOH^* + H_2O$	-1.11
$C_6H_5NOH^* + H^* \rightarrow C_6H_5NHOH^*$	0.38
$C_6H_5NHOH^* + H^* \rightarrow C_6H_5NH^* + H_2O$	-0.48
$C_6H_5NH^* + H^* \rightarrow C_6H_5NH_2^*$	0.14
$C_6H_5NH_2^* \rightarrow C_6H_5NH_2 + *$	2.23

S3. The GC Graphics







- (1) J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *J. Phys.: Condens. Matter.* 14 (2002) 2745.
- (2) J. Junquera, O. Paz, D. Sanchez-Portal and E. Artacho, *Phys. Rev. B: Condens. Matter.* 64 (2001) 235111.
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- (4) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- (5) M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, B. I. Lundqvist, *Phys. Rev. Lett.* 92 (2004) 246401.