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# Fe/Fe<sub>3</sub>C Encapsulated in N-Doped Carbon Tubes: A Recyclable Catalyst for Hydrogenation with High Selectivity

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**S** Supporting Information

ABSTRACT: Herein, a series of Fe-based catalysts have been designed and prepared by grinding a mixture of MIL-88d and melamine, and then the mixture was followed by pyrolysis. An unusual Fe/Fe<sub>3</sub>C-activated site is uniformly encapsulated in the Ndoped carbon tubes obtained by pyrolysis of the film-like nanocrystals of MIL-88d. Experimental characterizations and theoretical calculations demonstrate that the surface N sites can effectively trap the nitrobenzene and aniline by their phenyl groups with the formation of three C-N bonds that made the catalyst exhibit excellent catalytic activity (turnover frequencies of  $\leq 11268$  h<sup>-1</sup> calculated on the basis of nitrobenzene) and chemoselectivity for the reduction of nitro derivatives under facile conditions.



# INTRODUCTION

Over the past few years, catalysis has become an actual and important subject in chemistry; for example, obtaining functionalized amines by chemoselective hydrogenation of nitro compounds is an important chemical transformation, mainly in the agricultural chemistry and pharmaceutical industries.<sup>1–3</sup> Normally, noble transition metals (palladium, platinum, ruthenium, etc.) were used in catalytic hydrogenation reactions with an appropriate hydrogen source (such as H<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, etc.).<sup>4-6</sup> Of the diversified noble catalysts, palladium/carbon was the first choice as an industrial catalyst for hydrogenation to date. However, Pd/C has poor chemoselectivity of target products due to its very high activity.<sup>7-9</sup> The chemoselectivity and recycling of the catalysts are primarily present in the field of heterogeneous catalysis, so the development of alternative catalysts is required. Considering their price and abundance, cheaper metals have attracted the attention of more and more scientists, and supported cobalt-, iron-, and nickel-based catalysts have led to the efficient hydrogenation of many functional groups.<sup>10-15</sup> For example, the group of Matthias constructed a Co-based catalyst for chemoselective hydrogenation of quinolones.<sup>16</sup> The group of Zeng reported that Co<sub>4</sub>N exhibited excellent catalytic performance in CO<sub>2</sub> hydrogenation,<sup>17</sup> and the group of Li obtained the [Ni-DETA]<sup>2+</sup> catalyst showing good catalysis of the hydrogenation of acetylene.<sup>18</sup> However, those catalysts are very sensitive, requiring exact catalytic conditions and accompanied by lower chemoselectivity, separation, and reusability.<sup>19-22</sup> Additionally, non-noble metal catalysts easily

aggregate and leach, which usually causes irreversible inactivation under liquid phase conditions. Therefore, strategies for designing a new type of non-noble catalyst with greater stability, high activity, and chemoselectivity are urgently needed.

In recent years, the composites, fabricated from metal and heteroatom-doped carbon tubes, applied in heterogeneous catalysis have been interesting research hot spots.<sup>23,24</sup> Due to the fact that some heteroatoms modified in the non-noble metal catalysts could play important roles in highlighting the activities in the hydrogenation of nitro compounds,<sup>25-28</sup> our works are mainly focused on the N-doped porous carbon tubes with metal or metal oxide catalysts embedded for hydrogenation.<sup>29-31</sup> Generally, the N-doping materials were obtained by a one-pot pyrolysis with various templates that contained both carbon and nitrogen atoms at high temperatures.<sup>32</sup> Additionally, to design a metal-based catalyst that exhibits high performance and is reusable, fabricating metal or metal composite nanoparticles (NPs) with a small particle embedded in a porous carbon matrix would be a desirable strategy.33

Inspired by the considerations mentioned above, in this research, we used MIL-88d<sup>34</sup> and N-containing compounds as the precursor materials to construct a series of Fe-based catalysts encapsulated in NCTs (Fe/Fe<sub>3</sub>C@NCTs) to catalyze transfer hydrogenation for nitro compounds. The procedure

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for the preparation of Fe/Fe<sub>3</sub>C@NCTs is shown in Scheme 1. The experimental characterizations and theoretical calculations

#### Scheme 1. Illustration of the Synthesis of Fe/Fe<sub>3</sub>C@NCTs



demonstrate that the Fe/ $F_{e3}C@NCTs$  catalysts show highly efficient reduction of nitro derivatives under facile conditions.

#### RESULTS AND DISCUSSION

The as-synthesized catalysts have been characterized by PXRD (powder X-ray diffraction). The PXRD curves imply that the composition of the samples, which were produced at different pyrolysis times, melamine ratios, and pyrolysis temperatures, display distinct differences (Figures S3–S5). Obviously, all of the peaks of Fe/Fe<sub>3</sub>C@N<sup>2</sup>CT-900-1 could be indexed to the phase of Fe (JCPDS Card No. 06-0696), because the ratio of melamine was increased to >1:4, the change of Fe<sup>0</sup> to Fe/Fe<sub>3</sub>C (JCPDS Card Nos. 06-0696 and 35-0772). The peak at 26.5°, assigned to graphitic C, gradually appeared, for Fe/Fe<sub>3</sub>C@N<sup>4</sup>CT-900-1 and Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1 (Figure S3). When the pyrolysis temperature was increased, the graphitic carbon was more crystalline, which can be seen from PXRD curves (Figure S4). The Fe content of the catalysts was in the range of 18.26–46.02% as determined by ICP-AES (Table S1).

The microstructure characterized by scanning electron microscopy (SEM) shows that MIL-88d (Fe) microcrystals have a uniform thin sheet flower shape (Figure S6a). The sheet shape almost became carbon tubes when the admixture of MIL-88d (Fe) and melamine was calcined to 800-1000 °C (Figure S6b,c). The Fe/Fe<sub>3</sub>C hybrid nanocomposite was encapsulated in pea-pod-like carbon nanotubes through calcination of synthesized MIL-88d and melamine, and the obtained material was defined as Pod-Fe (see the Supporting Information). The scalable and good reproducibility of Pod-Fe was synthesized by the simple method, and none of the other Fe/Fe<sub>3</sub>C nanocomposites were outside of the carbon nanotubes. Electron microscopy was used to study the nanostructure of Pod-Fe. The transmission electron microscopy (TEM) images (Figure 1a) show that the as-synthesized materials show a well-demarcated pea-pod-like structure, and all of the particles are situated inside the carbon nanotubes when scanning randomly across the sample via high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) (Figure 1b) and the size of particle was approximately 20-50 nm. The high-resolution HAADF-STEM images of individual nanoparticles are shown in Figure 1c. Single nanoparticles have several crystal structures. STEM-EELS (scanning transmission electron microscope electron energy loss spectroscopy) elemental mapping (Figure 1d) showed that the C and N elements were uniformly welldistributed in the nanoparticle while Fe elements were mainly situated in the core. Notably, the distribution of C and N perfectly matched that of Fe, suggesting that Fe/Fe<sub>3</sub>C was



Figure 1. Microstructure of Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1. (a) TEM images of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1. (b and c) HADDF-STEM images and (d) EDS mapping of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1. (e) and (f) The lattice stripe of Fe<sub>3</sub>C and Fe. (g) The porous carbon enlarged image.

encapsulated in the compartments of carbon nanotubes. Enlarged images of selected areas tabbed by the squareness are displayed in panels e-g of Figure 1. The well-crystallized structure of lattice fringes with a *d* spacing of 0.21 nm is shown in Figure 1e, corresponding to the (211) plane of Fe<sub>3</sub>C. The *d* spacing of 0.203 (Figure 1f) was ascribed to the (110) plane of Fe. Figure 1g shows the porous carbon in the nanotube. In addition, the Fe/Fe<sub>3</sub>C NPs became smaller and the catalysts were more and more uniform when the amounts of melamine increased.

In the Raman spectra (Figure S7), two distinct bands change with pyrolysis temperature, which correspond to the D band at ~1345 cm<sup>-1</sup> (a carbon that defected from the catalysts) and the G band at 1590 cm<sup>-1</sup> (the in-plane vibration carbon atoms). The  $I_D/I_G$  ratio of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CTs-900-1 is 0.99, slightly higher than those of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CTs-800-1 (0.97) and Fe/Fe<sub>3</sub>C@N<sup>6</sup>CTs-1000-1 (0.97), which may imply more defects and may further affect the catalytic performance. The carbon's defection is thought to favor acceleration of mass transfer and could offer enough active site exposure for catalysis. To characterize porous Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1, the nitrogen adsorption isotherm of the sample was recorded. The N<sub>2</sub> curves at 77 K showed a typical IV isotherm with a BET surface area of 330 m<sup>2</sup>/g, typical of a mesoporous material (Figure S8).

To further explore the electronic structure and coordination environment of the Fe atoms in Pod-Fe, XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure) spectra were recorded (Figure 2). One can see that the Fe K-edge XANES of Pod-Fe is very distinct from those of Fe, FeO, and Fe<sub>2</sub>O<sub>3</sub>. The energy absorption threshold value (EATV) for Pod-Fe was located between those of Fe and Fe<sub>2</sub>O<sub>3</sub>, indicating that the Fe atom is a



Figure 2. (a) XANES of Fe foil, FeO, and  $Fe_2O_3$ . (b and c) FT at R space and k space. (d) Fe 2p and (e) N 1s XPS spectra.



Figure 3. Hydrogenation of ethynyl-4-nitrobenzene with different catalysts. Reaction conditions: hydrazine hydrate as the hydrogen source at a temperature of 40 °C.

Scheme 2. Catalytic Performance of the Fe/Fe<sub>3</sub>C Catalyst for Regioselective Hydrogenation of Ethynyl-4-nitrobenzene



in an ionic state (on the verge of  $Fe^{0+}$  or  $Fe^{3+}$ ). Additionally, the EATV of Pod-Fe is closer to that of the Fe foil, which indicates that the valence state of the Fe atom was similar to that of Fe. The oscillation  $k^{3}\chi(k)$  functions for Pod-Fe show a similar *k* value  $(4-6 \text{ Å}^{-1})$  in the low-*k* region with FeO and the high-k region  $(7-13 \text{ Å}^{-1})$ , which can be ascribed to the

|       |                  |  | R                     | $H_1, N_2 H_4, H_2 O, 40 $ °C | R                                 |           |                                |
|-------|------------------|--|-----------------------|-------------------------------|-----------------------------------|-----------|--------------------------------|
| Entry | Substrate        | Time(h)/TOF<br>(h <sup>-1</sup> ) <sup>b</sup> | Conv./Sele<br>ct. (%) | Entry                         | Substrate                         | Time (h)  | Conv./Select. (%) <sup>a</sup> |
| 1     | Br NO2           | 0.3/1825                                       | 100/>99               | 9                             | Br NO2                            | 0.3/1825  | 100/>99                        |
| 2     |                  | 0.3/1825                                       | 100/>99               | 10                            | O <sub>2</sub> N CH <sub>2</sub>  | 0.5/1095  | 100/>99                        |
| 3     | I                | 0.3/1825                                       | 100/>99               | 11                            | 0,1 ОН                            | 0.5/1095  | 100/>99                        |
| 4     | H <sub>3</sub> C | 0.3/1825                                       | 100/>99               | 12                            | NO2                               | 0.3/11268 | 100/>99                        |
| 5     | H3COC-NO2        | 0.3/1825                                       | 100/>99               | 13                            | H <sub>3</sub> CO NO <sub>2</sub> | 0.3/1825  | 100/>99                        |
| 6     | HOOC             | 0.3/1825                                       | 100/>99               | 14                            | HOH <sub>2</sub> CNO <sub>2</sub> | 0.5/1095  | 100/>99                        |
| 7     |                  | 0.5/1095                                       | 100/>99               | 15                            | NO <sub>2</sub>                   | 1/547.6   | 100/99                         |
| 8     |                  | 0.5/1095                                       | 100/>90               | 16                            |                                   | 18/35.6   | 97/>99                         |

Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1

#### Table 1. Hydrogenation of Different Nitro Derivatives by Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1

"Confirmed by gas chromatography spectra with *n*-dodecane as the internal standard. <sup>b</sup>Conversion percent: 97% for nitrobenzene acetylene, 30% for nitrobenzene, and 100% for the others. <sup>c</sup>The amount of hydrazine hydrate is 40 mmol in all of the hydrogenation processes but 0.75 mmol in the reduced reaction of entry 16.

distinct interactions between the Fe atom and the backscattering C and Fe atom. In addition, more structural information about Fe atoms was gained from EXAFS. Figure 2b shows the Fourier-transformed  $k^3$ -weighted  $\chi(k)$  function of the EXAFS curves of Pod-Fe, Fe<sub>2</sub>O<sub>3</sub>, and Fe foil. The main peak for Pod-Fe appeared at 1.7 Å, which may be assigned to Fe-C coordination. Together with the same position of the Fe foil, the other main peak appeared at 2.2 Å, which corresponded to Fe-Fe coordination. The XAFS conclusion was consistent with XRD and HADDF-STEM. To investigate the chemical state and the surface compositions of  $Fe/Fe_3C@$ N<sup>6</sup>CT-900-1, the XPS (X-ray photoelectron spectroscopy) spectrum was recorded. We can see from Figure 2 that Fe 2p shows four broad peaks at 707.3, 711.0, 720.4, and 724.0 eV, corresponding to Fe  $2p_{3/2}$  and  $2p_{1/2}$ . Their separations are as follows:  $\Delta 1 = 720.4 \text{ eV} - 707.3 \text{ eV} = 13.1 \text{ eV}$ , and  $\Delta 1 = 724.0$ eV - 711.0 eV = 13.0 eV. The character of this XPS spectra may be attributed to Fe and  $Fe_3C_1$ , which is consistent with the powder XRD patterns.<sup>35</sup>

The catalytic performance of the as-synthesized catalysts was investigated in the hydrogenation of functionalized nitroarenes with hydrazine hydrate as the hydrogen source. We can see from Figure 3 and Scheme 2 that reduction of ethynyl-4-nitrobenzene was carried out as a benchmark reaction. Interestingly, the performance of the catalysts was amazingly increased due to the nitrogen doped in the carbon tubes, which could be proof of the fact that the Fe/Fe<sub>3</sub>C@N<sup>0</sup>CT-900-1 catalyst exhibits little catalytic activity for the reduction of

ethynyl-4-nitrobenzene. However, under otherwise identical conditions, the Fe/Fe<sub>3</sub>C@N<sup>2</sup>CT-900-1 catalyst shows a conversion of 42.15%, many times higher than that of Fe/Fe<sub>3</sub>C@N<sup>0</sup>CT-900-1. As expected, the larger the amount of N doping, the higher the conversion of the hydrogenation. Then, the conversion achieves the maximum activity of hydrogenation of ethynyl-4-nitrobenzene with the Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1 catalyst. Such results unambiguously implied that the ratio of N doped in the mixture played an important role in the hydrogenation, which is consistent with the theoretical calculation results. Furthermore, the high hydrogenation catalytic performance may be due to the fact that the Fe/Fe<sub>3</sub>C@N<sup>n</sup>CT particles were smaller and showed a more uniform arrangement accompanied by an increase in the amount of melamine to 1:6.

To further prove the general applicability of the Fe/Fe<sub>3</sub>C@  $N^6$ CT-900-1 catalyst, the reduction of a diversity of nitroarenes with different functional groups was carried out, consistently giving the corresponding anilines with high conversion but without any byproduct. First, predominant conversion of the target products was obtained when a halogenated nitrobenzene was chosen as the substrate. Almost no dehalogenation occurred during the reaction even when the number of halogenation groups was increased (Table 1, entries 1–3, 9, and 10). Second, *o-*, *m-*, and *p*-substituted nitroarenes all provided excellent conversion to their corresponding products, which suggests that the steric effect of the substituent on phenyl rings is negligible (entries 9 and 10). Finally and also



Figure 4. (a) Energy profile for the reduction of nitrobenzene to aniline on N- and C-covered Fe (110). (b) Optimized structures of intermediates in the reduction of nitrobenzene to aniline: gray-blue for Fe, gray for C, blue for N, red for O, and white for H.

importantly, in the process of hydrogenation of the nitro compounds that possess challenging substituent radicals, for example, carbonyl, cynao, aldehyde, and carboxyl (entries 5-8, respectively), the catalyst shows high activity and selectivity as it provides the target products of aniline derivatives in >99% yields. More importantly, we can see from Scheme 2 that nitrobenzene acetylene can be reduced to amino-phenylacetylene with a trace amount of byproducts. The result was good evidence that the catalyst has high performance and selectivity for catalyzing nitro groups. These noticeable results illuminate the chemoselectivity of the Fe and Fe-carbide nanocatalyst, revealing its preeminent excellence compared to that of precious metal-based catalysts. To investigate the effect of the hydrogen source on the catalytic performance, the hydrogen source is substituted with NaBH<sub>4</sub> and isopropanol, and the conversion is only approximately <1% (Table S2).

The reusability and durability of the catalysts are vital for practical applications. To estimate the recyclability and reusability of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1, recycling tests of the reduction of ethynyl-4-nitrobenzene were carried out. Figure S9 shows that the catalytic cycles could maintain >96% conversion and >99% chemoselectivity after being used for six consecutive runs. Additionally, the catalyst could be magnetically separated using a magnetic field from the reaction mixture, due to the strong magnetism of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1 (Figure S9, right inset). Powder XRD patterns clearly demonstrated that the phase and composition of Fe/Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1 were very well maintained and the iron content was slightly reduced after recycling with a leaching rate of 1.8% (Figure S10 and Table S3).

Density functional theory (DFT) calculations were performed to estimate the intrinsic catalytic properties of the C- and N-covered Fe (110) surface. The hydrogenation of nitrobenzene to aniline was chosen as the model reaction. According to the literature, a double H-induced dissociation of the N–O bond was identified as being the favored pathway for the reduction of the nitro group in nitrobenzene on the Fe surface.<sup>36,37</sup> The two O atoms need to be hydrogenated first to activate the N-O bonds, and their cleavage can occur readily. The following overall mechanism was thus proposed: PhNO<sub>2</sub>\*  $\rightarrow$  PhNOOH\*  $\rightarrow$  PhN(OH)<sub>2</sub>\*  $\rightarrow$  PhNOH\*  $\rightarrow$  PhNHOH\*  $\rightarrow$  PhNH<sup>\*</sup>  $\rightarrow$  PhNH<sub>2</sub><sup>\*</sup>; the energy profiles on C- and Ncovered Fe(110) are presented in Figure 4a. The optimized structures of intermediates are displayed in Figure 4b, and all data are listed in Table S4. We found that the surface N sites can effectively trap the nitrobenzene and aniline by their phenyl groups with the formation of three C-N bonds. The adsorption energies for nitrobenzene and aniline were calculated to be -1.79 and -2.23 eV, respectively. H\* as the hydrogen source also was adsorbed on N sites with a sorption energy of -0.66 eV compared to that of half gaseous H<sub>2</sub>. The surface catalytic processes, including hydrogenation and deoxygenation, in general are thermodynamically reasonable, even though there are some slight endothermic elementary steps, i.e., PhN(OH)<sub>2</sub>\* formation (0.44 eV), PhNHOH\* formation (0.38 eV), and  $PhNH_2^*$  formation (0.14 eV). The two deoxygenation reactions involving N–O bond cleavage are both exothermic, i.e., PhNOH\* formation (-1.11 eV) and PhNH<sup>\*</sup> formation (-0.48 eV). By analyzing the theoretical results, we suggested that desorption of surface reaction products may be the rate-limiting step.

# CONCLUSIONS

In summary, low-cost, magnetically recyclable, and highhydrogenation activity metal catalyst  $Fe/Fe_3C$  NPs encapsulated in N-doped carbon tubes were designed and obtained from pyrolysis of MIL-88d and melamine. The considerable catalytic performance of functionalized nitro compounds under mild conditions is attributed to the core-shell structure of the NCTs, which could overwhelmingly decrease the extent of leaching and prevent the aggregation of Fe NPs. The Fe/ Fe<sub>3</sub>C@N<sup>6</sup>CT-900-1 catalyst is easily retrieved with a magnet. The catalyst could be reused for more than six cycles without any decrease in activity. Our work reveals a novel path for the design and construction of uniform dispersed metal/metal carbide embedded in nitrogen-doped carbon tubes with improved performance with respect to the catalytic hydrogenation reactions.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01332.

Experimental Section (including Figure S1), characterization (Figures S2–S10 and Tables S1–S4), gas chromatography graphs, and additional references (PDF)

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#### Notes

The authors declare no competing financial interest.

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