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A Highly Active Non-precious Metal Catalyst Based on Fe-N-C@CNTs for Nitroarenes Reduction

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Research on transition metal-nitrogen-carbon (M-N-C) materials revealed their potential as catalysts in several important traditional reactions. However, the activity of M-N-C still needs to be further improved and the real active center of M-N-C catalysts is still under debate. In this work, an efficient Fe-N-C@CNTs for the hydrogenation of nitroarenes was prepared by pyrolysis of FeCl₃, phenanthroline and CNTs. Fe-N-C supported on CNTs is much more active than that supported on activated carbon, showing the promotion effect of CNTs. The characterization results suggest that the high activity of Fe-N-C is mainly attributed to the formation of ϵ -Fe₃N, which is the active site for the hydrogenation reaction. Nitrogen/carbon atoms contacted to the active centers could serve as bridges to transport the dissociated hydrogen atoms via spillover effect. The catalytic performance of Fe-N-C was also tested on fixed bed reactor under continuous flow condition for the first time and could smoothly catalyze the reaction for over 300 hours.

Introduction

The Iron based heterogeneous catalyst is used in several important chemical industrial processes such as Fischer-Tropsch synthesis,¹ ammonia synthesis² and methane aromatization³ due to its ability for activating a series of small molecules like carbon monoxide, nitrogen,⁴ methane and etc. In recent studies iron-nitrogen-carbon catalysts were applied in hydrogenation reactions to transform nitroarenes into anilines.⁵ Compared to precious metal based catalyst,⁶ the hypothetical Fe-N-C catalysts show excellent chemoselectivity to aromatic nitro-group above sensitive functional groups such as aldehydes, ketones, olefins and etc., which made these catalytic systems especially suitable for the production of important intermediates of high economic value in pharmaceuticals, agrochemicals, dyes, and fine chemicals. Despite of its high selectivity, the activity of Fe-N-C catalyst was relatively low and usually long reaction time was needed to achieve complete conversion even at a substrate/catalyst ratio of around 20. Therefore, to improve the catalytic activity is now the main issue for fulfilling the potential practical applications of Fe-N-C catalysts.

Previously, activated carbon or metal oxides are usually used as support for the preparation of Fe-N-C catalysts.^{5,7} It is well known that activity of catalysts could be influenced largely

by the support material, for the support could impose structural, electrical and other differences on the active sites.⁸ Carbon nanotubes (CNTs) are widely used as catalyst support.^{9,10} Its nano-scale diameter, unique electronic properties and abundant surface groups could provide improved mass transfer properties and catalytic performance for active center.^{11,12} P. de Jong and co-workers found that iron nanocrystals supported on CNTs show excellent catalytic performance in F-T synthesis.¹³ Recently, C-Co₃O₄@N-doped CNTs are in-situ generated from D-glucosamine hydrochloride, melamine and Co(NO₃)₂•6H₂O, which was found to be more active than Fe-N-C/AC regarding the hydrogenation of nitroarenes.¹⁴

The M-N-C catalysts are very complicated and their active sites are still not very clear.¹⁵ In the pioneering work of Matthias et al. they declare that the unique activity of nitrogen doped carbon supported iron catalyst is derived from some particular FeNx centers.⁵ Zhang and co-workers indicate that Co single atoms bonded with N within graphitic sheets are the active sites of Co-N-C catalyst in C-C bond-forming reactions.¹⁶ Wang and co-worker attribute the high catalytic performance of C-Co₃O₄@N-doped CNTs to the synergistic effects of the unique structure of grapheme layers-coated Co⁰ and the electronic activation of doped nitrogen.¹⁴ Understanding the catalytic active sites is very important for the catalyst design. Herein, we report a very efficient Fe-N-C@CNTs catalyst for chemoselective hydrogenation of nitroarenes. Our studies suggest that ϵ -Fe₃N is the most active site for the hydrogenation of nitrobenzene.

Experimental section

Reagents.

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1,10-Phenanthroline and nitrobenzene was purchased from J&K Inc. All other nitro compounds were purchased from Inno-Chem Inc. Carbon nanotubes with a length of 0.5-2 μ m and an OD (Outer Diameter) of 10-20 nm was purchased from timesnano Inc. Solvents such as absolute ethanol and tetrahydrofuran were purchased from SINOPHARM Co. Ltd. All materials and reagents were used as received without further purification.

Characterization.

The transmission electron microscopy (TEM) was undertaken using a Hitachi HT-7700 at an acceleration voltage of 100 kV. The samples were placed onto an ultrathin carbon film supported on a copper grid. High resolution transmission electron microscopy (HRTEM) images were recorded on a FEI Tecnai F30 microscope with a point resolution of 0.20 nm operated at 300 kV. The powder X-ray diffraction data were collected on a Rigaku D/Max2500PC diffractometer with Cu Ka radiation (λ =1.5418 Å) over the 2 θ range of 5° - 80° with a scan speed of 5°/min at room temperature. The ⁵⁷Fe Mössbauer spectra of the prepared samples were recorded on a Topologic 500A spectrometer and a proportional counter at room temperature. ⁵⁷Co(Rh) moving in a constant acceleration mode was used as radioactive source. Ambient temperature highpressure hydrogen isotherms were recorded on a HPVA-2000 system.

CNTs treatment.

Firstly, 8 g of commercial CNTs (with diameter of 10-20 nm) were refluxed in 400 ml of concentrated nitric acid at 120 $^{\circ}$ C for 11 h. After cooling down to room temperature, the mixture was diluted and washed with copious amount of water to neutral. After that, the collected CNTs were dispersed in 400 ml of ethanol by ultrasound for 4 h. Treated CNTs was obtained after filtering and drying.

Synthesis of Fe-N-C@CNTs.

FeCl₃ (0.0145 g) and phenanthroline (0.0531 g) were refluxed in ethanol (50 ml) for 12 h to form solution A. CNTs (1 g) were dispersed in solution A with the aid of ultrasonic treatment for 4 h. The solid precursor was obtained by rotary evaporation of the solvent under vacuum. The precursor was pyrolyzed in nitrogen at 800 °C for 2 h with heating rate of 5 °C /min and the gas flow of 20 ml/min. Black powder of Fe-N-C@CNTs-0.5 was obtained after cooling to room temperature. For other Fe-N-C@CNTs, the synthetic process was similar, expect that FeCl₃ (0.043 g) and phenanthroline (0.1593 g) were used for the synthesis of Fe-N-C@CNTs-1.5 and FeCl₃ (0.0871 g) and phenanthroline (0.3186 g) were used for the synthesis of Fe-N-C@CNTs-3. Fe@CNT-1.5 was synthesized with the same conditions to Fe-N-C@CNTs-1.5 except that only FeCl₃ was used. Fe-N-C/CNT-1.5 was prepared in a similar method to Fe-N-C@CNT-1.5 but no ultrasonic treatment was performed after mixing solution A with CNTs.

Hydrogenation of nitrobenzene.

In a typical experiment (S/C=22), 80 mg of Fe-N-C@CNTs-1.5, 46 μl of nitrobenzene, 2 ml of H_2O and 2 ml of THF were placed in a 5 ml ampoule. After ultrasonic treatment, the ampoule

was placed in a stainless steel autoclave. The reactor was purged and sealed with 5 MPa H_2 and kept at 110 °C under stirring for a certain time. After the reaction, the autoclave was cooled to room temperature and the product was analyzed by Agilent 6890 gas chromatography equipped with a flame ionization detector and a HP-5 capillary column. **Stability test by fixed-bed reactor.**

A pre-degassed solution of nitrobenzene (6.9 ml) in 400 ml H_2O/THF (1/1 v/v) was fed continuously with a syringe pump over a catalyst bed of 350 mg of Fe-N-C@CNTs-1.5 (0.3 mmol) under 2.0 Mpa H_2 atmosphere at 140 °C. Simultaneously, H_2 was also continuously introduced with a flow rate of 7 ml/min. The outlet of the reactor was sampled at different time intervals. The crude mixtures were directly analyzed by GC.

Results and discussion

Synthesis and characterization of Fe-N-C@CNTs and Fe-N-C/CNTs-1.5.

Fe-N-C@CNTs was prepared using phenanthroline, FeCl₃ and CNTs as precursors (Scheme 1). For comparison, Fe-N-C/CNTs-1.5 was also prepared. The only difference in the preparation method is that ultrasonic treatment of phenanthroline, FeCl₃ and CNTs was performed for Fe-N-C@CNTs and Fe-N-C/CNTs-1.5 was prepared without the ultrasonic treatment. After solvent evaporation and successive pyrolysis at 800 °C under N₂ atmosphere, Fe-N-C@CNTs and Fe-N-C/CNTs-1.5 were obtained.



Scheme 1 Schematic illustration for the synthesis of Fe-N-C@CNTs.

The SEM images of Fe-N-C@CNTs-1.5 and Fe-N-C/CNTs-1.5 clearly show the tangles of CNTs with diameter of 10-20 nm (Fig. S1). The small metal particles with size less than 10 nm scatters in the CNTs and also small amount of particle with size about 30-50 nm and above 100 nm could be found in the SEM image of Fe-N-C@CNTs-1.5. In addition to small metal nanoparticles (less than 10 nm), larger metal particles (300-500 nm) also exist in the SEM image of Fe-N-C/CNTs-1.5. The TEM images confirm the above SEM results that both small nanoparticles and large metal particles co-exist in both samples and Fe-N-C/CNTs-1.5 has more amount of large-sized metal particles than Fe-N-C@CNTs-1.5 does (Fig. 1). For Fe-N-C@CNTs-1.5 and Fe-N-C/CNTs-1.5, most of metal particles are dispersed outside of the CNTs, although some metal particles still exist inside CNTs. According to the elemental mapping (Fig. S2), the N and Fe element are uniformly distributed in the entire skeletal framework, which suggests that Fe atom may

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have some interaction with N atom. The above characterization results suggest that the ultrasonic treatment could facilitate the uniform distribution of precursors on CNTs for the formation of small metal NPs. The TEM images of Fe-N-C@CNTs-0.5 and Fe-N-C@CNTs-3 shown in Fig. S3 are similar to that of Fe-N-C@CNTs-1.5. However, the particle size outside the CNTs steadily grows to over several hundred nanometers with the increment of iron loading. With Fe-N-C@CNTs-1.5



Fig. 1 TEM images of (A) Fe-N-C@CNTs-1.5 and (B) Fe-N-C/CNTs-1.5, (C) HR-TEM images of the typical metal particles with Fe-N-C@CNTs-1.5 as model: (a-b) iron nanoparticles wrapped with amorphous carbon shells inside CNTs, (c-d) iron nanoparticles wrapped with amorphous carbon shells outside CNTs, (e-f) iron crystals tightly encapsulated by highly graphitized carbon layers.

as model, metal nanoparticles could be classified as metal nanoparticles wrapped with amorphous carbon shells and iron crystals tightly encapsulated by highly graphitized carbon layers (Fig. 1C). These species were formed by pyrolysis of phenanthroline, FeCl₃ and carbon (or Al₂O₃).⁵ By measuring the d-space of iron containing crystals we could acquire some information on species inside different kinds of carbon layers. For particles wrapped with a layer of poorly graphitized carbon shell, lattice fringes attributed to (201) or (111) facet of Fe₃C (b and d in Fig. 1C) were observed while for particles coated with a layer of highly graphitized carbon lattice fringes attributed to (110) facet of α -Fe were identified (Fig. 1Cf).

The crystal phase of iron nanoparticles was further testified using X-ray powder diffraction technique (Fig. 2A). The diffraction peaks attributed to graphitic carbon, metallic iron (α -Fe, JCPDS-PDF: 65-4899) and metal nitrides (FeN0.076) could be clearly observed in the XRD patterns of Fe-N-C@CNTs and Fe-N-C/CNTs. As Fe loading increases from 0.5 to 1.5, the intensity of α -Fe species increases. This is probably due to the formation of iron species with larger particle size at high Fe loading based on TEM characterizations. It is noteworthy to mention that there was a set of diffraction patterns appeared in the XRD pattern of Fe-N-C/CNTs-1.5 (indicated by \blacksquare in Fig. 2A). After comparing with the standard pattern of different iron nitrides, carbides and oxides, it is still difficult to assign this new phase. Fe-N-C@CNTs and Fe-N-C/CNTs-1.5 were prepared with the same amount of iron and phenanthroline. Even with higher amount of iron and phenanthroline, the above mentioned diffraction peaks still could not be found in the XRD patterns of Fe-N-C@CNTs. The reason is still not clear at present stage, but in consideration of the only difference during the preparation of two kinds of catalysts (ultrasonic treatment), it is probably related with the higher dispersion degree of iron precursor, for long period ultrasonic treatment would result in changes to functional groups on the surface of highly oxidized CNTs,¹⁷ which may influence its interaction with iron precursors during the pyrolysis.



Fig. 2 (A) X-ray powder diffraction patterns of (a) Fe-N-C@CNTs-0.5, (b) Fe-N-C@CNTs-1.5, (c) Fe-N-C/CNTs-1.5, (d) Fe-N-C@CNTs-1.5 after storing in air for a month, (e) Fe-N-C@CNTs-1.5 after the 10th recycle and (f) Fe-N-C@CNTs-3.0 ($\triangledown Fe^0$, ■ unknown species, \blacklozenge FeN0.076, \bigstar Fe₃O₄). Dashed lines indicate the characteristic peaks of graphite. Mössbauer spectra (298K) of (B) Fe-N-C@CNTs-1.5, (C) Fe-N-C/CNTs-1.5, and (D) Fe-N-C@CNTs-3.0. The parameters of doublet and sextets were listed in Table S1.

Mössbauer spectra were employed to characterize iron species of Fe-N-C@CNTs and Fe-N-C/CNTs-1.5 because Mössbauer spectra may give more details on the state of iron species (Fig. 2). Due to low Fe content, no signals could be found for Fe-N-C@CNTs-0.5. For Fe-N-C@CNTs-1.5 and Fe-N-C@CNTs-3.0, the signals could be well fitted into one doublet and three sets of sextets. The doublet with the isomer shift (IS) of~0.2 mm s⁻¹ and the quadrupole splitting (QS) of~1.0 mm s⁻¹ might be attributed to Fe(II) or Fe(III) species of some poorly crystallized iron oxide.^{18,19} Sextet 1 and Sextet 2 could be attributed to α -iron and χ -Fe₂C₅/Fe₃C respectively;^{18,20,21} Sextet 3 may be ϵ -Fe₃N in which Fe was coordinated with 3 nitrogen atoms.²² It is interesting to mention than Fe-N-C@CNTs affords all three sets of sextets and Fe-N-C/CNTs-1.5 only shows one doublet and two of sextets (Sextet 1 and Sextet 2). This indicates that Fe-N-C/CNTs-1.5 with poorly crystallized iron oxide, α -iron and χ -Fe₂C₅/Fe₃C has no ϵ -Fe₃N species. The

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unknown species in the XRD pattern of Fe-N-C/CNTs-1.5 may be related with $\chi\text{-}Fe_2C_5/Fe_3C$ based on the results of Mössbauer.

Catalytic performance of Fe-N-C@CNTs in the hydrogenation of nitroarenes.

The catalytic performance of Fe-N-C@CNTs was tested in the hydrogenation of nitrobenzene and compared with Fe-N-C/CNTs-1.5 (Table 1). All samples tested could efficiently catalyze the hydrogenation of nitrobenzene with aniline as the only product. Fe-N-C@CNTs-0.5 and Fe-N-C@CNTs-1.5 could afford about 98% conversion in 0.5 h with H₂O/THF (1/1 v/v) as solvent. Under similar reaction conditions, the reaction time needs to prolong to 1 h for Fe-N-C@CNTs-3.0 to achieve >99% conversion. Due to the fast reaction rate of Fe-N-C@CNTs, it is hard to get precise kinetic curves to measure the turn over frequency. Thus, S/C was increased from 22 to 300 and TOF was calculated with conversion less than 30%. As Fe loading increases, the TOF increases and reaches the maximum at Fe loading of 1.5 wt%. Fe-N-C@CNTs-1.5 with TOF of 46.8 h⁻¹ shows the highest activity among all Fe-N-C@CNTs samples. Fe-N-C@CNTs-1.5 could also afford >99% conversion in 6 h, indicating that Fe-N-C@CNTs-1.5 is active enough to catalyze the reaction even with low catalyst amount. It takes 10 h for Fe-N-C/CNTs-1.5 to achieve full conversion. Due to its low activity, the TOF of Fe-N-C/CNTs-1.5 was measured at S/C of 22. Fe-N-C@CNTs-1.5 is much more active than Fe-N-C/CNTs-1.5 (TOF: 46.8 versus 5.1 h⁻¹). As far as we know, Fe-N-C@CNTs-1.5 is the highest active Fe-N-C based catalyst ever reported for nitrobenzene hydrogenation.

Table 1. The catalytic performance of Fe-N-C@CNTs and Fe-N-C/CNTs in the hydrogenation of nitrobenzene[a].

Cat.	S/C	Time (h)	Conv. (%)	TOF (h ⁻¹)
Fe-N-C@CNTs-0.5	22	0.5	98.5	-
Fe-N-C@CNTs-1.5	22	0.5	>99	-
Fe-N-C@CNTs-3.0	22	1	>99	-
Fe-N-C/CNTs-1.5	22	10	99	5.1
Fe-N-C/AC[b]	22	15	99	
Fe-N-C@CNTs-0.5	300	6	>99	33.5
Fe-N-C@CNTs-1.5	300	6	>99	46.8
Fe-N-C@CNTs-3.0	300	6	37	17
Fe-N-C@CNTs-1.5 ^[c]	300	6	>99	33.3
Fe-N-C@CNTs-1.5 ^[d]	300	6	69.5	-
Fe-N-C@CNTs-1.5 ^[e]	300	6	43.7	-

[a] Reaction conditions: 0.5 mmol nitrobenzene, S/C of 22, H₂O/THF (4 ml, 1/1 v/v), 110 °C, 5 MPa H₂. TOF was calculated based on kinetic curves with conversion less than 30%. [b] data from ref 5, reaction temperature is 120 °C. [c] No solvent was used. [d] H₂O was used as solvent. [e] THF was used as solvent.

It takes 10 h and 15 h respectively for Fe-N-C/CNTs-1.5 and Fe-N-C/AC to achieve full conversion, suggesting that Fe-N-C@CNTs-1.5 is much more active than Fe-N-C/AC reported in the literature. ⁵ Due to the fact that no TOF or the kinetic curves of Fe-N-C/AC was reported in the literature, it is reasonable to compare the activity of Fe-N-C/CNTs-1.5 and Fe-N-C/AC with reaction times needed to achieve full conversion

under the same reaction conditions, such as the same S/C ratio and the same solvent ect. Though Fe-N-C/CNTs-1.5 is less active than Fe-N-C@CNTs-1.5, it is still more active than Fe-N-C/AC, suggesting the promotion effect of CNTs.

With Fe-N-C@CNTs-1.5 as model catalyst, the influence of the solvent on the catalytic performance was tested (Table 1). Fe-N-C@CNTs-1.5 could efficiently catalyze the reaction to afford 99% conversion in 6 h under solvent free condition, which is quite important for energy saving and economic production of chemicals. Under similar reaction conditions, much lower conversion was achieved using pure H₂O and pure THF as solvent. The TOF of Fe-N-C@CNTs-1.5 is 46.8 h⁻¹ in TOF/H₂O and 33.3 h⁻¹ under neat conditions. The above results suggest that the mixture of TOF and H₂O is the best solvent for Fe-N-C@CNTs.

The active sites of Fe-N-C catalysts are still not fully understood though previous reports suggest that iron particles surrounded with C and N species are the active sites. Recently, Zhang and co-workers indicates that Co single atoms bonded with N within graphitic sheets are the active sites in the Co-N-C catalyst for C-C bond-forming reactions.¹⁶ In a just published report by Su et al., researchers attributed the real active center of Co-N-C catalyst to chelate complexes with cobalt atoms bonded to 2 to 3 nitrogen atoms in the graphene lattice which probably like the pyridinic vacancy.²³

Fe-N-C/CNTs-1.5 without ε-Fe₃N (Sextet 3) is less active than Fe-N-C@CNTs-x (x=1.5 and 3) possessing ε-Fe₃N, suggesting that ε-Fe₃N should be one kind of active sites. Fe-N-C/CNTs-1.5 shows catalytic activity for the hydrogenation of nitrobenzene though the activity is not very high. This indicates that there should be another kind of active sites in addition to ϵ -Fe₃N. The results of XRD and Mössbauer show that Fe-N-C/CNTs-1.5 has α -Fe, FeN0.076, iron oxide, and χ -Fe₂C₅/Fe₃C. A control sample, Fe@CNTs-1.5 was prepared under similar conditions to Fe-N-C@CNTs-1.5 but without the addition of phenanthroline. This sample shows only trace amount conversion of nitrobenzene, but the TEM and XRD result shows the presence of α -Fe in this sample (Fig. S3C and Fig. S4). Thus, another kind of active site may possibly involve FeN0.076 and χ -Fe₂C₅/Fe₃C. Comparing the activity of Fe-N-C@CNTs and Fe-N-C/CNTs-1.5, it can be stated that ϵ -Fe₃N should be much more active than other kind of active sites (FeN0.076 and χ-Fe₂C₅/Fe₃C). Fe-N-C@CNTs-1.5 and Fe-N-C@CNTs-3.0 have similar amount of ϵ -Fe₃N based on Mössbauer characterization, the higher catalytic activity of former sample is possibly due to its smaller particle size. This is reasonable due to the fact that smaller particles could increase the surface area of active sites.

Though the active sites for Fe-N-C based catalysts are very complicated, our results indicated that ϵ -Fe₃N should be the most active site for the hydrogenation of nitrobenzene. Also, smaller particle size benefits higher catalytic activity. Fe-N-C@CNTs-x and Fe-N-C/CNTs-1.5 all show higher activity than Fe-N-C/AC, suggesting the unique structure of CNTs brought about profound influences on the active species. Since the surface area of CNTs is much smaller than AC, the extension of

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dispersion of active sites should not be a reason for the difference in activity. The reason is not clear at present stage.

Another indispensable part of the catalyst was nitrogen atom. Langmuir-Hinshelwood mechanism of the nitroarenes reduction involves surface adsorption of reducing agent and substrate on the catalyst.^{24,25} Chen and his co-workers confirm that N doping is suitable to introduce active sites for the adsorption of substrates on catalyst, which is critical to the following catalytic process.²⁶ In Matthias' report they revealed that carbon/alumina supported iron catalyst could only yield trace amount of product under the same reaction conditions, indicating that N is an essential element for the reaction.⁵ Although from XPS results we got some information on the distribution of N species (Fig. S5 and S6), the contribution of interaction between iron and nitrogen towards the reaction still remained largely unknown. In a recent report, Gianvito Vilé claimed that nitrogen atoms around metal center may facilitate heterolytic dissociation of hydrogen molecule,²⁷ according to the result we applied high pressure hydrogen adsorption measurement on different materials to elucidate the function of nitrogen atoms in the catalyst (Fig. 3). The measurements were performed on a high pressure adsorption apparatus and the equilibrium time for each point was 20 min. Considering the possibility of chemical adsorption, the data acquired was a dynamic result rather than equilibrium. Pure CNTs could only adsorb trace amount of hydrogen, which is within the range of physical adsorption. The quantity of hydrogen gas adsorbed on Fe-N-C/CNTs-1.5 and Fe@CNTs-1.5 was even lower, indicating that the addition of iron and nitrogen via simple impregnation merely increased the weight of the material, while single component of iron could not fulfill the activation of hydrogen molecule either. The hydrogen adsorption amount for Fe-N-C@CNTs-1.5 increased significantly to ~0.6% at the pressure of 6 MPa, a value which is at the same level for carbon bridged Pd on AC.^{28,29} Similar high hydrogen take up was reproducible for Fe-N-C@CNTs-3.0. The difference in hydrogen adsorption between Fe-N-C@CNTs-1.5 and Fe@CNTs-1.5 should originate from the nitrogen/carbon coating layer derived from pyrolysis of phenanthroline. Fe-N-C@CNTs-1.5 and Fe-N-C/CNTs-1.5 synthesized with FeCl₃ and phenanthroline both have nitrogen/carbon coating layer. The higher H₂ adsorption properties of the former sample may be attributed to the existence of E-Fe₃N. Hydrogen molecules could be dissociated on the surface of iron containing active centers and then diffuse on to the surface of CNTs support.^{29,30} By comparing the catalytic results, we can conclude that the ability for activating and storing hydrogen under high pressure undoubtedly contributes to the high activity of Fe-N-C@CNTs catalysts.

With Fe-N-C@CNTs-1.5 as model catalyst, the general substrate scope of Fe-N-C@CNTs catalysts was tested in the hydrogenation of nitroarenes containing some sensitive functional groups such as aldehydes, C=C, CN and so on (Table 2). In addition of nitrobenzene, hydrogenation of halogen-substituted nitroarenes proceeds smoothly to produce corresponding haloaromatic amines without any

dehelogenation within 0.5 to 1 h. Amazingly, the substrates bearing other easily reducible functional group (aldehydes, CN, pyridine) could be also converted to corresponding substituted amines without affecting the substitution groups. It is noteworthy to mention that it takes no more than 3 h to achieve 96% to >99% conversion for all substrates listed in

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Fig. 3. High-pressure hydrogen isotherms at 298 K for pure CNTs and CNTs supported iron based catalysts with or without nitrogen/carbon bridges.

Table 2, showing the high catalytic activity of Fe-N-C@CNTs-1.5. For substrate bearing ethylene group, the product selectivity is 87%, slightly lower than Co-N-C or Fe-N-C catalysts reported in literature. This is probably due to the high catalytic activity of Fe-N-C@CNTs-1.5.

The stability of Fe-N-C@CNTs-1.5 was tested using batch reactor and fixed-bed reactor (Fig. 4). The recycle results based on batch reactor shows up to 99% conversion could be obtained for the nine cycles though the reaction time is extended from 1 h (for 1-5 cycles) to 2 h (for 6-10 cycles). For the tenth cycles, the conversion decreases from 99% to 95%. Compared with fresh catalyst, no obvious change in the particles size was found for Fe-N-C@CNTs-1.5 after ten cycles according to the TEM characterization (Fig. 1A and Fig. S7). The X-ray diffraction pattern of catalyst after recycling is also shown in Fig. 2A. Only Fe₃O₄ could be identified in the material. Though the catalyst could still convert nitrobenzene into aniline, iron oxide should not be an active site due to the insensitivity of XRD for detecting low content species. We also prepared an aged catalyst by exposing Fe-N-C@CNTs-1.5 to the open air for a month. There was no obvious change in the XRD result. However, this catalyst only affords 20% conversion in 0.5 h with S/C of 22 with THF/H₂O as solvent at 110 $^{\circ}$ C. The result shows the insensitivity of XRD for detecting the active species for Fe-N-C catalysts. The results of fixed-bed reactor show that 100% conversion could be obtained with flow rate of 0.06 ml/min for 120 h. The conversion drops to 70% with the flow rate increasing to 0.09 ml/min. After that the continuous decreasing of conversion from 70% to 42% could be observed. The above results suggest that the active site of Fe-N-C is not stable during the catalytic process and the stability of this kind of catalyst should be further improved.

Substra

NO₂

NO₂

CH3

0-1

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te	Product	Time (h)	Sel. (%)	Conv. (%)	T
,NO₂	NH ₂	0.5	>99	>99	e fo
, NO₂	CI NH2	0.5	>99	>99	C
NO ₂	NH ₂	1	>99	>99	A T

0.5

3

1.5

>99

>99

>99

>99

>99

>99

Table 2. Hydrogenation of different types of nitroarenes catalyzed by Fe-N-C@CNTs-1.5 $^{\rm [a]}.$

NH₂

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CH-

[b]	NH ₂ 1.5	>98	87
NH ₂ [b]	CN 3	>99	>99
) NH ₂ 3	>96	>99

[a] Reaction conditions: 0.5 mmol substrate, 4.5 mol% Fe, 2 ml H₂O+2 ml THF, 110 $^{\circ}$ C, 5 Mpa H₂, [b] 90 $^{\circ}$ C.



Fig. 4 (A) Recycling of Fe-N-C@CNTs-1.5 in batch reactor, reaction condition: 0.5 mmol nitrobenzene, 4.5 mol% Fe, H₂O+THF (1/1 v/v), 4 ml, 110 °C, 5 MPa H₂, 1 h for 1-5th cycle, 2 h for 6-10th. (B) The stability of Fe-N-C@CNTs-1.5 tested in fixed-bed reactor, reaction condition: 6.9 ml nitrobenzene, H₂O+THF (1/1 v/v), 400 ml, 350 mg Fe-N-C@CNTs-1.5 (0.3 mmol), 2 Mpa H₂ with a flow rate of 7 ml/min, 140 °C.

Conclusions

In this report a series of CNTs supported Fe-N-C catalysts were prepared and they show enhanced activity towards hydrogenation of nitroarenes while keeping a high chemoselectivity. Fe-N-C@CNTs possessing ϵ -Fe₃N is much more active than Fe-N-C/CNTs without ϵ -Fe₃N. We believe that

there are at least two kinds of active species for Fe-N-C catalysts and ϵ -Fe₃N is the most active site for catalyzing the nitroarene hydrogenation. Nitrogen/carbon atoms contacted to the active centers could serve as bridges to transport the dissociated hydrogen atoms and further enhance the activity. The sonication treatment is one of the key factors for the formation of ϵ -Fe₃N species. Fe-N-C@CNTs catalysts also show excellent durability which could run under continuous flow condition over 100 hours.

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References

- 1 H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan and K. P. de Jong, *Science*, 2012, **335**, 835.
- 2 N. Svend Erik, In Innovations in Industrial and Engineering Chemistry, American Chemical Society: 2008, Vol. 1000, p 15.
- 3 X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, D. Tan, R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan and X. Bao, *Science*, 2014, **344**, 616.
- 4 D. R. Strongin, J. Carrazza, S. R.Bare and G. A. Somorjai, *J. Catal.*, 1987, **103**, 213.
- 5 R. V. Jagadeesh, A.-E.Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner and M. Beller, *Science*, 2013, **342**, 1073.
- 6 H.-U. Blaser, H. Steiner and M. Studer, *ChemCatChem*, 2009, 1, 210.
- 7 H. Xiao, Z.-G. Shao, G. Zhang, Y. Gao, W. Lu and B. Yi, *Carbon*, 2013, **57**, 443.
- 8 Q. Fu and T. Wagner, *Surf. Sci. Rep.*, 2007, **62**, 431.
- 9 X. Tan, W. Deng, M. Liu, Q. Zhang and Y. Wang, Chem.
- Commun., 2009, 46, 7179.
 Y. Yao, H. Xiao, P. Wang, P. Su, Z. Shao and Q. Yang, J. Mater. Chem. A, 2014, 2, 11768.
- 11 W. Chen, X. Pan and X. Bao, J. Am. Chem. Soc., 2007, 129, 7421.
- 12 X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo and X. Bao, Nat. Mater., 2007, 6, 507.
- 13 M. Casavola, J. Hermannsdörfer, N. de Jonge, A. I. Dugulan and K. P. de Jong, *Adv. Funct. Mater.*, 2015, **25**, 5309.
- 14 Z. Wei, J. Wang, S. Mao, D. Su, H. Jin, Y. Wang, F. Xu, H. Li and Y. Wang, *ACS Catal.*, 2015, **5**, 4783.
- F. A. Westerhaus, R. V. Jagadeesh, G. Wienhöfer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brückner and M. Beller, *Nat. Chem.*, 2013, 5, 537.
- 16 L. Zhang, A. Wang, W. Wang, Y. Huang, X. Liu, S. Miao, J. Liu and T. Zhang, ACS Catal., 2015, 5, 6563.
- 17 R. Zeineldin, M. Al-Haik and L. G. Hudson, *Nano Lett.*, 2009, 9, 751.
- 18 S. Zhang, B. Liu and S. Chen, Phys. Chem. Chem. Phys., 2013, 15, 18482.
- 19 U. I. Kramm, I. Herrmann-Geppert, S. Fiechter, G. Zehl, I. Zizak, I. Dorbandt, D. Schmeißer and P. Bogdanoff, *J. Mater. Chem. A*, 2014, **2**, 2663.
- 20 Z. Yang, S. Guo, X. Pan and J. Wang, X. Bao, *Energ. Environ. Sci.*, 2011, **4**, 4500.
- 21 K. Cheng, M. Virginie, V. V. Ordomsky, C. Cordier, P. A. Chernavskii, M. I. Ivantsov, S. Paul, Y. Wang and A. Y. Khodakov, J. Catal., 2015, **328**, 139.

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Journal Name

- 22 S. Kurian and N. S.Gajbhiye, Chem. Phys. Lett., 2010, **493**, 299.
- 23 T. Cheng, H. Yu, F. Peng, H. Wang, B. Zhang and D. Su, *Catal. Sci. Technol.*, 2016, **6**, 1007.
- 24 T. Aditya, A. Pal and T. Pal, Chem. Commun., 2015, 51, 9410.
- 25 X. Kong, Z. Sun, M. Chen, C. Chen and Q. Chen, *Energ. Environ. Sci.*, 2013, **6**, 3260.
- 26 H. Hu, X. Wang, D. Miao, Y. Wang, C. Lai, Y. Guo, W. Wang, J. Xin and H. Hu, *Chem. Commun.*, 2015, **51**, 16699.
- 27 G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López and J. Pérez-Ramírez, *Angew. Chem. Int. Ed.*, 2015, **54**, 11265.
- 28 R. T. Yang and Y. Wang, J. Am. Chem. Soc., 2009, 131, 4224.
- 29 L. Wang and Yang R. T., *Catal. Rev.*, 2010, **52**, 411.
- 30 A. J. Lachawiec, G. Qi and R. T. Yang, *Langmuir*, 2005, **21**, 11418.

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Table of Contents Graphic and Synopsis Here

An efficient Fe-N-C@CNTs for the hydrogenation of nitroarenes was prepared by pyrolysis of FeCl₃, phenanthroline and CNTs. It was found that ϵ -Fe₃N is the most active site of Fe-N-C and nitrogen/carbon atoms contacted to the active centers could serve as bridges to transport the dissociated hydrogen atoms via spillover effect.

