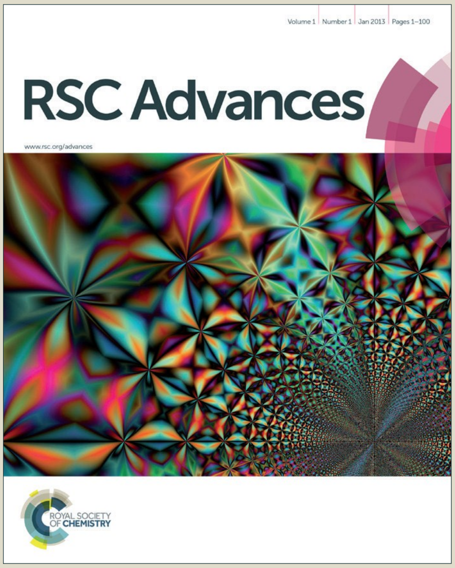
RSC Advances

This article can be cited before page numbers have been issued, to do this please use: S. Xu, D. Yu, S. Liao, T. Ye and H. Sheng, *RSC Adv.*, 2016, DOI: 10.1039/C6RA18935K.



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

View Article Online
DOI: 10.1039/C6RA18935K

RSC Advances

PAPER

Nitrogen-doped Carbon Supported Iron Oxide as Efficient Catalysts for Chemoselective Hydrogenation of Nitroarenes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shaodan Xu,[*a,b] Deqing Yu,[a] Shangfu Liao,[a] Tao Ye,[a,c] and Huadong Sheng[*a]

The chemoselective hydrogenation has been widely used in the production of fine chemicals, and developing heterogeneous catalysts with high activity and chemoselectivity is always a challengeable topic. Herein, we reported a new type of catalysts synthesized from biomass-derived chitosan and non-noble iron, which is denoted as nitrogen-doped carbon supported iron (Fe/N-C). TEM and XRD characterization indicate the presence of iron species. Interestingly, the Fe/N-C catalysts exhibited excellent catalytic performances in the hydrogenation of nitroarenes, and excellent yields of target aniline products could be obtained under industrially viable conditions.

Introduction

Chemoselective hydrogenation of easily available molecules into desired products using molecular hydrogen is always an important topic in the field of heterogeneous catalysis.[1-7] Many Pd, Au, Rh, Ir and Pt metals have been regarded as highly efficient catalysts for the hydrogenation, and already used in industrial scales.[8-14] Notably, the high price and limited availability of these metals make these applications high-cost, therefore, much interest has been attracted in developing earth-abundant alternative metal catalysts. Many earth-abundant metal salts coupled with soluble organic ligands have exhibited high activity in the hydrogenation reaction which used to be performed over noble metals previously.[15-19] However, the homogeneous feature makes these catalysts difficult in separation and regeneration from the reaction system, which strongly limited their wide applications in the future.[20-24] Recently, the Fe, Cu, Ni and Co-based heterogeneous catalysts have been found to be active for the hydrogenations, which have good feature in catalytic stability and recyclability, but their catalytic activity and chemoselectivity could not satisfy the application of these catalysts in chemoselective hydrogenations.[25-30] Therefore, developing efficient heterogeneous catalysts from earth-abundant metals is challengeable for chemoselective hydrogenations.

One great discovery in catalytic hydrogenations using H_2 is the chemoselective reduction of nitroarenes into anilines, which are industrially valuable intermediates for the production of agrochemicals and pharmaceuticals.[31-35] Such process has great limitation for the catalysts especially more than one reducible group are present in the nitroarene molecule, which easily leads to the hydrogenation of these substituted groups (C=O, C-Cl and so on), forming undesired products.[36] In order to solve this problem, many efforts have been focused on enhancing the chemoselectivity of noble metal catalysts. More recently, Beller and co-workers firstly found that the combination of nitrogen-doped carbon with Fe or Co oxides could produce a new type catalyst which could solely catalyze the hydrogenation of nitro-groups.[33,37] However, it should be noted that the preparation of these catalysts need expensive 1,10-phenanthroline (phen) ligand as carbon precursor and high pyrolysis temperature at as high as 800 °C. It is also found that other cheap ligands and low-temperature (400-600 °C) calcination leads to catalysts with poor activity.[27] Furthermore, the no-porosity and bulky metal oxides leads to relatively low frequency of the active sites in the hydrogenation.

In this work, we report a new type of nitrogen-doped mesoporous carbon supported iron catalysts (Fe/N-C-x, x denotes the calcination temperature). It is interesting to found that the Fe/N-C sample obtained at 500 °C (Fe/N-C-500) gives the highest activity and chemoselectivity in the hydrogenation of nitrobenzene. Importantly, the Fe/N-C-500 catalyst could catalyze the hydrogenation of a series of substituted nitroarenes to the corresponding anilines in good activities and chemoselectivities. More importantly, the Fe/N-C-500 catalyst is stable and can be easily reused for several recycles without any lost in activity and selectivity. The features of easy available, high activity, excellent chemoselectivity, and good recyclability make the Fe/N-C-500 catalyst potentially useful for the applications in the chemoselective hydrogenation of substituted nitroarenes in the future.

---

[a] Zhejiang Institute of Quality Inspection Science, Hangzhou 310018, China
E-mail: shaodanxu@zju.edu.cn; shd761002@163.com
[b] Department of Chemistry, Zhejiang University, Hangzhou 310027, China
[c] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

View Article Online
DOI: 10.1039/C6RA18935K

Experimental

Sample preparation

All commercial chemicals are directly used without further purification.

Synthesis of Fe/N-C-x

As a typical run, 1g of chitosan was dissolved in 22 ml of water and 0.5 g of acetic acid, then 0.7 g of borax, iron(III) acetylacetonate (~ 50 mg of Fe), and 5 ml of water were added. After stirring at room temperature for over night, the homogeneous gel was transferred into autoclave and heated at 200 °C for 12 h. Then the obtained solid was filtrated, washed, and calcined at different temperatures in N_2 flow for 4 h to obtain the final Fe/N-C-x catalyst.

Sample characterization

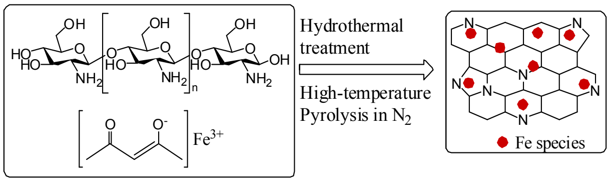
FEI Tecnai G2 F20 microscope equipped with an EDAX detector was employed to acquire TEM images. The microscope was operated at an accelerating voltage of 200 kV. The samples were ultrasonically dispersed in ethanol, and then a drop of the solution was deposited on a holey C/Cu TEM grid to be used for Transmission Electron Microscopy (TEM) characterization and elemental mapping. Rigaku powder X-ray diffractometer using Cu Kα (λ = 1.5418 Å) radiation. X-ray photoelectron spectra (XPS) were performed by Thermo ESCALAB 250, and the binding energy was calibrated by C1s peak (284.9 eV). Nitrogen isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP Tristar. The samples were outgassed for 10 h at 150 ºC before the measurement. Pore-size distribution was calculated using Barrett-Joyner-Halenda (BJH) model. The content of Fe was determined from inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer. Scanning electron micrograph (SEM) images were performed on Hitachi SU-1510 electron microscopes.

Catalytic tests

The hydrogenation reactions were performed in a 60-ml high pressure autoclave with a magnetic stirrer (1200 rpm). Typically, the catalysts, substrates, and solvent were mixed in the reactor. Then, the reaction system was filled with H_2 and heated to a desired temperature. The temperature was measured with a thermometer in an oil bath. After reaction, the product was taken out from the reactor and analyzed by gas chromatography (GC-2014C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with FFAP. The dodecane or decane was used as internal standard in the GC analysis. The recyclability of the catalyst was tested by separating from the reaction system by centrifugation, washing with a large quantity of methanol and water, and drying at 80 ^{o}C for 6 h.

Results and discussion

The Fe/N-C catalysts were directly obtained from the hydrothermal treatment of biomass-derived chitosan as nitrogen/carbon precursor and iron(III) acetylacetonate as iron precursor in the absence of any surfactants or templates, followed by calcination (Scheme 1).



Scheme 1. Synthesis of Fe/N-C-x samples.

Table 1. Structural parameters of various samples.

Sample	S_{BET} (cm^2/g)^a	Fe (*wt*%)^b	C/N molar ratio	Fe form^c	Ps(nm)^d
Fe/N-C-400	287	6.4	8.1	Fe_2O_3	2.8-6.8
Fe/N-C-500	309	6.7	8.3	Fe_3O_4, FeN_x	3.0-7.0
Fe/N-C-600	320	6.5	9.7	Fe_3O_4, FeC_x	3.0-9.0
Fe/N-C-800	270	6.9	16.4	Fe_3O_4, FeC_x	4.0-9.4

^{a} BET Surface area, by N_2 sorption; ^{b} Fe Loading, by ICP analysis; ^{c} By XRD patterns; ^{d} By counting ~80 nanoparticles in TEM images.

Figure 1A shows the scanning electron microscopy (SEM) images of the Fe/N-C-400, Fe/N-C-500, Fe/N-C-600, and Fe/N-C-800 samples. All samples exhibit an angular morphology, and the surface areas were established at 270-320 cm^2/g (Table 1), indicating the rich porosity. Figure 1e shows the scanning transmission electron microscopy (STEM) image of Fe/N-C-500, the Fe species and carbon support could be easily distinguished from each other by the image contrast because of the different atomic number of C and Fe. In the STEM image, the Fe species with bright contrast are highly dispersed on the carbon support with relatively dark contrast.[38] Furthermore, the Fe elemental EDX mapping analysis give the observation of the distribution of Fe element (Figure 1g), which is in good agreement with the distribution of Fe species in the STEM image (Figure 1f). By analyzing about 80 nanoparticles, more than 90% of the nanoparticles gave a small size distribution at 3-7 nm (Figure 1h). These results indicate the successful synthesis of nanoporous carbon supported small-sized FeOx particles.

View Article Online
DOI: 10.1039/C6RA18935K

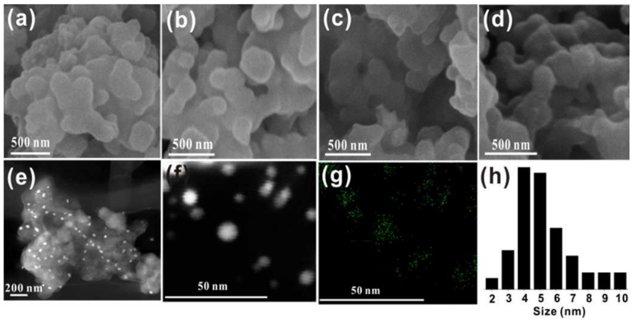


Figure 1. SEM images of (a) Fe/N-C-400, (b) Fe/N-C-500, (c) Fe/N-C-600, and (d) Fe/N-C-700; (e and f) STEM images of Fe/N-C-500, (g) the corresponding Fe elemental EDX mapping, and (h) FeO_x particle size distribution.

Figure 2A shows the Raman spectra of Fe/N-C-400, Fe/N-C-500, Fe/N-C-600, and Fe/N-C-800 samples, which have G band at about 1589 cm^{-1}, indicating the in-plane vibration of sp^2-derived aromatic carbons. The D band at about 1353 cm^{-1} presents the sp^2-derived carbons in the unperfected aromatic structure. Notably, the signal of D band is very strong, which is only slightly weaker than the G band.[38] In this work, this phenomenon should be due to the presence of rich nitrogen species on the carbon structure, where the C/N atomic molar ratio could be estimated by elemental analysis. As shown in Table 1, the C/N molar ratios of Fe/N-C-400, Fe/N-C-500, and Fe/N-C-600 is lower (8.1-9.7) than that of Fe/N-C-800 (16.4), which is reasonably attributed to the leaching of N atoms during high-temperature pyrolysis at 800 °C. Figure 2B shows the XRD patterns of Fe/N-C-400, Fe/N-C-500, Fe/N-C-600, and Fe/N-C-800 samples. Notably, the peaks are wide and weak in intensity, associating with the small size of Fe species, which is in good agreement with the results of STEM characterization. In the XRD pattern of Fe/N-C-400, typical peaks associated with Fe_2O_3 are presented. For Fe/N-C-500, the Fe species are mainly presented as Fe_3O_4. Notably, a peak at 42.4° is also observed, associated with FeNx species, which might be due to the Fe-N interaction on the surface of Fe_3O_4 nanoparticles. Furthermore, higher pyrolysis temperature of 600 and 800 °C could produce FeC_x species. Figure 2C gives the N1s XPS spectra of Fe/N-C-500, which exhibited two peaks at 398.3 and 400.2 eV, assigning to pyridinic nitrogen and FeN_x species, indicating the presence of interaction between Fe and N, which is in agreement with the observations of FeN_x species in the XRD pattern.

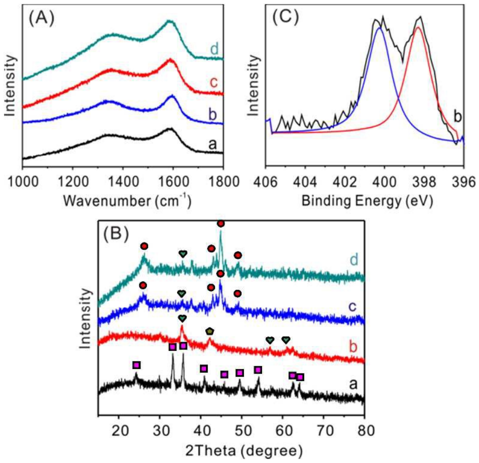


Figure 2. (A) Raman spectra, (B) XRD patterns of (a) Fe/N-C-400, (b) Fe/N-C-500, (c) Fe/N-C-600, and (d) Fe/N-C-800 samples (Square: Fe_2O_3; Heart-shape: Fe_3O_4; Pentagon: FeN_x; Cycle: FeC_x) and (C) N1s XPS spectra of Fe/N-C-500.

The study on the catalytic performances starts from employing the hydrogenation of nitrobenzene as a model reaction. Table 2 shows the catalytic reaction in different solvents of ethyl acetate, toluene, ethanol, and mixed THF-water, which were reported as favorable solvents for the nitroarene hydrogenation reactions in various reaction systems. Interestingly, the Fe/N-C-500 catalyst exhibit full conversion of nitrobenzene to aniline as sole product in ethyl acetate. In contrast, under the same reaction conditions, the nitrobenzene conversions could only reach 95.0, 58.0, and 72.1% in toluene, ethanol, and mixed THF-water solvent, respectively. These results indicate that ethyl acetate was a suitable solvent for obtaining high catalytic activity. Additionally, the other features including low price, low boiling point, and easy separation with aniline also suggest the great potentiality of ethyl acetate for wide application.

Table 2. Hydrogenation of nitrobenzene to aniline in different solvents.[a]

Entry	Solvent	Ph-NO_2 Conv. (%)	Ph-NH_2 Sel. (%)
1	ethyl acetate	>99.0	>99.0
2	toluene	95.0	>99.0
3	ethanol	58.0	>99.0
4	THF-water [b]	72.1	>99.0

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 50 mg of Fe/N-C-500, 4 ml of solvent, 120 °C, 4 MPa of H_2, 15 h; [b] 2 ml of THF and 2 ml of water.

View Article Online
DOI: 10.1039/C6RA18935K

Table 3. Hydrogenation of nitrobenzene to aniline over Fe/N-C catalysts obtained at different pyrolysis temperature.[a]

Entry	Pyrolysis temperature (°C)	Ph-NO_2 Conv. (%)	Ph-NH_2 Sel. (%)
1	400	88.0	>99.0
2	500	>99.0	>99.0
3	600	>99.0	92.0
4	800	72.0	95.1

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 50 mg of Fe/N-C catalyst, 4 ml of ethyl acetate solvent, 120 °C, 4 MPa of H_2, 15 h.

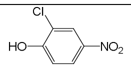
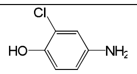
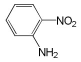
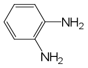
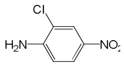
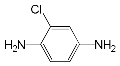
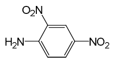
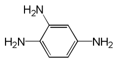
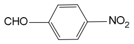
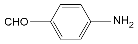
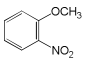
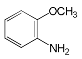
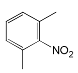
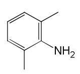
Table 4. Recycle data of Fe/N-C-500 catalyst in the hydrogenation of nitrobenzene to aniline.[a]

Runs	Ph-NO_2 Conv. (%)	Ph-NH_2 Sel. (%)
1	>99.0	>99.0
2	>99.0	>99.0
3	98.1	>99.0
4	98.5	>99.0
5	97.3	>99.0

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 50 mg of Fe/N-C-500 catalyst, 4 ml of ethyl acetate solvent, 120 °C, 4 MPa of H_2, 15 h.

Table 3 shows the catalytic data of various Fe/N-C catalysts obtained from different pyrolysis temperature. The Fe/N-C catalysts with different type of iron species are all active for the reaction. Notably, the Fe/N-C-500 and Fe/N-C-600 catalysts exhibited higher nitrobenzene conversion (>99.0%) than Fe/N-C-400 and Fe/N-C-800 catalysts (72.0-88.0%). Additionally, Fe/N-C-500 exhibited higher chemoselectivity to aniline (>99.0%) than Fe/N-C-600. The results indicate the good catalytic performance of the catalyst calcined at 500 °C. This phenomenon is reasonably related to the formation of FeN_x species on Fe/N-C-500 observing from the XRD patterns, which is reported as efficient catalytically active and selective sites for the hydrogenation reactions. Interestingly, the catalytic performance of Fe/N-C-500 catalyst is even more excellent than conventional nitrogen-doped carbon supported FeO_x catalyst obtained at 500 °C, and comparable with that obtained at 800 °C. This phenomenon might be attributed to the employment of 1, 10-phenanthroline as carbon precursor in the conventional catalyst, which required high pyrolysis temperature (e.g. 800 °C) to form FeO_x species with Fe-N interaction on the surface. In contrast, the biomass-derived chitosan has rich oxygen and nitrogen content, which could easily form FeO_x with Fe-N interaction at relatively low pyrolysis temperature (500 °C). Furthermore, the rich porosity of Fe/N-C-500 is favorable for the high dispersion of the metal nanoparticles and access with the reactants, thus leading to excellent catalytic performances. Table 4 gives the recycle data of Fe/N-C-500 catalyst, we can easily draw the conclusion that the Fe/N-C-500 catalyst is reusable. After each run, it can be easily recycled by filtration with negligible Fe leaching as confirmed by ICP analysis. Consequently, it exhibited constant catalytic performance during continuous recycles. When used for the hydrogenation of nitrobenzene, for example, it gives stable conversion of nitrobenzene (~97.5%) and aniline selectivity (>99.0%) in five reaction runs (Table 4). These results demonstrate that the Fe/N-C-500 catalyst has good recyclability, which is a very important parameter for a heterogeneous catalyst.

Table 5. Hydrogenation of various substituted nitroarenes to the corresponding anilines over Fe/N-C-500 catalyst.[a]

	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			15	>99.0	97.5
2			18	>99.0	>99.0
3			15	98.5	>99.0
4[b]			21	>99.0	97.0
5			14	>99.0	>99.0
6			12	>99.0	>99.0
7			19.5	>99.0	>99.0

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 50 mg of Fe/N-C-500 catalyst, 4 ml of ethyl acetate solvent, 120 °C, 4 MPa of H_2, 15 h. [b] 75 mg of catalyst.

A series of substituted nitroarenes as substrates have also been investigated. From table 5, we can know that the Fe/N-C-500 could efficiently catalyze the conversion of substituted nitroarenes to the corresponding substituted aniline products.

View Article Online
DOI: 10.1039/C6RA18935K

These results indicate the general applicability of Fe/N-C-500 catalyst, which makes it potentially useful for wide application in the hydrogenation of nitroarenes.

Conclusions

In summary, we successfully synthesize nitro-doped porous carbon supported Fe catalyst, which exhibited excellent catalytic activity and selectivity in the hydrogenation of nitroarenes, which attributes to the formation of FeN_x species. Very importantly, the Fe/N-C-500 catalyst has good recyclability for multiple reactions with nearly unchanged catalytic performance. The good features of Fe/N-C-500 catalyst, including easy available precursor, non-noble metals, simple synthesis route, and excellent catalytic performances, make it useful for developing more efficient catalysts for hydrogenations in the future.

Acknowledgements

This work is supported by the Science and Technology Project of General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ, No. 2014QK203).

Notes and references

1 H. Wei, X. Liu and T. Zhang, *Nat. Commun.*, 2014, **5**, 5634.
2 P. Mäki-Arvela, J. Hájek and D. Y. Murzin, *Applied Catal. A: General*, 2005, **292**, 1.
3 C. P. Casey, H. R. Guan, *J. Am. Chem. Soc.*, 2007, **129**, 5816.
4 M. Boronat, P. Concepcion and P. Serna, *J. Am. Chem. Soc.*, 2007, **129**, 16230.
5 M. Takasaki, Y. Motoyama and H. Nagashima, *Org. Lett.*, 2008, **10**, 1601.
6 X. F. Wu, J. K. Liu and J. L. Xiao, *Angew. Chem. Int. Ed.*, **2006**, 45, 6718.
7 H. Sajiki, K. Hattori and K. Hirota, *J. Org. Chem.*, 1998, **63**, 7990.
8 Y. Wang, J. Yao and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 2362.
9 T. Ward, L. Delannoy and B.D. Chandler, *ACS Catal.*, 2013, **3**, 2644.
10 M. Boronat, A. Corma, *Langmuir*, 2010, **26**, 16607.
11 B. Hu, T. Wu and B. Han, *J. Phys. Chem. C*, 2010, **114**, 3396.
12 W. Huang, J.N. Kuhn and G.A. Somorjai, *Nano Lett.*, 2008, **8**, 2027.
13 X. Zhang, H. Shi and B.-Q. Xu, *J Catal., 2011,* **279**, 75.
14 J. Liu, L. Xiao and J. Fan, *Catal. Sci. Technol.,* 2014, **4**, 441.
15 Y. Duan, L. Li and Y.-G. Zhou, *J. Am. Chem. Soc., 2014,* **136**, 7688.
16 L. Wang, F.-S. Xiao, *Green Chem.*, 2015, **17**, 24.
17 J.C. Huffman, J.G. Stone and K.G. Caulton, *J. Am. Chem. Soc.*, 1977, **99**, 5829.
18 M. Zhang, L. Zhu and D. Lowe, *Org. Lett.*, 2003, **5**, 1587.
19 J.D. Morrison, R.E. Burnett and C. Phillips, *J. Am. Chem. Soc.*, 1971, **93**, 1301.
20 A. Togni, L. M. Venanzi, *Angew. Chem. Int. Ed.*, 1994, **33**, 497.
21 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702.
22 D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem. Int. Ed.*, 2005, **44**, 7852.
23 D. J. Gorin, B. D. Sherry and F. D. Toste, *Chem. Rev.*, 2008, **108**, 3351.
24 G. C. Forman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151.
25 Y. Li, S. Yu and J. Gao, *J. Am. Chem. Soc.*, 2014, **136**, 4031.
26 J. Xiang, X. Wen and F. Zhang, *Ind. Eng. Chem. Res.,* 2014, **53**, 15600.
27 C.S. Spanjers, J.T. Held and R.M. Rioux, *J Catal.*, 2014, **316**, 164.
28 D. Srimani, A. Mukherjee and D. Milstein, *Angew. Chem. Int. Ed.*, 2015, **127**, 1.
29 X. Chen, Y. Cui and W.-L. Dai, *Chem. Commun.*, 2015, **51**, 13776.
30 C. Lian, F. Ren and Y. Li, *Chem. Commun.*, 2015, **51**, 1252.
31 S. Cai, H. Duan and Y. Li, *ACS Catal.*, 2013, **3**, 608.
32 K. Möbus, E. Grünewald and P.W. Albers, *J Catal.*, 2014, **311**, 153.
33 R.V. Jagadeesh, A.-E. Surkus and M. Beller, *Science*, 2013, **342**, 1073.
34 Z. Rong, W. Du and L. Lu, *Chem. Commun.*, 2010, **46**, 1559.
35 D. Cantillo, M. Baghbanzadeh and C.O. Kappe, *Angew. Chem. Int. Ed.*, 2012, **51**, 10190.
36 A. Corma, P. Serna, *Science*, 2006, 313, 332.
37 F.A. Westerhaus, R.V. Jagadeesh and M. Beller, *Nat. Chem.*, 2013, **5**, 537.
38 L. Wang, B. Zhang and F.-S. Xiao, *ChemSusChem,* 2014, **7**, 1537.

View Article Online
DOI: 10.1039/C6RA18935K

Nitrogen-doped carbon supported iron oxide as efficient catalysts for chemoselective hydrogenation of nitroarenes.