available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Carbon film encapsulated Fe₂O₃: An efficient catalyst for hydrogenation of nitroarenes

Yingyu Wang^a, Juanjuan Shi^a, Zihao Zhang^b, Jie Fu^b, Xiuyang Lü^b, Zhaoyin Hou^{a,*}^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China^b Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China

ARTICLE INFO

Article history:

Received 2 August 2017

Accepted 17 September 2017

Published 5 November 2017

Keywords:

Carbon film

Encapsulation

Iron catalysis

Pyrolysis

Hydrogenation

Nitroarene

ABSTRACT

Iron catalysis has attracted a wealth of interdependent research for its abundance, low price, and nontoxicity. Herein, a convenient and stable iron oxide (Fe₂O₃)-based catalyst, in which active Fe₂O₃ nanoparticles (NPs) were embedded into carbon films, was prepared *via* the pyrolysis of iron-polyaniline complexes on carbon particles. The obtained catalyst shows a large surface area, uniform pore channel distribution, with the Fe₂O₃ NPs homogeneously dispersed across the hybrid material. Scanning electron microscopy, Raman spectroscopy and X-ray diffraction analyses of the catalyst prepared at 900 °C (Fe₂O₃@G-C-900) and an acid-pretreated commercial activated carbon confirmed that additional carbon materials formed on the pristine carbon particles. Observation of high-resolution transmission electron microscopy images also revealed that the Fe₂O₃ NPs in the hybrid were encapsulated by a thin carbon film. The Fe₂O₃@G-C-900 composite was highly active and stable for the direct selective hydrogenation of nitroarenes to anilines under mild conditions, where previously noble metals were required. The synthetic strategy and the structure of the iron oxide-based composite may lead to the advancement of cost-effective and sustainable industrial processes.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Iron (Fe) is one of the most abundant elements on earth (4.7%) and the sixth most abundant element in the universe [1], playing a crucial role in life reactivity, especially in the human body as a “king metal” [2,3]. Unsaturated ferrous sites that are confined within nano-sized matrices are active centers in a wide range of enzyme and homogeneous catalytic reactions [4]. Currently, important applications of heterogeneous iron-based catalysts include ammonia synthesis [5–7], the production of olefins (*via* Fischer-Tropsch synthesis) [8,9], selective catalytic

reduction of NO_x [10–12], and so on. Recently, iron catalysis has attracted significant attention for its abundance, low price, and nontoxicity. It was found that iron-based catalysts exhibited excellent performance for direct coupling of methane to ethylene [13], in oxygen-reduction reactions [14], and for selective hydrogenation of nitroarenes [15], where noble metals were previously required. Selective hydrogenation of nitroarenes is of great importance as the aniline products are important commodity chemicals in the production of methylene diphenyl diisocyanate (MDI), polyurethanes, dyes, and explosives [16–18]. Aniline production is > 4 M tons per annum using

^{*} Corresponding author. Tel/Fax: +86-571-88273283; E-mail: zyhou@zju.edu.cn

This work was supported by the National Natural Science Foundation of China (21473155, 21273198) and Natural Science Foundation of Zhejiang Province (LZ12B03001).

DOI: 10.1016/S1872-2067(17)62917-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 11, November 2017

Entry	Sample	Fe loading (wt%)	Raman analysis	
			I_D/I_G	I_{2D}/I_G
1	acid-pretreated XC-72R	—	0.91	—
2	Fe ₂ O ₃ @G-C-800	0.76	0.93	0.11
3	Fe ₂ O ₃ @G-C-900	0.93	0.93	0.14
4	Fe ₂ O ₃ @G-C-1000	1.6	0.97	0.11
5	Fe ₃ O ₄ @XC-72R	4.9	—	—
6	Fe ₃ O ₄ @MgO	4.5	—	—
7	Fe ₃ O ₄ @Al ₂ O ₃	1.9	—	—
8	Fe ₃ O ₄ @SiO ₂	3.5	—	—

Fig. 3. (a) N₂ sorption isotherms and (b, c) pore size distribution of Fe₂O₃@G-C-900 and acid-pretreated XC-72R.

with Cu K α radiation ($\lambda = 0.154$ nm). Raman spectra were collected on a Rhenishaw 2000 Confocal Raman Microprobe (Rhenishaw, Instruments, England) using a 514.5 nm argon laser. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA System. The X-ray source was provided by a Mg standard anode (1253.6 eV) at 12 kV and 300 W. Scanning electron microscopy (SEM) images were obtained using a Zeiss Sigma field emission SEM (Model 8100). Scanning transmission electron microscopy (STEM) was utilized to observe the image of individual particles at atomic resolution with an aberration corrected JEOL 2200FS (S)TEM operating at 200 kV, coupled to an X-ray energy dispersive spectrometer (EDS) to obtain spectra relating to compositional details from individual particles larger than 1–2 nm. The Brunauer-Emmett-Teller (BET) specific surface areas and textural properties of the samples were measured using a micromeritics ASAP 2020 HD88 analyzer.

2.3. Catalytic reactions

Hydrogenation reactions were performed in a 50 mL custom designed stainless steel autoclave with a Teflon inner layer. In a typical procedure, the catalyst was dispersed in 16.0 mL ethanol prior to contacting a desired quantity of substrate. The autoclave was sealed, purged with H₂, pressurized to 2.0 MPa, and subsequently stirred with a magnetic stirrer (MAG-NEO, RV-06M, Japan) at a rate of 1000 rpm at the desired temperature. After the reaction, the solid catalyst was separated by centrifugation and the products analyzed by gas chromatograph (GC, HP 5890, USA) with a 30 m capillary column (HP-5) using a flame ionization detector. All products were confirmed by GC-mass spectrometry (GC-MS, Agilent 6890-5973N). For

each successive use, the catalyst was washed with ethanol three times to remove the remaining products, followed by drying at 40 °C for 6.0 h.

3. Results and discussion

3.1. Characterizations

Nitrogen adsorption-desorption isotherms of Fe₂O₃@G-C-900 and acid-pretreated XC-72R are shown in Fig. 3(a). Both materials display type II patterns according to the International Union of Pure and Applied Chemistry (IUPAC) classification. The specific surface area of the acid-pretreated XC-72R material was 225.9 m²/g. For Fe₂O₃@G-C-900 the specific surface area increased dramatically to 573.7 m²/g (Table 2). The pore size distribution was calculated and is presented in Fig. 3(b) and Table 2. A uniform microporous channel distribution having a mean value of 0.52 nm was observed for Fe₂O₃@G-C-900, with a micropore volume of 0.22 cm³/g. The textural properties of Fe₂O₃@G-C-900 are several times higher than that of the acid-pretreated XC-72R material (0.08 cm³/g) (Table 2). At the same time, an auxiliary mesoporous channel having a mean value of 3.56 nm was also detected in Fe₂O₃@G-C-900 (Fig. 3(c)), which is thought to relate to the slit-shaped pores between the parallel layers [29]. The results infer that additional carbon materials formed during the pyrolysis of iron-polyaniline complexes on XC-72R particles.

Raman analysis found that D-bands (~1350 cm⁻¹, evidence of defects, such as disorders, edges and boundaries of carbon) and G-bands (~1580 cm⁻¹, the vibration of E_{2g} phonons of sp² C atoms) were detected in all samples (Fig. 4) [30–32]. However, the 2D-band (~2700 cm⁻¹, information on the number of layers

Table 2
Structure of Fe₂O₃@G-C hybrids.

Sample	Particle size of Fe ₂ O ₃ (nm)	Pore volume (cm ³ /g) (pore size < 2 nm)	Pore size (nm)		A _{BET} (m ² /g)
			Micro-	Meso-	
Fe ₂ O ₃ @G-C-800	—	0.128	—	—	316.3
Fe ₂ O ₃ @G-C-900	2.33	0.220	0.52	3.56	573.7
Fe ₂ O ₃ @G-C-1000	50.5	0.192	—	—	437.6
acid-pretreated XC-72R	—	0.080	0.67	—	225.9

Fig. 4. Raman spectra of (1) acid-pretreated XC-72R, (2) Fe_2O_3 @G-C-800, (3) Fe_2O_3 @G-C-900 and (4) Fe_2O_3 @G-C-1000.

of the carbon films) can only be observed in the Fe_2O_3 @G-C composites. The I_D/I_G ratios of the Fe_2O_3 @G-C composites were higher than that of acid-pretreated XC-72R, and Fe_2O_3 @G-C-900 possesses the lowest I_D/I_G value (0.93) and the highest I_{2D}/I_G value (0.14) among the hybrid materials (Table 1). The results indicate that the additional amorphous carbon materials formed, and the newly appeared carbon films in Fe_2O_3 @G-C-900, were highly dispersed over a few layers.

XRD diffraction patterns of the Fe_2O_3 @G-C composites, prepared as a function of pyrolysis temperature, and acid-pretreated XC-72R are shown in Fig. 5. Broad peaks between 17° – 30° and 40° – 50° in all samples were assigned to the diffraction of (002) and (100) planes of graphite, which could be as-

Fig. 5. XRD patterns of (1) acid-pretreated XC-72R, (2) Fe_2O_3 @G-C-800, (3) Fe_2O_3 @G-C-900 and (4) Fe_2O_3 @G-C-1000.

cribed to the formation and stacking of carbon films. Both diffraction peaks of Fe_2O_3 @G-C-900 were obscure, indicating that the newly formed carbon films were well-exfoliated, and complements well with the Raman analysis. It's worth noting that no characteristic peaks of Fe_2O_3 could be fitted, because of the fine dispersion and/or the low loading amount of Fe_2O_3 .

SEM and TEM analyses of Fe_2O_3 @G-C-900 and acid-pretreated XC-72R further confirmed that the additional carbon materials formed on the pristine carbon particles. Separated particles of pristine XC-72R, within a 40–70 nm size range, having a clear outline were observed by SEM (Fig. 6(a)) and TEM images (Fig. 6(b)). While mainly hierarchically lamellar structured composites were detected in Fe_2O_3 @G-C-900 (Fig. 6(c)), and the newly formed carbon films and the pristine XC-72R particles could be clearly identified in the corresponding TEM images (Fig. 6(d)). The average width of the solid lamellar layer in Fe_2O_3 @G-C-900 was 200–250 nm.

The newly formed carbon films and the highly dispersed Fe_2O_3 NPs could be clearly identified in the high-resolution TEM (HRTEM) images of Fe_2O_3 @G-C-900 (Fig. 7). The carbon films bring enhanced surface area together with additional auxiliary pore channels, corresponding to the results presented in Fig. 3(b) and Table 2. HRTEM images also disclosed that the Fe_2O_3 NPs in this hybrid catalyst were surrounded by a thin carbon film (marked by red arrows in the image, Fig. 7(c), (g)). The Fe_2O_3 NPs in Fe_2O_3 @G-C-900 are homogeneously distributed and are typically in the range of 2 ± 2 nm in diameter. Lattice fringes show distances of 0.27 and 0.37 nm that corresponding to the (104) and (012) planes of Fe_2O_3 particles (JCPDS 33-0664), respectively.

HRTEM images of Fe_2O_3 @G-C composites prepared at 800 and 1000 °C are presented in Fig. 7. It was observed that the particle size of Fe_2O_3 was sensitive to pyrolysis temperature. The degree of homogeneity of the Fe_2O_3 NP dispersion was

Fig. 6. (a) SEM and (b) TEM images of acid-pretreated XC-72R; (c) SEM and (d) TEM images of Fe_2O_3 @G-C-900.

Fig. 7. HRTEM images of (a, b, c) $\text{Fe}_2\text{O}_3@\text{G-C-900}$, (d, e) $\text{Fe}_2\text{O}_3@\text{G-C-800}$ and (f, g) $\text{Fe}_2\text{O}_3@\text{G-C-1000}$.

observed to a lesser extent for the $\text{Fe}_2\text{O}_3@\text{G-C-800}$ catalyst (shown in Fig. 7(d), (e)) when compared with $\text{Fe}_2\text{O}_3@\text{G-C-900}$. However, increasing the pyrolysis temperature to 1000 °C resulted in small NP sintering to yield large NPs, which are shielded by a thick carbon shell (Fig. 7(f), (g)).

XPS analysis revealed the presence of C, N, O and Fe in all $\text{Fe}_2\text{O}_3@\text{G-C}$ composites (Fig. 8(a)), and the surface composition is summarized in Table 3. It was found that C content increased as a function of increasing pyrolysis temperature, while the contents of N and O showed the reverse trend. It is also notable that the detected surface Fe content was relatively low (Table 3). Deconvolution of N 1s spectra (Fig. 8(b)) further disclosed formation relating to pyridinic N (398.6 eV), pyrrolic N (399.8 eV) and graphitic N (401.2 eV) in $\text{Fe}_2\text{O}_3@\text{G-C}$ composites [33–37]. The relative content of each N species is compared in Fig. 8(c). With the loss of unstable N at higher temperatures, the content of graphitic N increased while the content of pyridinic N decreased as a function of pyrolysis temperature. Pyridinic N can reduce the energy barrier for reactant adsorption on adjacent carbon atoms, and accelerate the rate-limiting first-electron transfer, which leads to a significant enhancement of catalytic activity of the carbon surface [38,39]. Furthermore, recent reported results also indicated that doping graphitic N into a graphene structure can lead to a non-uniformed electron distribution, especially when two graphitic N atoms are doped into the same hexagon, leading to a significant enhancement of catalytic activity of the carbon surface [37].

Accordingly, N in the carbon films herein not only brought imperfect and porous encapsulation, but also enhanced the catalytic activity of the carbon surface around the Fe_2O_3 core.

3.2. Catalytic performance and active site analysis

The catalytic performance of the $\text{Fe}_2\text{O}_3@\text{G-C}$ composites was first assessed by the selective hydrogenation of nitrobenzene (NB) to aniline (AN) as a model reaction. Table 4 summarizes the conversion of NB and the selectivity to AN over the $\text{Fe}_2\text{O}_3@\text{G-C}$ composites and compares with a series of Fe-based catalysts on traditional supports. The activity of the resulting catalyst increased as a function of pyrolysis temperature up to 900 °C, and the conversion of NB over $\text{Fe}_2\text{O}_3@\text{G-C-900}$ reached 95.4% with a 99.1% selectivity to AN. However, further raising the pyrolysis temperature to 1000 °C resulted in a decrease of the catalyst activity (Entry 3). When acid-pretreated XC-72R particles (Entry 4) and other commonly used supports, such as SiO_2 (Entry 5), Al_2O_3 (Entry 6) and MgO (Entry 7) were used as the support, the conversion of NB decreased sharply to 27.3%, 17.8%, 19.3% and 19.5%, respectively. Selectivity towards AN over these catalysts were lower than that over $\text{Fe}_2\text{O}_3@\text{G-C-900}$. Hence, the nature of the support plays a crucial role on the performance of Fe_2O_3 NPs for selective hydrogenation of NB. The excellent performance of $\text{Fe}_2\text{O}_3@\text{G-C-900}$ is thought to be attributed to its higher specific surface area, large pore volume (Fig. 3 and Table 2), highly dispersed Fe_2O_3 NPs (Fig. 7) and the

Fig. 8. XPS spectra of (a) elemental analysis in survey, and (b) N 1s; and (c) percentage of nitrogen species as a function of pyrolysis temperature for $\text{Fe}_2\text{O}_3@\text{G-C}$ composites.

Table 3

Surface composition of the synthesized $\text{Fe}_2\text{O}_3@\text{G-C}$ composites.^a

Sample	Relative atomic percentage (%)				Relative elemental percentage (%)		
	C	O	N	Fe	Pyridinic N	Pyrrolic N	Graphitic N
$\text{Fe}_2\text{O}_3@\text{G-C-800}$	86.49	10.95	2.47	0.09	30.3	38.7	31.0
$\text{Fe}_2\text{O}_3@\text{G-C-900}$	88.08	9.54	2.32	0.06	20.1	33.4	46.5
$\text{Fe}_2\text{O}_3@\text{G-C-1000}$	90.09	8.02	1.84	0.05	19.7	28.0	52.3

^a Derived from X-ray photoelectron spectroscopy analysis.

synergetic interaction between the Fe_2O_3 NPs and the protective carbon films (Fig. 7(c)) [40,41]. Furthermore, N atoms in the carbon matrix of the $\text{Fe}_2\text{O}_3@\text{G-C}$ composites can further increase the projected density of states near Fermi level and reduce the local work function theory [42–45].

The performance of recycled $\text{Fe}_2\text{O}_3@\text{G-C-900}$ is shown in Fig. 9. During the recycle experiments, the initial catalyst was separated from the reaction solution *via* centrifugation, washed with ethanol and dried without further addition. The catalyst mass loss after the recycle experiment (in the 5th recycle) was ~12%. It was observed that the conversion of NB decreased slightly from 95.4% to 80.2% (in the 5th recycle), while the selectivity to AN remained higher than 98%. These results indicate that $\text{Fe}_2\text{O}_3@\text{G-C-900}$ could be recycled without a detrimental decrease in its performance. The decreased conversion of NB is thought to be attributed to the mass loss of the recycled catalyst and/or the abrasion of catalyst particles being

subjected to a magnetic stirrer at 1000 rpm during experiments.

More importantly, the time-on-stream of NB hydrogenation over $\text{Fe}_2\text{O}_3@\text{G-C-900}$ (Fig. 10) disclosed that AN formed mainly *via* a direct route (Fig. 1) as the selectivity to AN remained higher than 95% across all conversion levels of NB. The intermediates in the direct routine, such as nitrosobenzene (NSB) and *N*-phenylhydroxylamine (PHA) were observed. However, no condensation by-products, such as AOB, AB or HAB, were detected. The results show an important conceptual change when compared with that of Ni-catalyzed hydrogenation of NB [21], in which it was popularly accepted that AN formation is

Table 4

Hydrogenation of nitrobenzene over different catalysts.^a

Entry	Sample	Conversion (%)	Selectivity (%)	
			AN	Others ^b
1	$\text{Fe}_2\text{O}_3@\text{G-C-800}$	76.4	93.1	6.9
2	$\text{Fe}_2\text{O}_3@\text{G-C-900}$	95.4	99.1	0.9
3	$\text{Fe}_2\text{O}_3@\text{G-C-1000}$	94.1	94.2	5.8
4	$\text{Fe}_3\text{O}_4@\text{XC-72R}$	27.3	87.2	12.8
5	$\text{Fe}_3\text{O}_4@\text{SiO}_2$	17.8	92.1	7.9
6	$\text{Fe}_3\text{O}_4@\text{Al}_2\text{O}_3$	19.3	83.2	16.8
7	$\text{Fe}_3\text{O}_4@\text{MgO}$	19.5	88.8	11.2

^a Reaction conditions: 0.98 mmol nitrobenzene in 16.0 mL ethanol, $n(\text{Fe}) = 10 \mu\text{mol}$, 70 °C, $p(\text{H}_2) = 2.0 \text{ MPa}$, 2.0 h.

^b Mainly intermediates.

Fig. 9. Recycle experiment over $\text{Fe}_2\text{O}_3@\text{G-C-900}$ catalyst. (1) Conversion of NB; (2) Selectivity to AN. Reaction conditions: 0.98 mmol nitrobenzene in 16.0 mL ethanol, initial $n(\text{Fe}) = 10 \mu\text{mol}$, 70 °C, $p(\text{H}_2) = 2.0 \text{ MPa}$, 2.0 h.

Fig. 10. Time-on-stream of NB hydrogenation over $\text{Fe}_2\text{O}_3@\text{G-C-900}$. (1) Conversion of NB; (2) Selectivity to AN; (3) Selectivity to NSB; (4) Selectivity to PHA. Reaction conditions: 0.98 mmol nitrobenzene in 16.0 mL ethanol, $n(\text{Fe}) = 10 \mu\text{mol}$, 70°C , $p(\text{H}_2) = 2.0 \text{ MPa}$.

only initiated when NB conversion exceed 90%, because NB was strongly adsorbed on the Ni surface. Therefore, a large amount of Raney Ni catalyst ($\text{Ni}/\text{NB} > 1/10$) was needed to accelerate the formation of AN in industrial production [21,46].

At the same time, the formation of high boiling point by-products (AOB, AB and HAB) on the Ni surface during the reaction process would bring about a series of problems, such as the separation issues, impurities in the final product and catalyst deactivation.

On the basis of the above results, hydrogenation of a series of nitroarenes were performed to demonstrate the versatility of the $\text{Fe}_2\text{O}_3@\text{G-C-900}$ catalyst (Table 5). It was observed that nitroarenes with *para*-substitutions (entries 1–5) proceeded easily compared with *meta*- (entries 6–9) and *ortho*-substituted substrates (entries 10–12). These results are attributed to the primary pore channel of $\text{Fe}_2\text{O}_3@\text{G-C-900}$ (0.52 nm) and the resulting steric effect prolonging the conversion of nitroarenes with *meta*- and *ortho*-substitutions. At the same time, the direct hydrogenation route of NB over $\text{Fe}_2\text{O}_3@\text{G-C-900}$ (Fig. 1 and Fig. 10) could also result from the presence of the microporous channels. Among these nitroarenes, the aryl nitro-containing electron-donating substituents, such as $-\text{CH}_3$ and $-\text{NH}_2$, appeared to be easier for hydrogenation. Conversely, the hydrogenation of chloronitrobenzene exhibited a relatively modest activity because of the electron-withdrawing effect of $-\text{Cl}$ or $-\text{Br}$.

Table 5

Transfer hydrogenation of various substrates over $\text{Fe}_2\text{O}_3@\text{G-C-900}$.^a

Entry	Substrate	Temp. ($^\circ\text{C}$)	Time (h)	Conv. (%)	Product	Yield (%)
1		70	3	100		96.8
2		70	6	100		95.4
3		70	6	98.5		97.7
4		70	7	100		96.1
5		70	7	99.2		98.5
6		70	9	99.6		94.1
7		70	10	100		95.2
8		70	10	99.4		96.5
9		70	10	96.2		96.2
10		70	11	99.5		95.9
11		70	12	99.6		94.1
12		70	16	100		94.7
13		70	17	96.4		95.5

^a Reaction conditions: 0.98 mmol nitroarenes in 16.0 mL ethanol, $n(\text{Fe}) = 10 \mu\text{mol}$, 70°C , $p(\text{H}_2) = 2.0 \text{ MPa}$.

4. Conclusions

An effective strategy was developed to embed Fe₂O₃ NPs into carbon films by means of precursor polymerization and *in situ* pyrolysis. The thin carbon films surrounding the iron oxide NPs can restrain the NPs from detachment, dissolution, migration, and aggregation during heat treatment at 900 °C, and enhance their catalytic activity in the hydrogenation of nitroarenes to anilines. This strategy could be easily extended to produce a wide range of other metal-based catalysts with extraordinary stability.

References

- [1] P. A. Frey, G. H. Reed, *ACS Chem. Biol.*, **2012**, 7, 1477–1481.
- [2] G. Papanikolaou, K. Pantopoulos, *Toxicol. Appl. Pharmacol.*, **2005**, 202, 199–211.
- [3] A. C. Rosenzweig, H. Brandstetter, D. A. Whittington, P. Nordlund, S. J. Lippard, C. A. Frederick, *Proteins: Struct., Funct., Genetics*, **1997**, 29, 141–152.
- [4] Q. Fu, W. X. Li, Y. X. Yao, H. Y. Liu, H. Y. Su, D. Ma, X. K. Gu, L. M. Chen, Z. Wang, H. Zhang, B. Wang, X. H. Bao, *Science*, **2010**, 328, 1141–1144.
- [5] R. Schlögl, *Angew. Chem. Int. Ed.*, **2003**, 42, 2004–2008.
- [6] T. Kandemir, M. E. Schuster, A. Senyshyn, M. Behrens, R. Schlögl, *Angew. Chem. Int. Ed.*, **2013**, 52, 12723–12726.
- [7] A. Vojvodic, A. J. Medford, F. Studt, F. Abild-Pedersen, T. S. Khan, T. Bligaard, J. K. Nørskov, *Chem. Phys. Lett.*, **2014**, 598, 108–112.
- [8] X. Q. Chen, D. H. Deng, X. L. Pan, X. H. Bao, *Chin. J. Catal.*, **2015**, 36, 1631–1637.
- [9] X. H. Gao, J. L. Zhang, N. Chen, Q. X. Ma, S. B. Fan, T. S. Zhao, N. Tsubaki, *Chin. J. Catal.*, **2016**, 37, 510–516.
- [10] Y. Xia, W. C. Zhan, Y. Guo, Y. L. Guo, G. Z. Lu, *Chin. J. Catal.*, **2016**, 37, 2069–2078.
- [11] X. B. Wang, S. G. Wu, W. X. Zou, S. H. Yu, K. T. Gui, L. Dong, *Chin. J. Catal.*, **2016**, 37, 1314–1323.
- [12] X. Y. Shi, H. He, L. J. Xie, *Chin. J. Catal.*, **2015**, 36, 649–656.
- [13] X. G. Guo, G. Z. Fang, G. Li, H. Ma, H. J. Fan, L. Yu, C. Ma, X. Wu, D. H. Deng, M. M. Wei, D. L. Tan, R. Si, S. Zhang, J. Q. Li, L. T. Sun, Z. C. Tang, X. L. Pan, X. H. Bao, *Science*, **2014**, 344, 616–619.
- [14] M. Lefevre, E. Proietti, F. Jaouen, J. P. Dodelet, *Science*, **2009**, 324, 71–74.
- [15] R. V. Jagadeesh, A. E. Surkus, H. Junge, M. M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schunemann, A. Brückner, M. Beller, *Science*, **2013**, 342, 1073–1076.
- [16] H. U. Blaser, *Science*, **2006**, 313, 312–313.
- [17] C. H. Li, Z. X. Yu, K. F. Yao, S. F. Ji, J. Liang, *J. Mol. Catal. A*, **2005**, 226, 101–105.
- [18] A. S. Travis, in: Z. Rappoport ed., *The Chemistry of Anilines*, John Wiley and Sons, Hoboken, **2007**, 715–782.
- [19] X. H. Yan, J. Q. Sun, Y. W. Wang, J. F. Yang, *J. Mol. Catal. A*, **2006**, 252, 17–22.
- [20] J. Xiong, J. X. Chen, J. Y. Zhang, *Catal. Commun.*, **2007**, 8, 345–350.
- [21] J. H. Wang, Z. L. Yuan, R. F. Nie, Z. Y. Hou, X. M. Zheng, *Ind. Eng. Chem. Res.*, **2010**, 49, 4664–4669.
- [22] B. J. Zuo, Y. Wang, Q. L. Wang, J. L. Zhang, N. Z. Wu, L. D. Peng, L. L. Gui, X. D. Wang, R. M. Wang, D. P. Yu, *J. Catal.*, **2004**, 222, 493–498.
- [23] R. F. Nie, J. H. Wang, L. N. Wang, Y. Qin, P. Chen, Z. Y. Hou, *Carbon*, **2012**, 50, 586–596.
- [24] A. Corma, P. Concepcion, P. Serna, *Angew. Chem. Int. Ed.*, **2007**, 46, 7266–7269.
- [25] V. Höller, D. Wegricht, I. Yuranov, L. Kiwi-Minsker, A. Renken, *Chem. Eng. Technol.*, **2000**, 23, 251–255.
- [26] A. Corma, P. Serna, *Science*, **2006**, 313, 332–334.
- [27] X. C. Meng, H. Y. Cheng, Y. Akiyama, Y. F. Hao, W. B. Qiao, Y. C. Yu, F. Y. Zhao, S. I. Fujita, M. Arai, *J. Catal.*, **2009**, 264, 1–10.
- [28] W. C. Du, S. X. Xia, R. F. Nie, Z. Y. Hou, *Ind. Eng. Chem. Res.*, **2014**, 53, 4589–4594.
- [29] R. F. Nie, J. J. Shi, W. C. Du, W. S. Ning, Z. Y. Hou, F. S. Xiao, *J. Mater. Chem. A*, **2013**, 1, 9037–9045.
- [30] X. Y. Zeng, C. H. You, L. M. Leng, D. Dang, X. C. Qiao, X. H. Li, Y. W. Li, S. J. Liao, R. R. Adzic, *J. Mater. Chem. A*, **2015**, 3, 11224–11231.
- [31] J. L. Chen, X. P. Yan, *J. Mater. Chem.*, **2010**, 20, 4328–4332.
- [32] J. J. Shi, M. S. Zhao, Y. Y. Wang, J. Fu, X. Y. Lu, Z. Y. Hou, *J. Mater. Chem. A*, **2016**, 4, 5842–5848.
- [33] Z. S. Wu, A. Winter, L. Chen, Y. Sun, A. Turchanin, X. L. Feng, K. Müllen, *Adv. Mater.*, **2012**, 24, 5130–5135.
- [34] P. Chen, T. Y. Xiao, Y. H. Qian, S. S. Li, S. H. Yu, *Adv. Mater.*, **2013**, 25, 3192–3196.
- [35] J. J. Shi, Y. Y. Wang, W. C. Du, Z. Y. Hou, *Carbon*, **2016**, 99, 330–337.
- [36] J. K. Hu, M. Noked, E. Gillette, F. D. Han, Z. Gui, C. S. Wang, S. B. Lee, *J. Mater. Chem. A*, **2015**, 3, 21501–21510.
- [37] M. L. Xiao, J. B. Zhu, L. G. Feng, C. P. Liu, W. Xing, *Adv. Mater.*, **2015**, 27, 2521–2527.
- [38] Q. G. He, Q. Li, S. Khene, X. M. Ren, F. E. López-Suárez, D. Lozano-Castelló, A. Bueno-López, G. Wu, *J. Phys. Chem. C*, **2013**, 117, 8697–8707.
- [39] G. Wu, K. L. More, P. Xu, H. L. Wang, M. Ferrandon, A. J. Kropf, D. J. Myers, S. G. Ma, C. M. Johnston, P. Zelenay, *Chem. Commun.*, **2013**, 49, 3291–3293.

Graphical Abstract

Chin. J. Catal., 2017, 38: 1909–1917 doi: 10.1016/S1872-2067(17)62917-6

Carbon film encapsulated Fe₂O₃: An efficient catalyst for hydrogenation of nitroarenes

Yingyu Wang, Juanjuan Shi, Zihao Zhang, Jie Fu, Xiuyang Lü, Zhaoyin Hou*
Zhejiang University

Carbon film encapsulated Fe₂O₃ nanoparticles embedded in plate carbon (Fe₂O₃@G-C) were prepared *via in situ* pyrolysis. Fe₂O₃@G-C prepared at 900 °C was highly active and stable for the direct selective hydrogenation of nitroarenes to anilines.

- [40] R. V. Jagadeesh, K. Natte, H. Junge, M. Beller, *ACS Catal.*, **2015**, 5, 1526–1529.
- [41] D. F. Su, J. Wang, H. Y. Jin, Y. T. Gong, M. M. Li, Z. F. Pang, Y. Wang, *J. Mater. Chem. A*, **2015**, 3, 11756–11761.
- [42] Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum, Q. F. Li, *Angew. Chem. Int. Ed.*, **2014**, 53, 3675–3679.
- [43] D. H. Deng, L. Yu, X. Q. Chen, G. X. Wang, L. Jin, X. L. Pan, J. Deng, G. Q. Sun, X. H. Bao, *Angew. Chem. Int. Ed.*, **2013**, 52, 371–375.
- [44] J. P. Paraknowitsch, A. Thomas, M. Antonietti, *J. Mater. Chem.*, **2010**, 20, 6746–6758.
- [45] P. F. Zhang, Y. T. Gong, H. R. Li, Z. R. Chen, Y. Wang, *Nat. Commun.*, **2013**, 4, 1593.
- [46] H. D. Burge, D. J. Collins, B. H. Davis, *Ind. Eng. Chem. Prod. Res. Dev.*, **1980**, 19, 389–391.

碳膜包覆的氧化铁纳米颗粒：一种高效的芳硝基化合物加氢催化剂

王莹钰^a, 石娟娟^a, 张子豪^b, 傅 杰^b, 吕秀阳^b, 侯昭胤^{a,*}

^a浙江大学化学系, 生物质化工教育部重点实验室, 浙江杭州310028

^b浙江大学化学与生物工程学院, 浙江杭州310027

摘要: 铁是地球上最丰富的元素之一, 它在生命反应中起到至关重要的作用. 目前, 铁基催化剂广泛应用于合成氨、费托合成、 NO_x 的选择性催化还原等. 最近, 铁因其含量丰富、价格低廉、无毒等优势而在多相催化方面引起了重点关注. 最新研究发现, 铁基催化剂在甲烷直接偶联制乙烯、氧还原以及芳硝基化合物的选择性加氢等领域具有突出表现, 其中芳硝基化合物选择性加氢是一类具有重要应用前景的反应, 这是因为苯胺(AN)是一种重要的精细化学品和有机中间体, 广泛用于医药、染料、农药等行业, 苯胺的年产量超过了400万吨, 目前使用的催化剂主要有Raney Ni、负载镍、Ru/SnO₂及少量铂碳、钯碳催化剂. 但是, 在Ni基催化剂上, 硝基苯加氢主要经过间接缩合途径, 同时会伴有氧化偶氮苯(AOB)、偶氮苯(AB)和氢化偶氮苯(HAB)等副产物生成, 这些高沸点的副产物会带来一系列问题, 如产物分离困难、产品纯度较低以及催化剂失活等. 在这种情况下, 为了加速苯胺生成, 工业上一般采用过量的Raney Ni催化剂. 贵金属(如Pt, Pd和Ru等)对催化芳硝基化合物加氢具有极高的活性, 且苯胺的生成主要经过直接加氢途径. 然而, 由于成本过高, 贵金属催化剂的大规模应用还存在一定的困难.

本文采用简易的方法制备了一种铁基催化剂, 在这个催化剂中氧化铁纳米颗粒被碳膜包覆并嵌入至平板碳中($\text{Fe}_2\text{O}_3@\text{G-C}$). 该催化剂由活性炭、苯胺及醋酸亚铁热解所得. 通过扫描电镜(SEM)、拉曼光谱(Raman)及X射线衍射(XRD)分析, 我们证实原始碳颗粒上形成了新的碳膜. 同时高倍透射电镜图也清楚地揭示了氧化铁纳米颗粒被碳膜包覆的结构. 实验发现, $\text{Fe}_2\text{O}_3@\text{G-C-900}$ 催化剂(900 °C热解所得)在芳硝基化合物选择性加氢反应中具有很高的活性. 在2 MPa H_2 , 70 °C条件下反应2 h, 硝基苯(NB)转化率达到95.4%, 苯胺选择性达到99.1%, 远远高于其他载体(活性炭、 SiO_2 、 Al_2O_3 和 MgO)负载的铁基催化剂. 表征结果发现, $\text{Fe}_2\text{O}_3@\text{G-C-900}$ 催化剂的高活性可能与其具有较大的比表面积(573.7 m^2/g)、孔体积(0.22 cm^3/g , 孔径小于2 nm)、高度分散的氧化铁纳米颗粒以及氧化铁纳米颗粒和其表面碳膜的协同作用密切相关. 此外, 催化剂中引入的氮原子不仅可以在包覆的碳膜上形成缺陷, 也能进一步增强包覆在氧化铁纳米颗粒表面的碳膜的催化活性. 通过对 $\text{Fe}_2\text{O}_3@\text{G-C-900}$ 催化剂在硝基苯加氢反应中的循环使用活性的考察, 发现该催化剂在循环使用5次后, 仍具有良好的活性. 更重要的是, 在 $\text{Fe}_2\text{O}_3@\text{G-C-900}$ 催化剂上硝基苯的加氢主要是直接途径, 反应中没有高沸点AOB, AB和HAB等副产物生成.

鉴于 $\text{Fe}_2\text{O}_3@\text{G-C-900}$ 催化剂对NB加氢具有优异的活性, 我们还进行了一系列含有不同取代基团的芳硝基化合物的加氢实验, 发现对位取代的底物相对于间位及邻位的底物更容易发生加氢还原反应, 这应归因于该催化剂的孔径较小(0.52 nm). 这些研究方法可以扩展至其他金属催化剂的制备, 以促进高效益和可持续的工业生产的发展.

关键词: 碳膜; 封装; 铁催化; 热解; 加氢; 芳硝基化合物

收稿日期: 2017-08-02. 接受日期: 2017-09-17. 出版日期: 2017-11-05.

*通讯联系人. 电话/传真: (0571)88273283; 电子信箱: zyhou@zju.edu.cn

基金来源: 国家自然科学基金(21473155, 21273198); 浙江省自然科学基金(LZ12B03001).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).