Chinese Chemical Letters 24 (2013) 539–541

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

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

Original article

# Magnetic graphene nanocomposite as an efficient catalyst for hydrogenation of nitroarenes

Cheng Feng, Hai-Yan Zhang, Ning-Zhao Shang, Shu-Tao Gao, Chun Wang *

*College of Sciences, Agricultural University of Hebei, Baoding 071001, China*

ARTICLE INFO

*Article history:*
Received 21 January 2013
Received in revised form 12 February 2013
Accepted 27 February 2013
Available online 19 April 2013

*Keywords:*
Nitroarenes
Magnetic graphene
Reduction
Hydrazine hydrate

ABSTRACT

Graphene-$Fe_3O_4$ nanocomposite (G-$Fe_3O_4$) was synthesized by a chemical co-precipitation method which was used as an efficient catalyst for the reduction of nitroarenes with hydrazine hydrate. The method has been applied to a broad range of compounds with different properties and the yields were in the range of 75%–92%. The G-$Fe_3O_4$ catalyst can be readily recovered and reused 5 times without significant loss of the catalytic activity.

## 1. Introduction

Aromatic amines are central intermediates and key precursors in the synthesis of dyes, pigments, agrochemicals and pharmaceuticals [1,2]. The usual methods for preparation aromatic amines are reduction using Raney-nickel [2], which is combustible in air after the use. Pd-carbon [3], or Pt-Ni [4] are used frequently, but these precious metal complexes are expensive. The use of metals such as Fe or Zn powder in acidic media for the reduction of aromatic nitro compounds is also widely used [5,6]. However, the main drawback of all these methods is the lack of selectivity.

Among other nitro reducing agents, hydrazine hydrate has been applied successfully [1,7]. This method has following advantages: mild reaction conditions, simple post-reaction treatments, environment-friendly [8]. The catalysts employed in hydrazine hydrate reduction including iron-compound [9,10], mixed metal compounds [4,11] and zeolite [7] have been reported.

Graphene (G) is a type of novel and interesting carbon material and has caused wide attention in recent years [12]. The properties of graphene such as high thermal, chemical, and mechanical stability as well as high surface area also represent desirable characteristics as 2D support layers for metallic and bimetallic nanoparticles in heterogeneous catalysis applications [13]. In recent years, nanoscale magnetic catalysts have shown great potentials in catalysis because of their high dispersion, high reactivity and magnetic to easy phase separation [14,15]. Catalysts supported on magnetic nanoparticles can be quickly and easily recovered in the presence of external magnetic field for reuse.

The preparation of graphene-based magnetic nanocomposite has been reported recently [16]. However, to the best of our knowledge, there has been no report yet about the use of G-based magnetic nanocomposite as the catalyst for organic synthesis.

In continuation of our interest in exploring efficient catalysts for organic transformations [17], in this work, a superparamagnetic graphene-$Fe_3O_4$ nanocomposite (G-$Fe_3O_4$) was synthesized by a co-precipitation method and its catalytic activity was evaluated for the reduction of aromatic nitro compounds for the first time with hydrazine hydrate as a hydrogen donor.

## 2. Experimental

Graphite powder (320 mesh) and hydrazine hydrate (80%) were provided by the Bohaixin Co., Ltd. (Baoding, China). Nitroaromatic substrates were purchased from Aladdin Reagent Company. The size and morphology of the magnetic nanoparticles were measured by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at 200 kV The Fe content was determined by means of visible spectrophotometry with *o*-phenanthroline. Graphene and magnetic graphene nanoparticles (G-$Fe_3O_4$) were synthesized and characterized according to the method reported in our previous work [18]. $Fe_3O_4$ was synthesized by the same method for the preparation of G-$Fe_3O_4$ without adding graphene.

The nitroarenes were reduced with hydrazine hydrate catalyzed by G-$Fe_3O_4$. Typically, 2.0 mmol of nitroarene, 0.01 g of G-$Fe_3O_4$ and 4.0 mmol of 80% hydrazine hydrate were added sequentially into a 50 mL round-bottom flask. The mixture was

---

* Corresponding author.
*E-mail address:* wangc69@yahoo.com.cn (C. Wang).

1001-8417/$ – see front matter © 2013 Chun Wang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
http://dx.doi.org/10.1016/j.cclet.2013.03.036

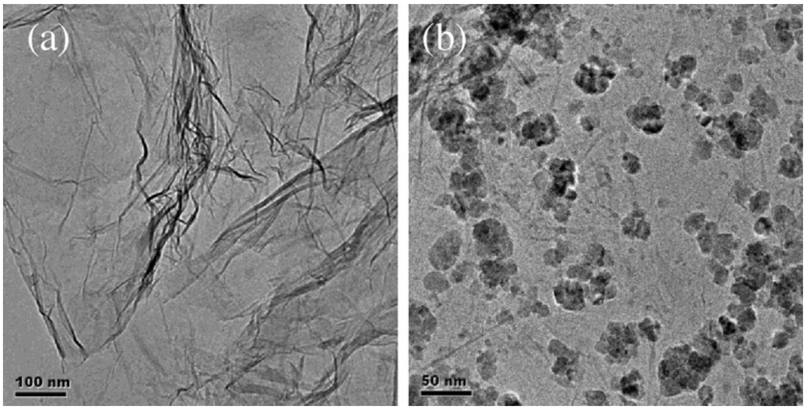


**Fig. 1.** TEM image of graphene (a) and G-$Fe_3O_4$ composite (b).

stirred at 70 °C for an appropriate time depending upon the nature of the substrate. Upon completion of the reaction (monitored by TLC), 5 mL of ethanol was added and a homogeneous solution was obtained. The mixture was cooled to room temperature and the catalyst was separated by a magnet for recycling tests. The reaction mixture was concentrated under reduced pressure. The residue was subjected to silica-gel column chromatography using petroleum ether-ethyl acetate as an eluent to give pure product.

## 3. Results and discussion

The morphology of the G and G-$Fe_3O_4$ was determined by TEM. As shown in Fig. 1(a), G consisted of randomly aggregated and crumpled sheets to form a disordered solid. It was clear that these graphenes were essentially transparent and no large graphitic crystallites were observed. Fig. 1(b) shows that iron oxide nanoparticles were successfully coated on the surface of the G to form a G-$Fe_3O_4$ nanocomposite and the size of $Fe_3O_4$ particles ranged from 25 nm to 50 nm.

The catalytic activity of G-$Fe_3O_4$ was evaluated by the reduction of aromatic nitro compounds with hydrazine hydrate. In our initial study, nitrobenzene was chosen as the model reactant in order to examine the efficiency of different catalysts (*i.e.* graphene, $Fe_3O_4$ and G-$Fe_3O_4$). As shown in Table 1, no product was obtained in the absence of the catalyst (Table 1, entry 1), indicating that the catalyst was necessary for the reaction. Among the catalysts tested, G-$Fe_3O_4$ was found to be the most effective catalyst since it gave the highest yield of product (Table 1, entry 5). Similar but lower yields were obtained when using graphene, $Fe_3O_4$ or their hybrid as the catalyst. The results indicated that the graphene [13] and $Fe_3O_4$ both were catalytically active for this reaction. From Fig. 1, one can observe that the $Fe_3O_4$ was distributed on the graphene sheets with an average size of 25–50 nm. This shows that the active sites of the catalyst were stabilized and dispersed on graphene and there may have a synergistic effect [19] on the catalytic activity of G-$Fe_3O_4$. Thus, it seemed to us that the graphene played an important role in this more efficient catalyst.

**Table 1**
Reduction of nitrobenzene with different catalysts.[a]

| Entry | Catalyst | Time (min) | Isolated yield (%)[b] |
|---|---|---|---|
| 1 | – | 90 | 0.0 |
| 2 | Graphene | 90 | 85.9 |
| 3 | $Fe_3O_4$ | 90 | 84.9 |
| 4 | G+$Fe_3O_4$ (1:1 wt) | 90 | 87.7 |
| 5 | G-$Fe_3O_4$ | 90 | 93.6 |

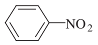
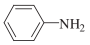
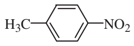
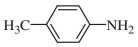
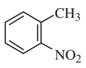
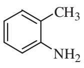
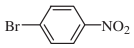
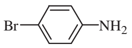
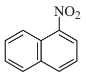
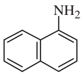
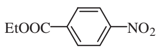
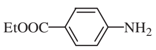
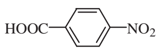
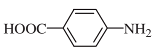
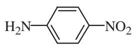
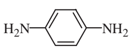
[a] Reaction condition: molar ratio of nitrobenzene to hydrazine hydrate is 1:2, amount of catalyst is 5%, reaction temperature is 70 °C.

[b] The products were identified by IR and $^1H$ NMR.

To demonstrate the generality of this model reaction, the reduction of a series of aromatic nitro compounds was studied under the optimized reaction conditions. As shown in Table 2, aromatic nitro compounds containing various electron-donating or electron-withdrawing groups were converted to the corresponding amines in good yields. In all cases, amines were found to be the only product of the reactions and the usual side products of nitro reduction were not observed in the final product mixtures. The present method was highly chemoselective in the presence of sensitive functional groups such as halogens and –COOH. In some cases, the catalytic activity was significantly influenced by the position of the substituents on the aromatic ring. For example, the presence of a methyl group *ortho* to the nitro group required a longer reaction time than the *para*-analogs due to steric effects.

The reusability and recycling of the G-$Fe_3O_4$ were also investigated under the same condition, except that amount of catalyst was reduced to 1%. At the end of the reduction, the catalyst was separated by a magnet, washed with ethanol, dried at 100 °C for 1 h and reused for the next reaction. The catalytic activity of the G-$Fe_3O_4$ did not show significant decrease even after five runs. The ferrum content in fresh G-$Fe_3O_4$ and used G-$Fe_3O_4$ (five times)

**Table 2**
Reduction of nitroarenes by hydrazine hydrate in the presence of G-$Fe_3O_4$.[a]

| Entry | Nitro compound | Product | T (°C) | Time (min) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 |  |  | 70 | 20 | 88.4 |
| 2 |  |  | 70 | 85 | 89.0 |
| 3 |  |  | 70 | 360 | 83.9 |
| 4 |  |  | 70 | 80 | 90.5 |
| 5 |  |  | 70 | 255 | 91.9 |
| 6 |  |  | Reflux | 240 | 91.4 |
| 7 |  |  | Reflux | 300 | 90.5 |
| 8 |  |  | Reflux | 300 | 82.4 |

[a] Reaction condition: molar ratio of nitroarenes to hydrazine hydrate is 1:2, amount of catalyst is 5%.

[b] The products were characterized by IR and $^1H$ NMR.

were determined by means of visible spectrophotometry to be 36.1 wt% and 35.9 wt%, respectively, indicating that the Fe in the catalyst exhibited very low leaching during the reaction.

## 4. Conclusion

In conclusion, an efficient, inexpensive and recyclable G-$Fe_3O_4$ catalyst was synthesized by a co-precipitation method. G-$Fe_3O_4$ was used as an efficient catalyst for the reduction of nitroarenes with hydrazine hydrate. The catalyst can also be reused without an observable loss of activity. We believe that this method is an important addition to the known procedures for the reduction of aromatic nitro compounds on both lab and larger scales.

## Acknowledgments

This work was financially supported by the Natural Science Foundation of Hebei Province (No. B2011204051) and the Natural Science Foundation of Agricultural University of Hebei (No. LG201107).

## References

[1] G.A. Heropoulos, S. Georgakopoulos, B.R. Steele, High intensity ultrasound-assisted reduction of sterically demanding nitroaromatics, Tetrahedron Lett. 46 (2005) 2469–2473.

[2] I. Pogorelić, M. Filipan-Litvić, S. Merkaš, Efficient and selective reduction of aromatic nitrocompounds with sodium borohydride and Raney nickel, J. Mol. Catal. A: Chem. 274 (2007) 202–207.

[3] M. Lakshmi Kantam, T. Bandyopadhyay, A. Rahman, N. Mahender Reddy, B.M. Choudary, Reduction of nitroaromatics with a new heterogenised MCM–silylamine palladium (II) catalyst, J. Mol. Catal. A: Chem. 133 (1998) 293–295.

[4] S. Kumar Ghosh, M. Mandal, S. Kundu, S. Nath, T. Pal, Bimetallic Pt–Ni nanoparticles can catalyze reduction of aromatic nitrocompounds by sodium borohydride in aqueous solution, Appl. Catal. A 268 (2004) 61–66.

[5] L. Pehlivan, E. Métay, S. Laval, et al., Iron-catalyzed selective reduction of nitro compounds to amines, Tetrahedron Lett. 51 (2010) 1939–1941.

[6] F.A. Khan, J. Dash, C. Sudheer, R.K. Gupta, Chemoselective reduction of aromatic nitro and azo compounds in ionic liquids using zinc and ammonium salts, Tetrahedron Lett. 44 (2003) 7783–7787.

[7] M. Kumarraja, K. Pitchumani, Simple and efficient reduction of nitroarenes by hydrazine in faujasite zeolites, Appl. Catal. A 265 (2004) 135–139.

[8] S.R. Boothroyd, M.A. Kerr, A mild and efficient method for the preparation of anilines from nitroarenes, Tetrahedron Lett. 36 (1995) 2411–2414.

[9] S. Farhadi, F. Siadatnasab, Perovskite-type $LaFeO_3$ nanoparticles prepared by thermal decomposition of the $La[Fe(CN)_6]\cdot 5H_2O$ complex: a new reusable catalyst for rapid and efficient reduction of aromatic nitro compounds to arylamines with propan-2-ol under microwave irradiation, J. Mol. Catal. A: Chem. 339 (2011) 108–116.

[10] S.K. Mohapatra, S.U. Sonavane, R.V. Jayaram, P. Selvam, Reductive cleavage of azo dyes and reduction of nitroarenes over trivalent iron incorporated hexagonal mesoporous aluminophosphate molecular sieves, Appl. Catal. B 46 (2003) 155–163.

[11] F. Cárdenas-Lizanaa, Z.M. de Pedrob, S. Gómez-Queroa, M.A. Keanea, Gas phase hydrogenation of nitroarenes: a comparison of the catalytic action of titania supported gold and silver, J. Mol. Catal. A: Chem. 326 (2010) 48–54.

[12] A.K. Geim, K.S. Novoselov, The rise of grapheme, Nat. Mater. 6 (2007) 183–191.

[13] Y.J. Gao, D. Ma, C.L. Wang, J. Guan, X.H. Bao, Reduced graphene oxide as a catalyst for hydrogenation of nitrobenzene at room temperature, Chem. Commun. 47 (2011) 2432–2434.

[14] S. Shylesh, V. Schunemann, W.R. Thiel, Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis, Angew. Chem. Int. Ed. 49 (2010) 3428–3459.

[15] A.H. Lu, E.L. Salabas, F. Schuth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed. 46 (2007) 1222–1244.

[16] X.P. Shen, J.L. Wu, S. Bai, H. Zhou, One-pot solvothermal syntheses and magnetic properties of graphene-based magnetic nanocomposites, J. Alloys Compd. 506 (2010) 136–140.

[17] J.J. Ma, X. Zhou, X.H. Zang, C. Wang, Z. Wang, A green and efficient synthesis of 9-aryl-3,4,5,6,7,9-hexahydroxanthene-1,8-dione using a task-specific ionic liquid as dual catalyst and solvent, Aust. J. Chem. 60 (2007) 146–148.

[18] C. Wang, C. Feng, Y.J. Gao, et al., Preparation of a graphene-based magnetic nanocomposite for the removal of an organic dye from aqueous solution, Chem. Eng. J. 173 (2011) 92–97.

[19] N.R. Khalid, Z.K. Hong, E. Ahmed, Y.W. Zhang, C.N. He, Synergistic effects of Fe and graphene on photocatalytic activity enhancement of $TiO_2$ under visible light, Appl. Surf. Sci. 258 (2012) 5827–5834.