

A chemoselective and green reduction of nitro arenes to aromatic amines with FeSO_4 , NaBH_4 , $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in water at room temperature

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Abstract

A new efficient and practical method for the room-temperature reduction of aromatic nitro compounds employing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaBH_4 , $\text{H}_3\text{PW}_{12}\text{O}_{40}$ system in H_2O under mild conditions is reported. The method is simple, inexpensive, easily scaled-up and applicable for the large scale preparation of different substituted anilines.

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1. Introduction

Aromatic amines, widely used as important intermediates in the synthesis of chemicals such as dyes, antioxidants, photographic, pharmaceutical and agricultural chemicals, can be obtained easily

by the reduction of corresponding aromatic nitro compounds using catalytic hydrogenation [1] and a variety of other reduction conditions. Many reducing agents have been recommended for this transformation and the most classic and practical reductants are zinc, tin or iron in the presence of an

acid [2]. Other reagents such as Cu nano particles/ HCO_2NH_4 [3], Pt and Pd nanoparticles/Carbon nanofibers [4], gold nanoparticles supported [5], nanostructured platinum catalyst [6], Pt-Ne bimetallic nanoparticles [7], Ni-Fe mixed oxide [8], Ni/ SiO_2 [9], Au/ Al_2O_3 [10], NiCo_2O_4 [11], metallic iron/ $\text{CO}_2\text{-H}_2\text{O}$ [12], NaBH_4 /Raney Nickel [13], polymer-Supported hydrazine hydrate/iron oxide hydroxide [14], activated iron [15], $\text{Pd}(\text{OH})_2$, KF, polymethyl hydrosiloxane [16], nanosized $\gamma\text{-Fe}_2\text{O}_3$, KOH, Me_2CHOH [17], silver nanoshell-coated polystyrene beads [18], MCM41-silylamine palladium(II) [19], Pd complex [20], Au/ SiO_2 [21], nanosized Ni [22], Au, Pt/MCM41 [23], Au/ Al_2O_3 [24], nanosized NiCoB [25], zero-valent iron powder [26], Au/ ZrO_2 , EtOH [27], $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ [28], Ni-MCM41 [29], $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}/\text{Fe}_x\text{O}_y$ [30], N_2H_4 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{MW}$ [31], N_2H_4 , $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ [32], FeCl_3/Zn [33], FeS, NH_4Cl [34], have also been used. However the selective reduction of a nitro group in the presence of other reducible functionalities in a molecule is a challenging task. In addition reduction of aromatic nitro compounds often stops at an intermediate stage, producing hydroxylamines, hydrazines and azoarenes as side products [35].

In recent years, nanoparticles have received increasing attention since such materials exhibit many fascinating chemical and physical characteristics and potential technological applications [36]. As part of a wider work in the reduction of different organic functionalities, and prompted by the known ability of iron in promoting the reduction of aromatic nitro groups, we decided to evaluate our active-iron-based reducing system in performing that transformation. A number of different synthetic routes have been developed to prepare iron nanoparticles. In this study iron nanoparticles were synthesized by

adding aqueous solution of NaBH_4 to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

In continuation of our previously reported catalytic properties of heteropolyacids (HPAs) [37-40] we wish to report herein our results on a reduction methodology of nitro aromatics. A facile and selective preparation of aromatic amines under mild reaction conditions, using nanoscale Fe particles generated in a simple and economic way from commercially available $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaBH_4 in presence of a catalytic amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ provide.

2. Experimental

In a typical experiment to a mixture of 1 mmol nitro aromatic compound, 3 mmol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 87mg $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.03mmol) in 4 ml H_2O were added 6 mmol NaBH_4 and stirred for the time indicated in Table 1. After compilation of the reduction (monitored by TLC) the reaction mixture was filtered and washed with EtOH and extracted with diethyl ether (2×10 mL). The combined organics layers were concentrated under vacuum and the crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1) to afford pure products.

3. Results and Discussion

3.1. Physico-chemical characterization

Fe nanoparticles were prepared in situ from iron sulfate by reduction with NaBH_4 in water. The identity of iron nanoparticles was established by TEM, XRD and BET studies. The TEM micrograph of the iron nanoparticles is shown in Fig.1 (10-20 nm). The structure of Fe nanoparticles was determined by powder X-ray diffraction (Fig.

2). From Fig. 2, it was observed that the XRD pattern of Fe nanoparticles sample shows no crystalline structure. BET specific surface area of the synthesized iron nanoparticles is $42 \text{ m}^2/\text{g}$ in comparison a commercially available Fe powder ($<10 \mu\text{m}$) has a specific surface area Just $0.9 \text{ m}^2/\text{g}$.

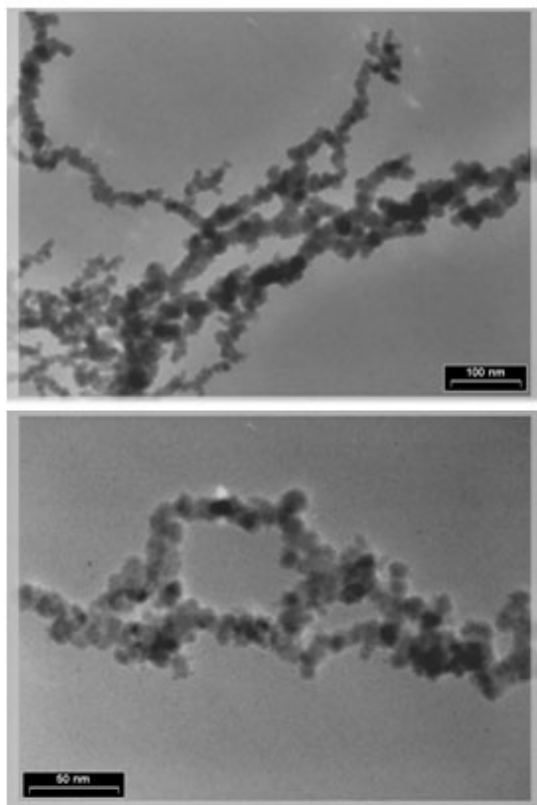


Fig.1. TEM images of Iron nanoparticles.

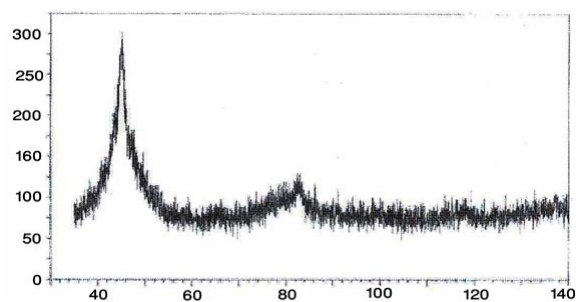


Fig. 2. XRD pattern of nano-Fe particles.

3.2. Reduction of Nitro Arenes to Aromatic Amines in the presence of catalytic amounts of polyoxometalate and Fe nanoparticles

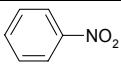
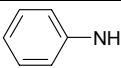
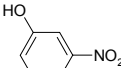
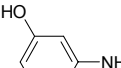
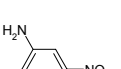
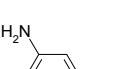

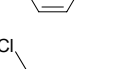
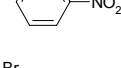
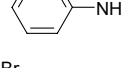
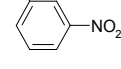
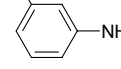
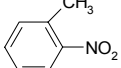
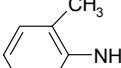
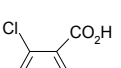
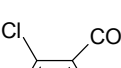
Table 1 shows the conditions and results for the reduction of different functionalized aromatic nitro compounds. It can be seen that chloro and bromonitrobenzene were cleanly reduced to the corresponding anilines in excellent yield without any dehalogenation, which was often encountered with several procedures such as hydrogenation (entries 4, 5).

The reducing systems were also efficient in the reduction of aromatic nitro compounds bearing additional substituents that is the case of o-nitrotoluene (entry 6), m-nitroaniline (entry 3) and m-nitrophenol ((entry 2) all of which were reduced to the amines in excellent yields. The carboxylic acid and ketocarbonyl, functionalities present in the aromatic ring also remained unaffected during reduction of the corresponding nitrobenzenes by this procedure (entries 7, 8).

In the case of p-nitroacetophenone (Table 1, entry 8) the reduction-dehydration of some extent of the carbonyl group in the starting material was observed by Gc-Mass yielding Ca. 8% of p-aminostyrens as by-product. The reaction with a vinylic nitro compound (β -nitrostyrene) and p-nitrobenzaldehyde were messy, giving a mixture of several unidentified compounds. Blank experiments, using nitrobenzene as test compound demonstrated the necessity of using the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaBH_4 (Table 2, entry 3).

The reaction was also not very effective with nano-scale Fe particles without $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Table 2, entries 1, 2). We have also studied the above mentioned reaction in the presence of HClconc instead of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Table2, entries 3).

Table 1. Chemoselective reduction of nitro compounds to corresponding amines.

Entry	Substrate	Time (h)	Product	Yields (%) ^{b,c}
1		0.5(2) ^d		100 (10) ^d
2		2		98
3		2.5		97
4		3		99
5		4		97
6		4		100
7		2.5		99
8		1.75		92

^aReaction condition: Aromatic nitro (1mmol), FeSO₄. 7H₂O (3 mmol), NaBH₄ (6 mmol), 87 mg H₃PW₁₂O₄₀ (0.03mmol), H₂O (4 ml), r.t. ^bAll the products were characterized by comparison of their ¹H NMR, ¹³C NMR and IR with those of authentic samples. ^cIsolated yield. ^dReaction condition: Aromatic nitro (1mmol), Fe powder (3 mmol), NaBH₄ (6 mmol), 87mg H₃PW₁₂O₄₀(0.03mmol), H₂O (4 ml), r.t.

Although HCl was active for this reaction, the yield was insignificant as compared to that with the HPA catalyst. Thus a combination of Fe nanoparticles and H₃PW₁₂O₄₀ is essential to carry out the reduction. To check efficiency of Fe nanoparticles for this reaction a comparison of results of representative reaction by metallic Fe powder is present in Table 1 (entry 1d).

Table 2. Optimaization of the reaction conditions for the reduction of nitrobenzene.

Entry	FeSO ₄ .7H ₂ O (mmol)	NaBH ₄	H ₃ PW ₁₂ O ₄₀ (mg)	Time (min)	Yield (%)
1	-	6	87	60	-
2	3	6	-	60	20
3	3	6	- ^b	60	25
4	3	-	87	60	-
5	3	6	87	30	100

^a Reagent and reaction conditions: nitrobenzene (1 mmol), H₂O (4ml). room temperature. ^b Reaction condition: Aromatic nitro (1mmol), FeSO₄. 7H₂O (3 mmol), NaBH₄ (6 mmol), HClconc(0.146 g), H₂O (4 ml), r.t.

It is worth noting that we have not detected the formation of nitroso and hydroxyl amines as intermediates with all of the substrates tested. Probably due to their fast conversion to the corresponding aniline derivatives in the reaction medium. A more detailed study about the role of the HPA and the reaction mechanism is in progress in our laboratory.

4. Conclusions

In conclusion the present procedure using iron nanoparticles in the presence of H₃PW₁₂O₄₀ provides a very simple and efficient methodology for highly chemoselective reduction of aromatic nitro compounds. Additionally other merits of our catalytic systems are as follows: (1) this catalyst can be in situ easily prepared and is low-cost, (2) the mild reaction conditions, (3) the catalytic systems is environmentally friendly, using water as solvent without remnants of chemicals, (4) high conversion and selectivity can be obtained almost without by-products, (5) sensitive functional group such as OH, Cl, Br, CO₂H, and COCH₃ remain unaffected in the reaction conditions.

Acknowledgements

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References

- [1] A. M. Tafesh, J. Weiguny, *J. Chem. Rev.* 96 (1996) 2035-2052.
- [2] G. H. Coleman, S. M. McClosky, F. A. Suart, *Organic Synthesis*; Wiley: New York, 1995; Collect. Vol. III, p 668-670.
- [3] A. Saha, B. Ranu, *J. Org. Chem.* 73 (2008) 6867-6870.
- [4] M. Takasaki, Y. Motoyama, K. Higashi, S.-H. Yoon, I. Mochida, H. Nagashima, *Org. Lett.* 10 (2008) 1601-1604.
- [5] A. Corma, P. Serna, *Science*, 313 (2006) 332-334.
- [6] P. Maity, S. Basu, S. Bhaduri, G. K. Lahiri, *Adv. Synth. Catal.* 349 (2007) 1955-1962.
- [7] S. K. Gosh, M. Mandal, S. Kundu, S. Nath, T. Pal, *Appl. Catal. A: Gen.* 268 (2004) 61-66.
- [8] Q. Shi, R. Lu, L. Lu, X. Fu, D. Zhao, *Adv. Synth. Catal.* 349 (2007) 1877-1881.
- [9] Y. Zheng, K. Ma, H. Wang, X. Sun, J. Jiang, C. Wang, R. Li, J. Ma, *J. Catal. Lett.* 124 (2008) 268-276.
- [10] F. Cardenas-Lizana, S. Gomez-Quero, M. K. Keane, *Cat. Commun.*, 9 (2008) 475-481.
- [11] T. Swathi, G. Buvaneswari, *Mater. Lett.* 62 (2008) 3900-3902.
- [12] G. Gao, Y. Tao, J. Jiang, *Green Chem.* 10 (2008) 439-441.
- [13] I. Pogorelic, M. Filipan-Litvic, S. Merkas, G. Ljubic, I. Cepanec, M. Litvic, *J. Mol. Catal. A: Chem.* 274 (2007) 202-207.
- [14] Q. Shi, R. Lu, K. Jin, Z. Zhang, D. Zhao, *Green Chem.* 8 (2006) 868-870.
- [15] P. Li, Z. Wu, J. Yan, M. Wang, Y. Ding, *Synthesis* (2003) 2001-2004.
- [16] J. Ronald. Jr. Rahaim, E. Robert, Jr. Maleczka, *Org. Lett.* 7 (2005) 5087-5090.
- [17] S. U. Sonavane, M. B. Gawande, S. S. Deshpande, A. Venkataraman, R. V. Jayaram, *Catal. Commun.* 8 (2007) 1803-1806.
- [18] S. Jana, S. K. Ghosh, S. Nath, S. Pande, S. Praharaaj, S. Panigrahi, S. Basu, T. Endo, T. Pal, *Appl. Catal. A: Gen.* 313 (2006) 41-48.
- [19] K. M. Lakshmi, T. Bandyopadhyay, A. Rahman, N. Mahender Reddy, B. M. Choudary *J. Mol. Catal. A: Chem.* 133 (1998) 293-295.
- [20] S. Xu, X. Xi, J. Shi, S. Cao, *J. Mol. Catal. A: Chem.* 160 (2000) 287-292.
- [21] Y. Chen, J. Qiu, X. Wang, J. Xiu, *J. Catal.* 242 (2006) 227-230.
- [22] Y. Du, H. Chen, R. Chen, N. Xu, *Appl. Catal. A: Gen.* 277 (2004) 259-264.
- [23] T. Joseph, V. Kumar, A.V. Ramaswamy, S. B. Halligudi, *Catal. Commun.* 8 (2007) 629-634.
- [24] F. Cardenas-Lizana, S. Gomez-Quero, M. A. Keane, *Catal. Commun.* 9 (2008) 475-481.
- [25] J-H. Shen, Y-W. Chen, *J. Mol. Catal. A:Chem.* 273 (2007) 265-276.
- [26] Y-S. Keum, Q-X. Li, *Chemosphere*, 54 (2004) 255-263.
- [27] D. He, H. Shi, Y. Wu, B-Q. Xu, *Green Chem.* 9 (2007) 849-851.
- [28] A. S. Kulkarni, R. V. Jayaram, *J. Mol. Catal. A:Chem.* 223 (2004) 107-110.
- [29] S. K. Mohapatra, S. U. Sonavane, R.V. Jayaram, P. Selvam, *Org. Lett.* 24 (2002) 4297-4300.
- [30] M. Lauwiner, P. Res, J. Wissmann, *Appl. Catal. A: Gen.* 172 (1998) 141-148.
- [31] C-R. Zhang, Y-L. Wang, *Indian. J. Chem. Sect. B: Org. Chem. Incl. Med. Chem.* 45 (2006) 510-511.
- [32] M. V. Joshi, D. Mukesh, *J. Catal.* 168 (1997) 273-277.

- [33] D. G. Desai, S. S. Swami, S. B. Hapase, *Synthetic. Commun*, 29 (1999) 1033-1036.
- [34] D. G. Desai, S. S. Swami, S. K. Dabhade, M. G. Ghagare, *Synthetic Commun*. 31 (2001) 1249-1251.
- [35] C. Yu, B. Liu, L. Hu, *J. Org. Chem*. 66 (2001) 919-924.
- [36] H. G. Zheng, J. H. Liang, J. H. Zeng, Y. T. Qian, *Mater. Res. Bull*. 36 (2001) 947-951.
- [37] R. Fazaeli, S. Tangestaninejad, H. Aliyan, M. Moghadam, *Appl. Catal. A. Gen*. 309 (2006) 44-51.
- [38] R. Fazaeli, S. Tangestaninejad, H. Aliyan, *Appl. Catal. A. Gen*. 318 (2007) 218-226.
- [39] R. Fazaeli, H. Aliyan, *Appl. Catal. A. Gen*. 331 (2007) 78-83.
- [40] R. Fazaeli, H. Aliyan, *Appl. Catal. A. Gen*. 353 (2009) 74-79.