

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

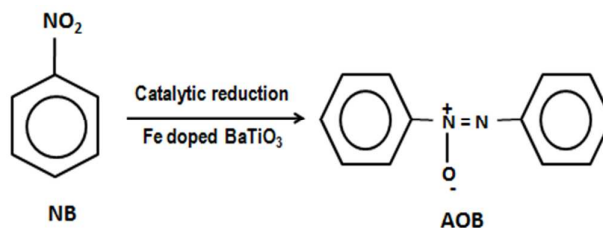
You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Graphical Abstract

Ch. Srilakshmi*, H. Vijay Kumar, K. Praveena, C. Shivakumara, M. Muralidhar Nayak

A Highly efficient Iron doped BaTiO₃ nanocatalyst for the catalytic reduction of nitrobenzene to azoxybenzene



A heterogeneous Fe doped BaTiO₃ efficient nanocatalyst for the synthesis of azoxybenzene via catalytic reduction of nitrobenzene in the presence of 2-propanol and molecular H₂ has been investigated. This method offers 100% conversion with 93-95 % azoxybenzene selectivity. This study marks the first time application of perovskites for the synthesis of azoxybenzene via selective catalytic reduction of nitrobenzene.

Text : Catalytic reduction of nitrobenzene over Fe doped barium titanate catalyst

COMMUNICATION

A Highly efficient Iron doped BaTiO₃ nanocatalyst for the catalytic reduction of nitrobenzene to azoxybenzene

Cite this: DOI: 10.1039/x0xx00000x

Ch. Srilakshmi^{a*}, H. Vijay Kumar^a, K. Praveena^b, C. Shivakumara^a, M. Muralidhar Nayak^cReceived 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

In the present study, we report an efficient and high yielding catalytic reduction of nitrobenzene in presence of 2-propanol or molecular H₂ over Fe doped BaTiO₃ nanocatalysts. This method provides 100 % conversion of nitrobenzene with 93% and 95 % AOB yield with 2-propanol and molecular H₂ under described experimental conditions, thus leading to efficient synthesis of azoxybenzene from nitrobenzene. The optimum Fe content to obtain high azoxybenzene yields was 2.5 % and 10 % in presence of 2-propanol and molecular H₂ respectively.

Azoxy compounds are versatile organic compounds have received considerable attention due to their physiological activity and their applications as liquid crystalline materials.¹⁻⁴ Azoxybenzene has been used as dyes, analytical reagents, reducing agents, stabilizers, food additives, pigments, polymerization inhibitors.⁵⁻⁸

The synthesis of azoxybenzene is carried out through the oxidation of aromatic amines and reduction of nitro compounds by using various stoichiometric reagents.⁹⁻²³ Due to environmental concern associated with homogeneous routes using stoichiometric routes it is desired to develop an alternative, efficient, reusable solid phase catalyst for the direct conversion of nitrobenzene to

azoxybenzene. To date, very few catalytic routes are reported on reduction of nitrobenzene to azoxybenzene.^{24, 25} However, known catalysts for hydrogenation reactions are less active and selective. Thus, a synthetic method that can differentiate and catalyze a selective reduction of nitrobenzene using a simple, inexpensive catalyst would be valuable and have potential synthetic applications. Recently, Zhu et al.²⁶ reported that gold nanoparticles supported on TiO₂ nanocrystals painted H-titanate nanofibers could selectively reduce nitrobenzene to azoxybenzene under visible light irradiation. In the present study we report selective reduction of nitrobenzene in presence of either 2-propanol and molecular H₂ over Fe doped BaTiO₃ catalysts.

Although Perovskite type mixed oxides have been used previously for a variety of reactions including oxidation of CO²⁷ and NH₃,²⁸ and NO_x decomposition.²⁹ Their application for catalytic reduction of nitrobenzene is still unexplored. Hence in the present manuscript we describe the development of solid phase, reusable and robust catalyst with high catalytic activity and selectivity for the selective reduction of nitrobenzene to azoxybenzene. The catalysts were thoroughly characterized using electron microscopy, XRD, FT-IR, (see, Fig. S2, ESI) N₂ physisorption methods (see, Table S1, ESI).

The indexed PXRD patterns of BaTi_{1-x}Fe_xO₃ (0.0 ≤ x ≤ 0.3) powders calcined at 850 °C for 4 h (Fig. S1, ESI) showed BaTiO₃ (BTO) phase (JCPDS no. 031-0174) with cubic symmetry and space group, *Pm-3m*. XRD patterns of the Fe doped samples were matched with the XRD of the BTO sample and shows doping at B site. Trace amounts of BaCO₃ was observed as impurity in the catalysts. The formation of BaCO₃ phase might be due to the reaction between BaO and CO₂ produced at the elevated temperature during calcinations.

Transmission electron microscopic images of the catalysts (Figure 1) illustrates a narrow distribution of particle sizes, in the range of 40-50 nm for BaTiO₃ (Figure 1A) and in the range of 30-40 nm for Fe doped BaTiO₃ catalysts (Figure 1B, 1C, 1D). The particles

^a Solid State and Structural Chemistry Unit (SSCU), Indian Institute of Science (IISc), Bangalore 560012, INDIA
Fax: (+91) 80 2360 1310

E-mail: ch.srilakshmi@sscu.iisc.ernet.in

^b Material Research Centre (MRC), Indian Institute of Science (IISc), Bangalore 560012, INDIA

^c Inorganic and Physical Chemistry Division (IPC), Indian Institute of Science (IISc), Bangalore 560012, INDIA

† Electronic supplementary information (ESI) available: XRD, FTIR, N₂ physisorption, XPS, Optimization of reaction conditions results.

are spherical in shape and are agglomerated. The particle size estimated from TEM reasonably agree (see, Table S2, ESI) with those obtained from XRD (30 to 60 nm) using Scherer equation. There is a decrease in the average particle size for Fe doped BTO catalysts with increase in Fe content in the catalysts, could be due to the particle growth hindrance caused by oxygen vacancies, lattice distortion as well as internal stress arising from the substitution of Ti with Fe as described by Wei. et.al.³⁰ Figure 1E shows a typical lattice image of a 50 nm nanocrystalline grain of BTO catalyst (Figure 1A). Clear lattice fringes with $d_{110} = 0.28$ nm reveal that well-crystallized BTO nanoparticles are formed. The surrounding edges of the particle are very smooth and no surface steps were observed. Figure 1F shows a surface profile HRTEM image of a 50 nm BTO grain (Figure 1A). It is noticed that the surface facets are parallel to the (100) and (110) planes. Small islands of 3 ~ 4 atom layer thickness were frequently observed around the edge of the particle. The contrast variations across Figure 1F are due to the thickness variations associated with the fine-scale surface facets and surface roughness.

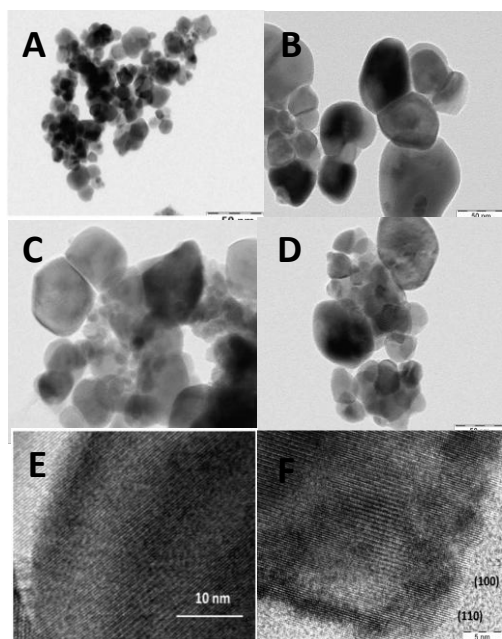


Figure 1 TEM images of (a) BTO (b) BTO-Fe-2.5 (c) BTO-Fe-5 (d) BTO-Fe-30 (e) Lattice image of a 50 nm nanocrystalline grain of BTO (f) Surface profile HRTEM image of 50 nm BTO grain

X-ray photoelectron spectra (XPS) spectra of the Fe 2p region (Fig. S3, ESI) showed very less intense peaks for BTO-Fe-2.5 and BTO-Fe-5 indicating the high dispersion of Fe particles. BTO-Fe-10 catalyst showed Fe $2P_{3/2}$ broad peak at 713.9 eV and Fe $2p_{1/2}$ at 726.5 eV which was due to Fe^{3+} . With further increase in the Fe content all the catalysts showed broad peaks for Fe $2P_{3/2}$ with maxima between 709.25 to 710.52 indicating the presence of both Fe^{2+} / Fe^{3+} in the catalysts.

The detailed investigation on the optimization of the reaction conditions and discussion is provided in ESI (see, pages S6-S8, ESI).

The catalytic reduction performed on pure BTO catalyst in presence of 2-propanol (Table 1, entry 1) showed 99 % conversion of nitrobenzene (NB) and 56.4 % AOB yield. Whereas, the reaction conducted on the Fe doped catalysts showed 100% NB conversion on all the catalysts with Fe content from 2.5 to 15% (BTO-Fe-2.5 to BTO-Fe-15). The decrease in conversion on BTO-Fe-20 and BTO-Fe-30 catalyst is due to presence of iron in its oxidized state as the reaction is conducted in the absence of H_2 . This is clearly understood as the reaction results obtained in H_2 atmosphere showed 100% conversion on all the catalysts (see, Table 2). The maximum yield of 93 % AOB was obtained on BTO-Fe-2.5 catalyst and was higher than that of other catalysts indicating 2.5% Fe is the optimal amount to obtain maximum AOB yield. The reduction in AOB yield with increase in Fe content in the catalysts is due to formation of other reduction products like azobenzene and aniline via side reactions (see scheme 2).

Table 1. Catalytic reduction of nitrobenzene in presence of 2-propanol

Ent.	Catalyst	Yield (%)			Conversion (%)	Selectivity (%) AOB
		AOB	AB	AN		
1	BTO	56.4	21.8	20.8	99	57
2	BTO-Fe-2.5	93	0	7	100	93
3	BTO-Fe-5	82	0	18	100	82
4	BTO-Fe-10	81	0	19	100	81
5	BTO-Fe-15	80	0	20	100	80
6	BTO-Fe-20	56	0.92	35	92	61
7	BTO-Fe-30	59	1	28	88	67
8	BaFeO ₃	38.8	8.61	31.7	79	49
9	BaO-TiO ₂ -Fe ₂ O ₃	36.5	9.12	35.8	82	44.5

Reaction conditions: Nitrobenzene (20mmol), KOH pellets (20mmol), catalyst (150mg) and 2-propanol (20ml), refluxed for 2-6 h at 80 °C; **AOB**-Azoxybenzene, **AB**-Azobenzene, **AN**-Aniline, Conversion % = $\frac{(C_i - C_f)}{C_i} \times 100$ (C_i & C_f initial and final amount of Nitrobenzene (mol%)), Yield% = $\frac{(\% \text{Conversion of nitrobenzene} \times \% \text{Selectivity of product})}{100}$

For comparison purpose, catalytic reduction of nitrobenzene was also studied on the respective mixed oxide and perovskite such as BaO-TiO₂-Fe₂O₃ and BaFeO₃ catalysts in the presence of 2-propanol. The conversion and yields obtained on these catalysts (see entries 8 and 9 in Table 1) are low compared to all the catalysts in the present study. This result clearly demonstrates the effect of Fe doping in the BaTiO₃ matrix in the catalytic reduction of nitrobenzene.

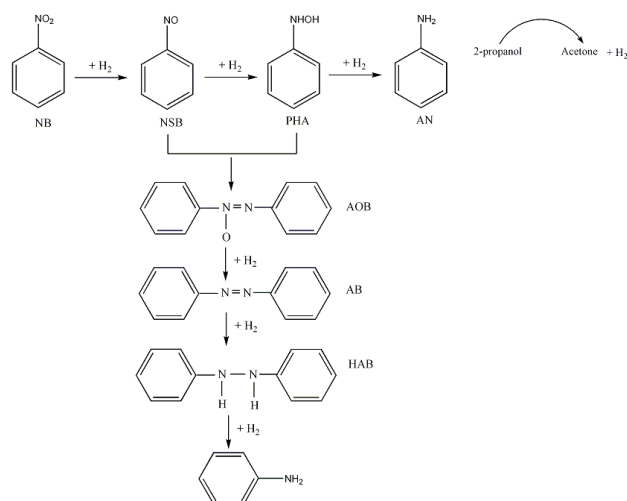
Molecular H_2 has been employed as the hydrogen source, and the catalytic reduction was performed at atmospheric pressure, (see Table 2). The conversion as well as yield indeed is improved in the presence of H_2 atmosphere. 100% conversion was achieved on all the catalysts. A maximum AOB yield of 95% was obtained on BTO-Fe-10 catalyst (see entry 4 in Table 3). The better results

obtained in the presence of H_2 atmosphere could be due to active metal i.e. iron remain in reduced state under reaction conditions.

Table 2. Catalytic reduction of Nitrobenzene in presence of H_2

Ent.	Catalyst	Yield (%)			Conversion (%)	Selectivity (%) AOB
		AOB	AB	AN		
1	BTO	64	0	26	90	71
2	BTO-Fe-2.5	92	4	4	100	92
3	BTO-Fe-5	93	0	7	100	93
4	BTO-Fe-10	95	0	5	100	95
5	BTO-Fe-15	86	0	14	100	86
6	BTO-Fe-20	85	0	15	100	85
7	BTO-Fe-30	87	0	13	100	87
8	$Fe(NO_3)_3 \cdot 9H_2O$	58	6	24	88	66

Reaction conditions: Nitrobenzene (20mmol), KOH pellets (20mmol), catalyst (150mg) and 2-propanol (20ml), refluxed for 2-6 h at 80 °C, %Selectivity = (Mole % desired product/Mole % of all products)*100



Scheme 1. Reaction pathway for the catalytic reduction of nitrobenzene to azoxybenzene

For the sake of comparison the catalytic reduction also conducted with homogeneous $Fe(NO_3)_3$ (150 mg) in the presence of H_2 and the results are presented in Table 2 (entry 8). The conversion of nitrobenzene and selectivity of AOB were found to be lesser compared to Fe supported on $BaTiO_3$. This result clearly indicates the influence of $BaTiO_3$ support for Fe for the conversion of nitrobenzene. Optimum content of Fe found to be 2.5 wt% on $BaTiO_3$ for the conversion of nitrobenzene with 2-propanol. The optimum contents of Fe is found to be 10 wt% on $BaTiO_3$ for the conversion of nitrobenzene using molecular hydrogen as reducing agent.

From the above results it can be understood that Fe doped catalysts exhibits similar or higher NB conversion, in particular, significantly higher yields towards AOB was achieved than on pure BTO catalyst.

The possible reaction pathways are outlined in Scheme 1. The two reaction routes possible in the catalytic reduction of nitrobenzene are direct route and condensation route. Direct route involves the formation of aniline as the major product. And the condensation route involves a condensation reaction between formed intermediates of nitrosobenzene (NSB) and phenyl hydroxylamine (PHA) leads to the formation of azoxybenzene. The formation of dimeric products of AOB and AB are mainly favoured by a basic reaction environment. Azoxybenzene is easily converted into azobenzene and hydrazobenzene (HAB) which can be subsequently hydrogenolysed to AN at atmospheric pressure. From the above results it can inferred that the Fe on $BaTiO_3$ is promoting the reductive coupling between NSB and PHA to selectively form the AOB. Whereas, the pure $BaTiO_3$, $BaO-TiO_2-Fe_2O_3$, $BaFeO_3$ and $Fe(NO_3)_3 \cdot 9H_2O$ are less selective towards AOB formation.

Conclusions

In conclusion, we have developed a highly efficient catalytic system consisting of Fe doped $BaTiO_3$, for the catalytic reduction of nitrobenzene to azoxybenzene using either 2-propanol or molecular H_2 as hydrogen source and KOH as promoter. This is the first demonstration of the selective catalytic reduction of nitrobenzene to azoxybenzene over solid phase perovskite catalysts using both 2-propanol and molecular H_2 as hydrogen source. This method provides 100 % conversion with 93% AOB yield with 2-propanol and 100% conversion with 95 % AOB yield with molecular H_2 thus leading to efficient synthesis of azoxybenzene from nitrobenzene. These results indicate that these materials provide great promise towards the important goal of developing improved catalysts for selective catalytic reduction.

Notes and References

1. T. Ikeda and O. Tsutumi, *Science*, 1995, **268**, 1873.
2. J. P. Snyder, V. T. Bandurco, F. Darack and H. Olsen, *J. Am. Chem. Soc.*, 1974, **96**, 5158.
3. D. Campbell, L. R. Dix, P. Rostron, *Dyes Pigm.*, 1995, **29**, 77.
4. T. L. Gilchrist, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, Vol. 7, p. 735; D. H. Rosenblatt and E. P. Burrows, in *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*, ed. S. Patai, Wiley, Chichester, 1982, p. 1085.
5. R. Egli, in *Colour Chemistry: The Design and Synthesis of Organic Dyes and Pigments*, A. P. Peter, H. S. Freeman, Eds. (Elsevier, London, 1991), chap. VII.
6. S. C. Catino, E. Farris, *Concise Encyclopedia of Chemical Technology* (Wiley, New York, 1985).
7. K. Venkataraman, in *The Chemistry of Synthetic Dyes* (Academic Press, London, 1970), chap. VI.
8. E. Buncl, *Acc. Chem. Res.*, 1975, **6**, 132.
9. O. D. Wheeler, D. Gonzales, *Tetrahedron*, 1964, **20**, 189.
10. H. E. Baumgarten, A. Staklis, E. M. Miller, *J. Org. Chem.*, 1965, **30**, 1203.

- 11 (a) R.W.Murray, K. Iyanar, J. Chen, J. T.Wearing, *Tetrahedron Lett.*, 1996, **37**, 805; (b) G. Barak, Y. Sasson, *J. Org. Chem.*, 1989, **54**, 3484.
- 12 R.W. Murray, R. Jeyaraman, L. Mohan, *Tetrahedron Lett.*, 1986, **27**, 2335.
- 13 A. McKillop, J. A. Tarbin, *Tetrahedron*, 1987, **43**, 1753.
- 14 R. A. Sheldon and J. Dakka, *Catal. Today*, 1994, **19**, 215.
- 15 S. Tollari, M. Cuscela and F. Porta, *J. Chem. Soc. Chem. Commun.*, 1993, 1510.
- 16 S. Tollari, D. Vergani, S. Banfi and F. Porta, *J. Chem. Soc. Chem. Commun.*, 1993, 442.
- 17 S. Satoru, M. Miura and M. Nomura, *J. Org. Chem.*, 1989, **54**, 4700; H. Huang, D. Sommerfeld, B. C. Dunn, C. R. Lloyd and E. M. Eyring, *J. Chem. Soc. Dalton Trans.*, 2001, 1301.
- 18 R. O. Hutchins, D. W. Lamson, L. Rua, C. Milewski, Br. Maryanoff, *J. Org. Chem.*, 1971, **36**, 803.
- 19 H. J. Shine, H. E. Mallory, *J. Org. Chem.*, 1962, **27**, 2390.
- 20 S.A. Buckler, L. Doll, F. K. Lind, M. Epstein, *J. Org. Chem.*, 1962, **27**, 794.
- 21 N. S. Kozlov, V. A. Soshin, *Uch. Zap. Permsk. Gos. Pedagog. Inst.*, 1965, **32**, 84, Chem. Abstr. 1967, **66**, 2290k.
- 22 E. F. Degering, E. F. Hitch, *J. Am. Chem. Soc.*, 1951, **73**, 1323.
- 23 H. E. Bigelow, A. Palmer, *Org. Synth.*, Coll. Vol. 1943, **2**, 57
- 24 D. K. Dutta, *Synth. Commun.*, 2006, **36**, 1903.
- 25 B. Pal, T. Torimoto, K. Okazaki and B. Ohtani, *Chem. Commun.*, 2007, 483.
- 26 Z. Zheng, J. Zhao, H. Liu, J. Liu, A. Bo, H. Zhu, *ChemCatChem*, 2013, **5**, 2382
- 27 G. Kremenec, J.M.L. Nieto, J.M.D. Tascon, L.G. Tejuca, *J. Chem. Soc. Faraday. Trans I* 1985, **81**, 939.
- 28 Y. Wu, T. Yu, B. Dou, C. Wang, X. Xie, Z. Yu, S. Fan, Z. Fan, L. Wang, *J. Catal.*, 1989, **88**, 120.
- 29 L.G. Tejuca, J. L.G. Fierro, J.M.D. Tascon, *Adv. Catal.*, 1989, **36**, 237.
- 30 X. Wei, G. XU, Z. Ren, Y. Wang, G. Shen, G. Han, *Mat. Lett.*, 2008, **62**, 3666.