

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

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Table of contents

Synthesis methods	S2
Catalyst characterization methods	S2
XRD	S3
FTIR	S4
BET surface area	S5
XPS	S6
Optimization of the reaction conditions for selective catalytic reduction of nitrobenzene to azoxybenzene	S6 to S8

Synthesis methods:

Synthesis of pure and Fe doped BaTiO₃(BTO) nanoparticles by oxalate route

The synthesis of BTO nanopowders by oxalate route¹ was carried out starting with titanium isopropoxide and barium nitrate as raw materials, and oxalic acid as chelating agent, in a molar ratio, Ti(OC₃H₇)₄: Ba(NO₃)₂: C₂H₂O₄·2H₂O=1:1:2 and 2-propanol as the solvent. The oxalate precursors were dried at 120°C, overnight and calcined at 850°C for 4h for obtaining BaTiO₃ nanopowders. For Fe substituted samples the same procedure was followed except for the addition of stoichiometric amount of Iron nitrate precursor to the above solution in the following ratio Ba(NO₃)₂: 1-xTi(OC₃H₇)₄: xFe(NO₃)₂: C₂H₂O₄·2H₂O=1:0.9:0.1: 2

Synthesis of BaFeO₃ nanoparticles by oxalate route

The synthesis of BaFeO₃ nanopowders by oxalate route was carried out starting with barium nitrate and iron nitrate as raw materials and oxalic acid as chelating agent, in a molar ratio, Ba(NO₃)₂:Fe(NO₃)₂: C₂H₂O₄·2H₂O=1:1:2 and 2-propanol as the solvent. The oxalate precursor was dried at 120°C, overnight and calcined at 850°C for 4h.

Synthesis of BaO-TiO₂-Fe₂O₃ mixed oxide by co-precipitation method

Appropriate amounts of respective soluble metals salts were dissolved in minimum amount of deionized water. To this, aqueous ammonia solution was added under vigorous stirring until pH 10.0 was achieved. Then the co-precipitated hydroxides were washed repeatedly to get neutral filtrate free of the anions of precursor materials. The precipitate was then dried in an air oven at 120°C for 12h. The hydroxide was then calcined in a muffle furnace at 500°C for 5h.

Catalyst characterization methods

The catalysts were characterized by X-ray diffraction recorded on a JEOL JDX-8030 X-ray diffractometer using Cu K α radiation. The BET surface area of the samples was measured using a Model-Quantachrome Autosorb iQ₂ automated gas sorption analyzer. Samples were initially pretreated in N₂ at 300°C for 6h and the surface area of the catalysts was obtained by adsorbing N₂ at liquid nitrogen temperature, 77K.

The infrared absorption spectra were measured at room temperature, in the wave number range of 4000 to 400 cm⁻¹ by a computerized spectrometer type Perkin FTIR-300 using the KBr pellet technique.

The particle size and morphology of the powders were studied using the transmission electron microscope (Model JEM-2010, JEOL, Tokyo, Japan).

X-ray photoelectron spectra (XPS) of the samples were recorded on an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) using Al K α radiation (1486.6 eV). Binding energies were calculated with respect to C(1s) at 285 eV and measured with a precision of ± 0.2 eV.

Details of GCMS analysis were as follows: Instrument: Thermo TRACE GC ULTRA (GC), Thermo DSQ II (MS); Ionization for MS: Electron Impact Ionization; Mass Analyzer: Quadrupole; Detector: Electron Multiplier

Discussion of the results

Powder X-ray diffraction

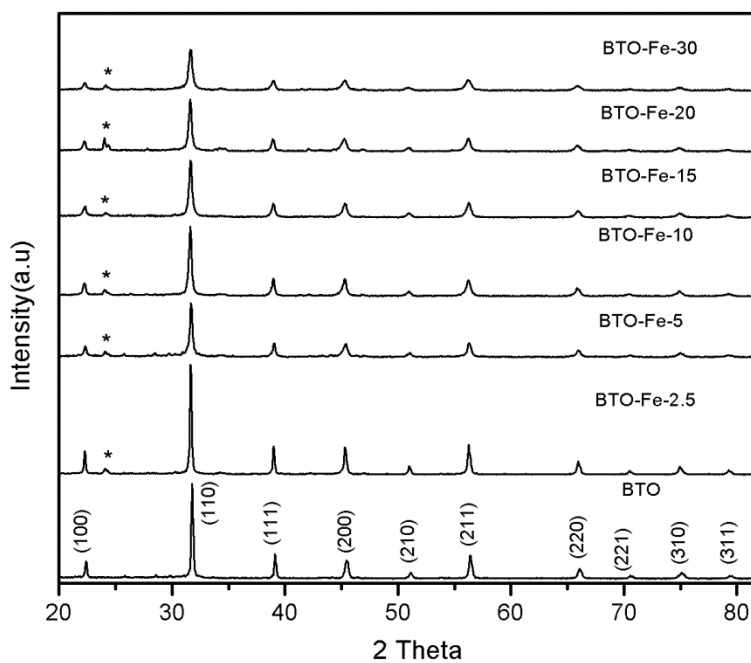


Figure S1. XRD patterns of the pure and Fe doped BTO catalysts

* refers to BaCO₃ phase

Fourier Transform Infra-Red Spectroscopy

The IR spectra of the catalysts measured are shown in Figure S2. The IR spectrum of the samples consists mainly of three regions: the first region shows bands at circa 3428-3436 and 1630 cm^{-1} , which are due to the OH stretching vibration (ν) and OH deformation vibration (δ), respectively, arising from the water and 2-propanol present in the porous structure of the barium titanate. The second region corresponds to the absorption bands in the region of 1430 -1435 cm^{-1} and 855-867 cm^{-1} , and 690-692 cm^{-1} are characteristic of the BaCO_3 phase present in the samples as impurity. The third region, in the range between 392-600 cm^{-1} , represents the characteristic infrared absorptions of the Ti-O vibrations. The band situated around $\sim 532 \text{ cm}^{-1}$ is due to TiO_6 stretching vibration connected to the barium. Finally, the peak at 396 cm^{-1} can be attributed to normal TiO_6 bending vibrations. IR bands observed in the region of 2340-2355 cm^{-1} in the samples were due to CO_2 present in the atmosphere.

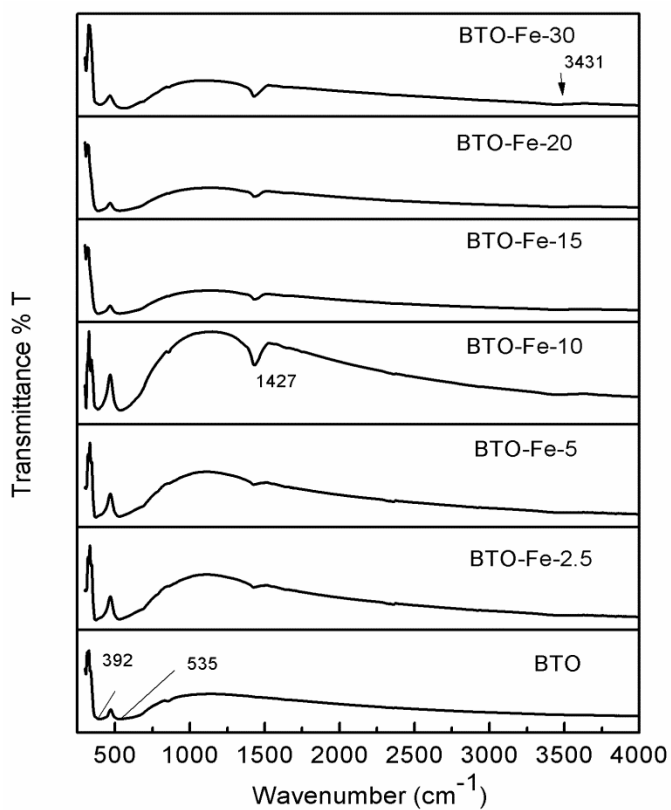


Figure S2. FTIR spectra of the pure and Fe doped BTO catalysts

BET Surface area

The BET surface area of the catalysts measured is given in the Table S1. The surface area of the BaTiO₃ catalyst is found to be 1.5 m²/g and the surface area increased with increase in Fe content in the samples. The increase in surface area of the catalysts might be due to contribution from BaTi_{1-x}Fe_xO₃ component.

Table S1. BET surface area of the catalysts

Entry	Catalyst	BET Surface area (m ² /g)
1	BTO	1.5
2	BTO-Fe-2.5	2.6
3	BTO-Fe-5	3.3
4	BTO-Fe-10	4.0
5	BTO-Fe-15	4.8
6	BTO-Fe-20	5.0
7	BTO-Fe-30	14.0

Particle size analysis by TEM (Transmission electron microscopy)

Table S2. Particle size of the samples estimated by TEM

Entry	Catalyst	Particle size (nm)
1	BTO	50
2	BTO-Fe-2.5	40
3	BTO -Fe-5	43
4	BTO-Fe-10	32
5	BTO-Fe-15	30
6	BTO-Fe-20	35
7	BTO-Fe-30	33

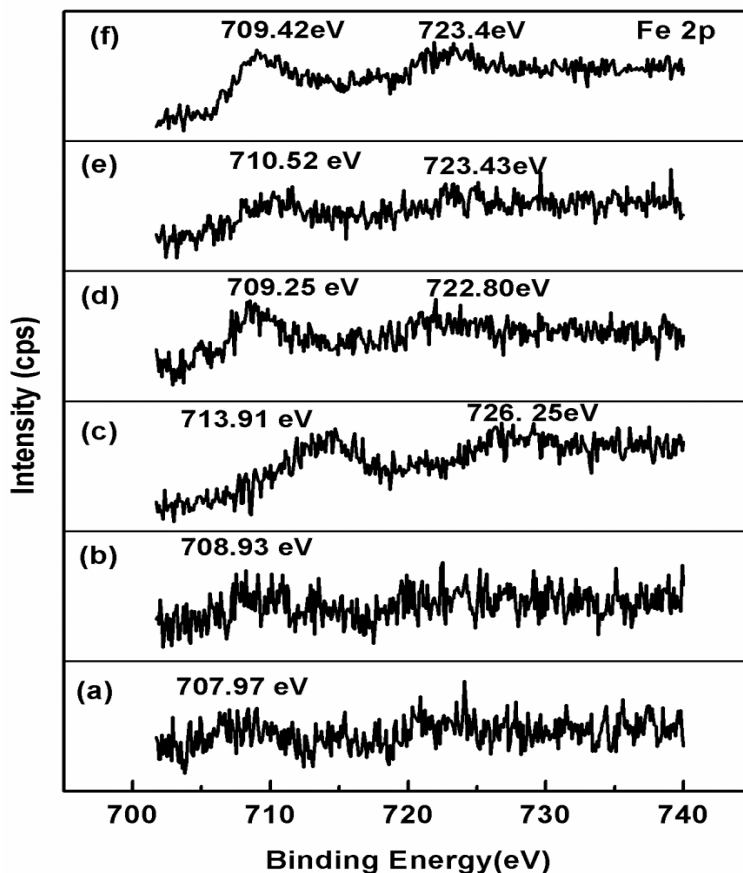


Figure S3: XPS profiles of Fe $2P_{3/2}$ over various Fe contents on BaTiO₃ catalysts
 (a) BTO-Fe-2.5 (b) BTO-Fe-5 (c) BTO-Fe-10 (d) BTO-Fe-15 (e) BTO-Fe-20 (f) BTO-Fe-30

Optimization of the reaction conditions for catalytic reduction in presence of 2-propanol are as follows

Effect of reaction temperature on catalytic reduction of nitrobenzene

The effect of reaction temperature on the catalytic reduction was studied on the most active BTO-Fe-2.5 catalyst. The data in the Table 3 reveals that the maximum conversion and yield to azoxybenzene was feasible at a reaction temperature of 80°C. Hence all the reactions were conducted at 80°C in the present study.

Table S3. Results of the catalytic reduction of nitrobenzene with 2-Propanol at various reaction temperatures

Ent.	Reaction temperature (°C)	Yield (%)			Conversion (%)	Selectivity (%)
		AOB	AB	AN		
1	60	47.8	2.88	2.65	53.4	89.6
2	70	53.6	30	0	83.6	64.2
3	80	94	0	6	100	94

Reaction conditions: Nitrobenzene (20mmol), KOH pellets (20mmol), BTO-Fe-2.5 (150mg) and 2-propanol (20ml), at 60-80°C for 2-6hr

Effect of KOH concentration on the catalytic reduction of nitrobenzene

The reaction did not proceed in the absence of either the catalyst or KOH. The effect of KOH concentration on the yield of azoxybenzene is illustrated in Table 4. It can be observed from the table that 20 mmol is the appropriate concentration of KOH where maximum conversion is 100% and azoxybenzene yield of 94% was obtained

Table S4. Results of catalytic reduction of nitrobenzene at various KOH concentrations

Ent.	Conc. of KOH (mmol)	Conversion (%)	AOB Yield (%)
1	0	0	0
2	10	60	46.2
3	15	73	62.8
4	20	100	94
5	25	90	68.7

Reaction conditions: Nitrobenzene (20mmol), KOH pellets (0-25mmol), BTO-Fe-2.5 (150mg) and 2-propanol (20ml), refluxed for 2-6hr at 80°C

Effect of catalyst weight on the catalytic reduction of nitrobenzene

The catalytic reduction of nitrobenzene was also studied by varying the catalytic amount in the reaction system (Table 5). 100% conversion obtained is with 150 mg of catalyst with 94% yield and interestingly no reaction was observed with overloading of the catalyst up to 200 mg.

Table S5. Results of catalytic reduction of nitrobenzene at different catalyst weight in mg

Ent.	Wt. of catalyst (mg)	Conversion (%)	AOB Yield (%)
1	100	37.4	37.4
2	150	100	94
3	200	No reaction	

Reaction conditions: Nitrobenzene (20mmol), KOH pellets (20mmol), BTO-Fe-2.5 (100-200mg) and 2-propanol (20ml), refluxed for 2-6hr at 80°C

Effect of solvent on the catalytic reduction of nitrobenzene

It can be observed from Table 6 that the reaction did not occur with solvents like methanol and 1-propanol whereas 100% conversion was obtained with 2-propanol; this could be due to easy dissociation of KOH in the 2-propanol solvent compared with other solvents.

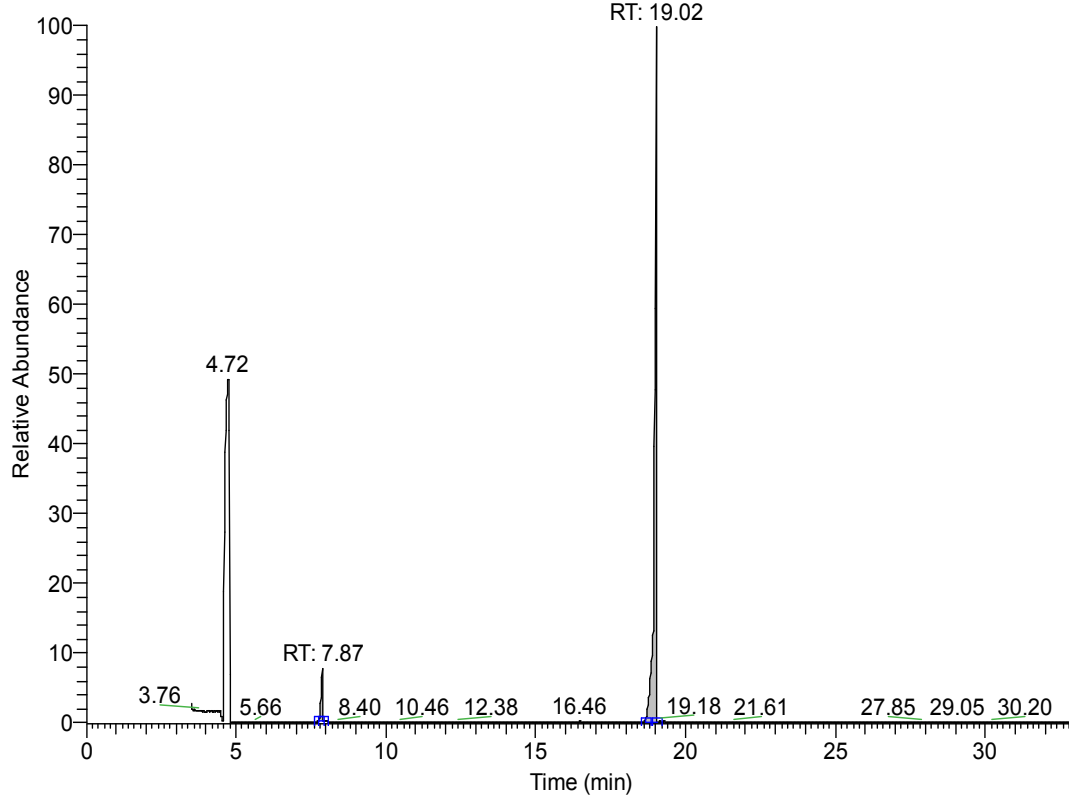
Table S6. Results of catalytic reduction of nitrobenzene with various solvents

Ent.	Type of solvent	Conversion (%)	AOB Yield (%)
1	1-Methanol	No reaction	
2	1-Propanol	No reaction	
3	2-Propanol	100	94
4	1- Butanol	35.5	24.3

Reaction conditions: Nitrobenzene (20mmol), KOH pellets (20mmol), BTO-Fe-2.5 (150mg) and 2-propanol (20ml), refluxed for 2-6hr at 80°C

GC-MS data analysis report for Catalytic reduction in presence of H₂ gas for BTO-Fe-10 catalyst

RT: 0.00 - 33.00



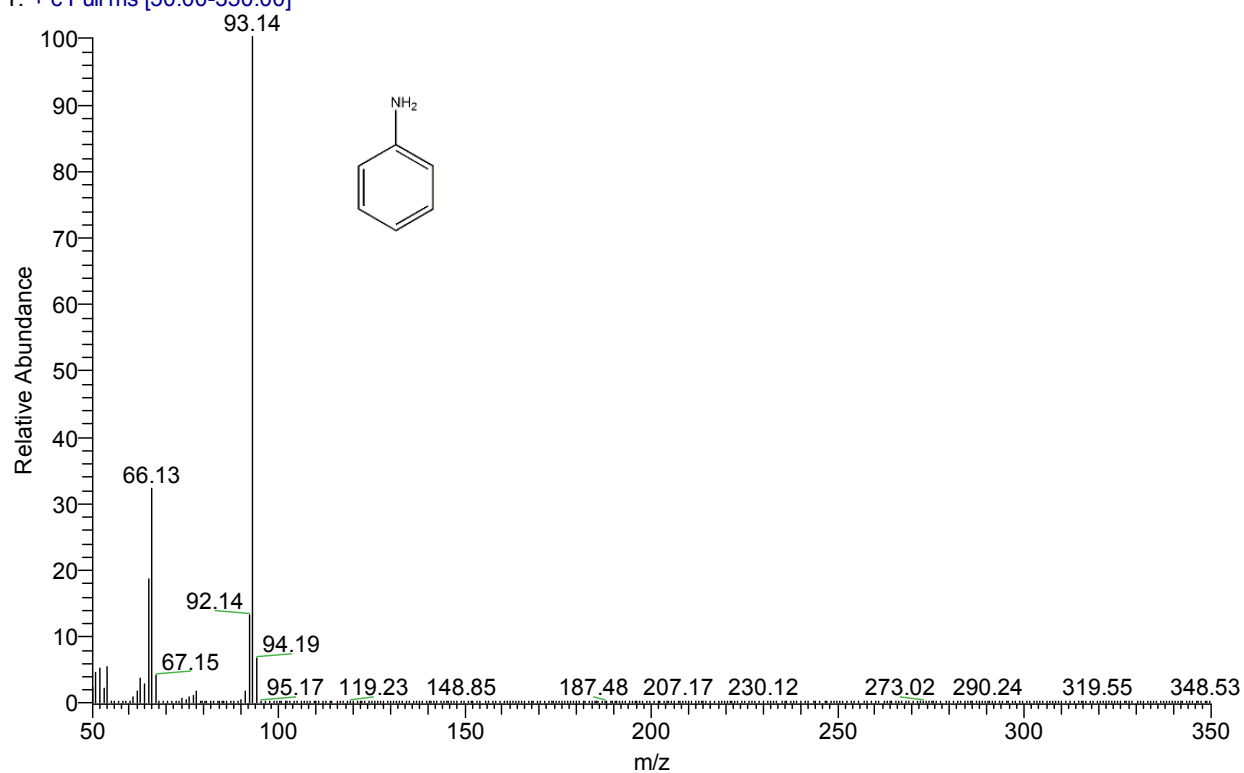
NL:
6.29E7
TIC MS
SGO5A-
80H-6hr

PEAK
LIST
SGO5A-80H-
6hr.raw
RT: 0.00 - 33.00

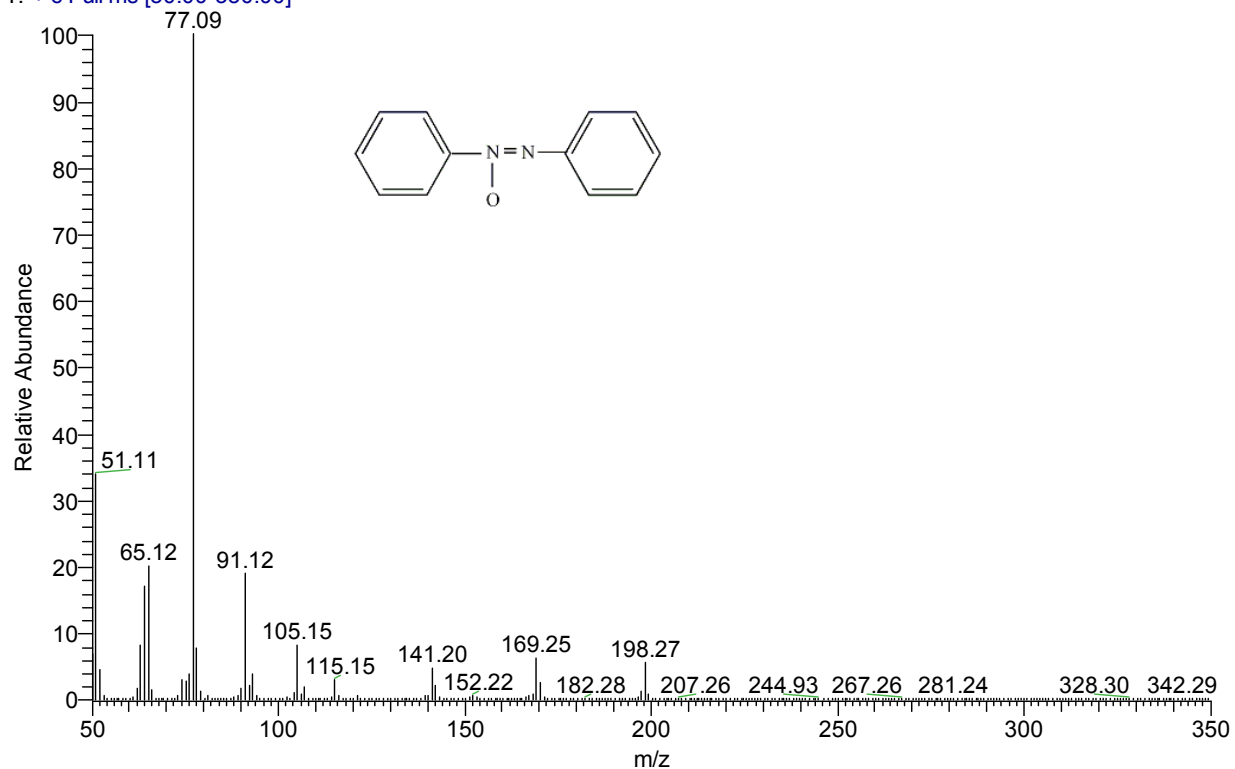
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
7.87	7.75	7.89	16159722	4.9	4739785	7.01
19.02	18.66	19.05	313528347	95.1	62908418	92.99

SGO5A-80H-6hr #396-438 RT: 7.59-8.03 AV: 43 NL: 3.48E5
T: + c Full ms [50.00-350.00]



SGO5A-80H-6hr #1437-1521 RT: 18.38-19.25 AV: 85 NL: 2.07E6
T: + c Full ms [50.00-350.00]



References

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