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## ARTICLE TYPE

Reduction of Organic Azides to Amines using Reusable Fe<sub>3</sub>O<sub>4</sub> Nanoparticles in Aqueous MediumSreenivasarao Pagoti,<sup>a,b</sup> Subham Surana,<sup>a</sup> Ajay Chauhan,<sup>a</sup> Bibudha Parasar,<sup>a</sup> and Jyotirmayee Dash<sup>a,b,\*</sup>

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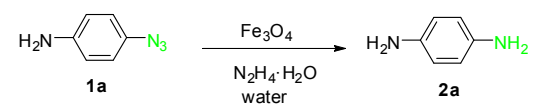
Aromatic, heteroaromatic and sulfonyl azides were conveniently reduced to the corresponding amines in excellent yields using hydrazine hydrate in the presence of iron oxide nanoparticles. The Fe<sub>3</sub>O<sub>4</sub>-MNPs could be easily separated by an external magnet, and recycled ten times without significant loss of the catalytic efficiency.

Magnetically separable catalysts have recently emerged as sustainable heterogeneous catalysts due to their rapid catalysis and efficient recycling.<sup>1</sup> Magnetic nanoparticles (MNPs) mimic homogeneous catalyst as they efficiently disperse catalytic active sites in the reaction medium. MNP catalysts are robust, readily available and can be effectively separated from the reaction mixture using an external magnet.

MNPs have recently been used for reduction of aromatic nitro groups, ketones, alkenes and alkynes.<sup>2-5</sup> The reduction of organic azides provides a straight forward access to the corresponding amines,<sup>6</sup> which are important class of compounds and have potential use in chemistry and biology, such as synthesis of pharmaceuticals, natural products, agrochemicals, polymers, rubbers and dyes. Although various methods are reported in the literature for the preparation of amines,<sup>2</sup> the reduction of azides is one of the important protocols because azides are easily accessible<sup>7</sup> from the corresponding halides and sulfonates. A variety of reducing reagents and metal-catalyzed hydrogenations has been reported in the literature for the transformation of azides into amines.<sup>6,8</sup> Most of these reactions have several disadvantages such as long reaction times, harsh reaction conditions, cost efficiency, poor selectivity, general applicability and tedious work-up procedures. Further the major drawback of these homogeneous catalysts is the difficulties in separating the catalysts from the products which limit their use in industrial applications.

Azido functional groups are versatile synthons<sup>9</sup> and have wide applications in the synthesis of triazoles and other heterocycles.<sup>7-10</sup> In continuation of our work on azido functional groups,<sup>11a-b</sup> and green chemical procedures,<sup>11c</sup> we herein report the reduction of aromatic, heteroaromatic and sulfonyl azides to the corresponding amines using hydrazine hydrate in the presence of iron oxide nanoparticles in aqueous medium.

Magnetite nanoparticles (MNPs) were prepared using the coprecipitation technique (see ESI†).<sup>12</sup> As a prototype, 4-azidoaniline **1a** was studied for reduction using Fe<sub>3</sub>O<sub>4</sub> in water (Table 1). The reaction did not proceed in the absence of any added hydrazine hydrate (entries 1, 2, Table 1). We observed that the reaction of 4-azidoaniline **1a** with 5 equiv hydrazine monohydrate in the presence of 50 mol% Fe<sub>3</sub>O<sub>4</sub> in water at RT proceeded with a 50% conversion of the azide **1a** affording the desired product **2a** in 47% yield (entry 3, Table 1). The reduction of azide **1a** took 2 h for completion at 120 °C to afford 1,4-diamino benzene **2a** in near quantitative yields (entry 5, Table 1). It is important to note that a 10 mol% Fe<sub>3</sub>O<sub>4</sub> could catalyze the reaction providing the product **2a** in excellent yield (entry 7, Table 1). As reported previously,<sup>8</sup> no reaction was observed using hydrazine monohydrate in the absence of Fe<sub>3</sub>O<sub>4</sub> (entry 9, Table 1).

Table 1. Reduction of 4-azidoaniline **1a** to the corresponding amine **2a**.<sup>a</sup>


entry	temp	Fe <sub>3</sub> O <sub>4</sub> mol%	Time (h)	Conv. (%), <sup>b</sup> Yield (%) <sup>c</sup>
1	rt	50	24	No reaction <sup>d</sup>
2	90 °C	50	12	No reaction <sup>d</sup>
3	rt	50	24	50, 47
4	80 °C	50	12	80, 73
5	120 °C	50	2	>99, 99
6	120 °C	20	3	>99, 99
7	120 °C	10	5	>99, 99
8	120 °C	100	1.5	>99, 99
9	120 °C	--	24	No reaction <sup>e</sup>

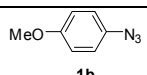
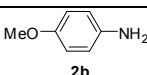
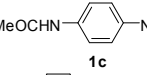
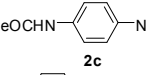
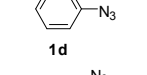
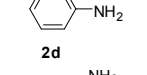
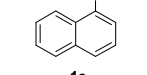
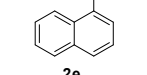
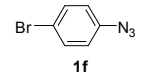
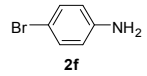
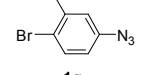
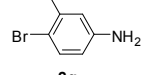
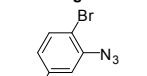
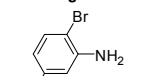
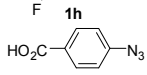
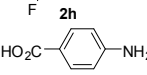
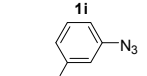
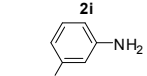
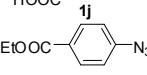
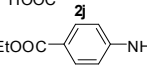
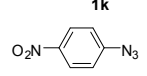
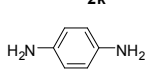
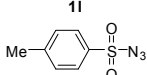
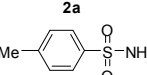
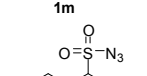
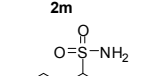
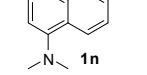
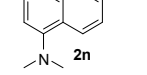
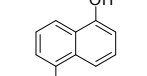
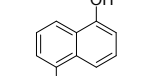
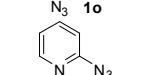
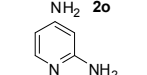
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<sup>†</sup>Electronic Supplementary Information (ESI) available: [Experimental procedures, characterisation data of compounds, PXRD data, AFM images and the copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra]. See DOI: 10.1039/b000000x/

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Table 2. Reduction of aryl/heteroaryl azides to the corresponding amines employing Fe<sub>3</sub>O<sub>4</sub> (50 mol%) with hydrazinemonohydrate in water.<sup>‡</sup>

Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>
	$\text{R-N}_3 \xrightarrow[\text{water, 120 } ^\circ\text{C}]{\text{Fe}_3\text{O}_4 (50 \text{ mol}\%), \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}} \text{R-NH}_2$			
1			1.5	99
2			1.5	85
3			2	90
4			5	84
5			2	98
6			3.5	99
7			2.5	81
8			1.5	92
9			3	98
10			2	81
11			4	80
12			1.5	99
13			1.5	99
14			6	82
15			1.5	97
16			2	99

<sup>a</sup>All reactions were carried out using azide **1** (1 mmol) and hydrazine monohydrate (5 mmol) in water (4 mL). <sup>b</sup>Isolated yield after column purification

To examine the scope of the reduction reaction using the Fe<sub>3</sub>O<sub>4</sub>-N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in water, we investigated the reduction of a series of aromatic, heteroaromatic and sulfonyl azides **1**. As shown in Table 2, the corresponding amines **2** were obtained for a wide range of azides **1**. The reactions were usually fast and yields are often excellent for all the tested azides. Aromatic azido derivatives **1f-1h** were efficiently reduced to the corresponding amines (Table 2, entries 5-7), which indicate that the halogen atoms such as fluorine and bromine remained intact under the reaction conditions. The azido group of **1** was chemoselectively reduced to the amino moiety in the presence of carboxylic acid, ester and amide groups (Table 2, entries 8-10). Aromatic azides containing *o*-, *m*- or *p*-substituents underwent facile reduction to the corresponding amines (Table 2). Azides containing free amino (**1a**) and hydroxyl (**1o**) groups produced the corresponding amines in high yields (Table 1, Table 2-entry 14).

It was found that the nitro group was reduced to the amines under the reaction condition,<sup>2c</sup> *p*-nitro phenyl azide **1l** reduced to give the corresponding diamine **2a** (Table 2, entry 11). Sulfonyl azides **1m** and **1n** (Table 2, entries 12 and 13) also produced the corresponding amines in near quantitative yields within 2 h. Similarly, heteroaromatic azides such as 2-azidopyridine (**1p**) and 2-azidothiazole (**1q**) reacted readily to afford the corresponding amines in excellent yields (Table 2, entries 15-16).

Table 3. Recycling experiments in reduction of azide **1a** to the amine **2a**<sup>a†</sup>

cycle	1	2	3	4	5	6	7	8	9	10
t (h)	2	2	2	3	3	4	4	4	4	5
yield (%) <sup>b</sup>	>99	>99	99	97	98	>99	99	98	99	97

<sup>a</sup>Reaction conditions: 1.0 mmol of azide **1a**, 5.0 equiv of hydrazine monohydrate, Fe<sub>3</sub>O<sub>4</sub> catalyst (50 mol%) in 4.0 mL of water at 120 °C. <sup>b</sup>Isolated yield after column purification.

We then investigated the recyclability of MNPs using the reduction of 4-azidoaniline **1a** (1 mmol) under the optimized conditions (ESI†). After completion of the reaction, the Fe<sub>3</sub>O<sub>4</sub> nanocatalysts were easily attracted using a magnet (Figure 1). The recovered MNPs were washed and dried at 60 °C for 30 min and reused in the next cycle (Table 3). This procedure was repeated for 10 times and it was observed that in each cycle, the recovered catalyst retained its efficiency, but required slightly longer reaction time after the 4th catalytic cycle. The reactions using recovered MNPs were fast and clean providing almost quantitative yield of the product **2a** (Table 3).

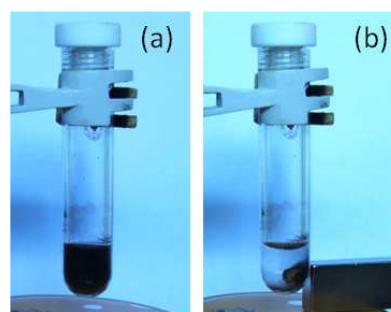
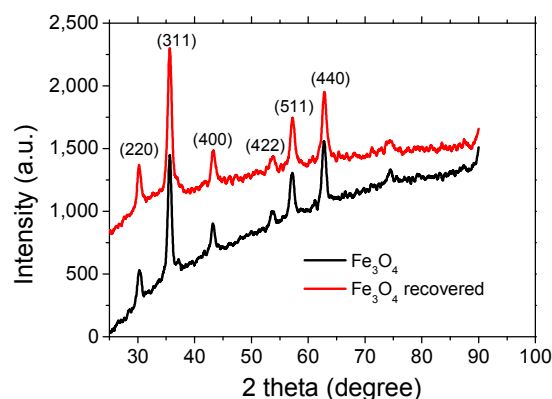


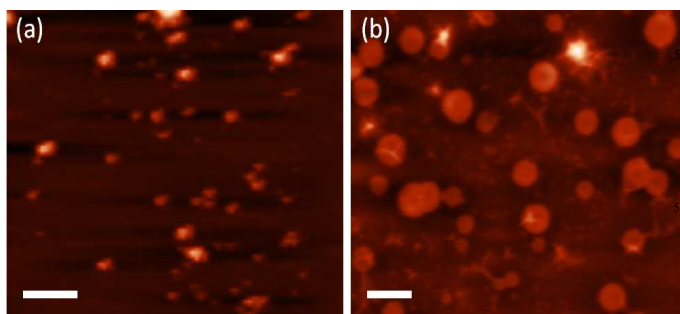
Figure 1. Magnetic separation of MNPs (a) during reduction reaction, (b) magnetic separation of the MNPs at ambient temperature using a magnet.

The powder X-ray diffraction (PXRD) patterns confirmed that the size of magnetite did not change before and after the catalysis

(Figure 2 and ESI†).<sup>12-13</sup> The average diameter of MNPs was estimated from the reflection at  $2\theta = 35.64^\circ$  using Scherrer's equation to be 10.14 nm, which is close to that calculated for the recovered MNPs after 10<sup>th</sup> catalytic cycle (11.04 nm). Atomic force microscopy (AFM) was used to study the morphology of the prepared and the recovered Fe<sub>3</sub>O<sub>4</sub>-MNPs. The average height of the recovered MNPs was determined to be 25 nm which is larger than the freshly prepared MNPs (11 nm, ESI†). AFM images revealed that the MNPs retained their spherical shape while an aggregation of the MNPs was observed after 10 consecutive catalytic cycles (Figure 3 and ESI†).

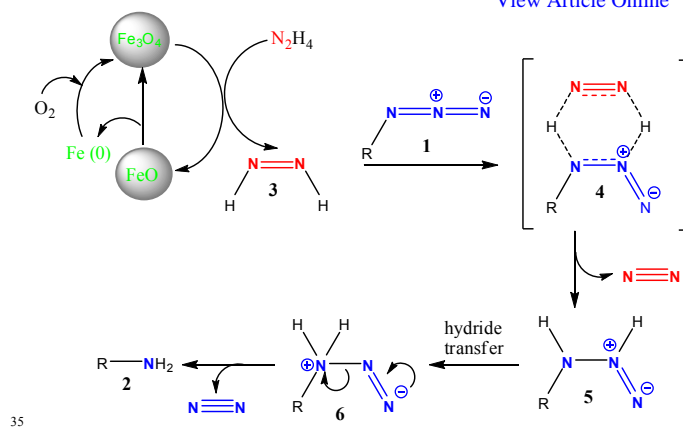


**Figure 2.** The powder X-ray diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> and recovered Fe<sub>3</sub>O<sub>4</sub> after the 10<sup>th</sup> catalytic cycle.



**Figure 3.** AFM images of (a) Fe<sub>3</sub>O<sub>4</sub> and (b) recovered Fe<sub>3</sub>O<sub>4</sub> after the 10<sup>th</sup> catalytic cycle (scale bar 200 nm).

A plausible mechanism has been proposed. The first step in the mechanism can be viewed as the reduction of the inverse spinel type magnetite (Fe<sup>II</sup>Fe<sup>III</sup><sub>2</sub>O<sub>4</sub>) structure to a NaCl type wustite (FeO) structure, where hydrazine donates its hydrogen ions. The H<sup>+</sup> ions upon interaction with the oxygen atom of magnetite forms water and hence leaves the magnetite backbone.<sup>14</sup> This redox reaction in turn generates the unstable reducing diimide species **3**. The reactive in-situ generated **3** then transfers both of its hydrogens in a concerted way<sup>15</sup> to the azide **1** possibly through the transition state **4**, which decomposes to release nitrogen. The resulting intermediate **5** then undergoes a hydride transfer to generate **6**, which then furnishes amine with the simultaneous elimination of nitrogen gas. The reduced form wustite is metastable, and hence disproportionates to Fe(0) and the original magnetite (Fe<sub>3</sub>O<sub>4</sub>). In the presence of oxygen, iron(0) transforms into Fe<sub>3</sub>O<sub>4</sub> and thereby completes the catalytic cycle.



**Scheme 1.** Proposed mechanism.

In summary, we have described reduction of a broad range of organic azides to the corresponding amines using hydrazine hydrate as the hydrogen source in the presence of 50 mol% of Fe<sub>3</sub>O<sub>4</sub>-MNPs in aqueous medium. The reactions were usually fast affording the amines in excellent yields. The MNPs could be magnetically recoverable and efficiently reused for ten catalytic cycles without significant loss of the catalytic efficiency. Since water is a green solvent,<sup>16-17</sup> and hydrazine hydrate produce nitrogen and water from the reaction, this catalytic system represents an environmentally benign alternative to other metal-based catalysts.

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## Notes and References

<sup>‡</sup> Brief experimental procedure: All experiments were carried out under an inert atmosphere of argon in flame-dried flasks. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100-200 mesh). Unless otherwise stated, yields refer to analytical pure samples. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 278K unless otherwise stated and are reported in ppm relative to tetramethylsilane (TMS). Infrared (FTIR) spectra were recorded with the KBr disk and KBr plate techniques for solid and liquid samples,  $\nu_{\max}$  cm<sup>-1</sup>. HRMS analyses were performed with Q-TOF YA263 high resolution instruments by positive mode electrospray ionization. AFM was carried out on a NT-MDT in semi-contact mode. 10 mL of an aqueous dispersion of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was deposited onto freshly cleaved mica (Agar Supplies) and allowed to dry in air for 12 h prior to imaging.

All of these starting materials and products are known compounds except 4-azido-1-bromo-2-methylbenzene **1g**. The known compounds are identified by comparison of their spectroscopic data (<sup>1</sup>H NMR, <sup>13</sup>C NMR) with those reported in the literature (see S.I.).<sup>7,18</sup>

**4-Azido-1-bromo-2-methylbenzene 1g:** 1-Bromo 2-methyl aniline **2g** (500 mg, 2.69 mmol) was suspended in 17% hydrochloric acid (25 mL) at

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room temperature. The solution was cooled to 0 °C using an ice bath. Then NaNO<sub>2</sub> (278 mg, 4.04 mmol) in 2 mL water was added in small portions. After stirring at 0 °C for 20-30 min, an aqueous solution of NaN<sub>3</sub> (263 mg, 4.04 mmol) was slowly added and the mixture was stirred for additional 2 h at room temperature. After completion, the reaction mixture was extracted with diethyl ether (3 x 40 mL). The combined organic fractions were washed with saturated NaHCO<sub>3</sub> solution (2 x 40 mL) and brine (2 x 40 mL). The organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to provide the azide **1g** (513 mg, 90%) as a brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.46 (d, *J* = 10.6 Hz, 1H), 6.88 (d, *J* = 3.0 Hz, 1H), 6.72 (dd, *J* = 10.6, 3.6 Hz, 1H), 2.38 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 139.5, 139.1, 133.3, 121.1, 120.2, 117.9, 22.9; IR: 3306.0, 3224.1, 2954.7, 2504.0, 2425.3, 2324.3, 2241.2, 2110.0, 2065.3, 1602.2, 1474.2, 1380.2, 1304.7, 1202.3, 1149.4; HRMS (ESI) calcd for C<sub>7</sub>H<sub>7</sub>BrN<sub>3</sub> [M+H]<sup>+</sup>: 211.9823; Found: 211.9785.

**General procedure for the reduction of azides using Fe<sub>3</sub>O<sub>4</sub>:** To a solution of azide **1** (1 mmol, 1 equiv) in water (4.0 mL), Fe<sub>3</sub>O<sub>4</sub> (116 mg, 0.5 mmol) and hydrazine monohydrate (0.243 mL, 5 mmol) were added to the mixture. The reaction mixture was refluxed or heated in a sealed tube at 120 °C under an argon atmosphere until completion, as monitored by TLC. The reaction was cooled and the Fe<sub>3</sub>O<sub>4</sub>-MNPs were separated using a magnet. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexanes eluent) to afford the desired pure amine. (Most of the amines were analytically pure before flash chromatography). The recovered catalyst was washed with methanol (2 x 5 mL), dried under vacuum, and reused for the next cycle of the reaction.

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