

Research Article

Morphology-Controlled Synthesis and Characterization of Magnetic Iron Oxide Nanocrystals and Their Potential Applications in Selective Oxidation of Alcohols and Olefins

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A protocol for the preparation of iron oxide nanocrystals of two different (nanorods and octahedrons) morphologies has been developed and the synthesized nanocrystals were well characterized by TEM and XRD. These two nanocrystals have been applied for the selective oxidation of aryl-methanol and vinyl-arene. Moreover, the magnetic catalysts have easily separated from reaction mixture by a magnet and are reused without appreciable loss of catalytic activity. The oxidation processes avoid the use of toxic catalysts and volatile and hazardous organic solvents.

1. Introduction

Selective oxidations of aryl-methanol and vinyl-arene to aryl-aldehyde are synthetically important because of the wide applications of these products in organic reactions and also it is difficult to control the further oxidation to acid. Traditionally, oxidation of benzyl alcohol to benzaldehyde is performed with many oxidizing agents and was used in stoichiometric amount [1–3]. These oxidants are generally expensive in nature and most importantly they generate toxic heavy-metal waste and were performed in hazardous chlorinated solvents. In recent years, the oxidation reactions using hydrogen peroxide (H_2O_2) as reagent in combination of a catalyst has attracted much attention because H_2O_2 is very mild in nature, inexpensive, and produce only water as product [4–6]. For this reason, a number of methodologies have been developed for oxidation of alcohols using H_2O_2 as oxidant and various metal as catalyst [7–18]. Thus, there is a thrust in search for new green catalysts. Very recently, various nano-particles such as NiO₂ NPs [19] and metal-oxide-supported nanogold [20] also applied as catalyst

for the benzylic oxidation. Iron-based catalysts have been extensively used because they are easily accessible, inexpensive, environmentally benign, and relatively nontoxic in comparison with other transition metals. Different iron (II) [21–23] and iron (III) compounds [24–28] have been used as for the oxidation reactions. Herein, we report the synthesis and characterization of iron oxide nanomaterials of two different morphologies (namely, nanorod and octahedron) and their successful applications in the selective oxidation of aryl-methanol and vinyl-arene with H_2O_2 under organic solvent-free condition.

2. Results and Discussions

At first, we have synthesized both the iron oxide nanorods and octahedrons using hydrogen peroxide by solvothermal technique. In a simple experimental procedure, a mixture of $FeCl_3$ and $FeCl_2$ was used in equimolar ratios as the precursor. Ethylenediamine and water were mixed in equal volume ratios before being used as the solvent. Appropriate

TABLE 1: The comparison of reactivity of nanorods and octahedron iron oxide nanomaterials for selective oxidation of benzyl alcohol with hydrogen peroxide.

Catalyst	Temperature	Time (h)	Yield (%)	Selectivity (%)
Nanorods	70°C	12	78	97
Octahedron	80°C	12	70	96
None	100°C	24	15	80

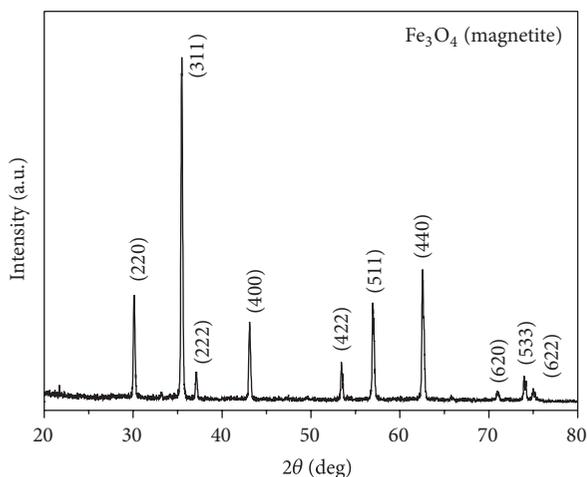
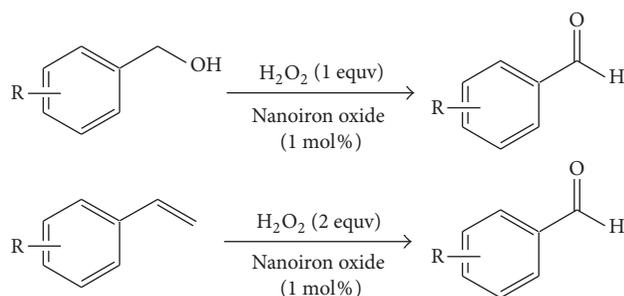


FIGURE 1: XRD pattern representing both the nanorods and octahedrons of iron oxide.

amounts of the precursor were dissolved in the selected amount of the solvent in such a way that the mixture filled up to 80% of a Teflon lined stainless steel autoclave used for the solvothermal process. Hydrogen peroxide was added to the chamber before being closed and placed in a preheated oven at 175°C for 8 h. 150 and 300 μL of H_2O_2 were used for the synthesis of magnetite (Fe_3O_4) nanorods and octahedrons, respectively. After the desired time of synthesis the deep brown products were washed several times in water and dried in vacuum for further characterization.

The powder products were characterized by X-ray diffraction (XRD) study to identify the products as well as their crystal structure. Both the products exhibited identical XRD patterns and literature survey (JCPDS) shows the formation of magnetite (Fe_3O_4) phase of iron oxide. Figure 1 shows the representative XRD pattern. No other phases of iron oxide or hydroxide were detected in the samples within the detection limit of the XRD. The precipitates were dispersed in water before being deposited in a thin carbon film coated Cu grid for transmission electron microscopic (TEM) studies in order to investigate the morphology of the products. The TEM image depicted in Figure 2(a) shows the formation of uniform nanorods with diameters ~ 150 nm and lengths ~ 400 nm when 150 μL of H_2O_2 was used.

Further high-resolution TEM (HRTEM) (not shown here) reveals that these nanorods were single crystalline in nature. Figure 2(b) shows the formation of Fe_3O_4 octahedrons when 300 μL of H_2O_2 was used for the synthesis. The dimensions of the octahedrons were quite polydispersed in nature.



SCHEME 1: Nanoiron oxide catalyzed oxidation of benzyl alcohol and styrene derivative by H_2O_2 .

The synthesized iron oxide nanorods and octahedrons were employed as catalysts for the selective oxidations benzylic alcohols by H_2O_2 (Scheme 1).

In a trial reaction, we have applied both iron oxide nanomaterials (i.e., nanorod and octahedron) for the oxidation of benzyl alcohol. We have observed a comparable reactivity and selectivity of the two nanomaterials with slightly higher reactivity for nanorods (Table 1). We have taken iron oxide nanorods to carry out all the oxidation reactions due to their higher reactivity. In a typical experimental procedure benzyl alcohol or styrene was heated with 30% (v/v) H_2O_2 at 70°C in presence of catalytic amount of iron oxide nanorod (1 mol%) and stirred till completion of reaction (TLC).

The product was extracted with ethyl acetate. The details of experimental procedure were given in the experimental section. The selectivity of all the oxidized products was determined from ^1H NMR spectroscopic analysis of crude product.

A variety of substituted benzyl alcohol and styrene derivative were oxidized by H_2O_2 catalyzed by nanoiron oxide. The results are summarized in Table 2 (oxidation of alcohol) and Table 3 (oxidation of styrene). It was observed that without nano-iron oxide catalyst the oxidation reactions by H_2O_2 proceeded marginally (10–12%). The yields for both oxidation reactions were moderate to good. A little higher selectivity (99%) of the oxidized products was also observed in benzyl alcohol derivatives containing $-\text{CH}_3$, $-\text{Cl}$, $-\text{OMe}$, $-\text{NO}_2$ group in aromatic moiety (Entries 2–5 Table 2) compared to benzyl alcohol (97%) (Entry 1, Table 2).

The improved activity of the catalyst most probably originates from the nanometer size of nano-iron oxide. In general, nanoscale heterogeneous catalysts should offer higher surface areas and low-coordinated sites, which are responsible for the higher catalytic activity. Importantly, note that the ferromagnetic property of the catalyst made the isolation and reuse of this catalyst very easy. In the presence of a magnetic stirrer bar, nano-iron oxide moved onto the stirrer bar steadily and the reaction mixture became clear within 10 s (Figure 3). The catalyst can also be isolated by simple decantation.

After washing with acetone and drying in air, the nano-iron oxide can be directly reused for five runs without significant loss of catalytic activity for selective oxidation of 4-methoxy benzyl alcohol to 4-methoxybenzaldehyde

TABLE 2: Iron oxide nanorod catalyzed oxidation of benzylic alcohol by H₂O₂.

Entry	R	Time (h)	Yield (%) ^a	Selectivity (%) ^b
1	H	12	78	97
2	4-Me	10	81	99
3	4-Cl	12	80	98
4	4-OMe	11	82 (80) ^c	99 (98) ^c
5	4-NO ₂	12	75 (65) ^c	98 (95) ^c

^aYield refer to those of pure products characterized by ¹H NMR and IR spectroscopic data. ^bSelectivity based on alcohol conversion. ^cThe results in the bracket are obtained after 4th cycle.

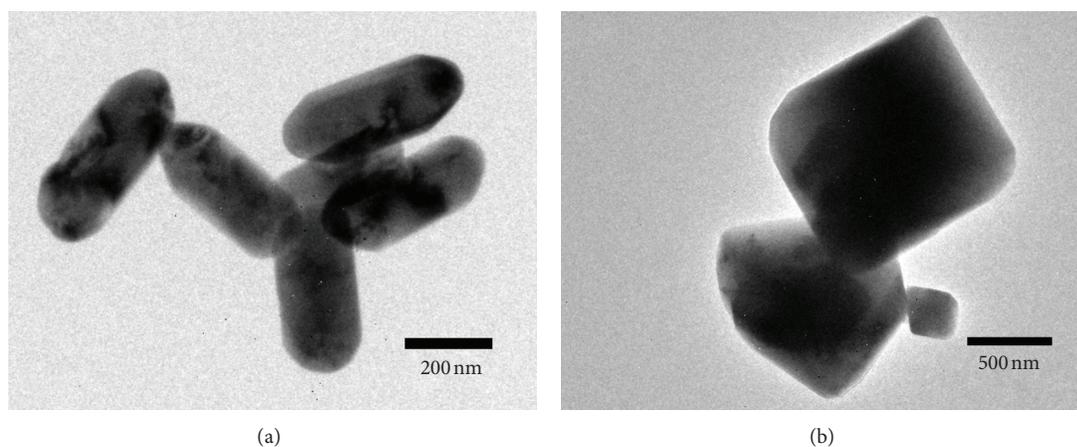
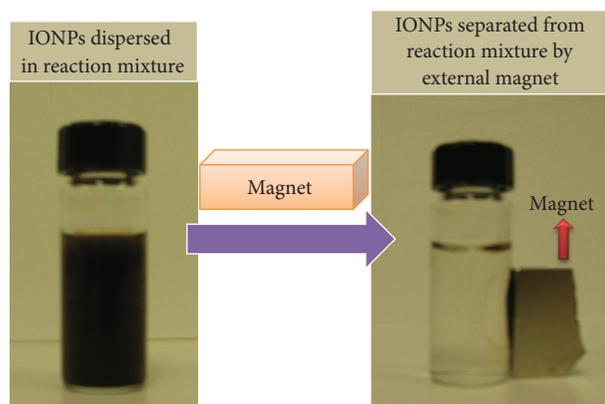
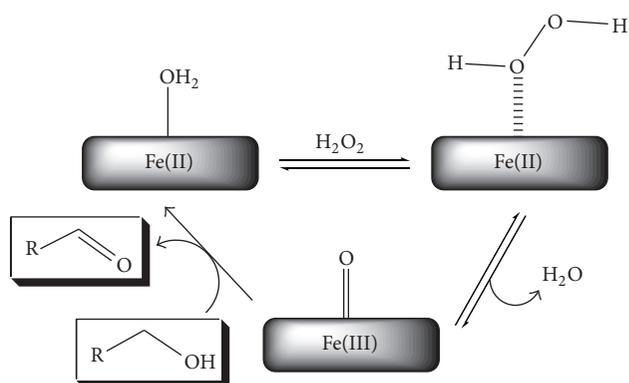
FIGURE 2: TEM images of the Fe₃O₄ (a) nanorods and (b) octahedrons.

FIGURE 3: Separation of the IONPs by using external magnet.



SCHEME 2: Plausible mechanism for the oxidation of alcohol.

(Table 4). The recyclability for the oxidation of 4-nitrobenzyl alcohol (entry 5, Table 2) and 4-methyl styrene (entry 5, Table 3) has also been checked and results were presented in tables.

A plausible mechanism for the iron oxide nanorod catalyzed oxidation of alcohol by H₂O₂ has been presented in Scheme 2.

In general, all these, oxidation reactions are simple, moderate to good yielding, and highly selective. This protocol did not require any solvent; thus, this procedure avoided volatile

and toxic organic solvents concerning green chemistry. Moreover, here we have used environment-friendly and easily accessible nano-iron oxide as catalyst. The oxidizing reagent (H₂O₂) is also a very cheap, mild, and an environment friendly reagent, which produced water as only by-product. The catalyst (nano-iron oxide) and reagent (H₂O₂) used in this protocol thus fulfilled the criteria for “green chemistry.”

In conclusion, a protocol has been developed for the preparation of iron oxide nanoparticles of two different

TABLE 3: Iron oxide nanorod catalyzed oxidation of styrene by H₂O₂.

Entry	R	Time (h)	Yield (%) ^a	Selectivity (%) ^b
1	H	12	72	98
2	4-Me	12	80 (70) ^c	99 (97) ^c
3	4-OMe	12	80	99
5	4-NO ₂	12	75	98

^aYield refer to those of pure products characterized by ¹H NMR and IR spectroscopic data. ^bSelectivity based on olefine conversion. ^cThe results in the bracket are obtained after 4th cycle.

TABLE 4: Iron oxide catalyzed oxidation of 4-methoxybenzaldehyde.

Runs	Time (h)	Yield (%) ^a	Selectivity (%) ^b
1	12	82	99
2	12	82	99
3	12	81	98
4	12	80	98
5	12	80	98

^aYield refer to those of pure products characterized by ¹H NMR and IR spectroscopic data. ^bSelectivity based on alcohol conversion.

(nanorods and octahedrons) morphologies and well characterized by TEM and XRD. These two nanomaterials showed comparable selectivity on the oxidation of aryl-methanol and vinyl-arene. Moreover, the magnetic catalysts have easily separated from reaction mixture by a magnet and are reused without appreciable loss of catalytic activity. The oxidation processes avoid use of toxic catalysts and volatile and hazardous organic solvents. Certainly, this observation provides great promise towards more practical applications.

3. Experimental Section

3.1. Details of Experimental Procedure for Nanoiron Oxide Catalyzed Oxidation Alcohol: Representative One for the Oxidation of Benzyl Alcohol (Table 2, Entry 1). 4-Methoxybenzyl alcohol (1 mmol) was heated with 30% (v/v) H₂O₂ (1 mmol) at 70°C in presence of catalytic amount of nano-iron oxide (1 mol%) and stirred at that temperature for 12 h (TLC). The reaction was cooled to room temperature and the product was extracted with ethyl acetate (2 × 10 mL). The combined organic layer was washed with water (2 × 5 mL) and brine solution (5 mL) and finally dried over anhydrous Na₂SO₄. Evaporation of solvent left the crude 4-methoxybenzaldehyde with 99% selectivity, which was purified by column chromatography over silica gel (ethyl acetate:hexane 5:1) to provide pure 4-methoxybenzaldehyde (115 mg, 85%).

The 4-methoxybenzaldehyde was indentified by IR and ¹H NMR spectroscopic data.

3.2. Details of Experimental Procedure for Nanoiron Oxide Catalyzed Oxidation Olefin: Representative One for the Oxidation of Styrene (Table 3, Entry 1). Styrene (104 mg, 1 mmol) was heated with 30% (v/v) H₂O₂ (2 mmol) at 70°C in presence of catalytic amount of nano-iron oxide (1 mol%) and stirred at that temperature for 12 h (TLC). The reaction was cooled to room temperature and the product was extracted with ethyl acetate (2 × 10 mL). The combined organic layer was washed with water (2 × 5 mL) and brine solution (5 mL) and finally dried over anhydrous Na₂SO₄. Evaporation of solvent left the crude benzyldehyde with 98% selectivity, which was purified by column chromatography over silica gel (ethyl acetate:hexane 5:1) to provide pure benzyldehyde (76 mg, 72%). The benzyldehyde was indentified by IR and ¹H NMR spectroscopic data.

All the products in Tables 1 and 2 are known. The ¹H NMR spectra of all the products in Tables 1 and 2 were given.

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