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 (H₂O₂) as reagent in combination of a catalyst has attracted much attention because H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 FeCl₃ and FeCl₂ 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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanorods</td>
<td>70 °C</td>
<td>12</td>
<td>78</td>
<td>97</td>
</tr>
<tr>
<td>Octahedron</td>
<td>80 °C</td>
<td>12</td>
<td>70</td>
<td>96</td>
</tr>
<tr>
<td>None</td>
<td>100 °C</td>
<td>24</td>
<td>15</td>
<td>80</td>
</tr>
</tbody>
</table>

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

The synthesized iron oxide nanorods and octahedrons were employed as catalysts for the selective oxidations benzyl alcohols by \( \text{H}_2\text{O}_2 \) (Scheme 1).

In a typical experimental procedure benzyl alcohol or styrene was heated with 30% (v/v) \( \text{H}_2\text{O}_2 \) 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 \( ^1\text{H} \) NMR spectroscopic analysis of crude product.

A variety of substituted benzyl alcohol and styrene derivative were oxidized by \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) 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.

Further high-resolution TEM (HRTEM) (not shown here) reveals that these nanorods were single crystalline in nature. Figure 2(b) shows the formation of \( \text{Fe}_3\text{O}_4 \) octahedrons when 300 μL of \( \text{H}_2\text{O}_2 \) was used for the synthesis. The dimensions of the octahedrons were quite polydispersed in nature.

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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

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 \( ^1\text{H} \) NMR spectroscopic analysis of crude product.
Table 2: Iron oxide nanorod catalyzed oxidation of benzylic alcohol by H$_2$O$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (h)</th>
<th>Yield (%)$^a$</th>
<th>Selectivity (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>12</td>
<td>78</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>4-Me</td>
<td>10</td>
<td>81</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>4-Cl</td>
<td>12</td>
<td>80</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>4-OMe</td>
<td>11</td>
<td>82 (80)$^c$</td>
<td>99 (98)$^c$</td>
</tr>
<tr>
<td>5</td>
<td>4-NO$_2$</td>
<td>12</td>
<td>75 (65)$^c$</td>
<td>98 (95)$^c$</td>
</tr>
</tbody>
</table>

$^a$Yield refer to those of pure products characterized by $^1$H NMR and IR spectroscopic data. $^b$Selectivity based on alcohol conversion. $^c$The results in the bracket are obtained after 4th cycle.

![a](image1.jpg) ![b](image2.jpg)

Figure 2: TEM images of the Fe$_3$O$_4$ (a) nanorods and (b) octahedrons.

![image3.jpg]

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

![image4.jpg]

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 H$_2$O$_2$ 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 (H$_2$O$_2$) 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 (H$_2$O$_2$) 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 $\text{H}_2\text{O}_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (h)</th>
<th>Yield (%)$^a$</th>
<th>Selectivity (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>12</td>
<td>72</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>4-Me</td>
<td>12</td>
<td>80 (70)$^c$</td>
<td>99 (97)$^c$</td>
</tr>
<tr>
<td>3</td>
<td>4-OMe</td>
<td>12</td>
<td>80</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>4-NO$_2$</td>
<td>12</td>
<td>75</td>
<td>98</td>
</tr>
</tbody>
</table>

$^a$Yield refers to those of pure products characterized by $^1$H NMR and IR spectroscopic data. $^b$Selectivity based on olefine conversion. $^c$The results in the bracket are obtained after 4th cycle.

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

<table>
<thead>
<tr>
<th>Runs</th>
<th>Time (h)</th>
<th>Yield (%)$^a$</th>
<th>Selectivity (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>82</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>82</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>81</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>80</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>80</td>
<td>98</td>
</tr>
</tbody>
</table>

$^a$Yield refer to those of pure products characterized by $^1$H NMR and IR spectroscopic data. $^b$Selectivity 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-Methoxy benzyl alcohol (1 mmol) was heated with 30% (v/v) $\text{H}_2\text{O}_2$ (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 ($2 \times 10$ mL). The combined organic layer was washed with water ($2 \times 5$ mL) and brine solution (5 mL) and finally dried over anhydrous Na$_2$SO$_4$. 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 $^1$H NMR spectroscopic data.

The 4-methoxybenzaldehyde was indentified by IR and $^1$H 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) $\text{H}_2\text{O}_2$ (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 ($2 \times 10$ mL). The combined organic layer was washed with water ($2 \times 5$ mL) and brine solution (5 mL) and finally dried over anhydrous Na$_2$SO$_4$. 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 $^1$H NMR spectroscopic data.

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

References


