

## Magnetic CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles as an Efficient Catalyst for the Oxidation of Alcohols to Carbonyl Compounds in the Presence of Oxone as an Oxidant

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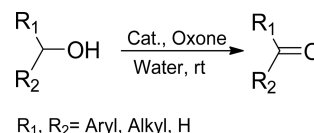
Received November 18, 2013, Accepted March 16, 2014

Magnetically nano-CoFe<sub>2</sub>O<sub>4</sub> efficiently catalyzes oxidation of primary and secondary benzylic and aliphatic alcohols to give the corresponding carbonyl products in good yields. The reactions were carried out in an aqueous medium at room temperature in the presence of oxone (potassium hydrogen monopersulfate) as an oxidant. In addition, the catalysts could be reused up to 6 runs without significant loss of activities. Catalyst was characterized by SEM, XRD and IR.

**Key Words :** Magnetic nanoparticles, Cobalt ferrite, Oxidation, Alcohols, Oxone

### Introduction

The synthesis and characterization of nanoparticles is of great interest in present study because of fundamental and technological benefits. A large number of applications such as catalysis entailing nanoparticles are now an industrial reality.<sup>1,2</sup> Nanoparticles of metals and metal oxides have been widely used as catalysts in many organic reactions because of their high surface area and facile separation.<sup>3</sup> Nanoparticles display high catalytic activity and chemical selectivity under mild circumstances.<sup>4</sup> The extremely tiny-size particles enlarge the surface area which, when exposed to the reactant, allow more reactions to take place simultaneously and hence accelerate the process.<sup>5</sup> Magnetic NPs have a wide variety of distinctive magnetic properties such as super paramagnetic, high coercivity, low Curie temperature, high magnetic susceptibility, *etc.* Magnetic NPs are of paramount importance for researchers from a broad range of fields, including magnetic fluids, data storage, catalysis, and bio applications.<sup>6-10</sup> Some defects have been found regarding homogeneous catalysts. For example, difficult workup of the perilous metal residues, and lack of recycling methods, which make them inconvenient for large-scale applications.<sup>11</sup> In heterogeneous reaction, tedious methods like centrifugation and filtration are utilized to recover catalysts and end in loss of solid catalyst in the process of separation. Magnetic separation supplies a convenient method to remove and recycle magnetized species by utilizing an appropriate magnetic field.<sup>12-14</sup> One of the significant transformations of organic synthesis is the oxidation of alcohols to carbonyl compounds and many methods have been probed in order to accomplish such a conversion and a variety of oxidants have been developed.<sup>15</sup> Many highly efficient systems have been developed for catalytic alcohol oxidation. Traditional methods



**Scheme 1.** Oxidation of alcohols with oxone in the presence of water at room temperature.

utilizing stoichiometric quantities of inorganic oxidants such as chromium (VI) reagents, permanganates, or *N*-chlorosuccinimide (NCS) are not environmentally friendly.<sup>16</sup> Even grave environmental problems are created using hypervalent iodine reagents. Thus, the development of greener oxidation systems using less poisonous catalysts, oxidants, and solvents became a crucial aim for catalysis. Among the numerous methods, oxidation of organic compounds to corresponding carbonyl by O<sub>2</sub> or TBHP required high temperatures and long times. Hence, mild, catalytic, economic and efficient alternative methods was needed.<sup>17-19</sup> The search for catalytic oxidation of alcohols in an aqueous medium in the absence of an additional base is still a significant challenge.<sup>20</sup> Oxone is a convenient, readily available, and relatively stable compound at room temperature, and therefore is utilized for various transformations in organic synthesis.<sup>21-29</sup> In this paper, cobalt ferrite nanoparticles were synthesized by co-precipitation method.<sup>30</sup> We have shown that CoFe<sub>2</sub>O<sub>4</sub> MNPs are an active and reusable catalysts for oxidation of alcohols with oxone in the presence of water at room temperature (Scheme 1).

### Experimental

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), sodium hydroxide (NaOH),

aliphatic and benzylic alcohols were purchased from Merck (Darmstadt, Germany) and Fluka (Switzerland) and used without further purification. The IR spectra were measured on a Jasco 6300 FT-IR spectrometer (KBr disks). The structural properties of synthesized nanoparticles were analyzed by X-ray powder diffraction (XRD) with a X-Pert Philips advanced diffractometer using Cu ( $K\alpha$ ) radiation (wavelength: 1.5406 Å), Pw3040/60, operated at 40 kV and 30 mA at room temperature in the range of  $2\theta$  from 4 to  $120^\circ$ . The particle size and morphology of the surfaces of sample were analyzed by a scanning electron microscopy (LEO Co., England, Model: 1455VP). The disc was coated with gold in an ionization chamber. TLC was used to follow the reactions. The aliphatic products detected by GC-FID (VARIAN C-P-3800 with FID detector, column CP-Sil 5 CB30 m  $\times$  0.32 mm).

**Preparation of  $\text{CoFe}_2\text{O}_4$  MNPs in Aqueous Solution.** Cobalt ferrite nanoparticles were synthesized by the coprecipitation of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ions (molar ratio 1:2) in sodium hydroxide solution<sup>30</sup>  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.54 g) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g) were dissolved in a 10 mL deionized water. NaOH (1.2 g) was dissolved in 10 mL water and this solution was added into the previously prepared solution while stirring at  $80^\circ\text{C}$ . The stirring was continued for 30 min and cooled to room temperature. The precipitate was isolated in a magnetic field, washed with deionized water three times, and finally dried.

**General Procedure for the Oxidation of Alcohol.** Alcohol (1 mmol), water (1 mL), and  $\text{CoFe}_2\text{O}_4$  MNPs (11.8 mg, 5 mol %) were added to a round-bottomed flask. The reaction mixture was stirred for the two minutes, and then oxone (0.6 mmol) was added in three portions. The reaction mixture was placed at room temperature and stirred for the specified time (Table 5). The reaction was followed by TLC (EtOAc-cyclohexane, 2:10). After the completion of the reaction, the product was extracted in dichloromethane. The solvent was evaporated under reduced pressure to give the corresponding aromatic products. Purification of the residue using plate chromatography (silica gel) provided the pure carbonyl compounds. The aliphatic products in dichloromethane was dried with anhydrous  $\text{MgSO}_4$  and detected by GC-FID.

## Results and Discussion

**Characterization of the Catalyst.** Figure 1 shows the FT-IR spectra of  $\text{CoFe}_2\text{O}_4$  MNPs, where the peak at  $580\text{ cm}^{-1}$  corresponds to the Fe–O bond. Generally, XRD can be used to characterize the crystallinity of nanoparticles, and it gives an average diameter of all the nanoparticles. The XRD pattern of the  $\text{CoFe}_2\text{O}_4$  MNPs sample is shown in Figure 2. The position and relative intensity of all diffraction peaks matched well with standard  $\text{CoFe}_2\text{O}_4$ . The results indicate that the discernible peaks in Figure 2 can be indexed to (220), (311), (400), (511) and (440) planes of a cubic unit cell, which corresponds to cubic spinel structure of cobalt iron oxide (card no. 003-0864). The diameter of the  $\text{CoFe}_2\text{O}_4$

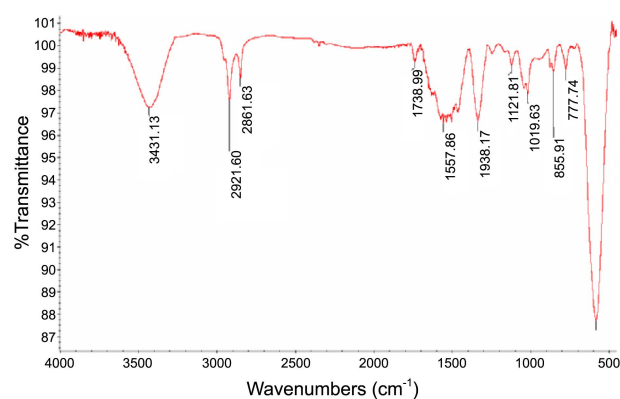


Figure 1. FT-IR spectra of  $\text{CoFe}_2\text{O}_4$  MNPs.

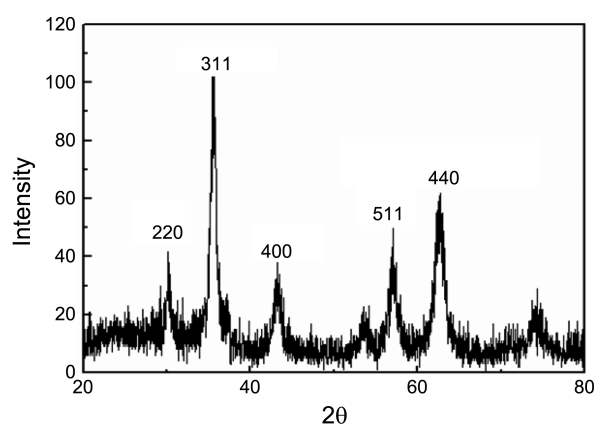


Figure 2. XRD pattern of  $\text{CoFe}_2\text{O}_4$  MNPs.

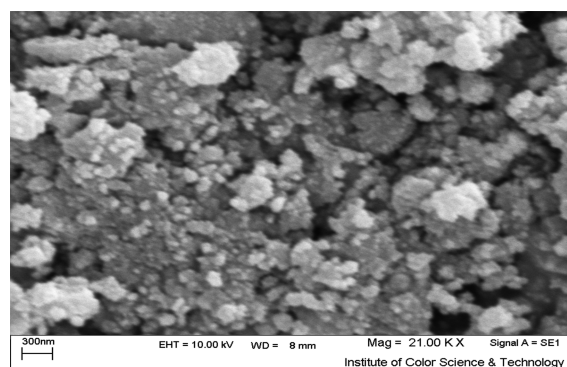


Figure 3. SEM image of  $\text{CoFe}_2\text{O}_4$  MNPs.

determined by Debye-Scherrer equation with XRD data ( $D = 0.94 \lambda / B \cos \theta$ ). The SEM analysis suggests that the  $\text{CoFe}_2\text{O}_4$  MNPs are nanocrystalline and their shape is spherical (Figure 3). These results are in good harmony with the XRD analyses. The results show that the diameter of the  $\text{CoFe}_2\text{O}_4$  MNPs, is about 60–90 nm.

**Optimization of Alcohol Oxidation Conditions.** For optimizing the reaction conditions, we tried to convert 2-chlorobenzyl alcohol (1 mmol) to 2-chlorobenzaldehyde in the presence of  $\text{CoFe}_2\text{O}_4$  as a nanomagnet catalyst (2.3 mg) and oxone (1 mmol was added in 3 stages in 30 minutes) in various solvents at room temperature. As shown in Table 1, 2-chlorobenzaldehyde was formed as the major product in

**Table 1.** Conversion of 2-chlorobenzyl alcohol to 2-chlorobenzaldehyde in different solvents with oxone and in the presence of  $\text{CoFe}_2\text{O}_4$  MNPs catalyst at room temperature

Entry	Solvent	Time (min)	Yield (%)
1	Cyclohexane	30	trace
2	Acetonitrile	30	45
3	Water	30	60
4	Ethanol	30	trace
5	Dry toluene	30	trace
6	Ethyl acetate	30	10

**Table 2.** Oxidation of 2-chlorobenzyl alcohol using various oxidizing reagents in water and in the presence of  $\text{CoFe}_2\text{O}_4$  MNPs catalyst at room temperature

Entry	Oxidizing reagent	Time (min)	Yield (%)
1	$\text{H}_2\text{O}_2$	30	40
2	$\text{O}_2$ atmosphere	30	10
3	Oxone	30	60
4	Absence	30	0

all cases, and the highest yield for 2-chlorobenzaldehyde was achieved in water (Entry 3).

Table 2 summarized the effect of different oxidants on the oxidation of 2-chlorobenzyl alcohol over nanomagnetic- $\text{CoFe}_2\text{O}_4$  catalyst at room temperature in water. These results showed that the higher yield was achieved with oxone as oxidant (Entry 3). We also observed that 2-chlorobenzyl alcohol was not oxidized with this system in the absence of oxidant under nitrogen atmosphere.

The amount of the catalyst and oxidant were also optimized. The results showed that 5 mol % of catalyst and 0.6 mmol of oxidant is the best choice for the oxidation of 1 mmol of alcohol (Tables 3 and 4). The competing reaction

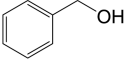

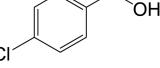

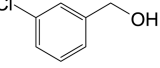

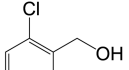

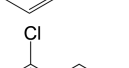

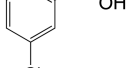

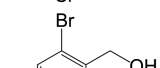

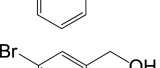

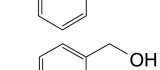

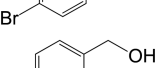

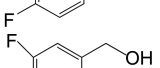

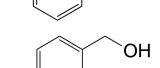

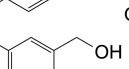

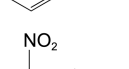

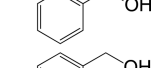

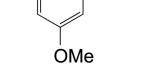

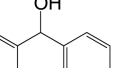

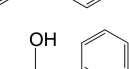

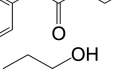

**Table 3.** Oxidation of 2-chlorobenzyl alcohol in water with Oxone (1 mmol) and different amounts of  $\text{CoFe}_2\text{O}_4$  MNPs at room temperature

Entry	Nanomagnetic- $\text{CoFe}_2\text{O}_4$ catalyst (mol %)	Time (min)	Yield (%)
1	10	30	90
2	5	30	90
3	3	30	80
4	1	30	60
5	0	30	20

**Table 4.** Oxidation of 2-chlorobenzyl alcohol (1 mmol) in water with different amounts of oxone and in the presence of  $\text{CoFe}_2\text{O}_4$  MNPs catalyst (5 mol %) at room temperature

Entry	Oxone (mmol)	Time (min)	Yield (%)
1	1	30	90
2	0.6	30	90
3	0.5	30	70
4	0.2	30	30

**Table 5.** Oxidation of various alcohols using  $\text{CoFe}_2\text{O}_4$  MNPs catalyst (5 mol %) in water with Oxone at room temperature

Entry	Substrate	Product	Time (min)	Yield (%)
1			20	93
2			30	90
3			25	88
4			30	90
5			45	88
6			30	85
7			30	88
8			35	85
9			35	88
10			40	86
11			120	85
12			120	83
13			120	82
14			15	94
15			30	88
16			150	70
17			240	99.7
18			240	82.6
19			240	99.5

**Table 6.** Recycling of the catalytic system for the oxidation of 2-chlorobenzyl alcohol to 2-chlorobenzaldehyde

Entry	Time (min)	Yield (%)
1	30	90
2	30	88
3	30	89
4	30	90
5	30	90
6	30	88

such as overoxidation of aldehydes to the corresponding carboxylic acids was not observed in any of the cases under the above conditions.

**Application Scope.** The reaction condition, which was optimized for 2-chlorobenzyl alcohol, can be easily applied to various primary and secondary alcohols. The results for the oxidation of a variety of alcohols are summarized in Table 5. The oxidation of various benzylic alcohols gave the carbonyl compounds in high yields and short reaction times. The electron withdrawing groups reduced the reaction rate dramatically (Entry 11) and the electron donating groups on the benzene ring accelerate the reaction rate (Entry 14). The oxidation for aliphatic alcohols proceeded quite slowly (Entry 17-19). The competing reaction such as overoxidation of aldehydes to the corresponding carboxylic acids was not observed, either.

The catalyst was easily separated from the products by exposure of the reaction vessel to an external magnet and decantation of the reaction solution. The remaining catalyst was washed with acetone and water to remove residual product, and then dried. This catalyst could be subsequently reused in more than six iterative cycles without no obvious decrease in activity (Table 6).

### Conclusion

We have introduced a straightforward and efficient method for oxidation of alcohols to their corresponding carbonyl compounds using oxone in the presence of nanomagnetic-CoFe<sub>2</sub>O<sub>4</sub> catalyst in water at room temperature. The use of nontoxic and inexpensive materials, stability of the oxidation condition, simple procedure, short reaction times, good yields, and mild reaction conditions are the advantages of this method. In comparison with the other oxidants such as O<sub>2</sub> or TBHP, oxidation by oxone accomplished at low temperatures and in short times.<sup>18,19</sup> The catalyst could be subsequently reused in six iterative cycles, without no obvious decrease in activity. The application of this nanocatalyst to different oxidation reactions is currently under investigation in our laboratory.

**Acknowledgments.** Publication cost of this paper was financially supported by the Korean Chemical Society.

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