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Magnetic $ZnFe_2O_4$ 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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ABSTRACT

Zinc ferrite ($ZnFe_2O_4$) nanoparticles were synthesized *via* the auto-combustion assisted sol-gel method of Zn^{2+} and Fe^{3+} ions (molar ratio 1:2) in ammonia solution. The prepared nanomagnetic catalyst was characterized by IR, XRD, SEM and ICP. The diameter of the $ZnFe_2O_4$ MNPs (63.7 nm) was determined by Debye-Scherre equation *via* their XRD pattern. Nanomagnetic $ZnFe_2O_4$ efficiently catalyzes oxidation of alcohols and gave the corresponding carbonyl-containing products in good yields. The reactions were carried out in an aqueous medium at r.t in the presence of oxone (potassium hydrogen monopersulfate) as an oxidant. In addition, the catalysts could be reused up to 5 runs without significant loss of activities.

Keywords: *Nanomagnetic catalyst, Zinc ferrite, Oxidation, Alcohols, Carbonyl compounds, Oxone.*

1. Introduction

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 [1]. Nanoparticles display high catalytic activity and chemical selectivity under mild circumstances [2]. Magnetic NPs are of paramount importance for researchers from a broad range of fields, including magnetic fluids, data storage, catalysis, and bio applications [3–7]. Recently, nanostructures of magnetic materials have received growing attention due to their new material qualities that are significantly different from those of their bulk counterparts [8-11]. Transition metal ferrites MFe_2O_4 show an important class of technological materials, because of their noticeable properties which give them proper for many requests in the next generation of electronics, magnetic information storage and catalysis [12].

In the heterogeneous reactions, tedious methods like centrifugation and filtration are utilized to recover catalysts and avoid the loss of solid catalyst particles in the separation process. Magnetic separation supplies a convenient method to remove and recycle magnetized species by utilizing an appropriate magnetic field [13-15]. Oxidation is one of the most fundamental reactions in synthetic organic chemistry and a variety of oxidants have been developed. Advances in the development of novel oxidation reagents and methodologies and their utilizations in both target- and diversity-oriented synthesis have been regularly probed, and constituted one of the most widely and actively investigated areas of present organic synthesis [16]. 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 [17]. Water can be counted as the most agreeable reaction medium for alcohol oxidation [18] and there is a thrust in search for new green catalysts [19]. Herein, zinc ferrite magnetic nanoparticles were synthesized *via* the auto-combustion assisted sol-gel method [20,21]. We have

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shown that $ZnFe_2O_4$ MNPs is an active and reusable catalyst through magnetic separation for the oxidation of alcohols with oxone in the presence of water at room temperature (Scheme 1).

2. Experimental

2.1. Material and methods

Ferric nitrate nonahydrate $Fe(NO_3)_3.9H_2O$, Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, citric acid $C_6H_8O_7$, 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 -PRO advanced diffractometer using Cu (Kα) radiation (wavelength: 1.5406 Å), operated at 40 kV and 40 mA at room temperature in the range of 2θ from 20 to 70°. The particulate morphology was characterized by using scanning electron microscopy (LEO Co., England, Model: 1455VP). The disc was coated with gold in an ionization chamber. Elemental analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP) using an ICP-OES (Model: VISTA-PRO) instrument. TLC and GC were used to follow the reactions. The aliphatic products detected by GC-FID (VARIAN CP-3800 with FID detector, column CP-Sil 5 CB30m×0.32mm).

2.2. Preparation of $ZnFe_2O_4$ MNPs in aqueous solution

Zinc ferrite nanoparticles were synthesized *via* the auto-combustion assisted sol-gel method of Zn^{2+} and Fe^{3+} ions (molar ratio 1:2) in ammonia solution [20,21]. Briefly, $Fe(NO_3)_3.9H_2O$, $Zn(NO_3)_2.6H_2O$ and chelating agent were dissolved in distilled water. The molar ratio of metal nitrate to citric acid was 1:1. The pH value was adjusted in 7 by dropwise adding ammonia solution (28%) to the reaction mixture under constant stirring. Then, the solution was evaporated on a water bath (60°C) to form a sticky gel. The temperature was increased to 80°C in order to obtain a thick gel. The gel was kept on a hot plate for auto combustion and the temperature was increased to *ca.* 200°C. A large amount of gases (CO_2, H_2O, and N_2) released and auto combustion occurred giving rise to a black ferrite powder. The powder washed with distilled water and acetone three times and isolated in a magnetic field.

2.3. General procedure for the oxidation of alcohol

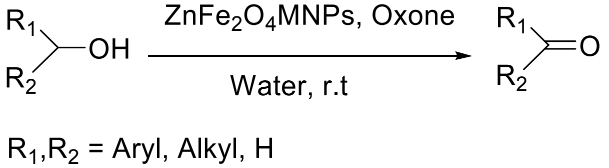
Alcohol (1 mmol), water (2 mL) and 10 mol% of nanomagnetic-$ZnFe_2O_4$ (24mg) were added into a round-bottomed flask. The mixture was stirred for two minutes. Then, oxone (0.8 mmol) was added in four portions (0.2 mmol every five minutes). The mixture was stirred at room temperature. The reaction was followed by TLC (EtOAc-cyclohexane, 2:10) in comparison with the standard samples of corresponding alcohols and carbonyl compounds. After the completion of the reaction, the product was extracted with dichloromethane. The solvent was evaporated under reduced pressure to give the corresponding pure aromatic products. Purification of the residue using flash column chromatography (silica gel) provided the pure carbonyl compounds. The products were characterized from their IR data and compared with authentic samples. The aliphatic products in dichloromethane were dried by using anhydrous $MgSO_4$ and detected by GC-FID in comparison with the standard samples of corresponding alcohols and carbonyl compounds. The GC yields of the aliphatic products were calculated based on their gas chromatogram. The selectivity of the oxidized products was determined from ^{1}HNMR spectroscopic analysis of crude product.

3. Results and Discussion

3.1. Characterization of the catalyst

The FT-IR spectrum of the $ZnFe_2O_4$ MNPs is presented in Fig. 1. A broad absorption band at about 3420 cm^{-1} represents a stretching mode of H_2O molecules and indicates that a large number of OH groups are presented on the surface of the MNPs. In the range of 1000–400 cm^{-1}, a typical metal–oxygen absorption band for the spinel structure of the ferrite at ~580 cm^{-1} was observed. This band strongly suggests the intrinsic stretching vibrations of the metal (Fe ↔ O) at the tetrahedral site [22].

Fig. 2 shows the XRD pattern of the $ZnFe_2O_4$ MNPs. Generally, XRD can be used to characterize the crystallinity of nanoparticles, and it gives average diameters of all nanoparticles. The results indicate that the discernible peaks in Fig. 2 [23], which corresponds to the cubic spinel structure of zinc, iron oxide (JCPDS card No. 01-077-0011). The broadening of all diffraction peaks indicates that the sizes of the prepared particles were small.



Scheme 1. Oxidation of alcohols in the presence of nanomagnetic catalyst at room temperature.

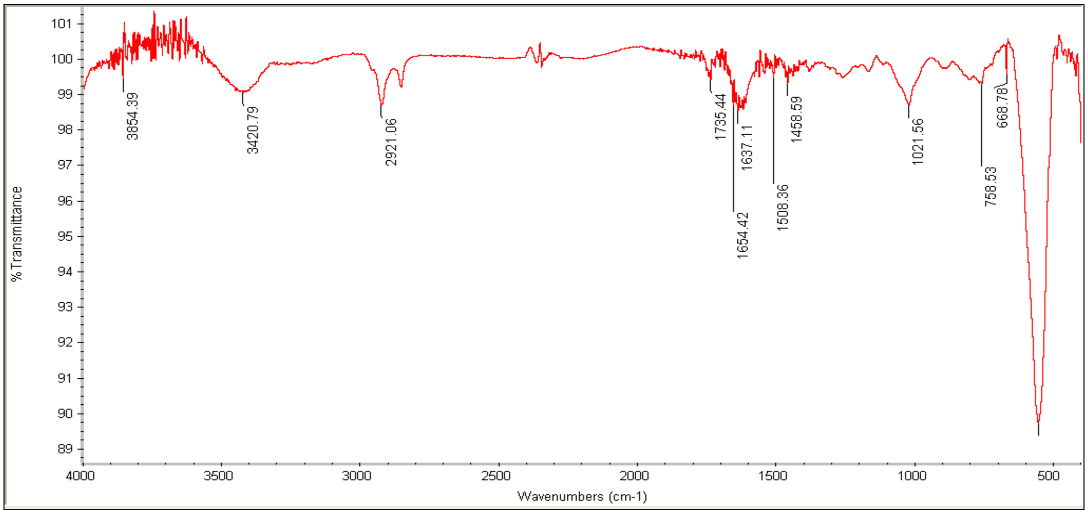


Fig. 1. FTIR spectrum of $ZnFe_2O_4$ MNPs.

The diameter of the $ZnFe_2O_4$ MNPs was determined by Debye-Scherre equation *via* their XRD data ($D = 0.94 \lambda / B \cos \theta$) and was 63.7 nm. From the ICP- result, the atomic ratio of Zn-Fe is 0.59, which is close to that of $ZnFe_2O_4$ and 27% of weight is Zinc. The SEM analysis suggests that the $ZnFe_2O_4$ MNPs are nanocrystalline and their shape is irregular spherical (Fig. 3). These results are in good harmony with the XRD analyses.

3.2. Optimization of alcohol oxidation conditions

For optimizing of the reaction conditions, first, we tried to convert 4-chlorobenzyl alcohol (1 mmol) to 4-chlorobenzaldehyde, as a model reaction in the presence of $ZnFe_2O_4$ as a nanomagnetic catalyst (12 mg) and oxone (1 mmol was added in four stages) in various solvents (2mL) at r.t and the results are given in Table 1. In the all conditions, 4-chlorobenzaldehyde was formed as the major product, but the highest yield for 4-chlorobenzaldehyde was achieved in the water (Table 1, Entry 4). We also studied the oxidation of 4-chlorobenzyl alcohol to 4-chloro benzaldehyde with other oxidants in the presence of nanomagnetic $ZnFe_2O_4$ MNPs catalyst in water at room temperature. These results showed that the higher yield was achieved with oxen as an oxidant (Table 2, Entry 3) We observed that in the absence of oxidant (under nitrogen atmosphere), 4-chlorobenzyl alcohol did not oxidize with this system, even in long reaction time.

The amount of the catalyst and oxidant were also optimized. The results show that 24mg of catalyst (10 mol%) and 0.8 mmol of oxidant is the best amount for 1 mmol alcohol (Table 3 and 4). In these reactions, the aldehyde selectivity was very high (>99%).

The competing reaction such as over oxidation of aldehydes to the corresponding carboxylic acids was not observed in any of the cases under above conditions, but the reaction produces by product (carboxylic acid) at high temperatures (>40ºC).

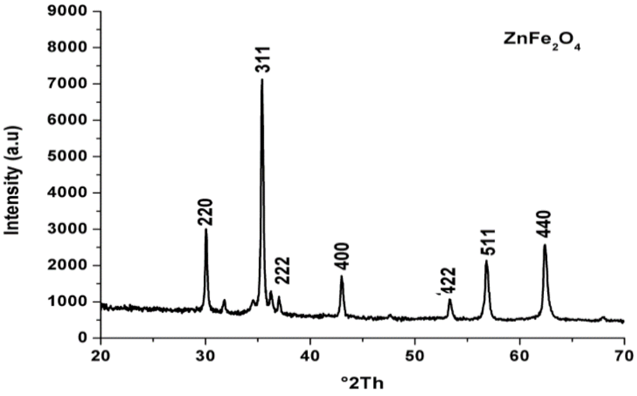


Fig. 2. XRD pattern of $ZnFe_2O_4$ MNPs.

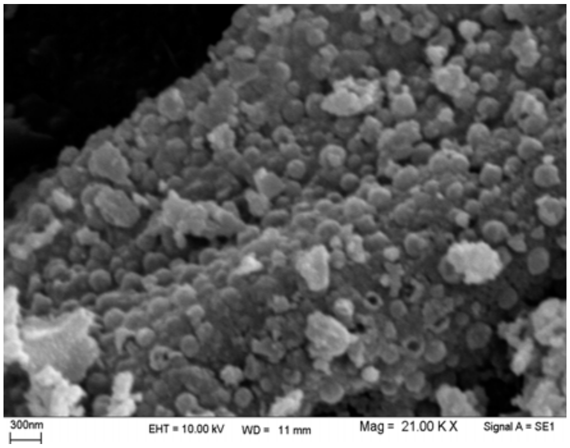


Fig. 3. SEM image of the obtained $ZnFe_2O_4$ MNPs.

Table 1. Conversion of 4-chlorobenzyl alcohol to 4-chlorobenzaldehyde in different solvents with oxone and in the presence of $ZnFe_2O_4$ MNPs catalyst at r.t.

Entry	Solvent	Yield (%)	Time (min)
1	Dichloromethane	10	90
2	Cyclohexane	trace	90
3	Acetonitrile	20	90
4	Water	60	90
5	Ethanol	trace	90
6	Dry toluene	trace	90
7	Ethyl acetate	15	90

3.3. Application scope

The optimized condition was used for various primary and secondary alcohols. As indicated in Table 5, $ZnFe_2O_4$ MNPs catalyst showed high activity/selectivity and excellent reusability in oxidation processes. In most cases, the aldehyde selectivity was quite high (>99%). 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 (Entry11) and the electron donor substituted group in the benzene ring of benzylic alcohols accelerates the reaction rate (Entry14). The oxidation times for aliphatic alcohols were fairly long (Entry17-19). The competing reaction such as over oxidation of aldehydes to the corresponding carboxylic acids was not observed in any of the cases under above conditions.

As indicated in Table 6, it can be concluded that in comparison with the other catalysts, oxidation in the presence of nanomagnetic $ZnFe_2O_4$ was accomplished at low temperatures and short reaction times. Among the numerous methods, oxidation of alcohols to the corresponding carbonyl compounds in the presence of O_2 or H_2O_2 required fairly high temperatures and long times.

Table 3. Oxidation of 4-chlorobenzyl alcohol with oxone (1 mmol) and different amounts of $ZnFe_2O_4$ MNPs in water at r.t.

Entry	Amount of catalyst (mol%)	Yield (%)	Time (min)
1	15	84	90
2	12	85	90
3	10	85	90
4	8	76	90
5	5	60	90
6	0	20	90

Table 2. Oxidation of 4-chlorobenzyl alcohol using various oxidantsin water and in the presence of $ZnFe_2O_4$ MNPs catalyst at r.t.

Entry	Oxidizing agent (1 mmol)	Yield (%)	Time (min)
1	H_2O_2	20	90
2	O_2 atmosphere	trace	90
3	Oxone	60	90
4	-	0	90

3.4. Catalyst recycling

The catalyst was easily separated from the products by exposure of the reaction vessel to an external magnet and decantation of the reaction mixture. The remaining catalyst was washed with acetone and water to remove residual product and dried. The catalyst could be subsequently reused in 5 further iterative cycles, no obvious diminishing activity was observed (Fig. 4).

4. Conclusions

To summarize, we have introduced a direct and effective method for the oxidation of alcohols to their corresponding carbonyl compounds utilizing oxone in the presence of nanomagnetic-$ZnFe_2O_4$ catalyst as a reusable, non-toxic, non-corrosive, inexpensive and commercially available heterogeneous catalyst in water. The method also offers some other advantages such as stability of the oxidative system, simple method, short reaction times, good yields of the products and mild reaction circumstances. The catalyst could be subsequently reused in 6 further iterative cycles, no clear abating activity was observed. The extension of the application of this nanocatalyst to various oxidation reactions is currently under investigation in our laboratory.

Acknowledgment

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Table 4. Oxidation of 4-chlorobenzyl alcohol (1mmol) in water with different amounts of oxone in the presence of $ZnFe_2O_4$ MNPs catalyst (10 mol%) at r.t.

Entry	Amount of oxone (mmol)	Yield (%)	Time (min)
1	0.9	85	90
2	0.8	85	90
3	0.7	76	90
4	0.3	50	90
5	0.1	18	90

Table 5. Oxidation of various alcohols using $ZnFe_2O_4$ MNPs as catalyst (10 mol%) in the presence of oxone (r.t) in water.

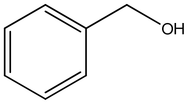
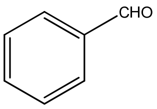
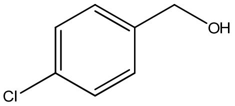
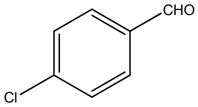
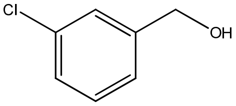
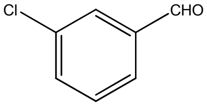
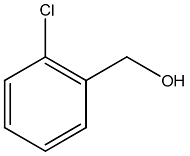
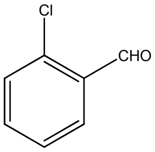
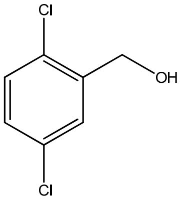
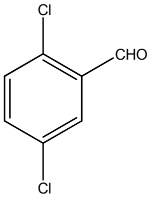
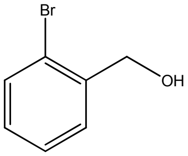
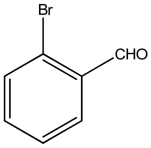
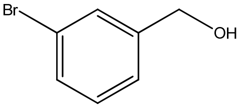
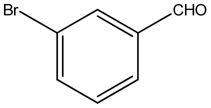
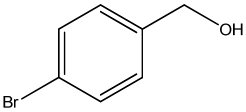
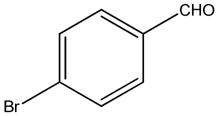
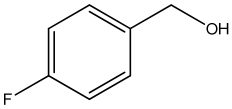
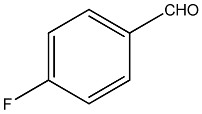
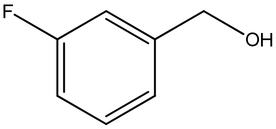
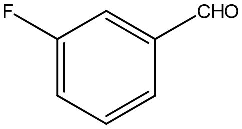
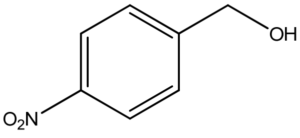
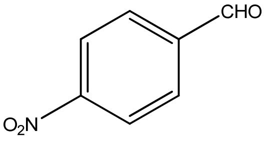
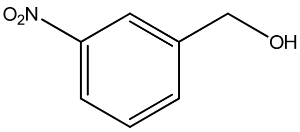
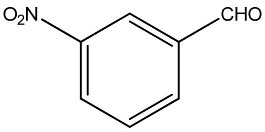
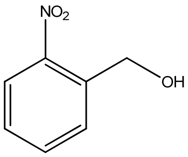
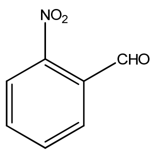
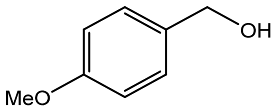
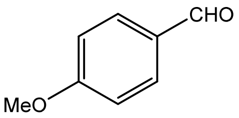
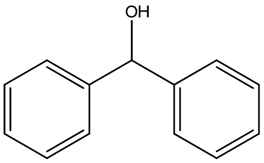
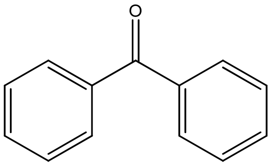
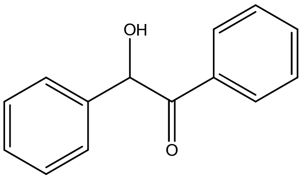
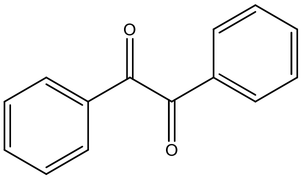
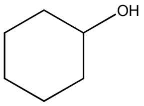
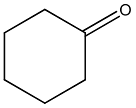
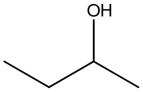
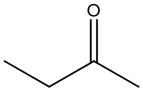
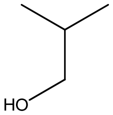
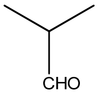
Entry	Substrate	Product	Yield[a](%)	Time (min)
1			88	90
2			85	90
3			83	95
4			83	95
5			80	95
6			86	95
7			84	95
8			85	90
9			82	90
10			80	95
11			82	120
12			82	120

Table 5. (*Continued*).

13			80	120
14			90	85
15			85	95
16			70	120
17[b]			99.68	150
18[b]			82.55	150
19[b]			99.17	150

[a] Isolated yield.

[b] The yields refer to GC analysis.

Table 6. Oxidation of benzyl alcohol to benzaldehyde using various catalysts and oxidants.

Catalyst	Oxidizing agent	Temp. (°C)	Time (h)	Ref.
Nano-γ-Fe_2O_3	H_2O_2	75	12	[24]
MgO-supported Nano-gold catalyst	O_2	120	5	[25]
TiO_2-supported gold nanoparticles	O_2	70	5	[25]
$ZnFe_2O_4$ MNPs	Oxone	r.t	1.5	This work

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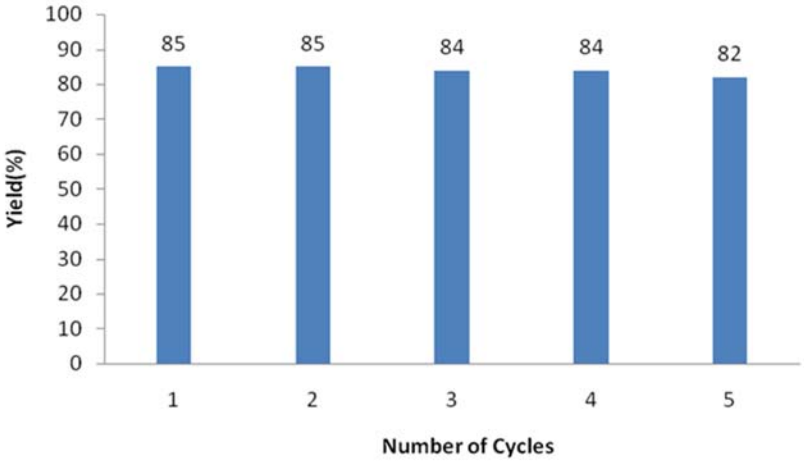

Fig. 4. Recycling of the catalyst for the oxidation of 4-chlorobenzyl alcohol.

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