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Magnetic $NiFe_2O_4$ 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

Nanomagnetic $NiFe_2O4$ was used as the efficient, stable, reusable catalyst for selective oxidation of alcohols to their corresponding carbonyl compounds using oxone (potassium hydrogen monopersulfate) as oxidant in the presence of water as solvent at room temperature. The oxidation of various primary and secondary alcohols has been examined and related corresponding products were obtained with good yields. The catalyst was investigated with XRD, SEM, ICP and IR techniques. Furthermore, the catalyst could be easily recovered and reused for several times without loss of activity.

Keywords: *Nanomagnetic catalyst, Nickel ferrite, Oxidation, Alcohols, Oxone.*

Introduction

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 [1]. Traditional methods utilizing stoichiometric quantities of inorganic oxidants such as chromium (VI) reagents, permanganates, or N-chlorosuccinimide (NCS) are not environmentally friendly. Even grave environmental problems are created

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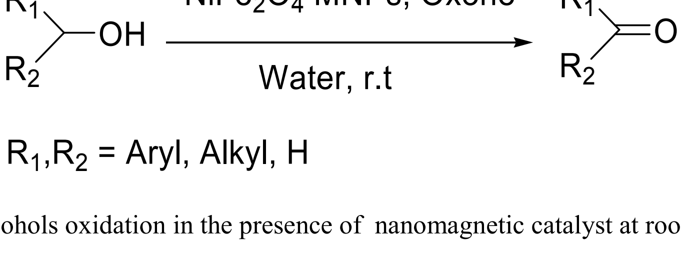
using hypervalent iodine reagents. Therefore, cleanliness, non-toxic and safe oxidation methods are needed [2-3].

In organic synthesis, oxone is a convenient, easy way of handling because its solid state, readily available, relatively stable at room temperature and inexpensive, which is utilized for various transformations in comparison with other oxidizing reagents [4-12]. Water can be counted as the most agreeable reaction medium for alcohol oxidation [13] and there is a thrust in search for new green catalysts [14]. Chemists have extensively used Iron-based catalysts because they are easily available, cheap, environmentally harmless, and relatively non-toxic in comparison with other transition metals.

Different iron (II) [15-17] and iron (III) compounds [18-22] have been used as for the oxidation reactions. Nanoparticles display high catalytic activity and chemical selectivity under mild circumstances [23]. Magnetic NPs are of paramount importance for researchers from a broad range of fields, including magnetic fluids, data storage, catalysis, and bio applications [24-28]. 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 [29-32]. The large surface area to volume ratio of metal oxide nanoparticle is mainly responsible for their catalytic performance [33]. Many unusual and interesting properties are show by ferrites in nanometer scale size. 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 [34].

Nickel ferrite (NiFe2O4) is an inverse spinal in which half of the ferric ions fill the tetrahedral sites and the rest occupy the octahedral [35]. Herein, nickel ferrite nanoparticles were synthesized via the auto-combustion assisted sol-gel method [36-37]. We have shown that $NiFe_2O_4$ MNPs are an active and reusable catalyst through magnetic separation for oxidation of alcohols with oxone in the presence of water at room temperature (Scheme 1).



Scheme 1. Alcohols oxidation in the presence of nanomagnetic catalyst at room temperature.

Experimental

Material and methods

Ferric nitrate nonahydrate $Fe(NO_3)_3.9H_2O$, Nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$, 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 particle size and morphology of the surfaces of sample was analyzed by a 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 C-P-3800 with FID detector, column CP-Sil 5 CB30m×0.32mm).

Preparation of $NiFe_2O_4$ MNPs in aqueous solution

Nickel ferrite nanoparticles were synthesized via the auto-combustion assisted sol-gel method of Ni^{2+} and Fe^{3+} ions (molar ratio 1:2) in ammonia solution[36-37]. Briefly, $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ 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 drop wise 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 oC 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 N2) 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.

General procedure for the oxidation of alcohol

Alcohol (1 mmol), water (2 mL) and 5 mol% of nanomagnetic-$NiFe_2O_4$ (12mg) were added into a round-bottomed flask. The reaction mixture was stirred for the two minutes and then oxone (0.6 mmol) was added in three portions due 15 minutes. The reaction mixtures were 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 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 indentified by IR data. 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.

Results and discussion

Characterization of the catalyst

The FT-IR spectrum of the $NiFe_2O_4$ MNPs is presented in Figure 1. A broad absorption band at about 3439 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. Two other principle absorption bands in the range of 400-600 cm^{-1} are also observed in the FT-IR spectrum. The first band is around 469 cm^{-1} and the second one is around 570 cm^{-1}, attributed to the long bond length of oxygen metal ions in the octahedral sites and the shorter bond length of oxygen-metal ions in the tetrahedral sites in the spinel structure, respectively [38].

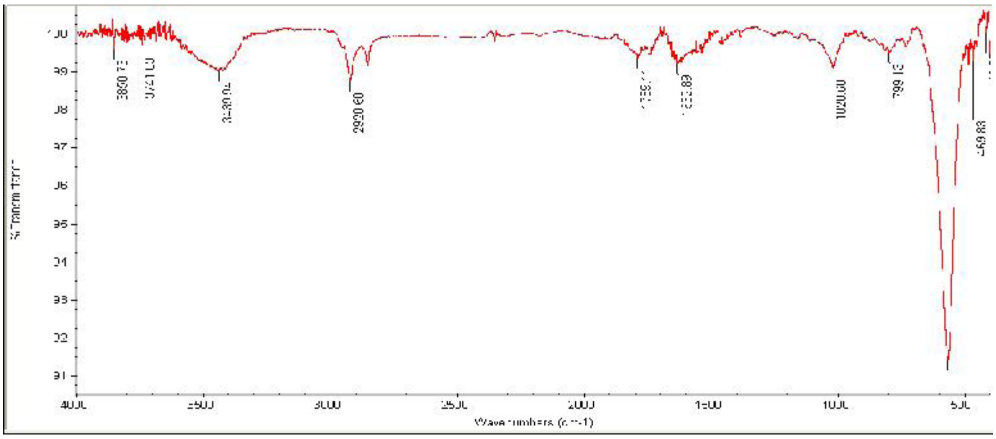


Figure 1. FT-IR spectrum of $NiFe_2O_4$ MNPs.

Figure 2 shows the XRD pattern of the $NiFe_2O_4$ 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 Figure 2 can be indexed to (220), (311), (222), (400), (422), (511), and (440) planes of a cubic unit cell [39], which corresponds to the cubic spinel structure of nickel iron oxide (JCPDS: 01-074-2081). The diameter of the $NiFe_2O_4$ MNPs determined by the Debye-Scherre equation via XRD data ($D = 0.94\ \lambda / B \cos \theta$) was 80.2 nm. The atomic ratio of Ni-Fe is about 0.53 (ICP), which is close to that of $NiFe_2O_4$ and 24.8% of weight is nickel.

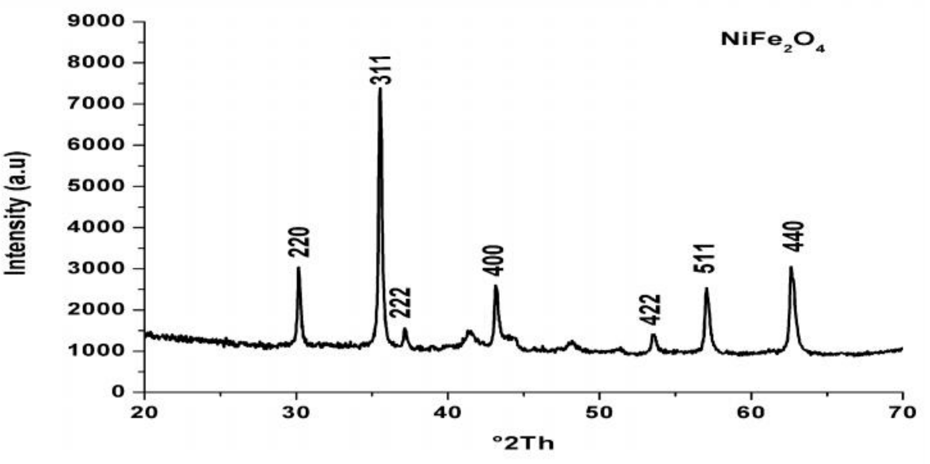


Figure 2. XRD pattern of $NiFe_2O_4$ MNPs.

The SEM images show the presence of voids and pores in the sample. This is attributed to the release of large amounts of gases during the combustion process. The sample has spongy structure and the formation of multigrain agglomerations consisting of very fine crystallites (Figure 3). These results are in good harmony with the XRD analyses.

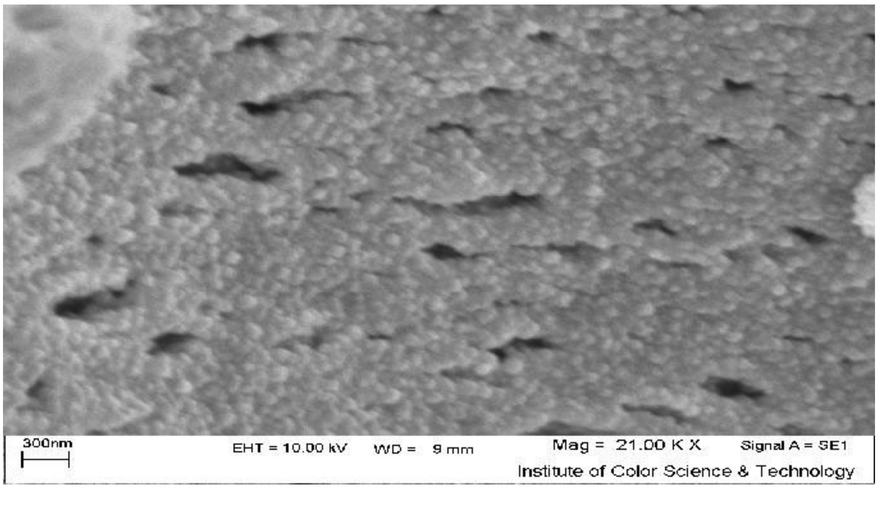


Figure 3. SEM image of the obtained $NiFe_2O_4$ MNPs.

Optimization of alcohol oxidation conditions

In a trial reaction, we tried to convert 4-chlorobenzyl alcohol (1mmol) to 4-chlorobenzaldehyde, as a model reaction in the presence of $NiFe_2O_4$ as a nanomagnetic catalyst (12 mg) and oxone (1 mmol was added in 3 stages) in various solvents (2mL) at room temperature. 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).

Table 1. Conversion of 4-chlorobenzyl alcohol to 4-chlorobenzaldehyde in different solvents with oxone and in the presence of $NiFe_2O_4$ MNPs as catalyst at room temperature.

Entry	Solvent	Time(min)	Yield (%)[a]
1	Dichloromethane	80	10
2	Cyclohexane	80	trace
3	Acetonitrile	80	20
4	Water	80	88
5	Ethanol	80	trace
6	Dry toluene	80	trace
7	Ethyl acetate	80	10

[a] Isolated yield

We also studied the oxidation of 4-chlorobenzyl alcohol to 4-chloro benzaldehyde with other oxidants in the presence of nanomagnetic $NiFe_2O_4$ catalyst in water at room temperature. These results showed that the higher yield was achieved with oxone as an oxidant (Table 2, entries 1- 3). The amount of the catalyst and oxidant were also optimized. The results showed that 12mg of catalyst (5 mol%) and 0.6 mmol of oxidant is the best choice for 1 mmol alcohol (entry 9). We observed that 4-chlorobenzyl alcohol was not oxidized with this system in the absence of oxidant under nitrogen atmosphere, even in long reaction time (entry 12) 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 temperature (>50 ºC).

Table 2. Oxidation of 4-chlorobenzyl alcohol (1mmol) in water and in the presence of $NiFe_2O_4$ MNPs catalyst at room temperature.

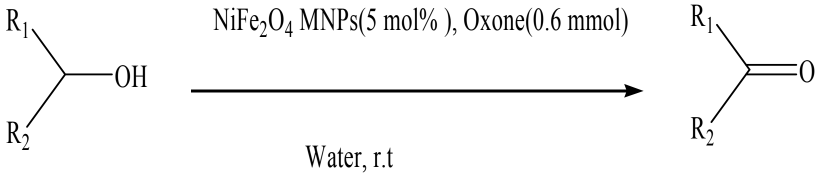
Entry	Catalyst(mol%)	Oxidizing reagent(mmol)	Time(min)	Yield(%)[a]
1	5	H_2O_2 (1)	80	20
2	5	O_2 atmosphere	80	trace
3	5	Oxone (1)	80	88
4	7	Oxone (1)	80	86
5	6	Oxone (1)	80	88
6	4	Oxone (1)	80	75
7	-	Oxone (1)	80	20
8	5	Oxone (0.7)	80	88
9	5	Oxone (0.6)	80	88
10	5	Oxone (0. 5)	80	70
11	5	Oxone (0. 2)	80	25
12	5	-	120	0

[a] Isolated yield

Application scope

The optimized condition was used for various alcohols to screen the generality of the work. As indicated in Table 3, $NiFe_2O_4$ MNPs catalyst showed high activity/selectivity and excellent reusability in oxidation processes. In these reactions, the aldehyde selectivity is very 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 (entries17-19). 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.

Table 3. Oxidation of various alcohols.



Entry	Alcohol	Product	Time (min)	Yield (%)[a]
1	Benzyl alcohol	Benzaldehyde	85	87
2	4-chlorobenzyl alcohol	4-chlorobenzaldehyde	80	88
3	3-chlorobenzyl alcohol	3-chlorobenzaldehyde	80	84
4	2- chlorobenzyl alcohol	2-chlorobenzaldehyde	85	86
5	2,4-dichlorobenzyl alcohol	2,4-dichlorobenzaldehyde	95	85
6	2- bromobenzyl alcohol	2- bromobenzaldehyde	85	83
7	3- bromobenzyl alcohol	3- bromobenzaldehyde	80	80
8	4- bromobenzyl alcohol	4- bromobenzaldehyde	80	85
9	4-fluorobenzyl alcohol	4-fluorobenzaldehyde	85	85
10	3- fluorobenzyl alcohol	3-fluorobenzaldehyde	85	86
11	4-nitrobenzyl alcohol	4-nitrobenzaldehyde	120	84
12	3- nitrobenzyl alcohol	3-nitrobenzaldehyde	120	84
13	2- nitrobenzyl alcohol	2-nitrobenzaldehyde	120	80
14	4-methoxybenzyl alcohol	4-methoxybenzaldehyde	75	90
15	Benzhydrol	Benzophenone	90	82
16	Benzoin	Benzil	120	75
17[b]	Cyclohexanol	Cyclohexanone	120	99.84
18[b]	2-butanol	Butanone	120	99.50
19[b]	Isobutanol	Isobutanal	120	99.16

[a]Yields refer to isolated products. The products were characterized from their spectral data (IR) and compared with authentic samples. [b]The yields refer to GC analysis.

Recycling of the catalyst

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 dried. This catalyst could be subsequently reused in 6 further iterative cycles, no obvious diminishing activity was observed (Figure 4).

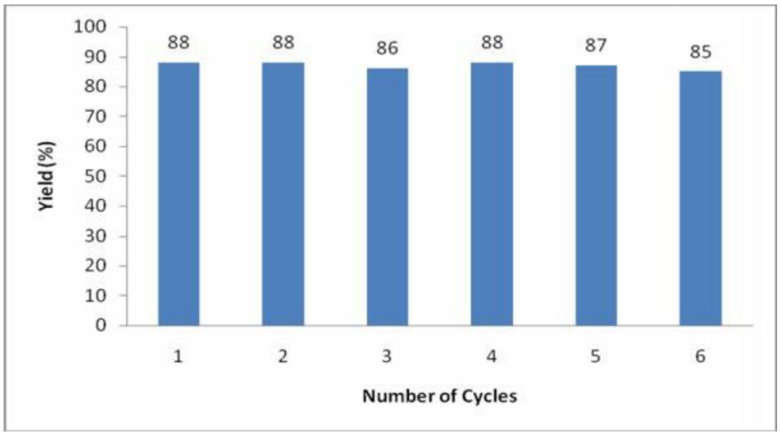


Figure 4. Recycling of the catalyst for the oxidation of 4-chlorobenzyl alcohol.

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-$NiFe_2O_4$ 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. In comparison with the other oxidants such as O_2 or TBHP, oxidation by oxone accomplished at low temperatures and in short times [40-41]. The catalyst could be subsequently reused in six 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.

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