

## Green synthesis of magnetic copper ferrite nanoparticles using tragacanth gum as a biotemplate and their catalytic activity for the oxidation of alcohols

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### ABSTRACT

During this study, we report the green synthesis of magnetic copper ferrite nanoparticles using tragacanth gum as a reducing and stabilizing agent by the sol-gel method. The green synthesized  $\text{CuFe}_2\text{O}_4$  MNPs are characterized by powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), vibrating sample magnetometer (VSM) and scanning electron microscopy (SEM). The X-ray powder diffraction (XRD) analysis revealed the formation of Cubic phase ferrite MNPs with average crystallite size of 14 nm. This study has demonstrated that  $\text{CuFe}_2\text{O}_4$  nanoparticles can act as an efficient catalyst for selective oxidations of alcohols applying oxone (potassium hydrogen monopersulfate) as oxidant in the presence of acetonitrile as solvent at 40 °C. Primary and secondary alcohols gave the corresponding products in good yields. Furthermore, the catalyst can be simply recovered and reused several times with almost no loss in activity.

**Keywords:** Copper ferrite, Nanomagnetic catalyst, Tragacanth gel, Oxidation, Alcohols.

### 1. Introduction

Spinel ferrites and their related structures have achieved huge attention in recent years because of their useful electrical and magnetic properties. Spinel ferrites have high thermodynamic stability, magnetic properties, high electrical resistivity and catalytic activity in addition to their resistance to corrosion and so they are used in storage systems, permanent magnet, electronic devices, telecommunication devices, magnetic refrigeration, microwave absorber, sensors, recording heads, catalyst, and drug delivery [1-7]. Molecular formula of magnetic spinel ferrites is  $\text{MFe}_2\text{O}_4$  in which M can be any divalent metal cation. In spinel ferrite,  $\text{M}^{2+}$  and  $\text{Fe}^{3+}$  occupy the tetrahedral (A) and octahedral (B) interstitial sites of the fcc lattice formed by  $\text{O}^{2-}$  ions, respectively [8-10]. Copper ferrite ( $\text{CuFe}_2\text{O}_4$ ) is one of the important spinel ferrite as it has paramount advantages over other type of magnetic

materials due to its unmatched flexibility in magnetic and mechanical parameters, high stability, high quality, low cost and low eddy current losses over a wide range of frequency [11]. Copper ferrite is one such reusable catalyst which shows great catalytic activity in organic synthesis [12]. There are many developed methods for the synthesis of spinel ferrite such as: sol-gel [13], thermal decomposition [14], electrochemical methods [15], hydrothermal methods [16] and co-precipitation [17].

In new synthetic organic chemistry the oxidation of alcohols into their corresponding carbonyl compounds shows a basically important functional group transformation and possesses a chief position [18]. A variety of different catalytic systems for catalytic oxidation of alcohols has been developed, there is a growing interest in the search for new efficient metal catalysts for this concern. But, cleanliness, non-toxic and safe oxidation methods are needed [19-22]. Oxone is a convenient, readily available, and relatively stable compound at room temperature, and therefore is utilized for various transformations in organic synthesis [23-26].

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The use of natural polymers is generating interest of researchers toward cost effective, non-toxic and eco-friendly green synthesis of nanoparticles [27]. Tragacanth gum (TG) is a naturally occurring complex, acidic polysaccharide derived as an exudate from the bark of *Astragalus gummifer* (Fabaceae family), a native tree of western Asia. It is commercially produced mostly in Iran and Turkey [28]. In this study, we have reported, the synthesis of copper ferrite nanoparticles using TG by the sol-gel method as a cheap, facile and friendly approach to the nature. The results show that  $\text{CuFe}_2\text{O}_4$  MNPs is an active and reusable catalysts through magnetic separation for oxidation of alcohols with oxone in the presence of acetonitrile at 40 °C (Scheme 1).

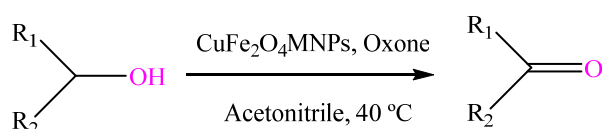
## 2. Experimental

### 2.1. General

The Tragacanth gum (TG) was obtained from a local health food store. All the chemicals were purchased from Merck and daijung (Darmstadt, Korea) were used without further purification. The structural properties of  $\text{CuFe}_2\text{O}_4$  MNPs were analyzed by X-ray powder diffraction (XRD) with a X'Pert-PRO advanced diffractometer using Cu ( $K\alpha$ ) radiation (wavelength: 1.5406 Å), operated at 40 KV and 40 MA at room temperature in the range of  $2\theta$  from 20 to 70. Infrared spectra were recorded on a Mattson (Unicam Ltd., Cambridge, UK) 1000 Fourier transform infrared spectrophotometer using KBr technique. The particle size and morphology of the sample surfaces was studied by a scanning electron microscope (Zeiss EVO 18). The magnetic properties of sample were detected at room temperature using vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran). The GC yields of the aliphatic products were calculated based on their gas chromatogram.

### 2.2. Preparation of $\text{CuFe}_2\text{O}_4$ MNPs

To prepare  $\text{CuFe}_2\text{O}_4$  MNPs,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were used as starting materials. Firstly, 0.2 g of the Tragacanth gum (TG) was dissolved in 40 ml of deionized water and stirred for 80 min at 70 °C to achieve a clear Tragacanth gel (TG) solution.



**Scheme 1.** Alcohols Oxidation in the presence of nanomagnetic catalyst.

After that, the 1mmol of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 2mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added to the TG solution and the container was moved to a sand bath. The temperature of the sand bath was fixed at 75 °C and stirring was continued for 12 h to obtain a brown color resin. The final product was calcined at 600 °C in air for 4h to obtain  $\text{CuFe}_2\text{O}_4$  MNPs.

### 2.3. General procedure for the oxidation of alcohol

Alcohol (1 mmol), Acetonitrile (1 mL) and 7 mol% of nanomagnetic- $\text{CuFe}_2\text{O}_4$  were added to a round-bottomed flask. The mixture was stirred for two minutes. Then, oxone (0.6 mmol) was added in three portions. The mixture was stirred at 40 °C. 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, purification of the residue using flash column chromatography (silica gel) provided the pure carbonyl compounds. The products were characterized from their spectral data (IR) and compared with authentic samples. The GC yields of the aliphatic products were calculated based on their gas chromatogram.

## 3. Results and Discussion

### 3.1. Characterization of the catalyst

The FT-IR spectrum analysis suggests two ranges of the absorption bands: In the range of 400–1000  $\text{cm}^{-1}$ , two absorption bands for the spinel structure of the ferrite  $\nu_1$  at 572  $\text{cm}^{-1}$  and  $\nu_2$  at 421  $\text{cm}^{-1}$  were observed. The band,  $\nu_1$ , suggests the intrinsic stretching vibrations of the metal ( $\text{Fe} \leftrightarrow \text{O}$ ) at the tetrahedral site and the  $\nu_2$  is attributed to stretching vibrations of the metal ( $\text{Cu} \leftrightarrow \text{O}$ ) at the octahedral site [29, 30]. A broad absorption band at about 3431  $\text{cm}^{-1}$  represents a stretching mode of  $\text{H}_2\text{O}$  molecules and indicates that a large number of OH groups are presented on the surface of the MNPs (Fig. 1).

Fig. 2 shows the XRD pattern of the  $\text{CuFe}_2\text{O}_4$  MNPs. XRD analysis showed a series of diffraction peaks at  $2\theta$  of 30.25°, 35.88°, 37.50°, 43.06°, 54.07°, 57.51° and 62.69° can be assigned to (220), (311), (222), (400), (422), (511) and (440) planes, respectively. All the diffraction peaks were readily indexed to a pure cubic structure ferrite (JSPDS Card no. 75-1517) with  $a=b=c=8.341$  Å. The diffraction patterns are well matched with the literature [29, 30] and no diffraction peaks of other impurities were observed. The average crystallite size of ferrite nanoparticles was determined from the full width at half maximum (FWHM) of the XRD patterns using the well-known Scherrer formula:  $D = 0.9\lambda/\beta\cos\theta$

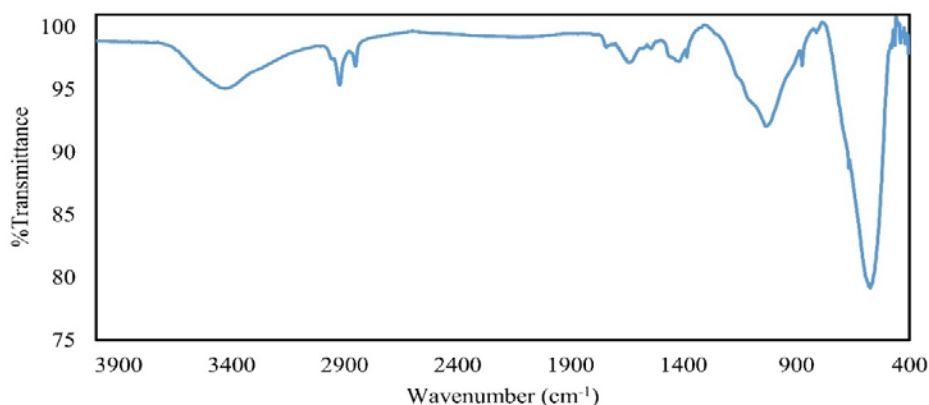


Fig. 1. FT-IR spectrum of CuFe<sub>2</sub>O<sub>4</sub> MNPs.

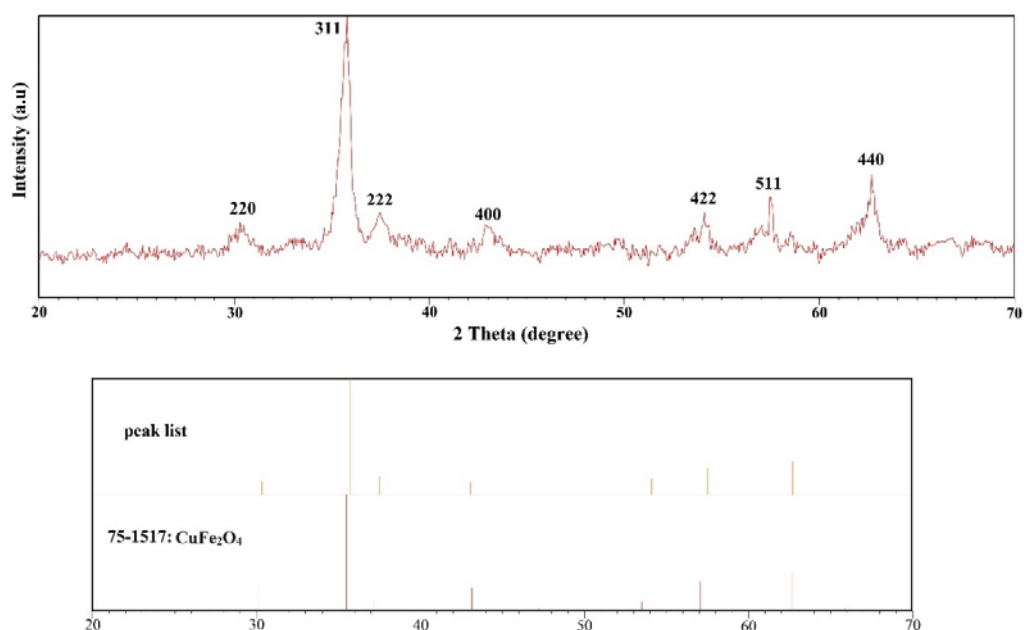


Fig. 2. XRD pattern of CuFe<sub>2</sub>O<sub>4</sub> MNPs.

Where  $D$  is the crystallite size (nm),  $\beta$  is the full width at half maximum of the peak,  $\lambda$  is the X-ray wavelength of Cu  $K\alpha = 0.154$  nm and  $\theta$  is the Bragg angle [31,32]. Using the above method we obtained an average size of 14 nm for CuFe<sub>2</sub>O<sub>4</sub> MNPs.

The SEM analysis suggests that the CuFe<sub>2</sub>O<sub>4</sub> MNPs are nanocrystalline and their shape is irregular spherical (Fig. 3). It can be seen from the image that the CuFe<sub>2</sub>O<sub>4</sub> MNPs range from 60-75 nm. These results are in good harmony with the XRD analyses.

To study the magnetic behavior of CuFe<sub>2</sub>O<sub>4</sub>-NPs, magnetization measurements recorded with VSM were performed. As can be observed in Fig. 4, the specific saturation magnetization value was measured to be 29.34 emu/g for CuFe<sub>2</sub>O<sub>4</sub>-NPs. coercivity (H<sub>c</sub>) values of the CuFe<sub>2</sub>O<sub>4</sub>-NPs calcined at 600 °C is 97.54 Oe, respectively.

The sample exhibited a magnetic property in the presence of a magnetic field.

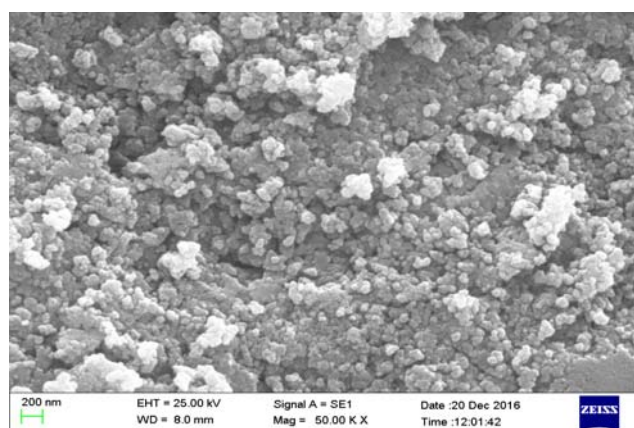


Fig. 3. SEM micrograph of the CuFe<sub>2</sub>O<sub>4</sub> MNPs calcined in air at 600 °C for 4 h.

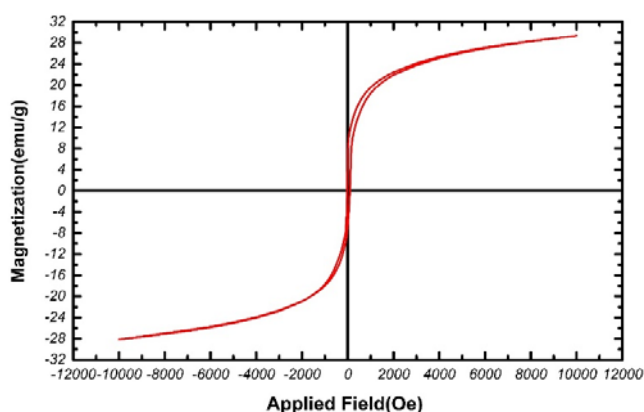


Fig. 4. Magnetization curve of  $\text{CuFe}_2\text{O}_4$  MNPs.

### 3.2. Optimization of alcohol oxidation conditions

For optimizing the reaction conditions, First, we tried to convert 2-chlorobenzyl alcohol (1 mmol) to 2-chlorobenzaldehyde in the presence of  $\text{CuFe}_2\text{O}_4$  as a nanomagnetic catalyst and acetonitrile with different oxidants ( $\text{H}_2\text{O}_2$ ,  $\text{O}_2$  and oxone) at 40 °C. In the all conditions, 2-chloro benzaldehyde was formed as the major product but the highest yield for 2-chloro

benzaldehyde was achieved with oxone. The amount of the catalyst and oxidant were also optimized. The results show that 7mol% of catalyst and 0.6 mmol of oxidant is the best amount for 1 mmol alcohol. We observed that in the absence of oxidant (under nitrogen atmosphere), 2-chloro benzyl alcohol did not oxidize with this system, even in long reaction time. The system (the same reaction conditions that optimized for 2-chloro benzyl alcohol) can be easily applied to various primary and secondary alcohols (Table 1). 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 donor substituted group on the benzene ring of benzylic alcohols accelerates the reaction rate. The oxidation times for aliphatic alcohols were fairly long (Entry 17-19). 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.

Table 1. Oxidation of various alcohols using  $\text{CuFe}_2\text{O}_4$  MNPs as catalyst (7 mol%) in the presence of oxone.

Entry	Alcohol	Product	Time (min)	Yield (%) <sup>a</sup>
1	Benzyl alcohol	Benzaldehyde	95	89
2	4-chlorobenzyl alcohol	4-chlorobenzaldehyde	95	81
3	3-chlorobenzyl alcohol	3-chlorobenzaldehyde	95	81
4	2- chlorobenzyl alcohol	2-chlorobenzaldehyde	95	86
5	2,4-dichlorobenzyl alcohol	2,4-dichlorobenzaldehyde	100	82
6	2- bromobenzyl alcohol	2- bromobenzaldehyde	95	86
7	3- bromobenzyl alcohol	3- bromobenzaldehyde	90	85
8	4- bromobenzyl alcohol	4- bromobenzaldehyde	95	88
9	4-fluorobenzyl alcohol	4-fluorobenzaldehyde	100	85
10	3- fluorobenzyl alcohol	3-fluorobenzaldehyde	100	86
11	4-nitrobenzyl alcohol	4-nitrobenzaldehyde	120	80
12	3- nitrobenzyl alcohol	3-nitrobenzaldehyde	120	83
13	2- nitrobenzyl alcohol	2-nitrobenzaldehyde	120	83
14	4-methoxybenzyl alcohol	4-methoxybenzaldehyde	90	94
15	Benzhydrol	Benzophenone	110	80
16	Benzoin	Benzil	120	78
17 <sup>b</sup>	Cyclohexanol	Cyclohexanone	120	95.5
18 <sup>b</sup>	2-butanol	Butanone	120	99.4
19 <sup>b</sup>	Isobutanol	Isobutanal	120	98.6

<sup>a</sup>Yields refer to isolated products. The products were characterized from their spectral data (IR) and compared with authentic samples.

<sup>b</sup>The yields refer to GC analysis.

This catalyst could be subsequently reused in five further iterative cycles (Yields were 86, 86, 85, 84 and 84 %, respectively) no obvious diminishing activity was observed. In these reactions, the aldehyde selectivity was quite 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 (>50 °C).

#### 4. Conclusion

In this study, we have reported tragacanth gum as a natural template for the preparation of CuFe<sub>2</sub>O<sub>4</sub> MNPS by the sol-gel method. A single phase with a cubic spinel structure was formed after heat treatment at 600 °C for only 4 h. This method has many advantages such as nontoxic, economic viability, ease to scale up, less time consuming and environmentally friendly approach for the synthesis of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles without using any organic chemicals. The catalytic activity of copper Ferrite nanoparticles has been evaluated for the oxidation of alcohols to their corresponding carbonyl compounds utilizing oxone. The method also offers some other advantages such as stability of the oxidation system, simple method, short reaction times, good yields of the products and mild reaction circumstances. The catalyst could be subsequently reused in five further iterative cycles, no clear abating activity was observed.

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