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# Imidazolium Chloride Immobilized on Copper Acetylacetonate-Grafted Magnetic Chitosan as New Metal/Ionic Liquid Bifunctional Catalyst for Selective Oxidation of Benzyl Alcohols in Water

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# Abstract

Copper acetylacetonate and 1-methyl-3-propylimidazolium chloride as an ionic liquid  $(Fe_3O_4/CS/Cu/IL)$  were immobilized to chitosan magnetite nanoparticles *via* covalent attachment. The prepared heterogeneous catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), X-ray powder detection (XRD), Thermogravimetric/Differential thermal analyses (TG/DTA), Vibrating sample magnetometry (VSM), Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Energy dispersive X-Ray (EDX). The Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL exhibits superior catalytic activity for the oxidation of various benzyl alcohols to the corresponding carboxylic acids using TBHP as an oxidant.

The catalyst could be simply recycled with the assistance of an external magnet and reused for five runs without significant loss of activity.

Keywords: Magnetic, Chitosan, Catalyst, Bifunctional, Water

# Introduction

Oxidation of benzylic position is one of the most significant and beneficial procedures in organic chemistry as the aldehydes and carboxylic acids are versatile intermediates in a diversity of

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During the last decades, RuCl<sub>3</sub>/H5IO<sub>6</sub>, <sup>2</sup> TEMPO/NaOCl, <sup>3</sup> and Chromium-catalyzed oxidation of primary and secondary alcohols to the acids and ketones with periodic acid (H5IO<sub>6</sub>) have been described. <sup>4</sup> A two-step process involving Swern oxidation in the first step, then oxidation of the resulting aldehyde with sodium chlorite (NaClO<sub>2</sub>) is another option. <sup>5, 6</sup>

In 2007, aerobic oxidation in 1-Butyl-3-methylimidazolium trifluoromethanesulfonate [bmim]OTf as ionic liquid converted various activated primary alcohols into their corresponding acids or aldehydes by using VO(acac)<sub>2</sub> and Copper(II) 2-ethylhexanoate in good to excellent yields (Eq 1).<sup>7</sup>

Later, various alcohols were transformed into the corresponding carboxylic acids and ketones in good yields with *t*-BuOOH in the presence of  $Bi_2O_3$  as catalyst (Eq 2). <sup>8</sup> Also, aerobic oxidation of benzyl alcohols to carboxylic acids in the presence of Pd/C along with NaBH<sub>4</sub> in aqueous ethanol or methanol by using K<sub>2</sub>CO<sub>3</sub> or KOH as base at room temperature was reported (Eq 3).<sup>9</sup> Tetrapropylammonium perruthenate (TPAP) could catalyze direct oxidation of primary alcohols to carboxylic acids through stabilized aldehyde hydrates in acetonitrile.<sup>10</sup>

Recently, *N*-heterocyclic carbene (NHC)–silver catalyst was able to oxidize benzyl alcohols to aldehydes or carboxylic acids in the presence of BnMe<sub>3</sub>NOH or KOH under dry air. <sup>11</sup> Photo oxidation of benzyl alcohols under visible light irradiation led to produce carboxylic acids using 2-chloroanthraquinone as an organocatalyst.<sup>12</sup>

Most of these methods involve toxic metals <sup>13</sup> and their applicability is limited in terms of substrate range, harsh conditions, using strong bases and so on alternative methods are still desirable.

The search for efficient catalysts that combine the advantages of both homogeneous and heterogeneous catalysts is one of the most exciting challenges of catalysis research. Then we decided to synthesize benzoic acid, with the highest possible yield, by oxidizing benzyl alcohol using a semiheterogeneous system (Eq 4).<sup>14</sup>



Scheme 1: Reactions toward benzoic acids

Chitosan is a linear aminopolysaccharide of glucosamine and *N*-acetylglucosamine units and is obtained by alkaline deacetylation of chitin extracted from the exoskeleton of crustaceans such as shrimps and crabs, as well from the cell walls of some fungi.<sup>15</sup> Recently, much attention has been paid to chitosan as a potential polysaccharide resource because of its unique physiochemical characteristics and biological activities.<sup>16</sup> Owing to its high biodegradability, nontoxicity, and antimicrobial properties, chitosan is widely-used as an antimicrobial agent either alone or blended with other natural polymers.<sup>17</sup> These properties have led to its increased utility in specific applications such as antibacterial/anti-biofouling coatings, controlled release coatings and microcapsules, nanofiltration, drug delivery hydrogels, gene delivery and tissue

engineering scaffolds.<sup>18-20</sup> Within the past decade, green chemistry has attained the status of a major scientific discipline due to safer solvents, energy efficient which lead to the development of cleaner and more benign chemical processes.<sup>21</sup> Immobilized ILs have attracted considerable interest due to their extended advantages such as their easy recovery and reusability, noncorrosive and non-hazardous nature, low cost and operational simplicity. <sup>22</sup> In extension to our recent works we have now prepared new bifunctional catalyst including copper acetylacetonate and ionic liquid supported on magnetic chitosan. This catalyst system shows additive effect and serves as a superb catalyst. Chitosan is an excellent adsorbent for metal removal in near-neutral solutions because of the large number of NH<sub>2</sub> groups. Interaction between NH<sub>2</sub> group of chitosan molecules and carbonyl group of Copper acetylacetonate led to imine bond formation then Copper acetylacetonate-grafted magnetic chitosan was obtained. A supported ionic liquid bearing imidazole groups was synthesized by anchoring 1propyltrimethoxysilane-3-methylimidazolium chloride onto chitosan. First, imidazole was treated with 3-chloropropyltrimethoxysilane to give 3-(3- trimethoxysilylpropyl)imidazole, and was further treated with magnetic chitosan to produce the supported zwitterion. The reason behind the incorporation of 1-methylimidazole in the catalyst system is that an ionic liquid can dissolve many polar and non-polar organic and inorganic molecules and also has good catalytic activity. Magnetic modified chitosan immobilized copper acetylacetonatate and ionic liquid  $(Fe_3O_4/CS/Cu/IL)$  was prepared as a novel catalyst. The combination of the metal and zwitterion sites in the same molecule could make the catalyst behave as a bifunctional catalyst hence facilitating its recovery and reuse. Thus, the interesting structural and chemical features as well as the good results obtained, led us to explore the ability of this catalyst in oxidation of benzyl alcohols in water. This catalyst was very effective and had several advantages such as being cost

effective, high yielding, involving shorter reaction times, no by-products formation and most importantly its easy usage with negligible reduction in catalytic activity. On the other hand, when water is used as the reaction medium, a repulsive hydrophobic interaction arises between the small organic molecules and water. Small organic molecules due to their insolubility in water are forced to form aggregates in order to decrease the organic surface area exposed to water. The combined effect of hydrophobic interaction and hydrogen bonding at the boundary accelerates the reaction and thus gives high yields. Herein, we report a new cooperative catalytic system comprising a bifunctionalized magnetic chitosan (MC) with a transition metal catalyst, Copper acetylacetonate, and a general ionic liquid, 1-propyltrimethoxysilane-3-methylimidazolium chloride. This bifunctional catalyst might find promising applications in green chemistry, as it can not only reduce costs and waste by saving separation/purification steps but also using water as solvent. The carboxylic acids were isolated by extraction with sufficient purity without the need for further chromatographic purification thus rendering this protocol both cost and time efficient.

# Experimental

All purchased chemicals were of analytical grade and used without further purification. Chitosan (ACROS, USA), acetic acid and ethanol were purchased from Merck. FT-IR spectra were obtained over the region 400-4000 cm<sup>-1</sup> with NICOLET IR100 FT-IR with spectroscopic grade KBr. The powder X-ray spectrum was recorded at room temperature by model: Philips X-Pert 1710 diffractometer using Co K $\alpha$  ( $\alpha$  =1.78897Å) voltage: 40 Kv, current: 40 mA and the data were collected from 10° to 90° (20) with a scan speed of 0.02/s. The morphology of catalyst was studied with scanning electron microscopy using SEM (Philips XL 30 and S-4160) with gold coating equipped with energy dispersive X-ray spectroscopy. The magnetic properties of

Fe<sub>3</sub>O<sub>4</sub>@CS@Cu(acac)<sub>2</sub>@IL nanoparticle was measured with vibrating sample magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co, Iran, www.mdk-magnetic.com). Thermogravimetric/differential thermal analyses (TG/DTA) was performed on a thermal analyser with a heating rate of 10 °C min<sup>-1</sup> over a temperature range of 25–800 °C under flowing compressed N<sub>2</sub> and O<sub>2</sub> and thermogravimetric analyses (TG) was done with a heating rate of 20 °C min<sup>-1</sup> over a temperature range of 25–1100 °C under flowing compressed N<sub>2</sub>.

# Synthesis of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL (a):

Scheme 2 illustrates the preparation of the  $Fe_3O_4/CS/Cu/IL$  bifunctional catalyst. Chitosan, a linear polymer of (1-4)-linked 2-amino-2-deoxy-gucopyranose, containing free amines provides a facile immobilization of the metal complex to its surface.

Fe<sub>3</sub>O<sub>4</sub> nanoparticles are prepared by chemical co-precipitation of Fe<sup>3+</sup> and Fe<sup>2+</sup> ions with molar ratio 2:1, in presence of chitosan, followed by the hydrothermal treatment. Unfortunately, chitosan is only soluble in acidic aqueous solutions with pH values lower than 6.5. Then 1.5 g of chitosan is dissolved in 100 mL of 0.05 M acetic acid solution; to which FeCl<sub>3</sub>.6H<sub>2</sub>O (3.51 g) and FeCl<sub>2</sub>.4H<sub>2</sub>O (1.29 g) are added. The resulting solution is mechanically stirred for 6 h at 80 °C under N<sub>2</sub> atmosphere. Consequently, 6 mL of ammonia solution 25% (Merck) is injected drop wise into the reaction mixture with constant stirring. After 30 min, the mixture is cooled to room temperature and chitosan coated over magnetic nanoparticles are separated by an external magnet, first washed with distilled water, then ethanol (Industrial Grade), and finally dried under vacuum at room temperature in 12 h.

Magnetic nanoparticles Fe<sub>3</sub>O<sub>4</sub> were chosen as the core magnetic support because of their simple synthesis, low cost, and relatively large magnetic susceptibility. The presence of the cross-linked

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chitosan polymer layer not only prevents the agglomeration but also protects the  $Fe_3O_4$  core from oxidation.

As synthesized magnetic chitosan (Fe<sub>3</sub>O<sub>4</sub>/CS) was subsequently used for the immobilization of copper acetylacetonate by using amino groups of the chitosan.

Copper acetylacetonate was immobilized on the magnetic chitosan via Schiff condensation at  $NH_2$  moiety. 0.5 g of modified magnetic chitosan was treated with 0.1 g of Cu(acac)<sub>2</sub> in 25 ml of ethanol (Merck, 99.9% purity) under refluxing condition for 24 h. Then Magnetic nanoparticles were washed using ethanol (Industrial Grade) 3 times to remove not reacted Cu(acac)<sub>2</sub>.

Finally the synthesized  $Fe_3O_4/CS/Cu(acac)_2$  was treated with 1-propyltrimethoxysilane-3methylimidazolium (synthesized reaction of chloride before from the 3-chloropropyltrimethoxysilane (IPTMS) and methylimidazol: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ : 0.51-0.55 (2H, m), 1.83-2.07 (2H, m), 3.57 (9H, s), 4.17 (3H, s), 4.33-4.37 (2H, m), 7.52-7.81 (2H, m), 10.47 (1H, m)) in ethanol (Merck, 99.9% purity) under reflux for 24 h to give magnetic modified chitosan immobilized copper acetylacetonate and ionic liquid (Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL) catalyst (Scheme 2). The solid material was separated by external magnate and thoroughly washed with ethanol (Industrial Grade) and dried under vacuum in 12 h at room temperature. The loading of the catalyst was determined by ICP-AES which was found to be 0.31 mmol Cu/g.



# **Scheme 2:** Preparation of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL bifunctional catalyst

#### **Typical Procedure**

The reactions were carried out in a 25 mL round flask equipped with a condenser and a magnetic stirrer. Into the flask were placed 30 mg of the catalyst (including: 1 mol% Cu, 0.5 mol % ionic liquid), 1 mmol of benzyl alcohol, 2 mL of deionized water, and 2 mmol TBHP. The resulting mixture was vigorously stirred at 60 °C for 4 h under Ar. After completion the reaction, the catalyst was separated by external magnet. The reaction mixture was purified by extraction. The recovered catalyst was washed with ethanol (Industrial Grade) and deionized water and then dried under a vacuum in 12 h at room temperature. The catalyst was then reused for the next reaction.

## **Result and Discussions**

The crystalline structure of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL NPs and phase purity were determined by powder X-ray diffraction (XRD) as shown in Fig 1. The XRD pattern of MNPs indexed to the spinal phases of iron oxide and six peaks ( $2\theta = 30.1$ , 35.5, 43.2, 53.5, 57.0 and 62.8) are related to their corresponding indices (220), (311), (400), (422), (511) and (440), respectively. The positions of all diffraction peaks matched well with those from the JCPDS card (**NO. 75-0033**). As amorphous chitosan has an amorphous structure is difficult to see the diffraction peaks. This result proves that chitosan coating and immobilization of copper and ionic liquid have not altered the structure of magnetic nanoparticles.



Figure 1: The X-ray diffraction pattern of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL

For discovering the surface, morphology and the size of nanoparticles, we used scanning electron microscopy. Figure 2 are properly magnified (20-40 KX) SEM micrographs indicating surfaces of particles. The result pictures show uniform and minuscule nanoparticles. The approximate size of particles is examined about 30-50 nm.



(Magnified 40000 x)

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Figure 2: SEM images of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL (Magnified 20000 x)

TGA technique is very helpful to understand the degradation temperatures, moisture content and percentage of inorganic and organic components in material. Figure 3 shows the TGA

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spectra of pure Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@Chitosan, Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu(acac)<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu(acac)<sub>2</sub>@Ionic Liquid which indicates that around 13% of the chitosan gets disintegrated between 200-400 °C. The variation in thermal events proved the formation of the new materials. According to the spectra, the quantity of Cu(acac)<sub>2</sub> was 2%. At the end of the experiment around 18% of the Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu (acac)<sub>2</sub>@Ionic Liquid gets decomposed and in comparison to Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu (acac)<sub>2</sub>, ionic liquid quantity was measured 3%.



Figure 3: TGA of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@Chitosan, Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu (acac)<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu(acac)<sub>2</sub>@Ionic Liquid

TGA/DTA with a heating rate of 10 °C min<sup>-1</sup> over a temperature range of 25–800 °C under flowing compressed N<sub>2</sub> and O<sub>2</sub> indicates the change in weight of material with change in temperature. As it has shown in Fig 4. Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu(acac)<sub>2</sub>@Ionic Liquid containing moisture is heated, with increase in temperature moisture get evaporated that result in decrease in

the weight of sample correspond to the moisture (endothermic). Combustion of the sample and decomposition of the surface around 200-600 °C (exothermic with weight loss), led to decrease in the sample weight.



Figure 4: TGA/DTA of Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu(acac)<sub>2</sub>@Ionic Liquid

In order to deduce the composition of the nanoparticles, energy-dispersive X-ray spectroscopy (EDS) analysis was carried out (Fig. 5). The EDS spectrum depicts no other peaks except those for  $Fe_3O_4/CS/Cu/IL$  (Fe, Si, O, C, N, Cl, and Cu) indicating the high purity of the composites.

The results of this analyses of the Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL are given in the following table. Weight percent of the elements of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL nanoparticles are 3.22%(C), 0.84%(N), 5.87%(O), 0.52%(Si), 0.93%(Cl), 1.96%(Cu) and 86.66%(Fe), respectively (Table 1).

This implied that copper and ionic liquid was on the surface of the covered chitosan on  $Fe_3O_4$  NPs.



Figure 5: EDX pattern of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL

Table 1: Quantitative	results of EDX analysis	s of Fe <sub>3</sub> O <sub>4</sub> /CS/Cu/IL
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Element	Line	Int	W%	A%
С	Ka	185.0	3.22	11.54
N	Ka	49.3	0.84	2.59
0	Ka	939.3	5.87	15.79
Si	Ka	137.5	0.52	0.80
Cl	Ka	169.9	0.93	1.13
Fe	Ka	1735.3	86.66	66.81
Cu	La	104.1	1.96	1.33
			0.31 mmol/g	

Bare nanocrystals of Fe<sub>3</sub>O<sub>4</sub> owner high saturation magnetization 73.7 emu/g at room temperature.<sup>23</sup> The results of VSM shows that the saturation magnetization value in Fe<sub>3</sub>O<sub>4</sub>/CS decreased to 50emug<sup>-1</sup> due to the coated chitosan polymer and in the case of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu(acac)<sub>2</sub> closed to 43 emug<sup>-1</sup> and finally reached to 37 emug<sup>-1</sup> in Fe<sub>3</sub>O<sub>4</sub>/CS/Cu(acac)<sub>2</sub>/IL NPs (Fig. 6)



Figure 6: Magnetization curves of Fe<sub>3</sub>O<sub>4</sub>/CS, Fe<sub>3</sub>O<sub>4</sub>/CS/Cu and Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL

The FT-IR spectra of magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>), chitosan, and magnetic nanoparticles coated by chitosan (Fe<sub>3</sub>O<sub>4</sub>@chitosan) are shown in Fig.7.

The FT-IR spectrum of pure chitosan were characterized by the following absorption bands: the (NH) of backbone polymer arising at 3435 (stretching characteristic), 1639 cm<sup>-1</sup> (bending

vibration) and C–O stretching vibration of alcoholic group at 1065 cm<sup>-1</sup>. The spectrum of  $Fe_3O_4$ @CS compared with  $Fe_3O_4$ , the presence of chitosan on magnetic nanoparticles covered the vibration of  $Fe_3O_4$ . The band shifted are significant. Electrostatic interaction between the negatively charged  $Fe_3O_4$  NPs surface and the positively protonated chitosan donates the IR spectrum change. The spectrum of the  $Fe_3O_4$ @Chitosan@Cu (acac)<sub>2</sub> catalyst showed a characteristic band at 1707 cm<sup>-1</sup> (C=N) and the absorption at 1581 cm<sup>-1</sup> is due to (CH<sub>2</sub>)<sub>3</sub>HC=N-stretching which is a characteristic absorption due to acethylacetonte crosslinking with chitosan. The peaks at 1576 cm<sup>-1</sup> is related to C=N stretching vibrations. It is worth mentioning that in Cu(acac)<sub>2</sub> anchored magnetic chitosan, the C=N stretching frequency is shifted to upper wavelength at ca.1707 cm<sup>-1</sup> indicating that C=N bond is coordinated to copper through the lone pair of nitrogen in the Schiff-base.

Also appeared peaks around 1370-1400 cm<sup>-1</sup> corresponding to  $CH_3$  group vibrations. These observations indicate that  $Cu(acac)_2$  has been successfully supported on the magnetic chitosan.

The FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu (acac)<sub>2</sub>@IL, a broad peak around 1584 cm<sup>-1</sup> corresponds to the C–N, C-C stretching vibrations of imidazole ring in the structure of catalyst.

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Figure 7: FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>@Chitosan@Cu (acac)<sub>2</sub>@IL

We developed a clean and single step method for the synthesis of benzoic acids. In completion of liquid phase reaction which contains both oil or solid and water phases, a co-solvent or a phase transfer catalyst is required to promote the reaction. The oxidation of benzyl alcohol to benzoic acid by TBHP was chosen as a probe reaction. The oxidation reactions were carried out under the solvent water with TBHP (70 % aq.) at r.t, a high conversion of benzyl alcohol was obtained when  $Fe_3O_4$ @Chitosan@Cu (acac)<sub>2</sub>@IL was used as a catalyst. It is interesting to notice that the activity of the catalyst in water increased when ionic liquid was supported on chitosan. This fact highlights the importance of supporting the zwitterions to stabilize catalyst in water medium. The higher activity of catalyst can be attributed to a cooperative effect between copper and IL.

To begin, benzyl alcohol was treated with various oxidants. As shown from the results summarized in Table 2, the reaction proceeded smoothly in other oxidants, such as hydrogen

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peroxide, urea hydrogen peroxide, *meta*-chloroperoxybenzoic acid, sodium hypochlorite. The isolated yields were significantly influenced by the oxidant employed. Among the oxidants tested, *tert*-Butyl hydroperoxide (TBHP) was proven to be the best compared to the others (Entry 6-10). A slightly better yield of benzoic acid resulted with increasing the temperature from r.t to 40 and then to 60 °C. (Entry 11, 12). Upon raising the temperature from 60 to 100 °C, the reaction rate and yield of the reaction did not change. After that, amount of the catalyst was also optimized. The effect of catalyst loading on the oxidation of benzyl alcohol is shown in this table. No benzoic acid was obtained without the use of a catalyst (Entry 17). When the catalyst loading was less than 20 mg, the yield of the product was relatively lower. A yield of 95% was obtained when 30 mg catalyst was applied (entry 15), and the yield was not apparently improved further when the catalyst loading was more than 30 mg. Thus the optimal reaction conditions were considered including benzyl alcohol (1 mmol), TBHP (2 mmol), 30 mg catalyst (including: 1 mol% Cu, 0.5 mol % ionic liquid) at 60°C for 4 h in deionized water under Ar atmosphere (Entry 15).

TBHP serves as a source of reactive oxygen radicals (e.g., tBuO), which would act upon the benzyl alcohol to generate benzaldehyde in situ. Then in the next step benzaldehye could convert to benzoic acid.

Our investigation implicated that the reaction proceeds *via* a radical mechanism as employing  $K_2CO_3$  or  $Et_3N$  as additives did not change product yield and also, the benzoic acid formation was suppressed in the presence of ascorbic acid.

Entry	Catalyst	mg	Oxidant	Temp.( °C)	Yield (%)
1	Fe <sub>3</sub> O <sub>4</sub>	10	TBHP	r.t.	N.D. <sup>b</sup>
2	Fe <sub>3</sub> O <sub>4</sub> @CS	10	TBHP	r.t.	N.D. <sup>b</sup>
3	$Cu(acac)_2$	10	TBHP	r.t	35 <sup>b</sup>
4	$Cu(acac)_2$	10	TBHP	r.t	45 <sup>b,c</sup>
5	$Fe_3O_4@CS@Cu(acac)_2$	10	TBHP	r.t.	20 <sup>b</sup>
6	Fe <sub>3</sub> O <sub>4</sub> @CS@Cu(acac) <sub>2</sub> @IL	10	TBHP	r.t.	40 <sup>b</sup>
7	Fe <sub>3</sub> O <sub>4</sub> @CS@Cu(acac) <sub>2</sub> @IL	10	$H_2O_2$	r.t.	35 <sup>b</sup>
8	$Fe_3O_4@CS@Cu(acac)_2@IL$	10	<i>m</i> CPBA	r.t.	30 <sup>b</sup>
9	$Fe_3O_4@CS@Cu(acac)_2@IL$	10	UHP	r.t.	20 <sup>b</sup>
10	$Fe_3O_4(a)CS(a)Cu(acac)_2(a)IL$	10	NaClO	r.t.	N.D. <sup>b</sup>
11	$Fe_3O_4(a)CS(a)Cu(acac)_2(a)IL$	10	TBHP	40	45 <sup>b</sup>
12	$Fe_3O_4(a)CS(a)Cu(acac)_2(a)IL$	10	TBHP	60	50 <sup>b</sup>
13	$Fe_3O_4 @CS @Cu(acac)_2 @IL$	10	TBHP	100	50 <sup>b</sup>
14	$Fe_3O_4@CS@Cu(acac)_2@IL$	20	TBHP	60	75 <sup>b</sup>
15	$Fe_3O_4@CS@Cu(acac)_2@IL$	30	TBHP	60	95 <sup>b</sup>
16	$Fe_3O_4@CS@Cu(acac)_2@IL$	40	TBHP	60	95 <sup>b</sup>
17	$Fe_3O_4@CS@Cu(acac)_2@IL$	-	TBHP	60	20 <sup>b</sup>
18	Fe <sub>3</sub> O <sub>4</sub> @CS@Cu(acac) <sub>2</sub> @IL	30	-	60	N.D. <sup>b</sup>

Table 2. Optimization of the reaction conditions <sup>a</sup>

<sup>a</sup> Condition: 1 mmol of benzyl alcohol, 2 mL of deionized water, and 2 mmol TBHP, 12 h <sup>b</sup> GC yield

<sup>c</sup> In the presence of TBAB

Benzylic alcohols, including with either electron withdrawing (b, d, f) or electron-donating groups (c, e, g), were oxidized to the benzoic acids in quantitative yield. Furfuryl alcohol was the only problematic substrate that the major product was furfural.



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**Scheme 2:** Oxidation of benzyl alcohols in the presence of Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL bifunctional catalyst, Isolated Yields

The proposed mechanism for the oxidation in the presence of catalyst is shown in Scheme 3.



Scheme 3: Plausible mechanism

In the first step by using of Cu and TBHP, activated benzyl alcohol in the presence of imidazole moiety produced benzaldehyde and *tert*-butanol. In the second step, benzaldehyde was activated and oxidized to benzoic acid.

This method is efficient and environmentally benign. Compared with the previously reported, offering significantly improved yields and purity of the desired products. Additionally, no chlorinated solvent is required.

After accomplishing the reaction, superparamagnetic nanocatalysts were separated from the medium, as usual with applying an external magnet, then washed and dried under vacuum at room temperature in 12 h and used for next reaction. Reusing nanocatalysts were repeated till the results were not satisfied. In this way, the catalytic recycle ability of synthesized nanocatalyst was examined. It showed excellent result for just 5 times and after that we were witness about its deterioration catalytic activities (Fig. 8). Also, there is no change in the structure of the catalyst after the reaction: all of the observed XRD peaks are the same as the recorded pattern of primary catalyst. Regarding recyclability of the catalyst, the image obtained (Fig. 10) do not reveal significant changes in the Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL morphology even after the fifth run (Fig. 10).



Figure 8: Activity lost as a function of the number of reused times of the catalyst in the synthesis of benzoic acid

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Figure 9: XRD pattern of the reused catalyst before using in the 6<sup>th</sup> run



Figure 10: SEM image of the catalyst after the 5<sup>th</sup> run

# **Conclusion:**

In summary, functional magnetic nanoprticles that combines catalytically active Copper acetylacetonate and 1-propyl-3-methylimidazolium chloride as ionic liquid (Fe<sub>3</sub>O<sub>4</sub>/CS/Cu/IL) was successfully prepared by imine band formation and silylanization.

We have disclosed a new catalyst system which proves to be very effective not only in reducing the reaction time, but also in increasing the yield of the product. It involves simple procedure, is environment friendly and also incorporates special features like reagent economy, easy workup and easy handling.

# Acknowledgment:

We are thankful to Tarbiat Modares University and National Elite Foundation of I.R. Iran for partial support of this work.

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Published on 13 September 2016. Downloaded by New York University on 13/09/2016 13:42:49

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