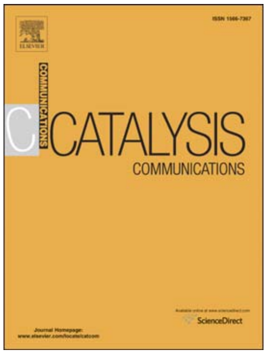

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Melad Shaikh, Mansingh Satanami, Kalluri V.S. Ranganath

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Efficient Aerobic Oxidation of Alcohols using Magnetically Recoverable Catalysts

Melad Shaikh, Mansingh Satanami and Kalluri V.S. Ranganath*

Guru Ghasidas University, Bilaspur, India-495009

E-mail: kallurivsr@gmail.com

Tel: +91-7752-260488; *fax*: +91-7752-260488

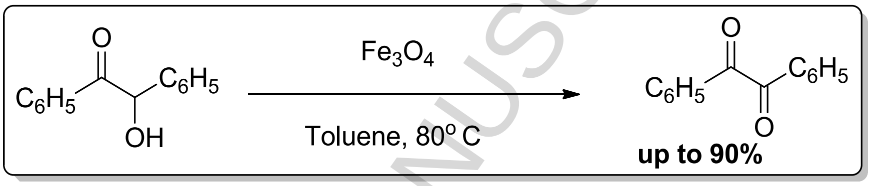
Abstract: A simple, highly efficient and mild catalytic aerobic oxidation of alcohol, in particularly benzoin was studied using iron oxide nanoparticles as a reusable catalyst. Moreover, benzyl was synthesized in large scale using inexpensive, readily available and environmentally friendly protocol in the presence of air. This novel and green methodology will allow further development not only in the geochemistry, but also in the oxidation of alcohols to replace expensive metals and corrosive reagents.

Key Words: Benzoin., Heterogeneous., Magnetite., Nitro alcohols., Oxidation.

1. Introduction

Magnetite nanoparticles (MNPs) are emerging as promising materials for applications in information recording, magnetic fluids, drug delivery, in-vivo magnetic imaging, and catalysis [1-4]. Heterogeneous catalysis has been around for a long time, but has still much to groom. Most heterogeneous catalysts are comprised of small nanometer sized, often a metal, and finely dispersed on a cheaper, high surface area support [5]. Industry favors a heterogeneous catalysis over homogeneous due to the advantage of recovery and recycling. The oxidation of alcohols to ketones is an important organic transformation since the resultant compounds are used in a variety of drugs, agro-chemicals and fragrances [6-7]. Alcohols have been conventionally oxidized by noncatalytic methods using stiochiometric amounts of hazardous oxidizing agents such as chromium and manganese compounds in the presence of mineral acids, which generate large amounts of waste materials. In addition to homogeneous catalysts, heterogeneous protocols have also been developed metal nanoparticles (NPs) on various supports [8-10]. Apart from these catalysts, iron, vanadium and ruthenium catalysts have also been successfully used in oxidation reactions [11-13]. The oxidation of benzoins to benzyl has also been reported by variety of homogeneous and heterogeneous catalysts [14-21]. In catalysis, it is highly desirable to find cheap replacements for the expensive metal and waste generated catalysts. Recently, Beller and coworkers have reported Fe_2O_3 NPs catalyzed oxidation of alcohols in the presence of hydrogen peroxide successfully [22]. Similarly, Oliver and coworkers have also reported the selective oxidation of primary alcohols in the presence of hydrogen peroxide [23].

Herewith, we report MNPs as a catalyst for the oxidation of benzoin to benzyl in high yields in the presence of air (up to 90%) as described in Scheme 1. This simple protocol overcomes the problems of homogeneous conditions and also in conventional heterogeneous conditions. The easy removal of the catalyst makes the procedure very simple and eco-friendly.



Scheme 1. Aerobic oxidation of benzoin using MNPs.

2. Experiment

2.1. Catalyst preparation

The MNPs were prepared by the so called wet-impregnation method as reported in the literature [24]. The ultra fine MNPs are prepared by co-precipitating aqueous solutions of ferrous ammonium sulfate $(NH_4)_2Fe(SO_4)_2$ and ferric chloride $(FeCl_3)$ mixture, respectively, in alkaline medium. The Fe (II) and Fe (III) salts were mixed in their respective stoichiometry (i.e., ratio Fe^{2+}: Fe^{3+} = 1:2). The resultant mixture was kept at 80°C in 80.0 mL of water. To this boiling solution, NH_4OH is added drop by drop till the precipitation occurs under constant stirring. Magnetite formed by conversion of metals into hydroxides, which takes place immediately, and transformation of hydroxides into ferrites. The resultant solution was maintained at 80°C for 2 hr. The brown color precipitate, thus formed is then washed several times by distilled water. The precipitate is then separated by the help of external magnet and is then kept for drying at 80 °C.

2.2. Catalytic Reaction:

An oven dried flask was charged with Fe_3O_4 (0.030 g), benzoin (0.127 g, 0.6 mmol). To the flask toluene (3.0 mL) was added and heated to 80 °C with magnetic stirring. After completion of the reaction (monitored by TLC and UV-Visible spectroscopy), the reaction mixture was cooled to rt, and catalyst was magnetically removed and washed several times with toluene.

3. Results and Discussion

The catalytic properties of the freshly prepared MNPs were initially evaluated in the oxidation of benzoin at 80 °C. We found that MNPs performed as a versatile nano catalyst in the oxidation reaction of benzoin, furnishing the corresponding product in 90 % yield in 15 h. There was no reaction in the absence of MNPs. Very interestingly MNPs not only acts as a heterogeneous catalyst, but also as an oxidant in the benzoin oxidation reaction.

We continued our study in the oxidation of benzoin using MNPs in the presence of air using various solvents and temperatures. Quite interestingly, oxidation reaction of benzoin to benzyl gave upto 24% yield at room temperature using MNPs in acetonitrile. The reaction rate appeared to be dependent on the amount of MNP and also on temperature (Fig. 1).

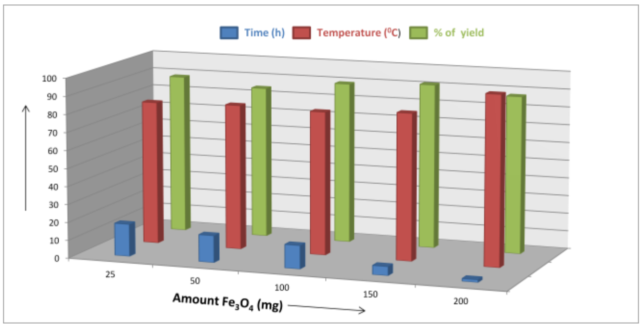


Fig. 1. Effect of various parameters (temperature, time and amount of MNPs) on the aerobic oxidation of benzoin.

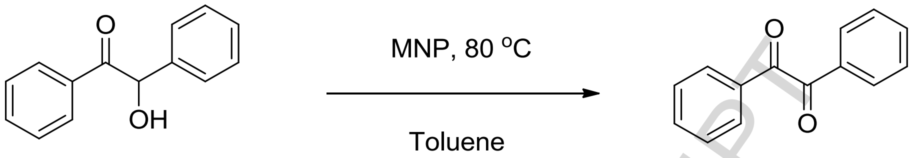
Very pleasingly, in toluene at 80 °C gave the best yields in the presence of MNPs in the oxidation reaction of benzoin to benzyl selectively (Table 1). Since magnetite has an inverse cubic spinel structure, it possesses both Fe^{2+} and Fe^{3+} ions and it is expected that Fe^{3+} take hydrogen from benzoin and reduced to Fe^{2+} ions. Fe^{2+} ion is oxidised to Fe^{3+} ions in the presence of air. The activity and selectivity of the oxide catalysts depends upon the oxidation state of the metal ions and their co-ordination in the lattice, the surface cation-oxygen bond strength, the extent of total oxygen (both surface and total) and morphology of the material. Surprisingly, no reaction was observed either in the presence of $FeCl_3$ or Ammonium iron (II) Sulphate, which is a precursor for the synthesis of MNPs. Interestingly, when the reaction was carried out in toluene in the presence of MNPs and 30% H_2O_2, benzyl product was formed in (up to 80% yield) in 4 h. However, catalyst lost its paramagnetic property after the reaction. No product formation was observed when the catalyst was only treated either with 30% H_2O_2 (convert all Fe^{2+} to Fe^{3+}) or with $NaBH_4$ (convert Fe^{3+} to Fe^{2+}) for one hr before addition of benzoin to the flask [25]. These results clearly indicate that both Fe^{2+} and Fe^{3+} are required for the oxidation.

Recycling of the experiment was carried out in toluene and the catalyst could be recycled for five times without loss of activity. Moreover, atomic absorption spectroscopy (AAS) analysis of the filtrate indicates, no iron was leaching from the MNPs. Moreover, the oxidation of benzoin was carried out in large scale (10 m.mol) and observed that benzyl was formed in 87% yield using MNPs (0.1 g)

The catalyst was characterized by X-ray photo electron spectroscopy (XPS), in order to understand the change of cations. The ratio of Fe (II) and Fe (III) remain constant after the oxidation reaction (Table 2). The XPS of the freshly prepared MNP catalyst exhibits the predominance of Fe (III) species. However, the heterogeneous catalyst, obtained after partial conversion of benzoin to benzyl shows the increasing of Fe (II) species (Figure 2). These results provide strong evidence that, upon treatment with benzoin, Fe (III) in MNP is reduced to Fe (II), which is in turn, oxidized to Fe (III) during the oxidation of benzoin

Table 1

Aerobic oxidation of benzoin in the presence of various catalysts[a]



Entry	Catalyst	Time (h)	Solvent	Oxidant	Temp(°C)	Yield (%)
1	-	36	Toluene	air	80	No reaction
2	$FeCl_3$	36	Toluene	air	80	-
3	$(NH_4)_2Fe(SO_4)_2$	36	Toluene	air	80	-
4	$FeCl_3$ + FAS	36	Toluene	air	80	-
5	Fe_3O_4	15	acetonitrile	air	R.T	24
6	Fe_3O_4	6	acetonitrile	air	60	71
7	Fe_3O_4	24	Toluene	H_2O_2	R.T	18
8	-	24	Toluene	H_2O_2	R.T	-
9	Fe_3O_4	15	Toluene	air	80	90
10	Fe_3O_4	6	Toluene	H_2O_2	RT	80

All the reactions were carried out in toluene or acetonitrile (3.0 mL), MNP (30.00 mg) and benzoin (1.0 m.mol)

To test the substrate scope of MNP catalyzed oxidation in the presence of air, variety of compounds were examined. Notably, simple primary and secondary alcohols also underwent using MNPs in the presence of air (Table 3, entries 2 & 3). These reactions were realized using expensive catalysts like Pd, Ru and Rh under homogeneous conditions [6]. Interestingly, nitro alcohols were converted into nitro ketones successfully in the presence of air using MNPs (Table 3, entry 4 & 5). Short reaction times and isolation of the product are the advantages of present work compared to earlier described methods [26-28]. Interestingly, there was no reaction with amino alcohols in the presence of MNP at 80 °C. (Table 3, entry 6)

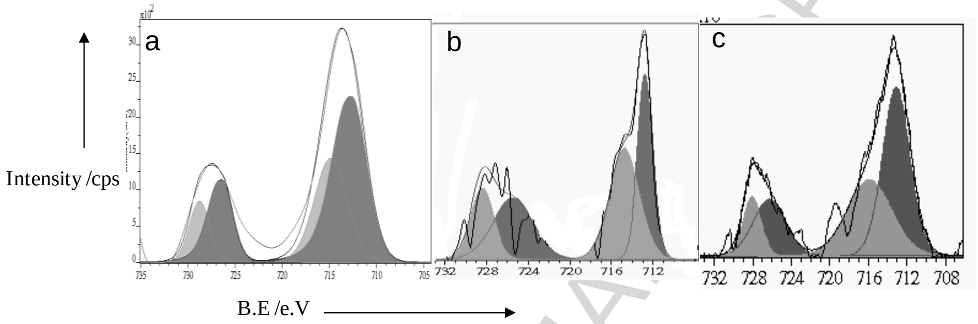


Fig. 2. XPS spectrum of Fe 2p ($2p_{3/2}$ and $2p_{½}$ peaks) a) Freshly prepared MPs b) Used Catalyst c) Partial conversion of benzoin to benzyl.

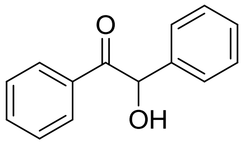
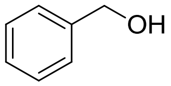
Table 2

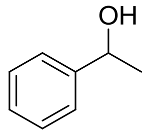
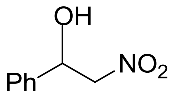
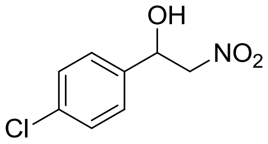
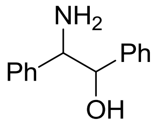
XPS data result of Fe_3O_4 before and after the reaction (after five cycles)

S.No	Catalyst	Fe^{3+}(%)	Fe^{2+} (%)
1	Fe_3O_4	55.5	44.5
2	Used Fe_3O_4	57.2	42.8
3	Fe_3O_4(partial conversion)	49.8	50.2

Table 3

Oxidation of various alcoholic groups in the presence of Fe_3O_4[a]

Entry	Substrate	Time (h)	Yield (%)
1		15	90
2		12	80

3		18	76
4		18	72
5		20	82
6		15	No Reaction

[a] All the reactions were carried out in toluene (3.0 mL), metal oxide (30.00 mg) at 80 °C

In conclusion, we have reported the oxidation of benzoin to benzyl selectively using MNPs as a reusable catalyst in the presence of air. We also proved that both Fe (II) and Fe (III) are necessary to complete the transformation. In addition, simple magnetic removal and recycling of the catalyst was shown to proceed without loss of activity.

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Highlights

- A simple, highly efficient and green protocol for the oxidation of benzoin.
- Fe(II) and Fe(III) are necessary for oxidation.
- Magnetite not only acts as a heterogeneous catalyst, but also as an oxidant.
- Nitro alcohols were converted into nitro ketones successfully in the presence of air.