



Short communication

# Ferrites catalyzed aerobic oxidation of benzoin and its extension to enantioselective version



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## ARTICLE INFO

## Article history:

Received 21 November 2014

Received in revised form 19 January 2015

Accepted 22 January 2015

Available online 28 January 2015

## Keywords:

Ferrites

Heterogeneous

Modifier

Oxidation

Spinel

## ABSTRACT

Ferrites have been used as efficient catalysts for the oxidation of  $\alpha$ -hydroxy ketones in the presence of air. The enantio selective version of the benzoin oxidation gave 30% yield with 43% ee using (*L*)-tartaric acid as chiral modifier on magnetite (inverse spinel).

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## 1. Introduction

An interesting family of mixed transition metal oxides, typically in a spinel structure has recently attracted research interest. The ferrites (designated as  $MFe_2O_4$ , where  $M = Fe, Zn, Co, Mg$ ) with magnetic properties are useful in electronic devices, magnetic fluids, and magnetic recording media and also in catalysis [1–3]. In addition, ferrites are also used as heterogeneous catalysts or catalyst support for organic reactions, adsorption and sensors [4–6]. Heterogeneous catalysis has been around for a long time, but has still much to groom. 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 [7,8]. The oxidation of benzoin to benzil is an important organic transformation since benzils have been using as ligands, biologically active compounds and also as photosensitive agent [9–11]. In view of significant drawbacks, such as toxic and expensive reagents, high temperature, stoichiometric amount of reagents, and low yield of these methods, more efficient catalytic system is highly demanded [12–15].

As a part of our interest in heterogeneous catalysis, we have been in hunt for development of new catalytic system [16]. The spinels have been used successfully in catalytic reactions; however this is our first attempt to utilize ferrites as catalyst in asymmetric reaction.

Herein, we report the aerobic oxidation of benzoin to 1,2-diphenylethane-1,2-dione in high yields in the presence of air using

cobalt ferrite as a heterogeneous catalyst (up to 94%) (Scheme 1). Initially various ferrites ( $MFe_2O_4$ ,  $M = Fe, Zn, Mg$  and  $Co$ ) were evaluated in the oxidation of benzoin in the presence of air. The easy removal of the catalyst from the reaction mixture makes the procedure very simple and eco-friendly.

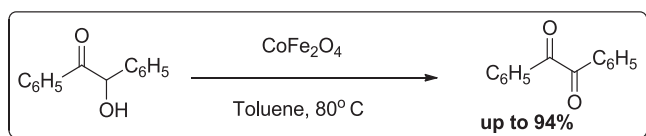
## 2. Experiment

### 2.1. Catalyst preparation

The magnetite was prepared by the so called wet-impregnation method as reported in the literature [17]. The substituted ferrites were synthesized by co-precipitation method depends mostly on parameters such as reaction temperature, pH of suspension, and initial molar concentration. The ultra fine particles of  $Fe_3O_4$  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.  $(NH_4)_2Fe(SO_4)_2$  and  $FeCl_3$  solutions are mixed in their respective stoichiometry (i.e., ratio  $Fe^{2+} : Fe^{3+} = 1:2$ ). The mixture is kept at 80 °C, and then the mixture is added 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 was formed by conversion of metals into hydroxides, which takes place immediately, and transformation of hydroxides into ferrites. The solution is maintained at 80 °C for 2 h.

The 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. Various ferrites were also synthesized using literature procedure [17].

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**Scheme 1.** Aerobic oxidation of benzoin using cobalt ferrite at 80 °C.

## 2.2. Base treatment of the $\text{Fe}_3\text{O}_4$ particles

A 5 g sample of  $\text{Fe}_3\text{O}_4$  particles was dispersed in 100 mL of NaOH solution (1.0 mol/L). The base treatment of the  $\text{Fe}_3\text{O}_4$  particles in a NaOH solution was performed for 8 h. The particles were then washed repeatedly by deionized water until the filtrate was neutral. The  $\text{Fe}_3\text{O}_4$  particle cake was dried at 60 °C for 20 h and crushed into dispersed particles. Then, the base-treated  $\text{Fe}_3\text{O}_4$  particles were ready for catalytic application.

## 2.3. Base titration of the $\text{Fe}_3\text{O}_4$ particle suspension

Base titrations were carried out in a flask equipped with a pH meter. A blank experiment was carried out by titrating a NaOH solution (0.010 mol/L) with a mixture of 5 mL of oxalic acid solution (0.010 mol/L) and 70 mL of deionized water to pH 10. The base titrations for the  $\text{Fe}_3\text{O}_4$  particles were performed as follow: (1) 50 mg of  $\text{Fe}_3\text{O}_4$  particles was dispersed into 70 mL of deionized water to form a suspension; (2) 5 mL of oxalic acid solution (0.010 mol/L) was uniformly mixed into the suspension; (3) NaOH solution (0.010 mol/L) was titrated into the suspension until pH 10.

## 2.4. Catalytic reaction

An oven dried flask was charged with respective ferrites (0.030 g), benzoin (0.127 g, 0.6 mmol). Toluene (3.0 mL) was added to the flask 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 the catalyst was magnetically removed and washed several times with toluene. The reaction mixture was monitored by using TLC with eluent of 9:1 hexane: EtOAc

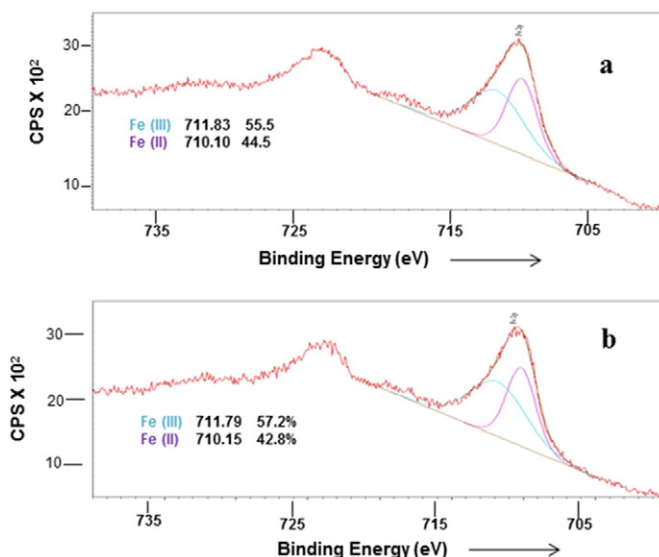
**Table 1**

Aerobic oxidation of benzoin in the presence of various ferrites.<sup>a</sup>

Entry	Spinel	Time (h)	Yield (%)	Fe (%)	Metal (%)
1	$\text{Fe}_3\text{O}_4$	15	90	69.1	–
2	$\text{ZnFe}_2\text{O}_4$	16	90	52.4	24.8
3	$\text{NiFe}_2\text{O}_4$	16	90	56.8	25.2
4	$\text{MgFe}_2\text{O}_4$	18	82	54.6	28.2
5	$\text{CoFe}_2\text{O}_4$	06	94	51.6	27.2
6	$\text{CoFe}_2\text{O}_4$	06	92	–	–
7	$\text{CoFe}_2\text{O}_4$	06	95	–	–
8	$\text{CoFe}_2\text{O}_4$	06	93	–	–
9	$\text{Fe}_3\text{O}_4$	16	88	–	–
10	$\text{CoFe}_2\text{O}_4$	6	90	–	–

Entry nos: 6–8 are 1st, 2nd and 3rd cycles respectively, entry nos: 9 and 10 are with base treated catalysts.

<sup>a</sup> All the reactions were carried out in toluene (3.0 mL), metal oxide (30.00 mg).



**Fig. 1.** XPS spectrum of a) fresh magnetite and b) (L)-TA modified magnetite.

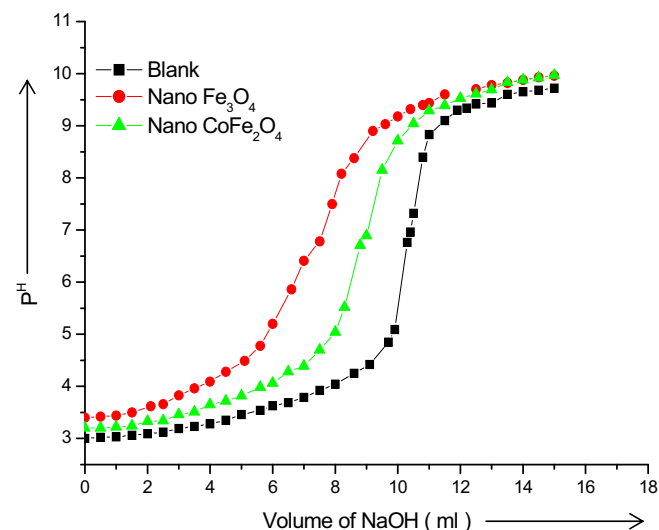
## 2.5. Characterization

The ferrites have been characterized by using X-ray photo electron spectroscopy (XPS), Scanning Electron Microscopy Energy Dispersive X-ray analysis (SEM-EDX) and Thermo Gravimetric Analysis (TGA).

## 3. Results and discussion

Initially catalytic application of benzoin was evaluated using inverse spinel like magnetite,  $\text{Fe}_3\text{O}_4$ . We found that magnetite performed as a versatile catalyst in the oxidation reaction of benzoin, furnishing the corresponding product in 90% yield in 15 h. The magnetite has an inverse cubic spinel structure; it possesses both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. The activity and selectivity of the oxide catalysts depend 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 the morphology of the material.

Various ferrites possessing magnetic properties like paramagnetic, antiferromagnetic, ferromagnetic and electromagnetic materials such as iron, zinc, magnesium, nickel and cobalt ferrites have been used in



**Fig. 2.** NaOH titration curves of  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and blank solution.

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