

RESEARCH PAPER

## Synthesis, Characterization and Catalytic Performance in the Selective Oxidation of Alcohols by Metallophthalocyanines Supported on Zinc Oxide Nanoparticles

Amin Ebadi\* and Sanaz Shojaei

Department of Chemistry, Kazerun Branch, Islamic Azad University, Kazerun, Iran

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### ABSTRACT

Unsubstituted phthalocyanines of Co, Fe and Mn supported on zinc oxide nanoparticles were prepared and were well characterized with X-ray diffraction and scanning electron microscopy. The oxidation of alcohols with tert-butylhydroperoxide, in the presence of metallophthalocyanines supported on zinc oxide nanoparticles was investigated. These MPc/ZnO nanocomposites were effective catalysts for the oxidation of alcohols such as cyclohexanol (83.4% conversion; 100% selectivity), benzyl alcohol (70.5% conversion; 100% selectivity) and hexanol (62.3% conversion; 100% selectivity). The influences of reaction time, various metals and type of substrates and oxidants on the oxidation of alcohols were also studied, and optimized conditions were investigated. Under these reaction conditions, the activity of the catalysts decreases in the following order: CoPc/nano-ZnO > FePc/nano-ZnO > MnPc/nano-ZnO. It shows that TBHP is more efficient oxidant due to weaker O-O bond with respect to H<sub>2</sub>O<sub>2</sub> and the following order has been observed for the percentage of conversions of alcohols: 2° > benzylic > 1°.

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### INTRODUCTION

Oxidation reactions are among the most important transformations in synthetic chemistry and offer important methodology for the introduction and modification of functional groups [1]. The selective oxidation of alcohols to aldehydes or ketones is a vital reaction in synthetic organic chemistry. In this way, chemists have used different kinds of metal salts and oxides in the form of homogeneous catalysts [2,3] or supported metal ions and supporting oxometal catalysts as heterogeneous systems [4,5].

Metallophthalocyanine (MPc) complexes have been used as alternative catalysts, because they have a similar structure to porphyrins and are cheaper and more stable to degradation [6]. The immobilization of MPc on solid supports is highly

desirable to synthesize heterogeneous catalysts [7]. In these catalysts, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> are commonly used as the supports. Bulk MPc in general cannot be used in industrial processes as they impart poor thermal stability that lead to fast deactivation of the catalyst. Furthermore, it is also known that bulk MPc leads to high combustion of organic molecules to carbon oxides [8]. There are some reports for the usage of cobalt and iron phthalocyanines as homogeneous catalysts for oxidation of alcohols [9,10]. Many different oxidants were used for the oxidation of alcohols such as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), KMnO<sub>4</sub>, MnO<sub>2</sub>, CrO<sub>3</sub> and so on. Most of these oxidizing reagents which can be used in a research laboratory in stoichiometric amounts are expensive or toxic

\* Corresponding Author Email: ebadiamin88@yahoo.com

[11-17]. Thus, the advantages of environmentally friendly oxidizing agents, such as  $H_2O_2$  and  $O_2$ , have been extensively studied.  $H_2O_2$  is attractive for producing active oxidation species in aqueous solution, with  $H_2O$  as a by-product. However, to the best of our knowledge, there is no report for application of MPC supported on zinc oxide nanoparticles for oxidation of alcohols. In this work, the catalytic effect of Fe, Mn and CoPc supported on zinc oxide nanoparticles are investigated for oxidation of alcohols in the liquid phase.

## MATERIALS AND METHODS

### Methods for characterization

The FT-IR spectra were recorded using a Perkin Elmer FT-IR spectrometer by employing KBr pellet technique. X-ray powder diffraction (XRD) patterns of the samples were recorded using a Bruker Advance D8 Diffractometer with Cu  $K\alpha$  radiation ( $\lambda=0.154$  nm). BET surface area was obtained from  $N_2$  adsorption isotherms at 77 K by a Strohlien. The SEM measurements were performed on a Holland Philips XL30 microscope. GC analysis of alcohols oxidation products was performed on a Shimadzu 8A, using authentic samples equipped with a TCD detector using OV-17, Propak-N, packed (2 m) columns and Helium as the carrier gas.

### Preparation of catalysts

ZnO nanoparticles were prepared by the chemical precipitation method. Zinc nitrate hexahydrate  $\{Zn(NO_3)_2 \cdot 6H_2O\}$  and ammonium hydroxide solution  $\{NH_4OH\}$  were used as starting chemicals. 12 M solution of aqueous ammonium hydroxide was added drop by drop to the 0/35 M solution of zinc nitrate hexahydrate in room temperature until pH of the solution reaches 7 and precipitate Zn cations in the form of hydroxides. After the white precipitate was formed, it was filtered and washed by deionized water. Metal salt ( $9.6 \times 10^{-5}$  mol), phthalonitrile ( $3.84 \times 10^{-4}$  mol), urea ( $1.92 \times 10^{-3}$  mol) and ammonium heptamolybdate ( $8 \times 10^{-4}$  mol) were mixed and finely grounded and were added to the white precipitate. This white precipitate was stirred and homogenized and was placed in an oven under temperature of 100 °C for 24 h. The mixture was heated in air to 300 °C at a heating rate of 2 °C/min and then the mixture was calcined at 400 °C under vacuum for 4 h [18,19]. Formation of ZnO nanoparticles was confirmed with XRD and for MPC with UV-VIS and IR spectra.

CoPc/nano-ZnO: IR (KBr):  $\nu$ ,  $cm^{-1}$  1520, 1428, 1336, 1289, 1161, 1120, 1088/3424, 1635, 1385, 1113.

FePc/nano-ZnO: IR (KBr):  $\nu$ ,  $cm^{-1}$  1518, 1414, 1332, 1293, 1164, 1119, 1084/3423, 1635, 1384, 1115.

MnPc/nano-ZnO: IR (KBr):  $\nu$ ,  $cm^{-1}$  1509, 1418, 1335, 1287, 1166, 1115/3424, 1636, 1385, 1113.

### Experimental procedure

In a typical reaction, a mixture of 0.5 g catalyst and 30 mmol of alcohol (cyclohexanol, n-hexanol or benzyl alcohol) were stirred under nitrogen in a 50 ml round bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 14 mmol of TBHP or  $H_2O_2$  was added as oxidizing reagents. The resulting mixture was then refluxed for 8 h under  $N_2$  atmosphere. After filtration, the solid was washed with solvent and then the reaction mixture was analyzed by GC (Shimadzu 8A). Products identification was done with GC-MS (Finnigan TSQ-7000).

## RESULTS AND DISCUSSION

### Characterization of the catalysts

Formation of MPC was confirmed with UV-VIS spectra (Fig. 1) and shows the same spectra of unsupported MPC. These spectra confirm formation of different polymorphs of MPCs in the zinc oxide matrix [20].

The XRD pattern presented in Fig. 2 indicates that ZnO nanoparticles are formed. There is no significant change in the XRD pattern with 10 wt.% CoPc supported on ZnO nanoparticles which confirms that CoPc dispersed through pores does not change the ZnO structure.

Scanning electron micrograph (SEM) of a typical sample of 10 wt.% CoPc supported on ZnO nanoparticles is shown in Fig. 3. It is clarified that the sizes of the particles are in the ranges of 30-50 nm. This result was coincident with the particle sizes calculated from the Scherrer equation.

Specific surface area measured with BET method was 65  $m^2/g$  for ZnO nanoparticles and 52  $m^2/g$  for 10 wt.% CoPc/nano-ZnO. This reduction in specific surface area for the supported CoPc may be an indication of encapsulation of CoPc in the ZnO pores.

### Catalytic oxidation of cyclohexanol with TBHP

The use of TBHP as an oxidant was based on the earlier studies on the oxidation of hydrocarbon [6], this oxidant was found to cause minimal destruction of the phthalocyanine catalyst, and

to give better selectivity of the products. The performance of the set of samples prepared as catalysts for the oxidation of alcohols was tested with TBHP. At first, the reactivity of a model compound, cyclohexanol, was examined under a variety of experimental condition (Table 1). In

all reactions were produced only one product (cyclohexanone) therefore, selectivity (%) is 100 with respect to it. The research results showed that three kinds of metallophthalocyanines could catalyze cyclohexanol oxidation with TBHP. The activity of the catalysts was as follows: CoPc/

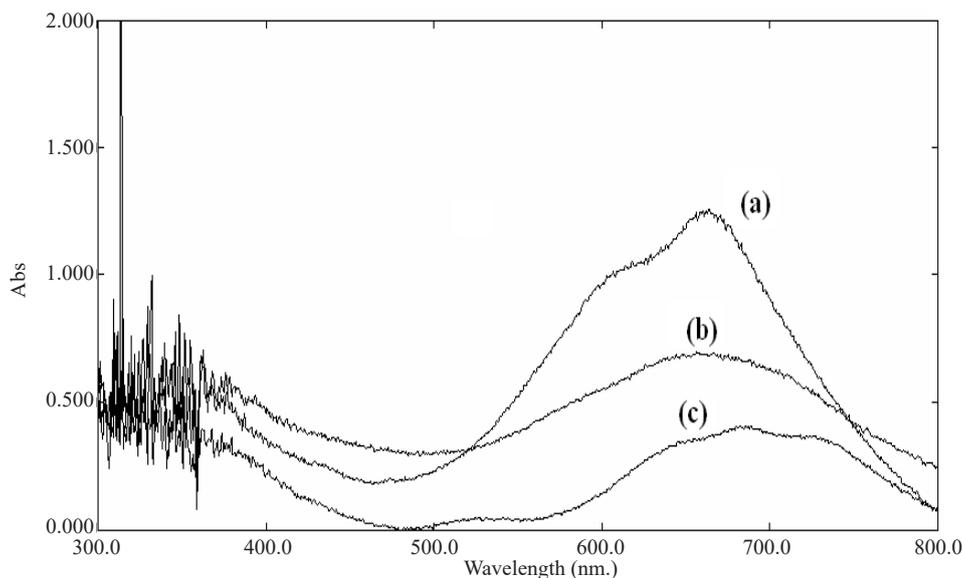


Fig. 1. Diffuse reflectance spectrum of: (a) CoPc/nano-ZnO (b) FePc/nano-ZnO, and (c) MnPc/nano-ZnO.

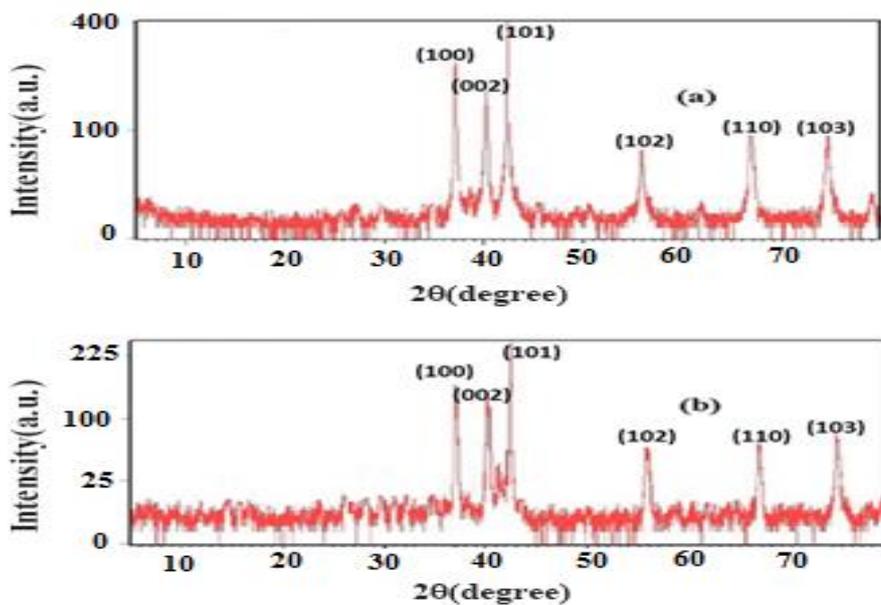


Fig. 2. XRD patterns of (a) ZnO nanoparticles, and (b) 10 wt.% CoPc/nano-ZnO.

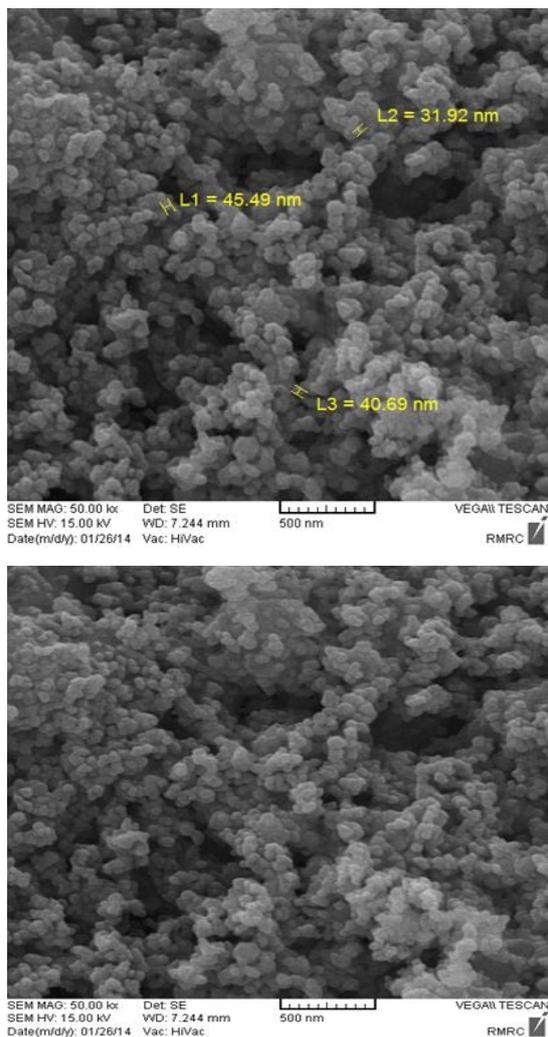


Fig. 3. SEM photographs of 10 wt.% CoPc/nano-ZnO.

nano-ZnO > FePc/nano-ZnO > MnPc/nano-ZnO. In the presence of 10% CoPc/nano-ZnO, conversion percentage of cyclohexanol was 83.4% with TBHP as an oxidant. Contrastive experiment results show that cyclohexanol oxidation with TBHP did not occur in the absence of the catalyst under the same reaction condition. In addition, unsupported ZnO has shown lower catalytic activity than the supported catalyst.

*Influences of reaction time on cyclohexanol oxidation reaction*

In this experiment, the change in conversion (%) of cyclohexanol in the presence of TBHP oxidant and 10% CoPc/nano-ZnO catalyst was monitored and plotted with respect to time (Fig. 4). The reaction was carried out at reflux temperature for 8 h with 0.5 g catalyst and 30 mmol cyclohexanol and 14 mmol TBHP in a round bottom flask and some samples was drawn out at regular intervals and analyzed by GC. Fig. 4 shows that the conversion of cyclohexanol increases continuously until 83.2% as time increases and then remains constant after 7 h, therefore duration about 7-8 h is proper reaction time.

*Influences of various metals on cyclohexanol oxidation reaction*

We have studied the catalytic properties of iron, cobalt and manganese phthalocyanines and to investigate the effects of different metals on cyclohexanol oxidation reaction under the same reaction conditions. Table 1 has summarized the results and confirms the high catalytic activities of

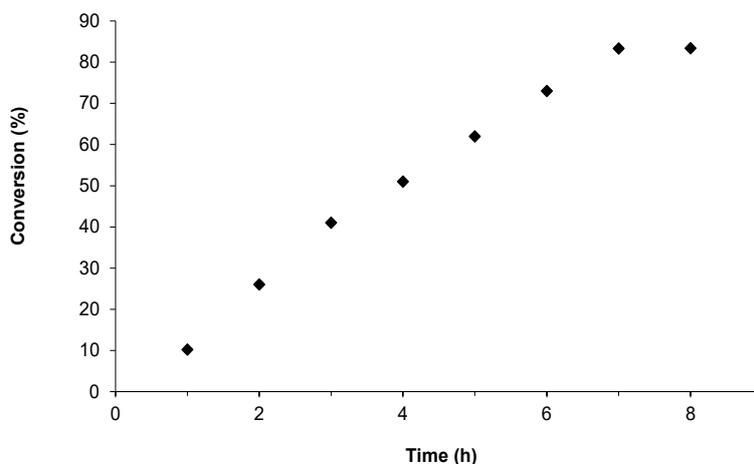


Fig. 4. The effect of reaction time on cyclohexanol conversion. Reaction condition: 0.5 g 10% CoPc/nano-ZnO catalyst, cyclohexanol 30 mmol, TBHP 14 mmol, reflux temperature.

Table 1. Oxidation of cyclohexanol with TBHP in the presence of metallophthalocyanines supported on zinc oxide nanoparticles

Catalyst	Conversion (%)	Selectivity (%)
10% CoPc/nano-ZnO	83.4	100
10% FePc/nano-ZnO	72.8	100
10% MnPc/nano-ZnO	61.4	100
nano-ZnO	23.5	100

Reaction condition: 0.5 g catalyst; cyclohexanol 30 mmol; TBHP 14 mmol; reflux temperature; reaction time 8 h

Table 2. Effect of the 10% CoPc/nano-ZnO catalyst in the oxidation of different alcohols.

Alcohol	Product	Conversion (%)		Selectivity (%)
		TBHP oxidant	H <sub>2</sub> O <sub>2</sub> oxidant	
Cyclohexanol	Cyclohexanone	83.4	67.4	100
Benzyl alcohol	Benzaldehyde	70.5	58.3	100
n-Hexanol	Hexanal	62.3	50.6	100

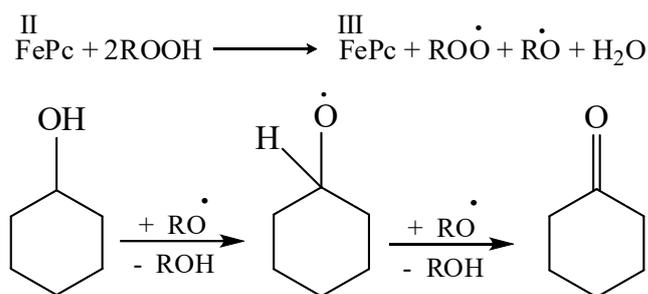


Fig. 5. Proposed mechanism for the production of cyclohexanone in cyclohexanol catalytic oxidation by metallophthalocyanine.

these MPCs. The research results indicated that all the three metallophthalocyanines could catalyze cyclohexanol oxidation with TBHP. The activity of the catalysts was as follows: CoPc/nano-ZnO > FePc/nano-ZnO > MnPc/nano-ZnO. Irfan Acar [21] has reported that Co phthalocyanine and in the liquid phase, a conversion percent of benzyl alcohol 42% was obtained. They also concluded that Co phthalocyanine acts better than Fe phthalocyanine.

#### Effect of substrates and oxidants on cyclohexanol oxidation reaction

In this study, experiments on various selected alcohols were performed and the comparisons with respect to conversion and product selectivity are represented in Table 2. Higher conversion was obtained for cyclohexanol on 10% CoPc/nano-ZnO catalyst using TBHP oxidant. Table 2 shows that

the reactivity of the alcohols toward oxidation with TBHP and H<sub>2</sub>O<sub>2</sub> on 10% CoPc/nano-ZnO catalyst depends on the particular structure of the substrate and type of oxidant. It shows that TBHP is more efficient oxidant due to weaker O-O bond with respect to H<sub>2</sub>O<sub>2</sub> and the following order has been observed for the percentage of conversions of alcohols: 2° > benzylic > 1°.

In this regard, it is worth noting that using H<sub>2</sub>O<sub>2</sub> as reactant the complexes lose their characteristic color during the course of the reaction. UV-VIS spectroscopy of the recovered catalysts evidenced the degradation of the MPC complexes. This behavior contrasts with that of TBHP which does not produce decomposition of the MPC complexes as assessed by UV-VIS and IR spectra at the end of the reaction. Similar UV-VIS and IR spectra were obtained for the catalyst before and after the reaction test with TBHP and the result confirms

that the catalyst is stable, decomposition of MPC was negligible and its reactivity was preserved.

#### Mechanism of catalytic oxidation

According to the literature [22], the electrocatalytic oxidation of cyclohexanol by metallophthalocyanine at first produces ROO· and RO· radicals as shown in Scheme 1. The RO· and ROO· radicals produced then react with cyclohexanol according to Fig. 5.

#### CONCLUSION

Metallophthalocyanines supported on zinc oxide nanoparticles were directly prepared with the addition of required materials for the formation of metallophthalocyanines to the white precipitate of Zn hydroxide and heated to 400 °C under vacuum. These metallophthalocyanines supported on zinc oxide nanoparticles prove to be reactive, effective and reusable catalysts for catalytic oxidation of different alcohols with excellent conversion percentage and 100% selectivity by using TBHP as oxidizing reagent.

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#### CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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