Journal of Ceramic Processing Research. Vol. 17, No. 6, pp. 560~563 (2016)

J O U R N A L O F
Ceramic Processing Research

Synthesis, characterization and catalytic activity of CuO/NiO nanoparticles for oxidation of olefins

Maryam Lashanizadegan*, Fahimeh Jarvand, Saeed Dehghanpour and Hoda Mirzazadeh
Department of Chemistry, Faculty of Physics and Chemistry, Alzahra University, P. O. Box 1993893973, Tehran, Iran

CuO/NiO nanoparticles were synthesized in the presence of PEG400 by depositional in alkaline environment. CuO/NiO nanoparticles were characterized by FT-IR, UV-Vis, SEM, X-ray diffraction (XRD), and EDAX. Results of XRD analysis show the crystal structure of Bunsenite (NiO) and Tenorite (CuO). The SEM photographs show granular and plate morphology of nanoparticles with high uniformity. The as-prepared nanoparticles are applied as catalyst in oxidation reaction. Effect of different parameters such as time, temperature, the kind of solvent and oxidant, and amount of oxidant on oxidation reaction were investigated in detail. The results show under the optimized reaction condition, between different substrates (cyclohexene, α-methyl styrene and styrene) using TBHP as oxidant, chloroform as solvent, and CuO/NiO as catalyst, 100% conversion of α-methyl styrene has been achieved where selectivity of acetophenone was 76%.

Key words: oxidation, CuO/NiO nanoparticles, Catalysis.

Introduction

Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner of edge surface sites [1]. It seemed likely that the use of oxide nanoparticles would benefit the catalytic activity due to the increase in catalyst surface area and physical chemical interactions. A great deal of fundamental researches has been done on mixed catalysts in the field of heterogeneous catalysis [2, 3]. Nickel oxide (NiO), a P type semiconductor, is used in adsorbents of solar thermal [4], catalyst and cathode electrode in battery [5]. CuO is in the wide range of applications such as gas sensors, magnetic storage, battery and heterogeneous catalysts [6-10]. Studies show the Mixed NiO/CuO nanoparticles, might enhance catalytic activity in oxidation and photocatalitic reactions [11-13]. In 2012, Kang and his colleagues used photocatalytic compounds including eosin Y and MW Carbone nano tube filled with NiO/CuO as an active center of the evolution of H_2 from water splitting [14]. In 2014, Ming Huang and his colleagues synthesized nano NiO/CuO flowers by a simple method and applied them as battery electrodes [15]. One of the reactions that use these metal oxides as catalysts is oxidation of olefins [16]. The oxidation of olefins is a very important reaction, because its products (epoxides and ketones) are widely used in the synthesis of many fine chemicals as well as pharmaceuticals and agro chemicals [17]. Consequently, studies on the oxidation of organic compounds containing C = C have received a lot of attention. In this study, CuO/NiO nanoparticles were synthesized in the presence of PEG400 by dispositional in an alkaline environment. Then catalytic activity of the nanoparticle in the oxidation of olefins by *tert*-butyl hydroperoxide (TBHP) was studied.

*Corresponding author:
Tel : +989124471085
Fax: +982188041344
E-mail: m_lashani@alzahra.ac.ir

Experimental

Instruments and reagents

All materials were commercial reagent grade. FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400-4000 cm^{-1} with a Bruker tensor 27DTGS. UV-VIS spectra were recorded on Lambda 35 spectrophotometer. Gas chromatography experiments (GC) were performed on Agilent Series 6890. The identity of the products was confirmed by GC-MS model Agilent Series 5973. XRD pattern was recorded by Jeol JDX-8030. Scanning electron microscope (SEM) of catalyst was performed on KYKY-EM3200.

Preparation of CuO/NiO nanoparticles

In a typical experimental procedure $Ni(CH_3COOH)_2.2H_2O$ was dissolved in distilled water to form a 0.1 M solution. The precursor solution obtaining 4 mL of this solution was added to a 100 mL conical flask containing mixed solutions of 50 mL distilled water, 2.5 mL NaOH 1 M, and 5 mL polymer blended well by stirring for 10 minutes. Subsequently, in another 100 mL conical flask, a mixed solution of 50 mL distilled water 10 mL NaOH 1 M, 5 mL polymer and 4 mL $CuSO_4$ 0.1 M were prepared. Then the contents of the each conical flask were added together and blended by stirring for

10 minutes. The mixed solution was placed for a 4 days at room temperature. After synthesis, the product was collected by centrifugation, washed with distilled water and ethanol several times and dried at 60 °C in a vacuum oven for 10 h. Then the product was calcinated at 500 °C for 2 hrs.

Epoxidation of Olefins

All reactions were carried out in a 25 mL glass reactor equipped with a reflux condenser and fitted with septum and water circulated condenser using a general procedure for catalysts; in a typical experiment, 5 mL chloroform, 10 mmol olefin and 5 mg catalyst were mixed and stirred at 80 °C. The reaction progress was monitored by GC and verified by GC-Mass.

Results and Discussion

Characterization study of the prepared sample

Fig. 1 shows a typical XRD Pattern of the synthesized NiO/CuO nanoparticles in an optimized condition. XRD pattern confirms that the synthesized sample is NiO/CuO nanoparticles. It has the crystal structure of Bunsenite (NiO) and Tenorite (CuO). The structure of the obtained XRD Pattern corresponds to) (JCPDS card No. 04-0835) and (JCPDS card No. 45-0937). Sharp and intense peaks prove the synthesis of typical quality crystalline NiO/CuO [18]. The surface morphology of the as-synthesized powder was studied using SEM and illustrated in Fig. 2. This figure shows a top view of SEM image of NiO/CuO nanoparticles. SEM images show nanoparticles have granular and plate morphology. Generally the morphology and uniformity of the nanoparticles are good. UV-Vis absorption spectrum of the as-synthesized solution of the sample illustrates a wide absorption peak centered at 276 nm with a long tail towards a higher wavelength side. This corresponds to maximum Absorbance of UV-Vis of the mixed structure of CuO/NiO [18]. The FTIR spectrum of the as-synthesized powder dispersed in KBr, are the resolved shoulders in the IR spectrum at 527, 473 cm^{-1} due to the characteristic vibrations of Cu-O and Ni-O, respectively [18].

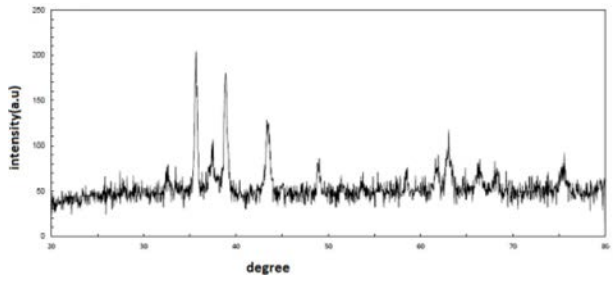

Fig. 1. Typical XRD pattern of the synthesized NiO/CuO.

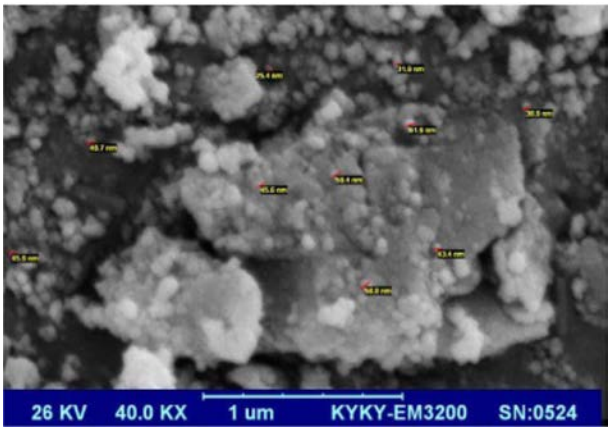

Fig. 2. SEM image of the synthesized NiO/CuO.

Catalytic activity of as-synthesized CuO/NiO nanoparticles

In order to study the catalytic effects of CuO/NiO in Oxidation of the olefin, first oxidation reaction of styrene is done using TBHP as oxidant to obtain an optimized condition. Then, in optimized condition, different substrates like styrene, α-methyl styrene and cyclohexene were applied for oxidation reaction.

Effects of time and temperature on reaction

For studying the effect of time and temperature, reactions were carried out at 60 °C in 12, 16, 18 hrs and 80 °C in 6, 8, 12 and 14 hrs. The results are shown in Figs. 3 and 4. Fig. 3 shows that at 60 °C with increasing time from 12 to 18 hrs, conversion%

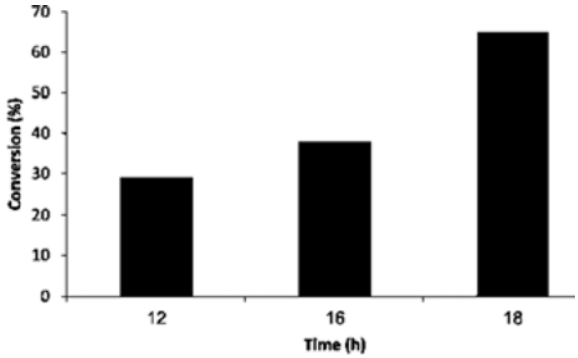

Fig. 3. Effect of time at 60 °C, reaction condition: catalyst 5 mg, styrene 10 mmol, TBHP 20 mmol, acetonitrile 5 mL.

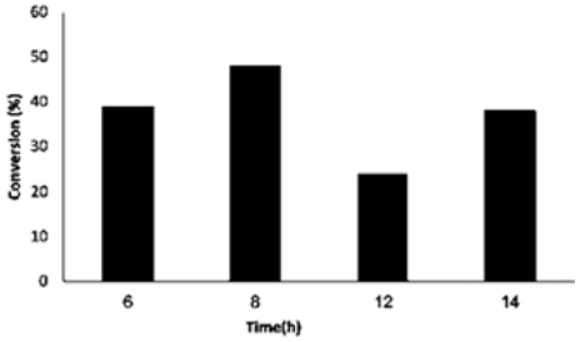

Fig. 4. Effect of time at 80 °C, reaction condition: catalyst 5 mg, styrene 10 mmol, TBHP 20 mmol, acetonitrile 5 ml.

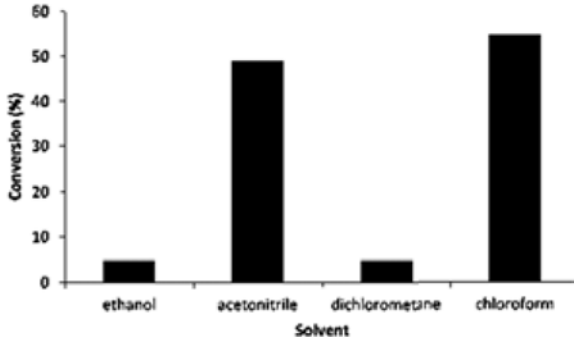

Fig. 5. Effect of solvent, reaction condition: catalyst 5 mg, styrene 10 mmol, TBHP 20 mmol, solvent 5 mL at 80 °C.

Table 1. Effects of oxidant.

Conversion %wt	Selectivity of product Styrene oxide))	Selectivity of product (benzaldehyde)	oxidant
–	–	–	H_2O_2
55	61	26	TBHP

Reaction condition: Catalyst 5 mg, Styrene 10 mmol, Oxidant 20 mmol, Chloroform 5 mL at 80 °C.

became higher, so the reaction was carried out in 80 °C. Fig. 4 shows that with increasing time from 6 to 8 hrs, conversion % is increased, so the optimized time and temperature for the reaction is 8 hrs at 80 °C.

Effects of solvent on reaction

To study solvent effect, oxidation of styrene was carried out in different solvents like ethanol, acetonitrile, dichloromethane and chloroform (Fig. 5). The results show the best solvent is chloroform.

Effects of oxidant

For finding the best oxidant, oxidation of styrene was carried out in TBHP and H_2O_2 (Table 1). The results show TBHP is the best oxidant. No reaction was done in H_2O_2.

Effects of amount of TBHP on oxidation reaction

For obtaining the best amount of TBHP, oxidation of styrene was done in the presence NiO/CuO as catalyst with different amounts of TBHP (Fig. 6). The results show 25 mmol is the best amount of TBHP.

Effects of amount of catalyst

Oxidation of styrene was carried out with different amounts of catalyst (Fig. 7) the results show 5 mg is the best amount of catalyst.

Effects of substrate on oxidation reaction

After optimizing all of the conditions of the reaction, in order to study the effects of the type of substrates on oxidation of olefins, the reaction was carried out with different substrates (styrene, α-methyl styrene,

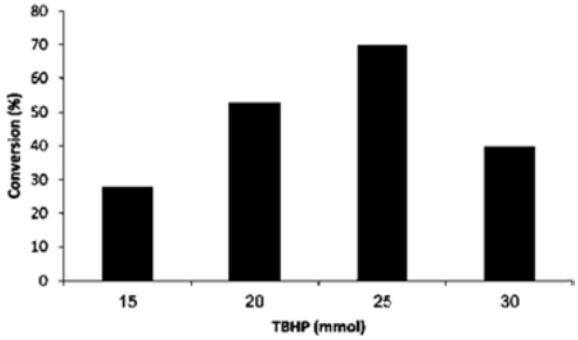

Fig. 6. Effect of amount of TBHP, reaction condition: catalyst 5 mg, styrene 10 mmol, oxidant amount 15, 20, 25, 30 mmol, chloroform 5 mL at 80 °C.

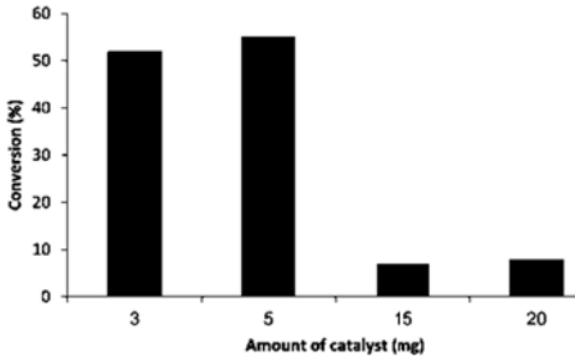

Fig. 7. Effect of amount of catalyst (mg), reaction condition: catalyst amount 3, 5, 15, 20 mg, styrene 10 mmol, TBHP 20 mmol, chloroform 5 mL at 80 °C.

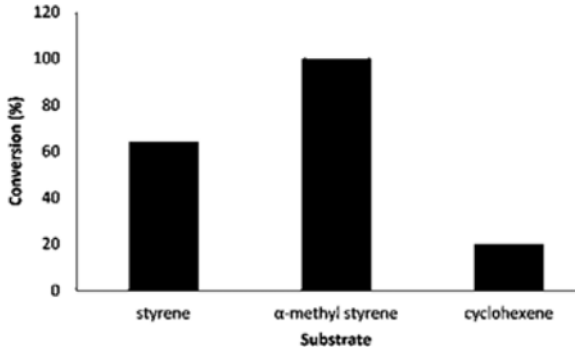

Fig. 8. Effect of substrates, reaction condition: catalyst amount 5 mg, substrate 10 mmol, TBHP 20 mmol, chloroform 5 mL at 80 °C.

cyclohexene) (Fig. 8). The schematic illustrations of reactions are shown in Fig. 9. The result shows that, under the optimized reaction condition, 100% conversion of á-methyl styrene has been achieved where selectivity of acetophenone was 76%.

Conclusions

This study demonstrates a method for synthesis of mixed nano particles using a short chain polymer PEG400. This polymer plays a crucial role in the growth of nanoparticles. Therefore by first adding polymer to

the solution of NaOH and then to the aqueous solution of metal salts, the process modifies the growth kinetics of the growing cells, which finally leads to the anisotropic growth of the crystals [19]. Notably, NiO/CuO nanoparticles are capable of catalyzing the oxidation of olefins in chloroform with TBHP oxidant. Oxidation reactions have rarely been attempted using CuO/NiO as catalyst before this study, and the prepared catalyst might be useful for industrial applications.

Acknowledgments

Supporting of this investigation by Alzahra University is gratefully acknowledged.

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