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Synthesis, characterization and catalytic property of CuO and Ag/CuO nanoparticles for the epoxidation of styrene

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Abstract−CuO nanorodes, CuO nanoplates and Ag/CuO nanoparticles were synthesized in the presence of polyethylene glycol by depositional in alkaline environment. Oxide nanoparticles were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared absorption spectra (FT-IR). CuO and Ag/CuO nanoparticles show high catalytic activity for the selective epoxidation of styrene to styrene oxide by TBHP. Under the optimized reaction condition, the oxidation of styrene catalyzed by CuO nanorods gave 100% conversion with 60 and 35% styrene oxide and benzaldehyde, respectively. Ag/CuO gave 99% conversion and styrene oxide (71%) and benzaldehyde (12%) being the major product.

Key words: Nano Oxide, Catalysis, Styrene Oxide, Copper (II) Oxide

INTRODUCTION

Many methods have been used to fabricate nanocrystal with different morphologies [1,2]. Among them, selective adsorption of surfactant molecules is typical for this kind of morphosynthesis [3,4]. To date, many kinds of surfactant molecules have been used to prepare nanocrystal. Of them, polyethylene glycols (PEG) have been used in preparing nanocrystal. A variety of PEG have been explored, including low and high molecular weight (PEG) [5,6] and copolymer of PEG [7].

However, studies about different morphology of CuO are reported. Xia and coworkers [8] reported the synthesis of CuO nanowires. CuO nanofibers have been synthesized by Hsieh et al. [9] and G.H. Du [10] describes a facile method to produce CuO nanowires and nanobelts.

CuO also has been exploited as a powerfully heterogeneous catalyst to convert hydrocarbons completely into carbon dioxide and water [11]. In the aqueous media CuO nano particles catalyze the one-pot synthesis of 4-keto-4,5,6,7-tetrahydrobenzofurans [12]. Styrene oxide is an important intermediate in the production of a number of fine chemicals and pharmaceuticals. However, in most cases, either styrene conversion or styrene oxide selectivity/yield was poor. Recently, Choudhary and coworkers [13-17] have reported a number of highly active nano-gold catalysts supported on different alkaline earth, rare earth and transition metal oxides for the selective epoxidation of styrene by anhydrous TBHP with high styrene oxide yield.

Studying a new type nano sized and morphology of copper oxide composites in order to improve catalytic activity remains a challenge. Also, addition of Ag in metal oxides can improve their catalytic activities [18-20] and only a few reports on the preparation of Ag/CuO composites with nanostructures have been published [21], so we have researched about this aspect. Herein, we present a simple and inexpensive method to synthesize CuO nanorods, CuO nanoplates and Ag/CuO nanoparticles. They are used as highly active and selective heterogeneous catalysts for the epoxidation of styrene by TBHP with high selectivity and yield for styrene oxide. Ag/CuO nanoparticles showed better catalytic performance than CuO nanorods.

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EXPERIMENTAL

All the reagents were of analytical grade and used without any further purification.

1. Preparation of CuO Nanorods

First, 4 ml $CuSO_4 \cdot 5H_2O$ (0.1 M) was added to the solution of 6 ml NaOH aqueous solution (10 M) in a 100 ml beaker. Then 50 ml distilled water and 2 g PEG6000 were added slowly. After that, the blue solution was stirred for 20 minutes and left standing at room temperature for four days. The obtained precipitate was then separated by centrifuge and washed several times with distilled water and alcohol and then calcined at 220 °C for 3 h.

2. Preparation of CuO Nanoplates

First, 4 ml $CuSO_4 \cdot 5H_2O$ (0.1 M) was added to the solution of 6 ml NaOH aqueous solution (10 M) in a 100 ml beaker. Then a mixed solution of 50 ml ethanol, 50 ml distilled water and 20 ml PEG400 was added. The resulting blue solution was stirred for 20 minutes and left at room temperature for 4 days. The precipitate was then separated by centrifuge and washed several times with distilled water and alcohol then calcined at 270 °C for 5 h.

3. Preparation of Ag/CuO Nanoparticles

First, 10 ml $CuSO_4 \cdot 5H_2O$ (0.1 M) was added to the solution of 15 ml NaOH aqueous solution (10 M) in a 100 ml beaker. Then 70 ml distilled water, 15 ml PEG400 and 0.2 ml of Silver nitrate solution (0.1 M) were added slowly. The resulting blue solution was stirred for 15 minutes and left at room temperature for four days. The precipitate was then separated by centrifuge and washed several times with distilled water and alcohol then calcined at 500 °C for 6 h.

4. Oxidation of Styrene

The catalytic oxidation of styrene was carried out in a 50 ml two necked flask fitted with septum and water circulated condenser using a general procedure for two catalysts; in a typical reaction, an aqueous 70% *tert*-butylhydroperoxide (TBHP) (15 mmol) and styrene (0.5 g, 5 mmol) were mixed in 10 ml of CH_3CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The catalyst (CuO or Ag/CuO nanoparticles) was added to the reaction mixture and the reaction was considered to begin. The resulting mixture was refluxed; the products were collected at different time intervals. The catalyst was separated from the reaction mixture by filtration. The products were identified and quantified by GC and verified by GC-MS. The used catalyst was dried and then it was reused for the oxidation.

RESULTS AND DISCUSSION

The mechanism of the formation of copper oxide is usually accepted as the following reaction equation [22].

$H_2O \rightarrow H^+ + OH^-$

$NaOH \leftrightarrow Na^+ + OH^-$

$Cu\,SO_4 \rightarrow Cu^{+2} + SO_4^{-2}$

$Cu^{+2} + OH^- \rightarrow Cu(OH)_2$

$Cu(OH)_2 \rightarrow CuO + H_2O$

1. FT-IR Study

The FT-IR spectra of CuO show the peaks at 494 and 610 cm^{-1} (Fig. 1(a)) confirming that CuO nanoparticles are formed [23]. The broad peaks at 3,419 and 1,634 cm^{-1} are related to the stretching and bending vibration of OH, respectively. These peaks indicate the presence of water linked to nanoparticles. Fig. 1(b) Shows the

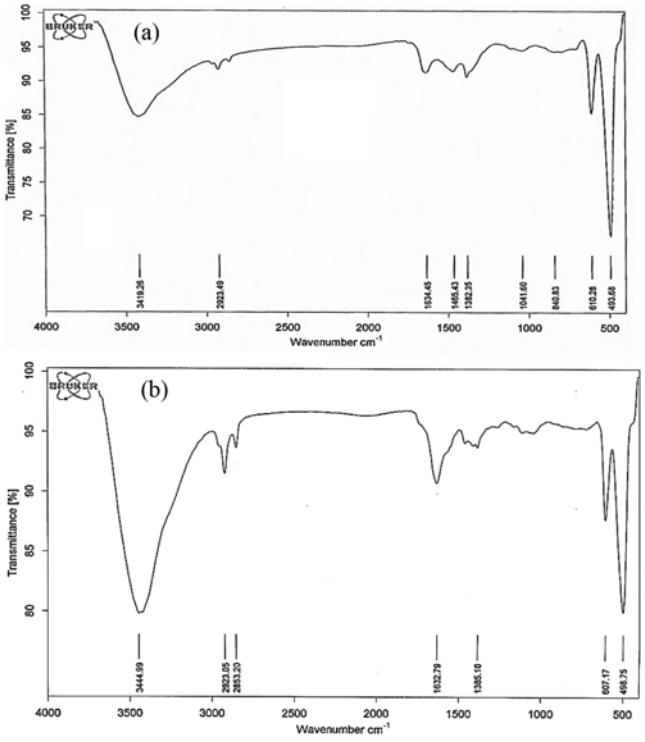

Fig. 1. FT-IR spectra of CuO (a) and Ag/CuO (b) nanoparticles.

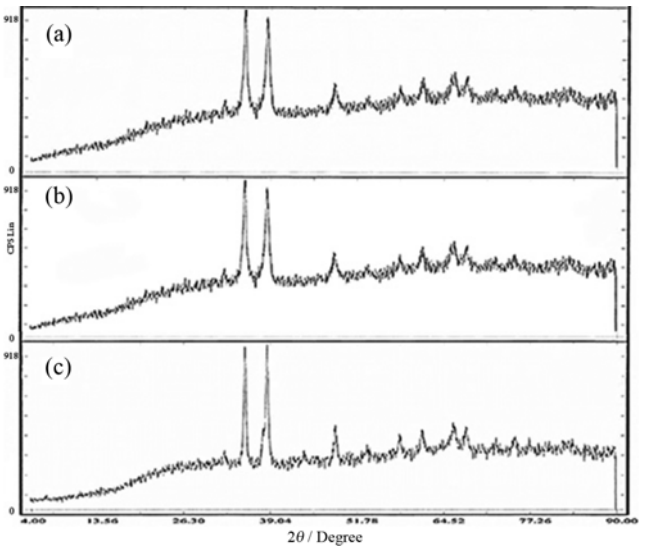

Fig. 2. XRD patterns of CuO nanorods (a), CuO nanoplates (b) and Ag/CuO nanoparticles (c).

FT-IR of Ag/CuO nanoparticles the peaks at 499 and 607 cm^{-1} confirming that CuO nanoparticles are formed and the peaks at 3,444 and 1,623 cm^{-1} are related to the stretching and bending vibration of OH. The absorption regions at 1,382 and 1,041 cm^{-1} are related to the vibration of longitudinal phonons, which are similar to the character commonly possessed by nanoparticles. Due to quite high ratio of surface atoms in nanosized sample, many suspended bonds that are up right to the particle surface may appear, and the stretching vibrations of suspend bonds become more active. So IR spectra band intensity increases [24]. In both spectra the peaks at 2924 and 2953 are related to alkene C-H stretching vibration modes of polyethylene glycol. It can be seen that only a slight shift in bands position was observed in the spectrum resulting from Ag addition. The observed shift may be due to the effect of Ag on metal-oxygen bands vibration of CuO [25].

2. XRD Study

The XRD patterns of the obtained nanorods, nanoplates and doped nano silver copper oxide are shown in Fig. 2(a)-(c). For all of the samples, characteristic diffraction peaks at 32.5°, 35.5°, 38.6° and 48.6° are evident, and these peaks agree well with the standard diffraction data for the tenorite CuO (JCPDS file No. 45 -0937). The characteristic diffraction peaks of Ag for Fig. 2(c) occur at 38°, 44°, and 77.3° which are well consistent with standard powder diffraction of Ag (JCPDS file No. 04-0783). The XRD patterns show that Fig. 2(a)-(b) are samples of CuO nanorods and CuO nanoplates, respectively, and Fig. 2(c) is a sample of Ag/CuO nano composites. Employing the Scherer equation, the sizes of nanorods, nanoplates and doped nano silver copper oxide are 18, 23 and 25 nm, respectively.

3. SEM Study

To investigate the morphology and particle size of CuO and Ag/CuO nanoparticles, scanning electron microscopy (SEM) was studied. Typical SEM images of CuO prepared in different condition are shown in Fig. 3(a)-(e). As can be seen, the sample was obtained in different amount of PGE400, 10 and 20 ml shown in Fig. 3(a) and 3(b), respectively, which leads to more uniform size distribution and

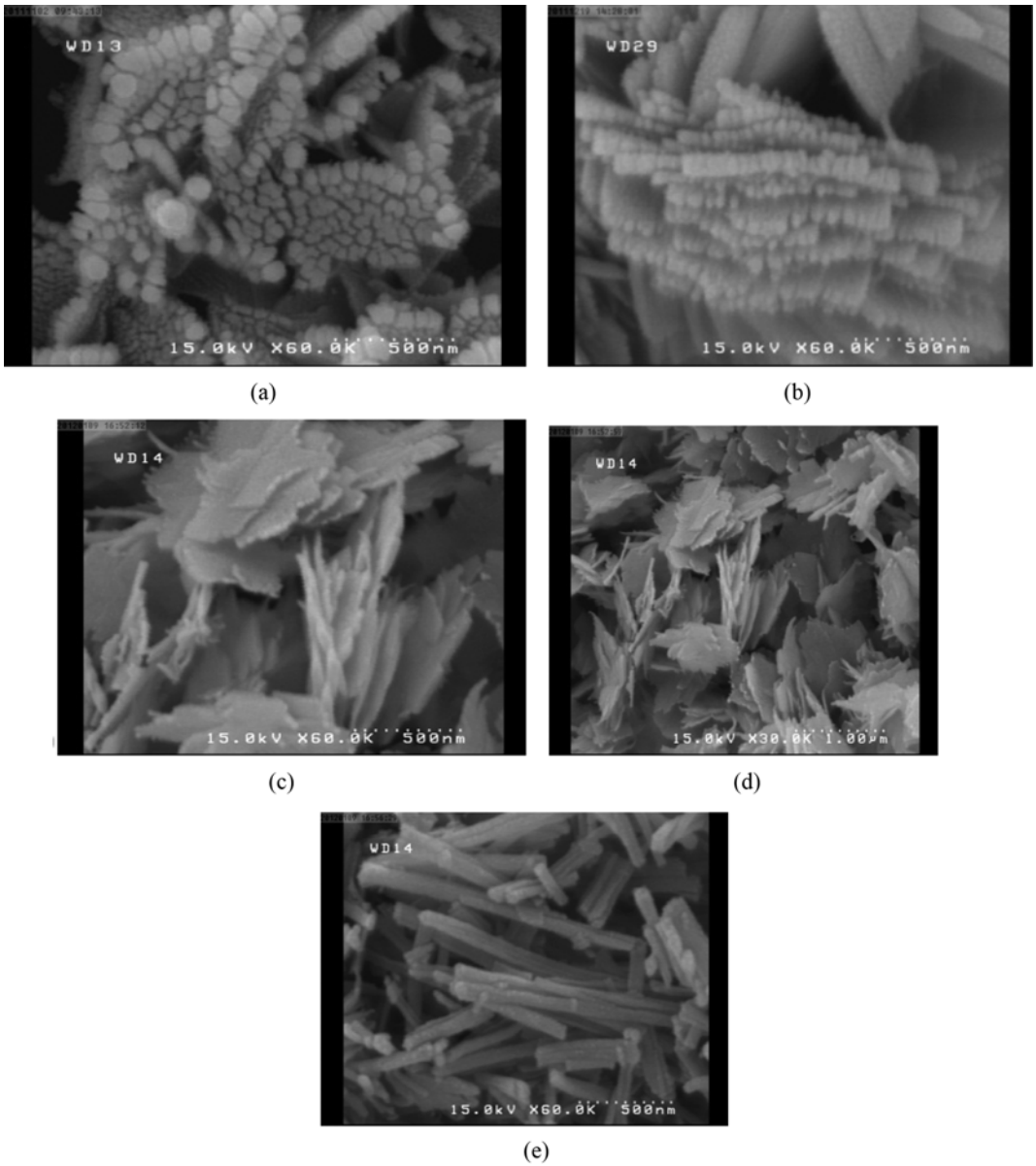

Fig. 3. SEM images of samples synthesized at different condition. (a) Typical procedure with 10 ml PEG400; (b) 20 ml PEG400; (c) and (d) nanoplates with different magnified; (e) nanorods from typical procedure with PEG6000.

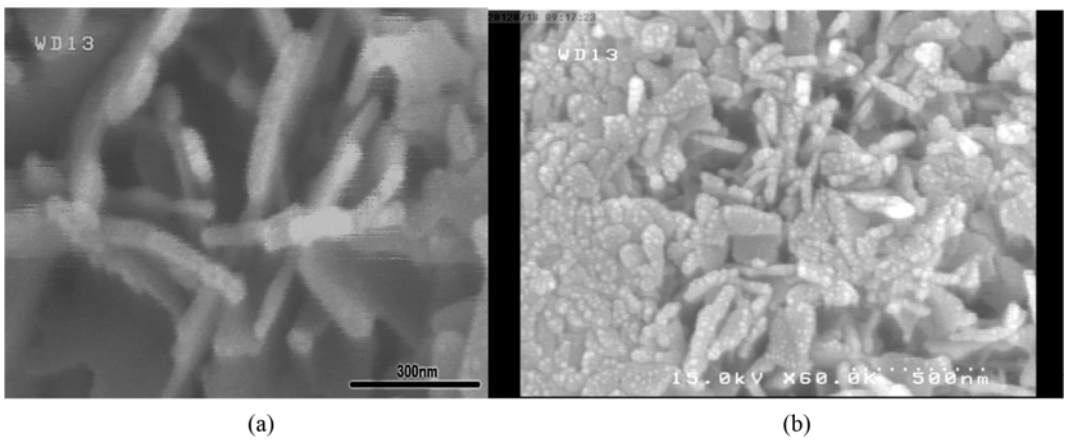

Fig. 4. SEM image of the Ag/CuO nanoparticles at different magnitude.

morphology of the structure, but is not the best one. Fig. 3(c) shows the image of the sample obtained in the mixture of ethanol and distilled water (50 : 50 wt%) in which we obtained plate morphology. Fig. 3(d) shows the same sample by different magnitude. By changing the molecular weight of PEG from 400 to 6,000, nanorod morphology with relatively good distribution is obtained (Fig. 3(e)). Fig. 4(a)-(b) shows the image size and shape of Ag/CuO nanoparticles extracted from mixture of distilled water in the presence of PEG400. PEG has been widely applied as an effective passivation agent in the fabrication of CuO and Ag/CuO nanoparticles. Its molecular weight and reaction conditions controlled the size, shape and structure of copper nanoparticles [26,27].

4. Oxidation of Styrene

The oxidation of styrene was carried out by TBHP using CuO nanorods and Ag/CuO nanoparticles as catalysts, and two oxidation products, styrene oxide and benzaldehyde were obtained. The catalytic potential of these catalysts has been optimized for the maximum oxidation of styrene by studying three different parameters: the effect of amount of oxidant (mole of TBHP per mole of styrene), amount of catalyst (amount of catalyst per mole of styrene), and solvent (CH_2Cl_2, C_2H_5OH, CH_3CN). Therefore, from these experiments, the optimized reaction conditions are: CuO (0.025 g), TBHP (1.45 ml, 15 mmol) CH_3CN (5 ml) and temperature (80 °C); Ag/CuO (0.025 g), TBHP (1.45 ml, 15 mmol) CH_3CN (5 ml) and temperature (80 °C) for the maximum oxidation of 5 mmol of styrene. The result is shown that the selectivity for styrene oxide is much higher, while benzaldehyde is much lower. Fig. 5 shows the products and selectivity of these catalysts under the optimum condition. As shown in the Fig. 5 the conversion is almost the same for both catalyst, but the selectivity of styrene oxide for Ag/CuO is better than CuO. Only very small amount of the formation of other products is possibly due to no further oxidation of styrene oxide to other oxidized products as observed above due to the mild oxidizing nature of TBHP [28]. Catalytic potential of CuO nanorods and Ag/CuO nanoparticles compares well with similar transition metal oxides. The observed conversion for transition metal oxides was NiO (52%), CoO (35%), MnO_3 (32%) and TiO_2 (5.4%) [29], Ti/SiO_2 (30%) [30]. Epoxidation of styrene with O_2 catalyzed by Fe_3O_4 (38%) [31]. Nano gold catalysts supported on transition metal oxides [13-17] show high activity for epoxidation of styrene only at high gold loadings and, therefore, are quite costly.

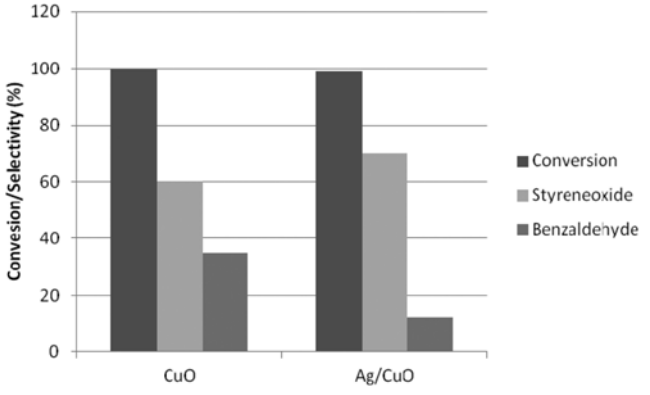

Fig. 5. Oxidation of styrene by CuO nanorods and Ag/CuO nanoparticles. Reaction condition; styrene (5 mmol), catalyst (25 mg), TBHP (15 mmol) and solvent CH_3CN 5 ml.

CONCLUSION

CuO nanorods, CuO nanoplates and Ag/CuO nanoparticles with average sizes in the range of 18-50 nm were synthesized by a polymer (polyethylene glycol) by depositional in alkaline environment. Simple and inexpensive transition metal oxides, such as CuO nanorods and Ag/CuO nanoparticles are highly promising environmentally-friendly (easily separable and reusable) catalysts for the oxidation of styrene by TBHP, with high selectivity and yield. The catalytic experiments reveal that Ag/CuO nano-composites display higher catalytic activity than CuO nanoparticles.

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