



Short communication

Preparation and characterization of nanosized copper (II) oxide embedded in hyper-cross-linked polystyrene: Highly efficient catalyst for aqueous-phase oxidation of aldehydes to carboxylic acids



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ABSTRACT

Preparation and catalytic properties of nanosized copper (II) oxide embedded in hypercrosslinked polystyrene (HPS) were investigated in this article. The CuO@HPS nanocomposite was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES), Fourier transform infrared spectroscopy (FT-IR), N₂-sorption analysis, X-ray powder diffraction (XRD), energy dispersive X-ray spectroscopy analysis (EDS), and transmission electron microscopy (TEM). The TEM analysis showed that the mean diameter of the resulted particles is ~4 nm. The nanocomposite was found to be efficient and durable catalyst in the oxidation of aldehydes to the corresponding carboxylic acids in water. The catalyst can be recycled and reused in 4 reaction runs.

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1. Introduction

Nano-sized metal and metal oxide particles have found their pertinent from industrial and economic points of view. Catalysts containing metal nanoparticles have been revealed a subject of interest due to their enhanced efficiency, selectivity, and stability. This impressive success would have been possible considering to the factors that severely control the size, size distribution and morphology of nanoparticles, whose understanding control the catalyst properties [1]. However, small size particles are susceptible to agglomeration and the formation of larger particles that lead to unstable catalytic properties. In addition, the application of the nanoparticles is limited by further obstacles, such as simple separation and regeneration of the nanocatalysts from the reaction mixture. In this pursuit, the development of supports for the preparation of heterogeneously supported nanocatalysts permits the formation of nanosized and highly monodisperse particles while preventing agglomeration.

As a consequence, the various types of support, such as zeolites, silicas, and carbon compounds have been extensively employed [2–5]. In recent years, efforts have been made to replace inorganic materials with porous organic supports [6].

Inorganic nanoparticles incorporated into well-defined organic polymer matrix represent a very favorable method for the preparation

of nanoparticles. Metalated polymer nanocomposites combine the particular properties of both inorganic nanoparticles and demanded processing characteristics of polymers. These materials have potential applications in various fields especially as efficient catalysts [7]. Hypercrosslinked polystyrene (HPS) with unique porosity is one of the few examples of hydrophobic porous polymers. It possesses several advantages like high porosity, nanoscale rigid pores, the ability to swell in wide variety of liquid mediums, large internal surface area (1000–1500 m² g^{−1}), high diffusivity, low viscosity, and low cost. Similar to the other supports, metal compounds can be incorporated into the porous polymers. According to the reports, metal nanoparticles were introduced into the polymer matrix of HPS represent a peculiar possibility for the modification of catalytic properties along with catalyst stability [8,9].

Copper and copper based compound gained considerable attention due to several properties and consequences of its application [10,11]. In comparison with expensive and air-sensitive catalyst, the copper (II) oxide is easily handled and remarkably stable under acidic and basic conditions. According to the low toxicity, high stability and recyclability, besides the ease of production, copper (II) oxide nanoparticles have been of intense interest in semiconductors [12], sensors [13] and catalysis. On this basis, CuO was utilized as an effective nanocatalyst for various organic transformations [14,15], cross coupling reactions [16], and thermal decomposition [17].

Recent work demonstrated that CuO in combination with ZrO₂ [18], CeO₂ [19], Ce_{0.3}Ti_{0.7}O₂ [20], and Ag₂O [21] were found to be the effective

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catalysts for organic compound synthesis, CO and NO oxidation as well as for the oxidation of organic chemicals by molecular oxygen.

In this work, we attempt to ascertain if HPS as porous polymer support can serve to immobilization of copper (II) oxide particles. Herein, for the first time, we show that the resulting nanocomposite can be used as a heterogeneous catalyst for oxidation of aldehydes to carboxylic acids. In this clean, mild and simple procedure, the transformation can be performed under air atmosphere in water as green and abundant resources. The optimized aerobic oxidation is attractive, since as opposed to most methodologies, this environmentally benign method does not require ligands and stoichiometric amounts of oxidant.

2. Experimental

2.1. Material

HPS Macronet- MN270 (Purolite Int., United Kingdom) was washed with water and acetone twice and dried under vacuum for 24 h. All chemicals were obtained from commercial suppliers. Sodium hydroxide and sulfuric acid were used as received but other chemicals were distilled or recrystallized before use. Deionized water was used for washing and solution preparation.

2.2. Instruments and measurements

The IR spectra were obtained using FT-IR Brucker-Vector in KBr/Nujol mull in the range of 400–4000 cm^{-1} . NMR spectra (^1H NMR and ^{13}C NMR) were recorded using a 250 Bruker Avance instrument. Merck silica gel 60 F_{254} plates were used to monitor the reaction progress in thin-layer chromatography (TLC).

X-ray powder diffraction patterns were collected on a Bruker D8 advance X-ray powder diffractometer with the 2θ range from 5 to 90° and Cu electrode as anode. The step size of each run was maintained at $0.07^\circ 2\theta$.

Transmission electron microscopy was performed with a Philips CM120 electron spectroscopic microscope operated at 120 kV.

JEOL JSM-7100 field-emission scanning electron microscopy (FESEM) and energy dispersive X-ray analyses (EDS) were used to study the morphology and elemental composition.

Nitrogen adsorption–desorption isotherms were investigated at 77 K with a BELSORB-max system (SIP). The surface area and pore size distribution were calculated with the BET and BJH methods.

The initial and final concentrations of metal in the nanocomposite were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro-Genesis).

2.3. Incorporation of copper(II) oxide in HPS

In a typical procedure, 0.5 g HPS and 3 mL of ethanol were placed in a Schlenk tube and the HPS sample was allowed to swell for 30 min in the solution. After forward, the solution of 0.2 g Copper (II) acetate monohydrate in 12 mL of ethanol and 0.15 mL acetic acid were added separately. When the temperature reached 78°C , the NaOH aq. (1 M, 5 mL) was subsequently dropped into the flask under continuous stirring. The mixture was refluxed for 1 h more. The catalyst (CuO@HPS) was then recovered by filtration, washed with water and ethanol and dried in vacuum overnight.

2.4. Oxidation of aldehydes catalyzed by CuO@HPS

In a two-necked round bottom flask equipped with a condenser, the aldehyde (1 mmol), was dropped into the mixture of catalyst (4 mol%) and NaOH (1.5 mmol) in deionized water (3 mL). The resulting mixture was stirred at room temperature under air atmosphere for 15 min and then the temperature reached 75°C . The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture

was filtered off and the catalyst rinsed with deionized water and ethanol. The filtrate was treated with H_2SO_4 (30 wt.%). The precipitated carboxylic acid was filtered, washed with water and dried in vacuum. (For liquid products after addition of H_2SO_4 , the product was extracted using diethyl ether (4×5 mL)).

3. Result and discussion

The preparation of nanocomposite is quite straightforward. To do this, briefly, hypercrosslinked polystyrene (HPS) sample was swelled in ethanol. The resulting support was then subjected to mixing with an appropriate concentration of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in the presence of acetic acid in ethanol. Next, the obtained slurry was allowed to react with a freshly prepared aqueous solution of NaOH (1 M) to obtain the corresponding CuO nanoparticles supported in HPS (CuO@PMO). The Cu content is 3.7 wt.% in the resulting nanocomposite, a value which was confirmed by inductively coupled plasma analysis (ICP-OES).

The porosity of parent HPS and HPS–CuO samples has been evaluated using liquid nitrogen physisorption analysis. The shape of nitrogen adsorption–desorption isotherms (Figs. A1 and A2, ESI†) can be signify that HPS-based samples encompass both mesopores and micropores [22]. The analysis demonstrated that the HPS prior to copper oxide addition has the BET surface area of $1537 \text{ m}^2 \text{ g}^{-1}$ and primary pore volume of $1.22 \text{ cm}^3 \text{ g}^{-1}$. Both surface area and the volume fraction of the HPS–CuO nanocomposite significantly decrease, due to copper oxide nanoparticles deposition within the pores and on the surface. This is in agreement with porosimetry results, in which a reduction of the pore volume $0.75 \text{ cm}^3 \text{ g}^{-1}$ and surface area $1171 \text{ m}^2 \text{ g}^{-1}$ was observed. The fraction of pores decreases by 38%.

Fig. 1 shows the FT-IR spectra of investigated HPS (a) and CuO@HPS (b). In the present investigation, the low frequency region 400–700 cm^{-1} assigned the vibrational properties of CuO nanoparticles. The peaks at 531 cm^{-1} and 579 cm^{-1} correspond to Cu–O bond stretching modes. In addition, observed broad absorption band at 3420 cm^{-1} might be due to vibrations of the O–H group that adsorbed on the surface.

As shown in Fig. 2, all of the diffraction peaks of the XRD pattern of the CuO at 2θ values of 33.1° , 35.2° , 38.4° , 42.2° , 48.5° , 53.3° , 58.3° , 61.3° , 65.8° , 67.9° , 72.1° , and 74.9° are observed and are consistent with the JCPDS data (card no: 044-0706). This indicated that CuO nanoparticles were obtained.

The EDS measurement has been used to confirm the presence of copper oxide components on the surface of nanocomposites. The EDS analysis, presented in Fig. 3, is supporting the CuO stoichiometry.

Fig. 4 shows TEM images of HPS–CuO sample prepared by impregnation of HPS with the copper(II) oxide. Diameter of the CuO compound NPs is ~ 4 nm.

It is worth mentioning that since the catalyst is prepared in the presence of sodium hydroxide, the copper (II) oxide and copper (II) hydroxide embedded in hyper-cross-linked polystyrene (HPS) is believed to be

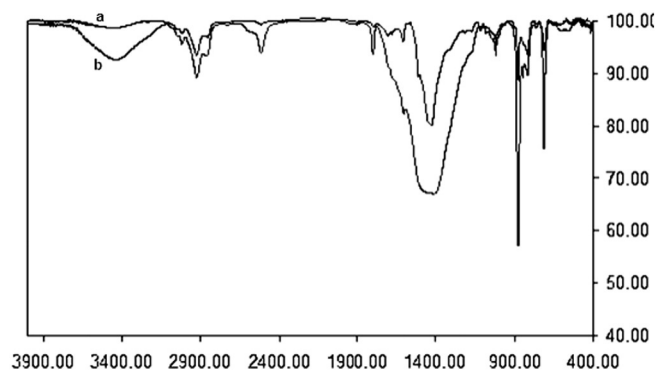


Fig. 1. FT-IR spectra of HPS (a) and CuO@HPS nanocomposite (b).

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