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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) was 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.

Keywords: Copper (II) oxide; Hypercrosslinked polystyrene; Nanocomposite; Oxidation; Aldehyde; Carboxylic acid.

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 the 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

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heterogeneously supported nanocatalysts permits the formation of nanosized and highly monodispers particles while prevent 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 m²g⁻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, beside 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 ZrO_2 [18], CeO₂ [19], Ce_{0.3}Ti_{0.7}O₂ [20], and Ag₂O [21] were found to be the effective 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 hours. 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 ¹³C 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 °2 θ .

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 was 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. (1M, 5 mL) was subsequently dropped into the flask under continuous stirring. The mixture was refluxed for 1 hour 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 Cu(CH₃COO)₂.H₂O in the presence of acetic acid in ethanol. Next, the obtained slurry were allowed to react with a freshly prepared aqueous solution of NaOH (1M) 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 m²g⁻¹ and primary pore volume of 1.22 cm³g⁻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 cm³g⁻¹ and surface area 1171 m²g⁻¹ was observed. The fraction of pores decreases by 38%.

Fig. 1 showes 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.



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

As shown in Fig. 2, all of the diffraction peaks of the XRD pattern of the CuO at 20 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. 3. EDS analysis of CuO@HPS

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.



Fig. 4. Transmission electron microscopy (TEM) image of CuO@HPS

It is worth mentioning that since the catalyst are 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 the active sites. The catalytic performance of CuO@HPS was investigated in the transformation of aldehydes to carboxylic acids. Several reagents such as chromium compounds [23], potassium permanganate [24], sodium perborate [25], chlorite species [26], hydrogen peroxide [27] and oxone [28], also several transition metal, for example, copper [29, 30], vanadium [31], gold [32], silver [33], have been developed the oxidation of aldehydes. In addition, Ag_2O/CuO [21], , Fe_3O_4 nanoparticles [34], and iron oxalate capped iron-copper nanomaterial [35] catalyzed oxidation of aldehyde has been reported. Using of stoichiometric amount of reagent, limited substrate scope, high catalyst loading, high cost and environmental contamination are particular drawbacks of previous methods. These were reasoned that a revision in reaction conditions to introduce efficient heterogeneous catalyst systems in green solvents such as water under air atmosphere.

To study the nanocomposite performance for aldehydes oxidation, the temperature, base, atmospheric conditions and catalyst loading were screened as the main factors affecting the transformation. For this purpose, a model oxidation of benzalehyde was initially carried out by using 2 mol% of CuO@HPS in the presence of NaOH under air atmosphere in water at room temperature for 24 h. A study of the same reaction identified that increase in the reaction temperature to 75 °C greatly enhanced the reaction efficiency from 10 % to 70% yield (Table1, entries 1, 3). Next, four variations of the catalyst loading (1, 2, 3, 4 mol %) were examined (Table1, entries 2-5). It was found that by a slight increase in the catalyst loading to 4 mol% greatly enhanced the reaction efficiency. Furthermore, the reaction was also carried out at atmospheric pressure of O_2 and Ar when the product yield was decreased to 75 and 50% respectively (Table1, entries 6, 7). To further determine the co catalyst effect, K₂CO₃ was also studied (Table 1, entry 8) and in comparison, NaOH was employed as base to obtain

satisfactory results. Notably, the present reaction is sluggish in the absence of NaOH at 75 °C (Table 1, entry 9).

Table 1. Optimization of the oxidation of benzaldehyde using CuO@HPS catalyst in water

Having established the optimal reaction conditions we further examined the scope of oxidation reaction in the presence of 4 mol% nanocomposite at 75 °C in water for various types of aromatic aldehydes (Table 2).

 Table 2 Oxidation of aldehydes using CuO@HPS nanocatalyst ^a

Table 2 shows that oxidation is completed under desired reaction conditions with good to excellent yields. It is worth noting that alcohol byproduct wasn't detected in this transformation.

To demonstrate the ability of HPS to stabilize nanoparticles, the recyclability of nanocatalyst was examined by isolating the catalyst from the reaction mixture of oxidation of 4-methyl benzaldehyde under optimal reaction conditions. In each run, after the completion of the reaction, the used nanocatalyst was filtered off and then washed with ethanol and large amounts of water to remove any remaining impurity. The recovered catalyst experiments were performed for four times. The results are shown in Fig. 5. These results indicate that catalyst activity slowly decreases over the consecutive runs. Therefore, this might be due to leaching of copper oxide particles and also the partial loss of the catalyst during the recovery and washing stages. However, copper leaching of the catalyst after the four reaction run was determined by inductively coupled plasma (ICP- OES) to be less than 1.5 ppm.



Figure 5. Recyclability chart of the oxidation of 4-methylbenzaldeyde using CuO@HPS.

4. Conclusions

In conclusion, a novel heterogeneous nanocatalyst was successfully prepared through the incorporation of copper (II) oxide in porous polymeric support. The hypercrosslinked polystyrene was used as a stable and effective support to the preparation and stabilization of copper oxide nanoparticles. In the present approach, the resulting nanocomposite is utilized as an efficient catalyst for oxidation of aldehydes in water as the environmentally benign conditions. Besides the heterogeneous catalysis advantages such as the easy separation, reusability and minimization of the metal contamination in the product, the easy set up and the absence of any organic solvent make this catalyst system a peculiar candidate for green chemistry processes.

Acknowledgments

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Appendix A. Supplementary data

Table 1. Optimization of the oxidation of benzaldehyde using CuO@HPS catalyst in water

		о с ^Щ н_	CuO@HPS (X mol Base (1.5 equiv)	%)	\sim	о Д _{ОН}	
		–	Atmosphere H ₂ O, t °C Time (h)			OIT	K
	Catalyst (mol %)	Base (mmol) ^a	Atmosphere	t [°C]	Time [h]	Yield (%) ^b	Q
1	2.0	NaOH	Air	rt	24	10	
2	1.0	NaOH	Air	75	20	45	
3	2.0	NaOH	Air	75	20	70	\sim
4	3.0	NaOH	Air	75	20	75	.O
5	4.0	NaOH	Air	75	20	80	0
6	4.0	NaOH	O_2	75	20	75	
7	4.0	NaOH	Ar	75	20	50	
8	4.0	K_2CO_3	Air	75	20	57	
9	4.0	-	Air	75	24	47	

 a The reaction was carried out in the presence of the benzaldehyde (1 mmol); base (1.5 mmol); water (3 mL) as solvent b Isolated yield

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Table 2 Oxidation of aldehydes using CuO@HPS nanocatalyst ^a

(Ar	CuO@HPS (4mol%) O NaOH (1.5 mmol)				
Ai	Air H ₂ O, 75°	C A OI			
Entry	ntry Aldehyde	Carboxylic acid	Time	Yield	
Linuy	machyac		[h]	[%] ^b	
1	C ₆ H ₅ CHO	C ₆ H ₅ COOH	20	80	
2	4-BrC ₆ H ₄ CHO	4-BrC ₆ H ₄ COOH	20	90	
3	4-ClC ₆ H ₄ CHO	4-ClC ₆ H ₄ COOH	20	90	
4	4-CH ₃ OC ₆ H ₄ CHO	4-CH ₃ OC ₆ H ₄ COOH	18	91	
5	4-CH ₃ C ₆ H ₄ CHO	4-CH ₃ C ₆ H ₄ COOH	18	97	
6	4-(CH ₃) ₂ CHC ₆ H ₄ CHO	4-(CH ₃) ₂ CHC ₆ H ₄ COOH	18	93	
7	4-CH ₃ SC ₆ H ₄ CHO	4-CH ₃ SC ₆ H ₄ COOH	20	85	
8	3-ClC ₆ H ₄ CHO	3-CIC ₆ H ₄ COOH	20	87	
9	3-CH ₃ C ₆ H ₄ CHO	3-CH ₃ C ₆ H ₄ COOH	20	85	
10	3,5-(CH ₃) ₂ C ₆ H ₃ CHO	3,5-(CH ₃) ₂ C ₆ H ₃ COOH	20	87	
11	3-NO ₂ C ₆ H ₄ CHO	3-NO ₂ C ₆ H ₄ COOH	20	90	
12	2-NO ₂ C ₆ H ₄ CHO	2-NO ₂ C ₆ H ₄ COOH	20	85	
13	2-ClC ₆ H ₄ CHO	2-CIC ₆ H ₄ COOH	20	92	
14	2,4-Cl ₂ C ₆ H ₃ CHO	2,4-Cl ₂ C ₆ H ₃ COOH	24	71	
15	4-CHOC ₆ H ₄ CHO	4-COOHC ₆ H ₄ COOH	24	60	
16	Nicotinaldehyde	Nicotinic acid	24	50	
17	2-Naphthaldehyde	2-Naphthoic acid	24	75	

^a Conditions: Substrate (1 mmol); NaOH (1.5 mmol); Catalyst (4 mol %); Water (3 mL) as solvent; 75 °C

^b Isolated yield.

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Highlights

- Copper (II) oxide nanoparticle was incorporated in crosslinked polystyrene matrix.
- The CuO@HPS nanocomposite was fully characterized.
- The nanocomposite is utilized as an efficient catalyst for oxidation of aldehydes.
- The reaction was done in water as the environmentally benign conditions.
- The nanocatalyst can be successfully recycled and reused in 4 reaction runs.

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