

## Feature Article

# Liquid phase oxidation of cinnamyl alcohol to cinnamaldehyde using multiwall carbon nanotubes decorated with zinc-manganese oxide nanoparticles



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## ABSTRACT

Zinc-manganese (Zn-Mn) oxide nanoparticles were prepared and loaded on functionalized multiwall carbon nanotubes (FMWCNTs) (Zn-Mn oxide/FMWCNT) using co-precipitation and developing condensation methods, respectively. The Zn-Mn oxide and Zn-Mn oxide/FMWCNTs were characterized using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). The catalytic efficiencies of the prepared catalysts were tested for liquid phase oxidation of cinnamyl alcohol (CnOH) to cinnamaldehyde (CnHO) in a modified batch reactor. The reaction parameters were optimized and compared in green (water and heptane), blue (toluene, acetonitrile, and cyclohexane), and red (benzene) solvents and molecular oxygen. The maximum CnOH-to-CnHO conversion of 97.2 and 99.9% with productivity of 63.2 and 65 mmol g<sup>-1</sup> h<sup>-1</sup> was achieved with 0.1 g of each Zn-Mn oxide and Zn-Mn oxide/FMWCNT, respectively in water at 60 °C and time = 120 min. Both catalysts showed high conversion, high productivity, low cost, recyclability, and true heterogeneous behavior and therefore, can be used effectively for the conversion of CnOH-to-CnHO.

## 1. Introduction

The selective oxidation of alcohols to aldehydes with molecular oxygen has paramount importance due to their applications in perfume, agrochemical, and fine chemicals industries. The aldehydes have been usually synthesized with a stoichiometric amount of oxidizing agents such as dichromate, hypochlorite, permanganates, and others [1–3]. These oxidant were harmful and environmental malignant, expensive, and yield a large amount of byproducts [4,5]. Therefore, the researcher switched to utilized homogenous catalysts such as metal alkoxides. These catalysts have poor recovery, non-reusability, and poor separation from the product [6,7]. To overcome these problems heterogeneous catalysts have been utilized. For example, Mallat et al. utilized platinum supported on alumina (Pt/Al<sub>2</sub>O<sub>3</sub>) for the conversion of cinnamyl alcohol (CnOH) to cinnamaldehyde (CnHO), showed a better conversion (88.5%), selectivity, and separation of catalyst from the reaction medium [8]. A bimetallic Pt-Bi catalyst supported on activated carbon in the presence of hydrogen peroxide has been used, which

showed better selectivity (84%), but poor conversion (34%) [9]. Scott et al., utilized metallic and bimetallic nanocrystal as a catalysts in aqueous medium and achieved ~34% conversion [10]. Similarly, Pt or palladium (Pd) catalysts with comparable results have also been utilized [8,11–13]. These catalysts have limitations of poor catalytic activity, loss of sensitivity due to deactivation, low selectivity, and high cost [14]. Several new models of catalysts have also been introduced recently. For example a two dimensional tungsten disulfide was hybridized with carbon dots and utilized for photocatalytic applications [15]. For enhanced photocatalytic activity Ga<sub>2</sub>O<sub>3</sub> nanoparticles were incorporated into liquid metal/metal oxide framework [16]. Lithium ion were partially intercalate into the two dimension molybdenum disulfide for enhanced catalytic properties for the hydrogen evolution reaction [17]. However, it is desirable to develop a green, costly effective and highly efficient catalyst.

Zinc (Zn) oxide nanomaterials have a promising role as a catalyst in oxidation of organic compounds due to high selectivity and stability, large excitation binding energy (60 meV) at room temperature, wide

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band gap (3.37 eV), low cost, and ecofriendly properties [18]. Zn oxide have been synthesized in a variety of shapes, however, it is well established that, doping a selective element into Zn is a primary method for controlling the properties such as band gap or electrical conductivity [19]. Recently, metals such as manganese (Mn), iron (Fe), nickel (Ni), cobalt (Co), and chromium (Cr) have been doped into Zn oxide due to their potential applications in drug delivery, cosmetics, and filling in medical devices [20,21]. Moreover, carbon nanotubes (CNTs) have been used as a support or scaffold for the hybrid assembly of metal nanoparticles. The CNTs enhances the oxidation ability of metal oxide nanoparticles via the retardation of electron-hole recombination. However, the CNTs due to their tangled ropes structure showed poor dispersion and therefore, difficult to decorate with nanoparticles uniformly [22]. To efficiently synthesize the nanoparticles-CNTs hybrid, it is worthy to activate the CNTs surface. The Zn-Mn oxide as a bimetallic compound may show a good combination of properties such as high catalytic activity, easy separation, and good durability and to the best of our knowledge Zn-Mn oxide or Zn-Mn oxide supported on MWCNTs has not been reported to be used in catalytic oxidation of CnOH-to-CnHO. Thus, the investigation of Zn-Mn oxide and supported Zn-Mn oxide as an oxidizing catalyst can be an interesting issue.

In this study, functionalized multiwall carbon nanotubes (FMWCNTs) were decorated with Zn-Mn oxide nanoparticles (Zn-Mn oxide/FMWCNTs). The Zn-Mn oxide and Zn-Mn oxide/FMWCNTs have been utilized for catalytic oxidation of CnOH-to-CnHO in the presence of different solvents (acetonitrile, benzene, cyclohexane, heptane, toluene, or water) and molecular oxygen. The catalysts showed high efficiency in term of productivity, high stability, and true heterogeneity, and thus can be vital for applications in oxidation of alcohols.

## 2. Material and methods

### 2.1. Materials

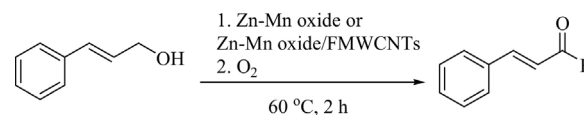
MWCNTs (Tokyo chemical industry, Japan), Nitric acid (HNO<sub>3</sub>, Sigma-Aldrich), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Sigma-Aldrich), Zinc chloride (ZnCl<sub>2</sub>, Sigma-Aldrich), manganese chloride (MnCl<sub>2</sub>, Sigma-Aldrich), and sodium hydroxide (NaOH), were used as received. Oxygen and nitrogen gases (BOC Pakistan) were purified with appropriate filters (C.R.S.Inc.202268). Traps specific for oxygen (C.R.S.Inc.202223) were used for removing traces of oxygen from the nitrogen gas. Deionized water (DIW) was used in the synthesis of catalysts and preparation of reagent solution, while other solvents were used as received.

### 2.2. Synthesis of Zn-Mn oxide nanoparticles

A 200 mL (1:1 v/v) solution of ZnCl<sub>2</sub> (0.1 M) and MnCl<sub>4</sub> (0.1 M) was titrated against NaOH (0.2 M) solution. The mixture was stirred at 60 °C for 2 h and aged for 12 h. The Zn-Mn oxide was precipitated and separated by centrifugation at 5000 rpm for 30 min and dried at 110 °C.

### 2.3. Functionalization and decoration of MWCNTs

The FMWCNTs were prepared from addition of MWCNTs (0.5 g) to a conical flask containing 100 mL solution of HNO<sub>3</sub> (6 M) and H<sub>2</sub>SO<sub>4</sub> (2 M). The mixture was sonicated for 30 min and subsequently refluxed at 170 °C for 6 h, thoroughly washed with distilled water to remove the un-reacted materials, and dried in oven at 100 °C. In order to obtain Zn-Mn oxide/FMWCNTs, to 200 mL (1:1 v/v) solution of ZnCl<sub>2</sub> (0.1 M) and MnCl<sub>4</sub> (0.1 M) the FMWCNTs (0.5 g) was added. The mixture was titrated against NaOH (0.2 M) solution and stirred at 60 °C for 2 h and aged for 12 h. The product Zn-Mn oxide/FMWCNTs were separated by centrifugation at 5000 rpm for 30 min.



Scheme 1. Liquid phase oxidation of CnOH-to-CnHO.

### 2.4. Catalytic test

A 20 mL CnOH (0.013 M) solution in a given solvent and desire amount of Zn-Mn oxide or Zn-Mn oxide/FMWCNTs was introduced into a sealed three necked tubular glass reactor wrapped in a heating cord connected to a temperature controller (Digi-Sense, ColeParmer, USA) on a preheated hotplate under molecular oxygen and stirred at a given temperature (Scheme 1). The optimal reaction parameters were surveyed in the range of temperature = 30–70 °C, time = 30–150 min, catalyst loading = 0.025–0.125 g, oxygen pressure 80–750 Torr, and stirring 150–1500 rpm. The product was collected and the conversion (%) and productivity were measured using formulae given in Eqs. (1) and (2), respectively.

$$\text{Conversion} = \frac{\text{mole of reactants disappeared}}{\text{mole of initial reactants}} \times 100 \quad (1)$$

$$\text{Productivity} = \frac{\text{product (mmole)}}{\text{Catalyst (g)} \times \text{time (h)}} \quad (2)$$

### 2.5. Instrumentations

The morphologies of Zn-Mn oxide and Zn-Mn oxide/FMWCNTs were measured by scanning electron microscopy (SEM, JSM5910, Jeol, Japan). The relative amount in weight percent of each element was found using energy dispersive X-ray spectroscopy (EDS, INCA200/Oxford instruments, U.K). The x-ray analysis was carried out with X-ray diffractometer (XRD, Rigaku D/Max-II, Cu Tube, Japan). The functional groups on the catalysts surface were found by a Fourier transform infrared spectrophotometer (FTIR, Prestige, Shimadzu, Japan). The FTIR samples were dried, mixed with KBr, and pressed into 1.3 mm-diameter pellets. Thermal gravimetric (TGA) analysis was carried out by a TGA thermal analyzer (PerkinElmer, Thermal Analysis, Japan) in a temperature range of 40–800 °C under the nitrogen flow at a rate of 10 °C/min. The conversion of CnOH-to-CnHO was analyzed by gas chromatography (GC, Clarus 580, Perkin Elmer, USA) provided with a flame ionized detector connected to a hydrogen generator (PGXH2 100, Perkin Elmer, USA). Nitrogen was used as a carrier gas produced with a nitrogen generator (G6010E, Parker domnick hunter, UK) at a flow rate of 20 psi.

## 3. Result and discussion

### 3.1. Characterization of the Zn-Mn oxide and Zn-Mn oxide/FMWCNTs

Fig. 1 shows the surface morphologies of Zn-Mn oxide and Zn-Mn oxide/FMWCNTs observed through SEM. The Zn-Mn oxide nanoparticles have a uniform geometrical structure and size of ~50–100 nm (Fig. 1a). The FMWCNTs was successfully decorated with Zn-Mn oxide (Fig. 1b) exhibit a homogenous dispersion and less aggregation. This smooth morphology of the catalyst may help in better adsorption leads to a good conversion. Fig. 1c shows the relative weight in percent (%) of various elements present in Zn-Mn oxide and Zn-Mn oxide/FMWCNTs derived from EDX results shown in Figure Supporting information (Fig. SI 1). The Zn-Mn oxide/FMWCNTs have high carbon contents with small proportion of Mn and Zn reveals the presence of metals nanoparticles on the surfaces of FMWCNTs.

Fig. 2 illustrates the FTIR spectra of the FMWCNTs and Zn-Mn oxide/FMWCNTs. The activation with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> generate carboxylic (COOH) groups on the external surface of the MWCNTs.

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