



Significant improvement of styrene oxidation over zinc phthalocyanine supported on multi-walled carbon nanotubes

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ABSTRACT

A novel hybrid catalyst (ZnPc–MWCNTs) was facilely prepared by a ultrasonic impregnation method. The as-prepared hybrid materials were characterized by FT-IR spectra, X-ray diffraction (XRD), diffuse reflectance spectra (DRS), scanning electron microscope (SEM), Raman spectroscopy and transmission electron microscopy (TEM). This hybrid material was employed as catalyst for styrene oxidation in presence of hydrogen peroxide as oxidant. The results showed that styrene was oxidized efficiently in the ZnPC–MWCNTs/H₂O₂ system. The enhancement of the catalytic activity of ZnPC–MWCNTs hybrid materials was investigated in terms of different oxidation conditions. It was found that the optimum oxidation condition was 40 mg catalyst, 8 h reaction time and reaction temperature of 60 °C. Under this condition, the conversion and the selectivity of styrene oxide was up to 94% and 90.6%, respectively. Moreover, the catalytic mechanism of styrene oxidation to benzaldehyde by the ZnPC–MWCNTs hybrid was also discussed.

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1. Introduction

Styrene oxidation at the side chain is of considerable interest in catalytic studies. Consequently, there is a growing concern in the synthesis of fine chemicals via this versatile reaction, such as the oxidative conversion of styrene to styrene oxide [1]. Styrene oxide is a very valuable chemical which has widespread applications as an important intermediate for the production of pharmaceuticals and fine chemicals. Since styrene has terminal olefinic group, its epoxidation is difficult, requiring long period (several hours) for obtaining appreciable styrene oxide yield [2]. Conventionally, styrene oxide is produced by the epoxidation of styrene using stoichiometric amounts of peracids [3]. However, peracids are expensive, corrosive, unsafe to handle and their use in the styrene epoxidation creates lot of waste due to formation of undesirable products. Therefore, it is a great practical interest to find such a catalyst which is much better for the epoxidation of styrene.

Metal-catalyzed oxidation of styrene can give rise to a whole variety of organic products. Metallophthalocyanine (MPc) has analogous structure to metalloporphyrin, and it has been researched in applications of solar cell materials, optical data materials and catalytic oxidation materials due to its optical and electronic properties [4–8]. MPcs are known to catalyze the oxidation of alkenes and alkanes. Metallophthalocyanines like Zn(II) phthalocyanines are readily available oxidation catalysts and found to transfer oxygen from various oxygen donors to alcohols, alkenes, phenols and thiols, numerous studies are carried out [9,10]. However, metallophthalocyanines are easy to aggregate, leading to markedly decrease the catalytic activity. Thus, design and synthesis of new hybrid materials to prevent aggregation of phthalocyanines become very urgent and necessary.

Nowadays, the heterogenization of transition metal complexes onto robust supports is especially attractive due to combining the advantages of homogeneous (activity and selectivity) and heterogeneous (facile recovering and recycling of catalyst) catalyses. Mangematin and Sorokin [11] described the catalytic behaviors of iron tetraaminophthalocyanine grafted onto silica for oxidation reaction of cyclooctene, cyclohexene and styrene. Carbon nanotubes (CNTs) received much attention because of their outstanding

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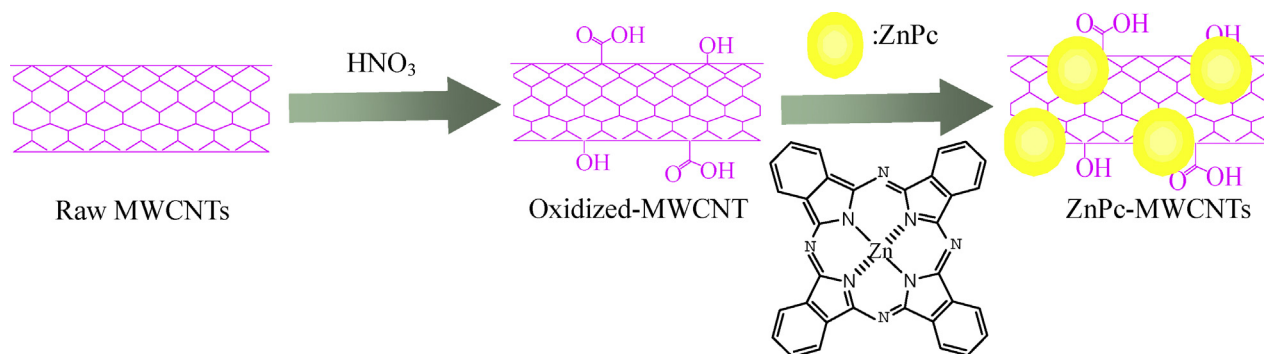


Fig. 1. Schematic representation of synthesis of ZnPc-MWCNTs.

thermal, mechanical, and electrical properties. It is well known that the CNTs are extremely promising as supports for metal catalyst for organic synthesis and fuel cell applications [12–17]. Up to now, some studies have indicated that CNTs as the catalyst support can prevent the aggregation of nanoparticles, increase the catalytic active sites and improve the catalytic activity due to the high surface areas, special hollow interiors and excellent electronic properties. To our knowledge, catalytic oxidation of styrene metal complex embedded in multi-walled carbon nanotubes (MWCNTs) has not been reported by now. Therefore, we reported firstly the fabrication of ZnPc embedded in MWCNTs by an ultrasonic impregnation method, and studied the catalytic activity of styrene oxidation of the as-prepared ZnPc-MWCNTs hybrid materials.

2. Experimental

2.1. Preparation of ZnPc-MWCNTs hybrid materials

All the reagents are analytical grade and used without further purifications. Zinc phthalocyanine (ZnPc) was synthesized from phthalonitrile, zinc acetate and 1-pentanol as described procedure [18]. The facile ultrasonic impregnation method of ZnPc-MWCNTs hybrid materials is shown in Fig. 1. Before preparing the ZnPc-MWCNTs hybrid materials, multi-walled carbon nanotubes must be purified in order to remove amorphous carbon fibers, amorphous carbon particles and other impurities such as graphite particles. In brief, 2 g of MWCNT was grinded in the agate mortar for 20 min, and then added to 100 ml of concentrated nitric acid, sonicated for 30 min to obtain a well dispersed MWCNT solution. The suspension was magnetic stirred and regurgitated at 120 °C for 10 h, then cooled down to room temperature naturally. Washed with absolute ethanol and distilled water repeatedly, then dried under vacuum at 60 °C for 12 h to obtain the carboxylic acid-functionalized MWCNTs. The synthesis procedure of ZnPc-MWCNTs is as follows: 0.8 g ZnPc were added into 100 ml ethanol under magnetic stirring. Then 0.1 g oxidized-MWCNTs were added and sonicated for 2 h. The mixture solution was then centrifuged and the supernatant was collected. Finally, the ZnPc-MWCNTs were obtained after dried in a vacuum at 80 °C for 4 h.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out at room temperature using a Rigaku D/MAX-2500PC diffractometer (Rigaku Co., Japan) with Cu K_{α} radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 100 mA. Morphologies of the prepared samples were observed on a JSM-6360LA scanning electron microscope (SEM, JEOL, Japan) and a JEM-2100 transmission electron microscope (TEM, JEOL, Japan). UV–vis diffuse reflection spectra (DRS) of the photocatalysts

were measured by a UV–vis scanning spectrophotometer (Shimadzu UV-2550) using an integrating sphere and BaSO₄ as white standard. Fourier transform infrared spectra (FT-IR) of samples were collected with a Nicolet (PROTÉGÉ 460) spectrometer in the range from 400 to 4000 cm⁻¹. The thermal stability of the materials was carried out using the TG-209-F3 thermogravimetric analysis meter (Nestlé Company, Germany). Raman spectra were measured at room temperature using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon, France) with a 532 nm laser focused on a spot of about 3 nm in diameter.

2.3. Evaluation of catalytic activity

The oxidation reaction of styrene was carried out in a three-necked 100 ml round bottom flask equipped with a reflux condenser. Typically, 40 mg of catalyst, 2.8 ml (27.3 mmol) of 30 wt.% aqueous H₂O₂ and 0.46 ml (3.9 mmol) of styrene along with 5 ml acetonitrile were mixed together. The pH value of the solution was adjusted to 8 and the solution was stirred at 60 °C for 8 h. After the reaction, ZnPc-MWCNTs were separated by filtration. Then the chloroform was used to extract the organic phase. The content of liquid products was analyzed by HP5890 gas chromatography (GC) equipped with a flame detector and a HP-5 capillary column (0.32 mm × 0.25 μm, Agilent, USA). The products were confirmed by the retention time of the standard samples. The sample (0.5 ml) was taken during the reaction at certain intervals each sample was injected into the GC to measure the content of resultant of reaction.

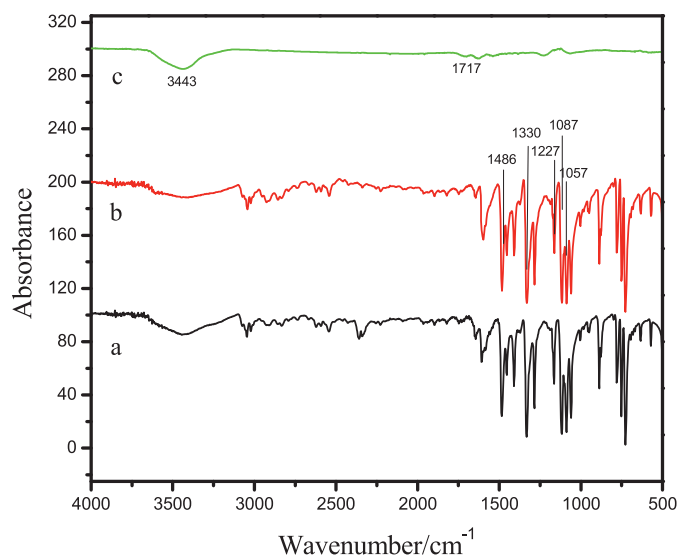


Fig. 2. FT-IR spectra of oxidized ZnPc-MWCNTs (a), ZnPc (b) and MWCNTs (c).

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