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Article

Efficient oxidation of cinnamon oil to natural benzaldehyde over β -cyclodextrin-functionalized MWCNTs

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ABSTRACT

We have designed and prepared β -cyclodextrin (β -CD)-functionalized multi-walled nanotubes (MWCNTs-g-CD) for the oxidation of cinnamon oil to natural benzaldehyde under aqueous conditions. The synergistic effect of combining MWCNTs with β -CD led to a remarkable increase in the performance of the MWCNTs-g-CD for the catalytic oxidation of cinnamaldehyde, which exhibited 95% cinnamaldehyde conversion and 85% selectivity to natural benzaldehyde with a short reaction time of 10 min. The MWCNTs-g-CD also exhibited outstanding recyclability with good stability, showing no discernible decrease in their catalytic activity over five reaction cycles.

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1. Introduction

Benzaldehyde (BzH) is the second most commonly used flavor compound in the world, with a wide range of important applications in the food and drink, cosmetics and pharmaceutical industries [1–5]. Increasing concerns surrounding food quality has led to a growing demand for natural benzaldehyde. The natural benzaldehyde used in commercial applications is mainly obtained by the aqueous hydrolysis of natural cinnamon oil, which contains more than 80% cinnamaldehyde [6,7]. However, the widespread application of this process has been limited by the poor aqueous solubility of cinnamon oil and the

low selectivity of this transformation towards natural benzaldehyde [8–10]. The oxidation of cinnamaldehyde in the liquid phase therefore represents a promising route for the manufacture of natural benzaldehyde under mild conditions [11]. However, the biggest challenge to realizing this approach is the availability of an effective catalyst, especially economically viable noble metal-free catalysts.

Cyclodextrins (CDs) are an important class of cyclic oligosaccharides that contain 6–8 D-glucose units linked together by α -1,4-glucose bonds, which are called α -, β - and γ -CDs, respectively. The central cavity of a CD system provides a hydrophobic space in which a suitable guest molecule can be sequestered

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under aqueous conditions. CDs are known to form inclusion complexes with a wide range of compounds, especially aromatic compounds [12–14]. Considerable research efforts have been directed towards the development of CDs capable of mimicking natural enzymes with high catalytic activity and substrate selectivity during the last decade. Among them, β -CD has been widely used to mediate a broad range of organic transformation under aqueous conditions, including oxidation, reduction, ring opening and hydrolysis reactions [15–20]. However, β -CD is soluble in water and must be immobilized on an appropriate solid support so that it can be readily recycled. β -CD was recently immobilized on cellulose and chitosan, and the resulting supported systems were applied to the catalytic oxidation of cinnamaldehyde under aqueous conditions [21–24]. The results revealed that β -CD and the functional groups of the support acted synergistically to allow for the oxidation of cinnamaldehyde. However, from an industrial production perspective, the application of these catalysts could be limited by their low mechanical strength and poor durability towards successive reaction cycles.

Carbon nanotubes (CNTs) have also been studied extensively as catalysts (or supports) and adsorbent materials for liquid phase reaction-adsorption systems because of their unique properties, including their excellent electrical and thermal conductivity, good chemical stability and recyclability, environmental acceptability and low cost [25–28]. Several studies have shown that CNTs are effective adsorbents than activated carbon for the removal of organic pollutants from aqueous solutions because of their excellent adsorption capacity [29,30]. CNTs have also been used as metal-free catalysts in numerous reactions, including the oxidative dehydrogenation of aromatic hydrocarbons and alkanes, the reduction of oxygen, the oxidation of hydrocarbons and phenols, and the decomposition of ammonia [31–34]. Furthermore, CNTs have been used to catalyze the oxidation of benzyl alcohol to benzaldehyde using molecular oxygen as an oxidant [35,36]. There have been numerous reports in the literature aimed at modifying the surfaces of CNTs by the introduction of specific functional groups to improve their performance as catalysts and adsorbents [37–39]. As part of our ongoing interest in such materials, we report herein the development of surface-modified CNT system bearing β -CDs as a high performance catalyst for the oxidation of cinnamaldehyde. To the best of our knowledge, this study represents the first reported example of the systematic evaluation of β -CD-functionalized multi-walled CNTs (MWCNTs) as a recyclable heterogeneous catalyst for the oxidation of cinnamon oil for industrial application.

The main goal of this work was to design β -CD grafted MWCNTs (MWCNTs-g-CD) for the oxidation of cinnamon oil to natural benzaldehyde under aqueous conditions (Scheme 1). It was investigated that the MWCNTs-g-CD would allow for the supramolecular recognition of β -CD, as well as showing good adsorption and chemical stability properties. The resulting catalyst was initially evaluated for the oxidation of cinnamaldehyde using hydrogen peroxide as the terminal oxidant under the mild reaction conditions. A plausible mechanism was proposed for the oxidation of cinnamaldehyde. The MWCNTs-g-CD exhibited enhanced catalytic activity comparison with the MWCNTs and β -CD in isolation, which was attributed to the occurrence of a synergistic effect between β -CD and the MWCNTs.

2. Experimental

2.1. Materials

MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). β -CD (>99%) was purchased from Shanghai Boao Biotechnology (Shanghai, China). Cinnamaldehyde (>99%) was obtained from Sinopharm Chemical Reagent (Shanghai, China). All of the other chemicals used in this study were purchased as the analytical grade and used without further purification. All of the aqueous solutions were prepared using Milli-Q water under ambient conditions.

2.2. Preparation of MWNTs-g-CD

MWNTs were purified and oxidized according to a previously reported procedure [40]. Briefly, MWCNTs (200 mg) were added to a solution of HNO_3 (3 mol/L, 20 mL), and the resulting mixture was agitated under ultrasonic irradiation at 25 °C for 30 min. The mixture was then heated at 120 °C with an agitation speed of 120 r/min for 24 h. Upon completion of the reaction, the mixture was cooled to room temperature and the solids were separated by centrifugation (1 min), washed to neutral pH with distilled water and dried under vacuum to give MWNTs-COOH. A small portion of this material (60 mg) was dispersed in SOCl_2 (25 mL) under sonication conditions for 30 min in the presence of DMF (1 mL). The mixture was then heated at 80 °C under nitrogen overnight. Upon completion of the reaction, the solvent and excess SOCl_2 were removed under reduced pressure to give the acyl chloride-functionalized MWNTs (MWNTs-COCl). This material was immediately dispersed in DMF (10 mL) under sonication conditions for 5 min



Scheme 1. Schematic diagram of the MWCNTs-g-CD preparation process.

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