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Aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by carbon nanotubes without any promoter

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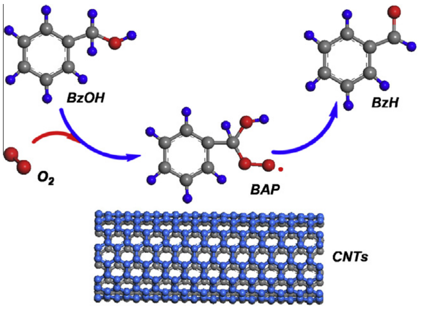
HIGHLIGHTS

- Carbon nanotubes (CNTs) can catalyzes benzyl alcohol (BzOH) to benzaldehyde (BzH).
- A reasonable mechanism for the liquid-phase oxidation of BzOH on CNTs is proposed.
- Electron transfer in graphene skeletons plays an important role.
- Nitrogen doping efficiently enhances the catalytic activity of CNTs for BzOH to BzH.
- Carbon catalyst displays outstanding recyclability.

GRAPHICAL ABSTRACT

Carbon nanotubes (CNTs) as a metal-free catalyst exhibited high activity and excellent stability for the selective oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) in solution phase with molecule oxygen as the terminal oxidant in the absence of any promoter.



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ABSTRACT

Carbon nanotubes (CNTs) were used as metal-free catalysts for selective oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) with molecular oxygen as the terminal oxidant in the absence of any promoter. The effects of reaction conditions, solvent and surface chemistry of CNTs on the catalytic performances have been investigated. The results showed that the solvent has a remarkable effect on oxidation of BzOH. The effect of the CNTs surface chemistry on the catalytic activity was revealed, and the surface carboxylic groups were particularly detrimental for the catalytic activity. A reasonable mechanism responsible for the liquid-phase oxidation of BzOH on CNTs was proposed, and electron transfer in graphene skeletons played an important role. Nitrogen doping efficiently enhanced the catalytic activity of CNTs for aerobic oxidation of BzOH, arising from improving electron transfer. In addition, the NCNTs revealed outstanding recyclability and exhibited excellent potential for industrial application of the BzOH oxidation to BzH.

1. Introduction

Selective oxidation of alcohols to their corresponding aldehydes or ketones is one of the most important and challenging functional group transformations in organic synthesis, both for fundamental research and industrial manufacturing [1–4]. Especially, the selective oxidation of benzyl alcohol (BzOH) to higher-value added product benzaldehyde (BzH) has received increasing attention, because the BzH has tremendous application in perfumery, pharmaceutical, dyestuff and agrochemical industries [5–7]. Commercially, the BzH is synthesized by the hydrolysis of the benzal chloride and the vapor/liquid-phase oxidation of toluene [3,8–10]. However, in the former process, traces of chlorine inevitably exist in the product BzH,

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and in the latter, the selectivity to BzH is very poor. Alternatively, direct oxidation of BzOH in liquid phase is a promising route for the manufacture of BzH, because it completely overcomes the major drawbacks of as above mentioned. Recently, such transformation with molecular oxygen as the terminal oxidant and water as the sole by-product has received enormous attention [11]. Consequently, a remarkable number of metal-catalyzed aerobic processes, especially based on noble metals, such as Ru [12,13], Pd [14,15], Pt [16,17], Ag [18,19], Au [20,21], have been developed. However, considering the high cost of the noble metals, it would be still desirable to develop metal-free catalysts to carry out BzOH oxidation. Comfortingly, carbon nanotubes (CNTs), owing to their unique π–π electrostatic interactions, excellent electrical and thermal conductivity, high specific surface areas, good chemical stability and recyclability, environmental acceptability, readily surface modification and low cost [22–26], have been proved promising as new-generation metal-free catalysts for a broad range of important chemical transformations, such as the oxidative dehydrogenation (ODH) of aromatic hydrocarbons [27] and alkanes [28], oxygen reduction reaction [29], oxidation of hydrocarbons [30,31] or phenols [32], as well as decomposition of ammonia [33]. It is of particular interest to know whether it is possible to oxidize benzyl alcohol (BzOH) to get higher-value added product benzaldehyde (BzH) by using cheap CNTs catalysts.

To this end, in our very recent work [34,35], we have reported that CNTs as a metal-free catalyst could successfully catalyze the oxidation of BzOH to BzH using molecular oxygen as the terminal oxidant and a small number of nitric acid (HNO_3) as the promoter under atmospheric pressure. Unfortunately, CNTs alone could not catalyze oxidation of BzOH with molecular oxygen at atmospheric pressure. Moreover, considering the strongly acidic nature and recycling issues of HNO_3, it is impractical for industrial use. In this letter, we have extended our studies on CNTs in the liquid phase aerobic oxidation of BzOH in the absence of any additives at a relative low operational pressure (1.5 MPa O_2). The main goal of this work is to reveal the effect of the CNTs surface chemistry and doping nitrogen atoms into the carbon lattice on the catalytic activity, and propose a reasonable mechanism pathway of BzOH oxidation over CNTs. In addition, the effects of reaction temperature, O_2 pressure, catalyst amount, reaction time and solvent on the catalytic performances of CNTs were investigated in detail in the selective oxidation of BzOH. These results provide an attractive metal-free alternative to noble-metal-catalyzed systems for BzOH oxidation, and push forward the research on carbon catalysis.

2. Experimental

2.1. Preparation of catalysts

Pristine commerical carbon nanotubes (CNTs-0, d_{out} = 30–50 nm, d_{in} = 6–12 nm) was purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). One grams of pristine carbon nanotubes was placed in a 500 mL round bottom flask and 200 mL of concentrated HCl was added, then the mixture was stirred using magnetic stirrer for 24 h to remove residual metal impurities, subsequently, diluted in deionized water, filtered, washed with deionized water until pH = 6–7, and dried in air at 110 °C overnight [36], denoted as CNTs-1. Subsequently, 0.5 g of the CNTs-1 were dispersed in 100 mL of 9 mol L^{-1} HNO_3 in a 250 ml round bottom flask equipped with a condenser and the dispersion was refluxed under magnetic stirring for 2 or 4 h to introduce oxygen-containing groups into surface of CNTs-1, then diluted in deionized water, filtered, washed with deionized water until pH 6-7 was reached, and dried in air at 110 °C overnight, the corresponding materials were denoted as CNTs-2 or CNTs-3, respectively. In addition, CNTs-3 was subjected to heat treatment in a horizontal tubular quartz furnace with 4 cm inner diameter under flowing argon at 600 °C or 900 °C for 2 h, and then samples were cooled under argon to room temperature prior to exposure to air, denoted as CNTs-4 or CNTs-5, respectively [37].

Nitrogen-doped carbon nanotubes (NCNTs) were produced by chemical vapour deposition (CVD) using Fe–Mo/Al_2O_3 as catalyst and a mixture of xylene as carbon source and aniline as nitrogen source in a horizontal tubular quartz furnace in 4 cm inner diameter [35]. Typically, 10 mL mixtures of aniline and xylene, which the concentration of aniline in the mixture was 30 v%. When the temperature of reaction region reached 800 °C, the solutions were injected by a syringe pump at a rate of 2.5 mL h^{-1} for 4 h, accompanied with 300 °sccm Ar. To remove residual Fe–Mo/Al_2O_3 catalyst, the prepared catalysts were stirred in concentrated HCl using magnetic stirrer for 6 h, diluted in water, filtered, washed with deionized water until pH 6–7 was reached, and dried in air at 110 °C overnight, the as-prepared sample was denoted as NCNTs. For comparison, undoped carbon nanotubes were also produced using the same procedure with xylene as precursor without aniline, denoted as CNTs-6.

Activated carbon (AC) was purchased from Liyang Convoy Activated Carbon Factory, then the AC was subjected to heat treatment in a horizontal tubular quartz furnace with 4 cm inner diameter under flowing argon at 900 °C for 2 h, and then samples were cooled under argon to room temperature prior to exposure to air, denoted as AC-900.

FeO_x was loaded on the CNTs-3 in the same way as described in the literature [30,38], and the loading of FeO_x was controlled at 4.1 wt.% by atomic adsorption spectroscopy.

2.2. Characterization of catalysts

The BET specific surface areas were measured by N_2 adsorption at liquid N_2 temperature in an ASAP 2010 analyzer. Raman spectra were obtained in a LabRAM Aramaic micro Raman spectrometer with an excitation wavelength at 633 nm with 2 μm spot size to investigate the carbon nanotubes structure. The Fe content of purified sample was measured by atomic adsorption spectroscopy (Shimadazu AAS-6800). The Ni content of purified sample was measured by electron probe micro-analyzer (EPMA-1600) with the accelerating voltage of 15 kV and beam current of 10 nA. X-ray photoelectron spectroscopy (XPS) were performed with a Kratos Axis ultra (DLD) spectrometer equipped with an Al Ka X-ray source, and the binding energies (±0.2 eV) were referenced to the C_{1s} peak at 284.6 eV. SEM images were obtained in a LEO 1530VP scanning electron microscope. TEM and HRTEM images were obtained in a JEM-2100 microscope operating at 200 kV. Specimens for TEM and HRTEM were prepared by ultrasonically suspending the sample in acetone and depositing a drop of the suspension onto a grid with amorphous carbon film.

2.3. Selective oxidation of BzOH

The oxidation reactions were carried out in a Teflon-lined 100 mL stainless steel autoclave equipped with a magnetic stirrer, at 1100 rpm. 5 mL of BzOH, 30 mL of DMF as solvent were added into the autoclave, and the air in the reactor was flushed over three cycles with Argon. Then, the reactor was heated to a stable operational temperature, and subsequently pure O_2 was fed into the reactor, and the pressure was kept constant by supplying pure O_2 during the reaction. Oxygenated products were identified by GC–MS and quantitated by GC. GC–MS analysis was performed on a SHIMAZDU GCMS-QP2010. GC analysis was performed on an Agilent GC-6820 equipped with a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column and a flame ionization detector using naphthalene as the internal standard [34]. Furthermore, for the test of reusability, the used catalyst was removed from the reaction