



Editor's choice paper

Promoting the aerobic Baeyer-Villiger oxidation of ketones over carboxylic multi-walled carbon nanotubes

Shao-Yun Chen^a, Xian-Tai Zhou^{b,*}, Jie-Xiang Wang^a, Rong-Chang Luo^a, Qing-Jin Luo^c, Liang-Jun Yu^c, Hong-Bing Ji^{a,*}

^a Fine Chemical Industry Research Institute, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, PR China

^b Fine Chemical Industry Research Institute, School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai, 519082, PR China

^c Huizhou Yussen Chemical Co. Ltd, Huizhou, 516081, PR China

ARTICLE INFO

Article history:

Received 3 April 2017

Received in revised form 28 May 2017

Accepted 1 June 2017

Keywords:

Multi-walled carbon nanotubes

Baeyer-Villiger oxidation

Radical

Dioxygen

ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) as metal-free catalysts presented excellent activity and selectivity in the Baeyer-Villiger oxidation of ketones to corresponding lactones in the presence of molecular oxygen and benzaldehyde. Different factors including catalyst, solvents, amount of catalyst were systematically investigated. Compared with MWCNTs, carboxylic multi-walled carbon nanotubes (c-MWCNTs) catalyst exhibited higher performance for the oxidation of ketones, showing good recyclability and reusability. The yield of ϵ -caprolactone was obtained with 94% under the optimum conditions. Also, c-MWCNTs presented excellent activity towards the oxidation of various cyclic ketones to the corresponding lactones. The introduced carboxyl group on the surface of MWCNTs was favorable to obtain high dispersion in the reaction solution. In addition, the recording of *in situ* Electron Paramagnetic Resonance (EPR) and Raman spectroscopy indicated that carboxyl group could significantly stabilize the radical species in the reaction.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The Baeyer-Villiger (B-V) oxidative reaction, a valuable process for preparing esters or lactones [1–3], is gathering much attention due to the wide applications of the products [4–7]. B-V reaction have been conducted traditionally by organic peracids as oxidants, but either intrinsic hazardous or a high economic costs of the such oxidants limit their practical application [8]. The oxidation with dioxygen or air is more desirable in the viewpoints of environment and costs. Recently, O₂/aldehyde system with metal-based catalyst such as Fe₂O₃, Sn/Fe-MCM-41 showed good catalytic performance toward B-V reaction [9–11]. Metal catalyst can accelerate the initiation of the free radical chain reaction, but there are disadvantages in the use of metal-based catalysts such as high costs, unfriendly environmental effects and undesirable by-products.

Carbon materials such as activated carbon, graphite and graphite oxide have received a great potential for B-V oxidation because it is more eco-friendly compared with conventional metal catalysts [12–14]. Nabaie reported the pioneer works that Ketjen

Black carbon materials catalyzed the B-V oxidation in the presence of dioxygen and aldehyde [15]. Recently, outstanding work by Yin has resulted in the highly efficiency of graphite and carbon nanotubes towards the B-V oxidation of cyclic ketones to lactones [16]. As a new class of metal-free catalyst, multi-walled carbon nanotubes (MWCNTs) have been attracted attention as catalyst in the application of oxidation reactions [17–19]. It suggested that MWCNTs can accelerate the electron-transfer which induces decomposition of radical precursors, including organic peroxides, and also can accept and stabilize the radical, which was studied by theoretical calculation performed at the B3LYP level of DFT theory [17,20]. However, some problems were encountered with the application of MWCNTs as catalysts, such as aggregation and poor dispersion in reaction solution. The functionalization of MWCNTs is an effective way to change their surface chemical properties [21]. Carboxyl group on the nanotube surface is commonly used to increase the adsorption affinity and dispersibility [22–24]. Wang reported the application of carboxyl surface modified multi-walled carbon nanotubes in the targeted delivery of drugs and imaging [25]. In the application of electrochemical performance, compared to non-modified electrocode, carboxyl functionalized multi-walled carbon nanotubes electrocode exhibited higher conductivity [26].

* Corresponding authors.

E-mail addresses: zhouxtai@mail.sysu.edu.cn (X.-T. Zhou), jihb@mail.sysu.edu.cn (H.-B. Ji).

The objective of this work is to introduce carboxyl group on the surface of MWCNTs and establish a protocol of preparing lactones from the aerobic oxidation of ketones. Compared with MWCNTs, the improvement of interfacial interaction and dispersibility could be achieved when MWCNTs was functionalized with carboxylic group, resulted in the enhancement of catalytic performance. More important, the evidences of interaction between reactive radicals and c-MWCNTs were obtained from *in situ* Electron Paramagnetic Resonance (EPR) and Raman spectroscopy, which confirmed that carboxyl group could significantly stabilize the radical species in the reaction.

2. Experimental

2.1. General

Ketones, *N-tert-butyl-alpha-phenylnitron* (PBN) were analytical grade and purchased from Alfa Aesar or Aldrich without further purification unless indicated. All other solvents are analytical grade. Activated carbon (AC) and graphite samples were purchased from Tianjin Kemiou Chemical Reagent Co. (carbon content no less than 99.0% and iron content no less than 0.02%). Graphite oxide, multi-walled carbon nanotubes (MWCNTs, length, 10–20 μm ; diameter, 5–15 nm) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. All materials were used with no further treatment before the reactions. The carboxylic acid functionalized MWCNTs (c-MWCNTs) were prepared according to previous reported method [27]. The pristine MWCNTs (0.5 g) were suspended in a mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v) and ultrasonicated for 3 h. The suspension was refluxed with vigorous stirring at 90 °C for 12 h. After cooling to room temperature, the mixture was filtered. The filtrated solid was then washed thoroughly with deionized water until neutral pH. The collected solid was dried in vacuum oven at 80 °C for 12 h.

The c-MWCNTs was quantitatively analyzed by back titration to determine the carboxylic acid (COOH) concentrations on the surface of MWCNTs. The c-MWCNTs (50 mg) were added into a 15 mL NaOH solution (0.1 mol/L). The mixture was stirred for 48 h to allow the solid MWCNT material to equilibrate with the NaOH solution. The mixture was then filtered and the filtrate was titrated with a HCl solution (0.1 mol/L) to determine the excess NaOH in the solution and the concentration of COOH on MWCNTs. The result of back titration of the functionalized MWCNTs shows that the COOH concentration on the surface of MWCNTs is 3.86 wt%.

2.2. Characterization techniques

XPS analysis was performed with an ESCALAB 250 spectrometer with an Al K α monochromatized radiation operated at 150 W (15 kV, 10 mA). The content of metal ions in solution (5% HNO_3 digested) was determined by a TJA IRIS (HR) inductively coupled plasma-atomic emission spectrometer (ICP-AES). Binding energies were calibrated versus the carbon signal at 284.8 eV. The Raman spectrum analysis was performed on a Renishaw inVia Laser micro-Raman spectrometer with a 633 nm excitation laser. TEM images were performed using a JEM-2010HR transmission electron microscopy with an operating voltage of 120 kV. FTIR spectroscopic measurements were carried out on a Bruker Equinox 55 FTIR spectrometer with pressing KBr troche. All spectra were recorded from 400 to 4000 cm^{-1} at room temperature. XRD patterns were recorded on an Empyrean X-ray diffractometer using Cu K α photon source (40 kV, 40 mA). Electron paramagnetic resonance (EPR) spectroscopy was recorded by a JESFA-200 (JEOL, Japan) EPR spectrometer at 50 °C. Instrument conditions for all analyses were as follows: microwave frequency, 9.05 GHz; mod-

Table 1

Catalytic performance of carbon materials in the cyclohexanone oxidation.^a

Entry	Catalyst	S _{BET} (m ² /g)	Conv. (%)	Select. (%)
1	Blank	–	17	>99
2	MWCNTs	74.5	76	>99
3	c-MWCNTs	76.8	94	>99
4	c-MWCNTs ^b	74.2	90	>99
5	Graphite	14.3	68	>99
6	Graphite oxide	–	66	>99
7	Activated carbon	320.5	60	>99

^a Conditions: cyclohexanone (2 mmol), benzaldehyde (4 mmol), DCE (10 mL), catalyst (10 mg), O₂ balloon, 50 °C, 4 h.

^b c-MWCNTs after annealing under flowing argon.

ulation amplitude, 2 mT; modulation frequency, 100 kHz; power, 0.998 mW; time constant, 0.03 s. All spectra are the signal-averaged sum of six scans unless otherwise noted. All reactions were carried out in triplicate. The BET specific surface areas were measured by N₂ adsorption at liquid N₂ temperature in an ASAP 2020C analyzer. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 plus equipped with Rtx-5 capillary column (30 m \times 0.25 mm \times 0.25 μm) and GC-MS analysis was performed on a Shimadzu GCMS-QP2010 plus equipped with Rxi-5 ms capillary column (30 m \times 0.25 mm \times 0.25 μm).

2.3. Catalytic tests

In a typical experiment, a mixture of benzaldehyde (4 mmol), ketone (2 mmol), biphenyl (1 mmol, inert internal standard), catalyst (10 mg) and 1,2-dichloroethane (DCE, 10 mL) was placed into 25 mL reaction tube equipped with condenser and balloon with dioxygen. The reaction mixture was stirred with magnetic stirrer at 50 °C for 8 h. The product for each reaction was analyzed by GC (Shimadzu GC-2010 plus) and GC-MS (Shimadzu GCMS-QP2010 plus).

2.4. Recycling tests

Recycling tests were carried out by repeating the catalytic reaction after separating the catalyst powder from the reactants and products. The catalyst was filtered and washed with acetone. After washing, the acetone solution was checked for the existence of reactants/products using gas chromatography. The recycled catalysts were then dried in vacuum at 80 °C for 6 h. The recycled catalyst was reused under the same reaction conditions.

3. Results and discussion

3.1. Catalytic performance of different carbon materials

Using cyclohexanone as the starting substrate, the catalytic performances of carbon materials, including MWCNTs, c-MWCNTs, activated carbon, graphite and graphite oxide in the B-V oxidation were tested and the results were summarized in Table 1. All carbon materials were dealt with HNO_3 and no metal were determined from XPS and ICP-AES measurements, which then were employed as catalysts in the B-V oxidation.

The blank experiment without any catalysts gave a cyclohexanone conversion of 17% after a reaction time of 4 h, as a result of peroxybenzoic acid generated from benzaldehyde and dioxygen [15,28]. Carbon materials as catalyst were active and exhibited good catalytic activities towards the aerobic B-V oxidation of cyclohexanone. It should be noted that high selectivity (>99%) of ϵ -caprolactone was obtained with all tested carbon materials. High yield of ϵ -caprolactone (76%) was obtained over MWCNTs catalyst, which was higher than activated carbon, graphite and graphite

Download English Version:

<https://daneshyari.com/en/article/4751847>

Download Persian Version:

<https://daneshyari.com/article/4751847>

[Daneshyari.com](https://daneshyari.com)