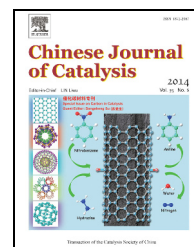


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Article (Special Issue on Carbon in Catalysis)

Catalytic performance of heteroatom-modified carbon nanotubes in advanced oxidation processes

João Restivo, Raquel P. Rocha, Adrián M. T. Silva, José J. M. Órfão, Manuel F. R. Pereira, José L. Figueiredo*

Laboratory of Catalysis and Materials-Associate Laboratory LSRE/LCM, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:

Received 3 April 2014

Accepted 17 April 2014

Published 20 June 2014

Keywords:

Advanced oxidation processes

Catalytic ozonation

Catalytic wet air oxidation

Sulfur groups

Nitrogen groups

Oxygen groups

Carbon nanotubes

Surface chemistry

ABSTRACT

Multi-walled carbon nanotubes (CNTs) were submitted to chemical and thermal treatments in order to incorporate different heteroatoms on the surface. O-, S- and N-containing groups were successfully introduced onto the CNTs without significant changes of the textural properties. The catalytic activity of these heteroatom-modified CNTs was studied in two liquid phase oxidation processes: catalytic ozonation and catalytic wet air oxidation (CWAO), using oxalic acid and phenol as model compounds. In both cases, the presence of strongly acidic O-containing groups was found to decrease the catalytic activity of the CNTs. On the other hand, the introduction of S species (mainly sulfonic acids) enhanced the removal rate of the model compounds, particularly in the CWAO of phenol. Additional experiments were performed with a radical scavenger and sodium persulfate, in order to clarify the reaction mechanism. Nitrogen functionalities improve the catalytic performance of the original CNTs, regardless of the process or of the pollutant.

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1. Introduction

The presence of organic pollutants that show some resistance to conventional treatment technologies for water and wastewater led to a growing interest in the development of more efficient methods for their removal [1–3], such as the so-called advanced oxidation processes, which include catalytic wet air oxidation (CWAO) and catalytic ozonation processes [4–7].

Several heterogeneous catalysts based on supported or unsupported metal oxides and noble metals have been investi-

gated in CWAO [8] and catalytic ozonation [9]. However, deactivation phenomena are frequent, in particular leaching of active metals. In spite of advances in the development of heterogeneous catalysis with minimal leaching effects [10,11], the use of metal-free catalysts has been recently preferred in many advanced oxidation processes, not only to avoid possible lixiviation of metals, but also because these materials are stable in both acidic and alkaline media.

The ability of carbon materials to enhance the removal of organic pollutants by the ozonation process is well-known, and has been demonstrated with activated carbons [12–16], mul-

* Corresponding author. Tel: +351-225081663; Fax: +351-225081449; E-mail: jlfig@fe.up.pt

This work was supported by FREECATS, the European Union 7th FP (2007-2013) grant no. 280658, PEst-C/EQB/LA0020/2013, FEDER through COMPETE-Programa Operacional Factores de Competitividade, by FCT-Fundação para a Ciência e a Tecnologia, NORTE-07-0124-FEDER-0000015, NORTE-07-0162-FEDER-000050, QREN, ON2, FEDER.

DOI: 10.1016/S1872-2067(14)60103-0 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 6, June 2014

ti-walled carbon nanotubes (CNTs) [17–21], carbon xerogels [22] and carbon nanofibers [17,23–26]. Similarly, various carbon materials have been used as catalysts for wet air oxidation, including activated carbons [27–29], carbon fibres [30], carbon foams [30], carbon xerogels [27,31] and CNTs [32–36]. The catalytic activity of carbon materials in liquid phase oxidation processes can be enhanced by modification of their textural and chemical properties [37,38]. While the effect of the textural properties, such as pore size and surface area, is well understood [21,35,39–41], the role of surface chemistry is still not completely established. In particular, the presence of surface heteroatoms, such as O, S, and N, has been shown to significantly affect the catalytic activity of carbon materials in catalytic ozonation [16,21,39,42–48] and in the CWAO process [29,30, 32–34,49].

In this work, a systematic study was performed to assess the influence of O, S, and N heteroatoms on the surface of carbon nanotubes in catalytic wet air oxidation and catalytic ozonation. For this goal, CNTs were prepared with different surface chemical properties, which were applied in the oxidation of two model compounds: oxalic acid and phenol. The performance of the catalysts was then related to their chemical properties, and the oxidation mechanisms for the CNTs with different surface groups were discussed.

2. Experimental

2.1. Materials

Commercial multi-walled carbon nanotubes (CNT-O), purchased from NANOCYL™ (NC3100), were subjected to different chemical and thermal treatments in order to modify the original surface properties. Four samples were obtained: CNT-N, prepared by liquid-phase oxidation of the pristine CNTs with nitric acid at boiling temperature; CNT-NUT, obtained by treating CNT-N with urea at 200 °C to incorporate nitrogen-containing surface groups, followed by gas-phase thermal treatment under nitrogen at 600 °C; CNT-S, obtained by sulfuric acid treatment of the pristine CNTs at 50 °C in order to introduce strong acidic functional groups (sulfonic groups); and CNT-NS, by refluxing the pristine CNTs with a HNO₃/H₂SO₄ mixture (1:3 v/v) at 50 °C. More detailed information about the experimental conditions can be found elsewhere [32,34].

2.2. Characterization

Textural properties of the pristine and modified CNT samples were based on the N₂ adsorption isotherms determined at –196 °C using a Quantachrome Nova 4200e apparatus. Surface chemistry of the samples was characterized by combining different techniques: temperature programmed desorption (TPD) in a fully automated AMI-300 Catalyst Characterization apparatus (Altamira Instruments) connected to a Dycor Dymaxion Mass Spectrometer monitoring CO, CO₂ and SO₂ released during the thermal analysis; X-ray photoelectron spectroscopy (XPS) performed in a Kratos AXIS Ultra HSA using a monochromatic Al K_α X-ray source (1486.7 eV); determination of the

pH at the point of zero charge (pH_{pzc}) using a drift method [21]. Further description of the techniques can be found elsewhere [32,34].

2.3. Experimental procedure

Ozonation experiments were performed in a stirred semi-batch tank reactor at room temperature and pressure. A volume of 700 mL of solution was used, consisting of a 90 mg/L solution of oxalic acid or 75 mg/L of phenol. Ozone, generated from pure oxygen using a BMT 802X ozone generator, was bubbled into the bulk of the solution using a diffusor (total flow rate = 150 cm³/min; ozone concentration = 50 g/m³). Ozone in the gas phase was monitored using a BMT 964 ozone analyser. 100 mg of the powdered catalysts with a particle size between 0.1 and 0.3 mm were introduced into the solution before starting gas flow admission and kept in suspension by stirring at 200 rpm. Blank (no catalyst) and adsorption (no ozone) tests were also performed. In the adsorption experiment, pure oxygen was kept flowing to maintain the mixing conditions of the ozonation tests.

CWAO experiments with phenol and oxalic acid were performed in a 160 mL 316-SS high pressure batch reactor housing a glass liner (Parr Instruments, USA Mod. 4564). 200 mg of catalyst were added to 75 mL of the organic pollutant solution and placed into the reactor. The reactor was flushed with pure nitrogen till complete removal of oxygen, pressurized with 5 bar of N₂ and then pre-heated up to the desired temperature under continuous stirring at 500 rpm in order to ensure proper mass transfer of oxygen in the liquid phase [27,31]. When the desired temperature was reached, pure air was injected to obtain a total pressure of 40 bar inside the reactor (corresponding to 7 bar of O₂ partial pressure), this being considered time zero for the reaction. The temperatures and the initial concentrations of oxalic acid and phenol were selected after preliminary experiments and by taking into account the concentration of oxygen that is dissolved in the liquid phase at the selected temperatures and pressures [32]. Therefore, CWAO of oxalic acid was performed at 140 °C (1000 mg/L of oxalic acid as starting solution) and phenol experiments at 160 °C (75 mg/L of phenol as starting solution). In addition, non-catalytic wet air oxidation (WAO) and adsorption experiments (absence of oxygen, 40 bar of N₂) were performed.

CWAO and ozonation experiments were carried out at the natural pH of the solutions, no buffer being added. The carbon materials were recovered at the end of each run for further characterization.

In order to obtain additional mechanistic information, experiments were also performed in the presence of a radical scavenger, *tert*-butanol (*t*-BuOH), with a concentration ten times higher than the organic compound. Additionally, experiments using sodium persulfate (Na₂S₂O₈) in the absence and presence of carbon material were performed under the same operating conditions, to provide further insight into the role of the S-containing groups. The amount of sodium persulfate used in the ozonation and CWAO experiments was fixed taking into account the amount of catalyst used in each process and the S

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