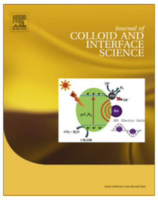
Journal of Colloid and Interface Science 483 (2016) 211–219

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



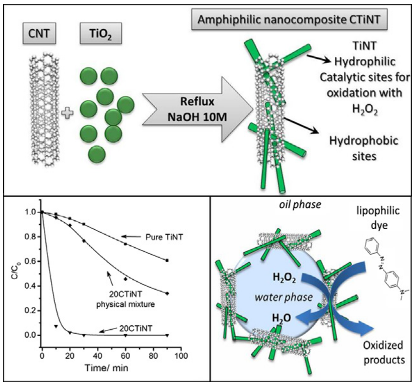
Regular Article

Multifunctional catalysts based on carbon nanotubes and titanate nanotubes for oxidation of organic compounds in biphasic systems

S.R.A. Santos [a], I.S. Jardim [a], H.A. Bicalho [a], I. Binatti [a], E.M.B. Sousa [b], A.M. Peres [b], R.R. Resende [c,d], E. Lorençon [a,*]

[a] Centro Federal de Educação Tecnológica de Minas Gerais, Departamento de Química, Av. Amazonas, 5253, Belo Horizonte, MG, Brazil
[b] Centro de Desenvolvimento da Tecnologia Nuclear, Serviço de Nanotecnologia, Av. Antônio Carlos, 6627 Belo Horizonte, MG, Brazil
[c] Universidade Federal de Minas Gerais, Departamento de Bioquímica e Imunologia, Av. Antônio Carlos, 6627 Belo Horizonte, MG, Brazil
[d] Instituto Nanocell, Rua Sto. Antônio, 420 Divinópolis, MG, Brazil

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 July 2016
Accepted 10 August 2016
Available online 13 August 2016

Keywords:
Titanate nanotubes
Carbon nanotubes
Hydrogen peroxide
Amphiphilic catalysts
Oxidation

ABSTRACT

Amphiphilic catalysts composed of carbon nanotubes (CNTs) and titanate nanotubes (TiNTs) have been successfully synthesized by refluxing anatase TiO_2 and functionalised CNTs in concentrated NaOH solution. The prepared materials were characterized by transmission electron microscopy, scanning electron microscopy, X-ray diffraction, thermogravimetric analysis (TGA), and N_2 physisorption isotherms. The catalytic activity of the synthesized composites was first evaluated in the oxidation of methyl yellow (MY) using H_2O_2 as oxidant in a single liquid phase system and in a biphasic water/oil mixture. The results of these experiments indicated that the catalytic activities of nanocomposites were very similar in the single liquid-phase oxidation. However, the modification of TiNTs with CNTs led to a substantially enhanced MY oxidation in the biphasic system. The nanocomposites show excellent interaction with both hydrophilic and hydrophobic compounds and thus stabilise emulsions. Under biphasic conditions, the catalysts can be easily separated and recycled, retaining catalytic activity even after eight runs. Additionally, the hybrid materials show superior catalytic activity and selectivity in the biphasic oxidation of benzyl alcohol with H_2O_2, as compared to pure TiNTs.

---

* Corresponding author.
E-mail address: eudesquimica@hotmail.com (E. Lorençon).

http://dx.doi.org/10.1016/j.jcis.2016.08.025

1. Introduction

Since the discovery of carbon nanotubes (CNTs), substantial interest has been directed towards the synthesis of one-dimensional (1D) transition metal oxides, owing to their exceptional physicochemical, optical, and electronic properties [1–3]. In this context, titanate nanotubes (TiNTs) have emerged as promising materials in many fields, such as electrochemistry [4], photochemistry [5,6], adsorption [7,8], and catalysis [9,10] due to their low cost of synthesis, chemical stability, large surface area, semiconducting nature, and high ion-exchange capacity [3,11,12].

The applications of TiNTs directly as catalysts or catalyst supports have been extensively investigated [13,14]. For example, Hara et al. [15] demonstrated that protonated TiNTs exhibit remarkable performance as Lewis acid catalysts in Friedel-Crafts alkylation. Zhang et al. [16] reported that protonated TiNTs possess high catalytic efficiency in the hydroxyalkylation/alkylation of 2-methylfuran and *n*-butanal under mild reaction conditions. Sodium titanate nanotubes were successfully applied as catalysts for biodiesel production, showing good activity and reusability [17]. We have demonstrated that terminal Ti(IV)–OH groups present on the TiNT surface can interact with H_2O_2, producing reactive superoxide radicals [9]. These results indicate that TiNTs are very efficient catalysts for the oxidation of methylene blue and dibenzothiophene with hydrogen peroxide [9,10]. Furthermore, TiNTs have been widely used as catalyst supports, since the abundant terminal Ti(IV)–OH groups help achieve a high loading of transition metal cations by an ion-exchange mechanism, resulting in the formation of small active nanoparticles with a narrow size distribution and high dispersion [3].

Nowadays, from the environmental point of view, the biphasic oxidation of organic substrates with hydrogen peroxide using amphiphilic materials is a suitable strategy for developing catalytic systems with high performance and recyclability, since aqueous hydrogen peroxide is a desirable oxidant that yields an environmentally benign by-product (H_2O) [18]. Recent studies have shown that nanocomposites of hydrophobic carbon nanotubes and hydrophilic inorganic materials can be used as alternative amphiphilic catalysts [19–21]. Moura et al. [22] produced magnetic amphiphilic nanocomposites via CVD growth of CNTs over Fe-Mo/nano-Al_2O_3. These materials were applied as biphasic oxidation catalysts, showing very promising results. Krambrock et al. [23] have synthesized amphiphilic catalysts by decoration of hydrophobic CNTs with Au NPs, with the resulting composites showing interesting results in the biphasic oxidation of organic substrates.

In this work, an amphiphilic catalyst composed of carbon nanotubes and titanate nanotubes (CTiNTs) was synthesized and characterized. These materials were produced by incorporating functionalised carbon nanotubes into titanate nanotubes during the synthesis of the latter. Initially, the catalytic performance of synthesized materials was studied in the oxidation of methyl yellow using H_2O_2 as oxidant in a single liquid phase system and in a biphasic water/oil mixture. The catalytic activity of TiNT and CTiNT nanocomposites was very similar in single liquid-phase oxidation. However, the modification of TiNTs with CNTs led to a substantial enhancement of the biphasic oxidation of MY. The nanocomposites show excellent interaction with both hydrophilic and hydrophobic compounds and thus stabilise emulsions. Under biphasic conditions, the catalysts can be easily separated and recycled, retaining catalytic activity even after eight runs. Additionally, the hybrid materials show superior catalytic activity and selectivity in the biphasic oxidation of benzyl alcohol with H_2O_2, as compared to pure TiNTs.

2. Experimental

2.1. Synthesis of CTiNT composites

Carbon nanotubes (CNTs) were produced by the CVD method using ferrocene as catalyst and ethylene as carbon source at 850 °C [24]. CNTs were functionalized by nitric acid treatment before use. 2 g of CNTs were refluxed in 6 M HNO_3 for 36 h. The resulting product was filtered, washed with distilled water on a PTFE filter (0.4 μm), and dried at 80 °C overnight.

Carbon nanotubes/titanate nanotubes composites were produced by reflux of functionalized CNTs and anatase TiO_2 (Sigma Aldrich) in aqueous solution of concentrated aqueous NaOH [10]. 0.5 g de TiO_2 were suspended in 100 mL de NaOH 10 M under ultrasonication with suitable amounts CNTs to produce mass ratio of CNT/TiO2 of 0, 5, 10, 20 wt%. The suspension was transferred into a PTFE (Teflon) flask and refluxed at 120 °C for 24 h under vigorous stirring. The precipitate was cooled to room temperature and washed with dilute hydrochloric acid (0.1 M) until pH ~ 1; and then with deionized water three times to remove residual Na^+ and OH^- ions. Finally, the solids were dried in a furnace at 80 °C overnight. The obtained materials were labelled as 0CTiNT, 5CTiNT, 10CTiNT, and 20CTiNT, according to the CNT/TiO_2 ratio used.

2.2. Catalytic activity

2.2.1. Methyl yellow oxidation

Methyl yellow (MY) oxidation tests were performed in a reactor at room temperature under magnetic stirring (300 rpm). The catalytic activity was evaluated by monitoring the intensity of the MY absorbance peak at 404 nm. Single liquid phase experiments were conducted in alcoholic solution. CTiNT composites (100 mg) were dispersed in MY alcoholic solution (50 mL, 30 mg L^{-1}), and the oxidation was started by adding hydrogen peroxide (2 mL) to the suspension.

The oxidation of MY in the biphasic (water/oil) system was conducted in a similar way. CTiNT composites (100 mg) were dispersed in MY solution in mineral oil (50 mL, 30 mg L^{-1}), and the oxidation was started by adding hydrogen peroxide (2 mL) to the suspension.

The concentration of methyl yellow was periodically monitored based on the intensity of its absorbance peak at 404 nm. The intermediates formed during MY oxidation were evaluated using mass spectrometry with electrospray ionization (ESI-MS) in positive extraction mode. For ESI-MS analysis, the reaction was stopped at a suitable time interval by addition of MnO_2, and the solids were separated from the solution of interest by centrifugation. Subsequently, an aliquot of the MY solution (1 mL) was diluted to 25 mL with methanol prior to analysis.

Recycling tests with 10CTiNTs were carried out in a biphasic solution for 60 min. The catalyst was removed from the reaction mixture by centrifugation and used in the next catalytic run without purification.

2.2.2. Benzyl alcohol oxidation

Benzyl alcohol oxidation reactions were performed at 90 °C in a 50 mL two-necked flask equipped with a magnetic stirrer and a reflux condenser. The catalyst (50 mg) was dispersed in a cyclohexane solution of benzyl alcohol (20 mM, 10 mL), and the reaction was started by addition of H_2O_2 (10 M, 0.1 mL) to the suspension. During the reaction, aliquots were removed from the organic phase, and the concentration of reactants and products was monitored by gas chromatography (GC) using an FID detector (Agilent 6890N). Assignments and quantification of products were made by comparison with authentic samples.