Generation of reactive oxygen species in titanates nanotubes induced by hydrogen peroxide and their application in catalytic degradation of methylene blue dye

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ABSTRACT

The present work describes the application of sodium (Na-) and hydrogen (H-) titanate nanotubes (TiNTs) as catalysts in oxidation reactions with aqueous hydrogen peroxide. By applying a combination of characterization techniques, it is shown that the interaction of TiNTs with H_2O_2 leads to a modification in the color and vibrational structure of the TNT, which can be attributed to the formation of superoxide radicals. Electron paramagnetic resonance measurements reveal that fraction of generated radicals increases asymptotically with H_2O_2 concentration. Catalytic tests of methylene blue discoloration revealed that TiNTs are very active in the discoloration of the dye, being the catalytic activity dependent on the concentration of H_2O_2. The analysis of the reaction products by electrospray ionization mass spectrometry showed that the dye was successively oxidized in different intermediate compounds. The effects of previous thermal treatment of the TiNTs were also investigated, and it was found that the active catalytic sites are progressively deactivated as the treatment temperature is increased. The overall results suggest that terminal groups present in the titanate structure, such as $TiO^{:-}$ are active catalytic sites that convert into highly reactive superoxide radicals upon interaction with H_2O_2 molecules.

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1. Introduction

In the last three decades remarkable advances in the catalytic oxidation of organic compounds by hydrogen peroxide have been achieved. In particular, the utilization of heterogeneous catalysts such as titanosilicates [1], titanium substituted zeolites and amorphous silica has been extensively studied [2–4]. The catalytic activity of these materials is in part due to the ability of transition metals such as Ti (IV) to interact with H_2O_2 producing radical species [5]. More recently hydrogen and sodium titanate nanotubes (TiNTs) have attracted much attention due to their exceptional physico-chemical properties and unusual morphology [6]. TiNTs can be produced by low cost, simple alkaline treatments of TiO_2 precursors [7]. They consist of multilayered open-ended tubular structures having length on the scale of several hundred nanometers, well defined diameter around 10 nm and large specific surface area containing essentially a mesoporous texture [6,7].

Although titanate nanotubes present features that make them ideal for high performance heterogeneous catalysis, most of the catalytic studies performed so far were restricted to their application as support for highly dispersed metal nanoparticles [6–9]. Only few works have explored the catalytic properties of pristine titanate nanotubes. For example, Kitano et al. [10] have demonstrated that hydrogen titanate nanotubes exhibit remarkable catalytic performance as Lewis acid catalyst with active Brønsted acid sites. In the other hand, studies on the photocatalytic activity of titanate nanotubes for degradation of organic dyes have revealed that the oxidation capacity of pristine TiNTs is very limited. Guo et al. [11] investigated the photocatalytic oxidation of Rhodamine B (RhB) and methyl orange (MO) in the presence of titanate nanotubes and nanowires synthesized by a hydrothermal method using Degussa P25 TiO_2 as a precursor. The authors found that prior to calcination, the photocatalytic activities of both materials towards RhB and MO degradation have efficiency less than of P25. Similar results

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were reported by Xiao et al. [12] for RhB degradation. Baiju et al. [13] studied the photocatalytic degradation of methylene blue (MB) on a mixture of titanate nanobelts and nanotubes obtained by hydrothermal process. The results showed that pristine titanates presented good adsorption capacity towards MB, however no significant photocatalytic activity was observed. In addition, Xiong et al. [14] have demonstrated that titanate nanotubes exhibit favorable photocatalytic activity for MB degradation after controlled calcination at 400 °C.

Furthermore, few researchers have investigated the interaction of titanate nanotubes with hydrogen peroxide, which has been previously established as an ideal oxidant for green oxidation. Khan et al. [15] showed that crystalline anatase TiO_2 nanotubes can be synthesized by treatment of hydrogen titanate nanotubes with 2 wt% of hydrogen peroxide aqueous solutions at 40 °C followed by calcination at 350 °C. The authors found that the anatase nanotubes have higher photocatalytic efficiency in the oxidation of trimethylamine when compared to pristine TiNT, however, the effects of H_2O_2 as oxidant were not studied.

In this work, we have studied the catalytic behavior of titanate nanotubes for the oxidation of organic substrates in the presence of H_2O_2 in the absence of light and demonstrated their great potential for environmental decontamination. The interaction of the TiNTs with H_2O_2 was systematically investigated by using several techniques. Electron paramagnetic resonance (EPR), UV–vis, Raman spectroscopy results revealed that TiNTs have specific sites for radical production from H_2O_2, contrary to what occurs for TiO_2 materials. The catalytic performance of TiNTs was evaluated by monitoring the discoloration of methylene blue (MB) aqueous solutions with varying H_2O_2 concentration, whereas ESI-MS measurements confirm that MB that the dye was successively oxidized in different intermediate compounds before the mineralization.

2. Experimental

2.1. Synthesis of titanate nanotubes

Titanate nanotubes were synthesized by reflux of TiO_2 powder in concentrated NaOH aqueous solution [16]. 500 mg of TiO_2 anatase (Sigma–Aldrich) was added to 100 mL of 10 M NaOH aqueous solution into a PTFE (Teflon) flask. The mixture was refluxed at 110 °C for 24 h under vigorous stirring. After cooling to room temperature, the white precipitate was washed with deionized water until neutral pH was reached, resulting in sodium titanate nanotubes. Alternatively, hydrogen titanate nanotubes were obtained through the washing of the precipitate with dilute hydrochloric acid (0.1 M) and then with deionized water three times to remove Na^+ ions. Finally, the solids were dried in a furnace at 60 °C overnight.

2.2. Interaction of titanate nanotubes with hydrogen peroxide

The obtained titanate nanotubes were treated with different concentrations of hydrogen peroxide. 50 mg of nanotubes were dispersed in 50 mL of aqueous H_2O_2 (0.1 M) for 10 min. After treatment the product (yellow solid) was separated by filtration and dried at 60 °C for 1 h.

2.3. Characterization

High-resolution transmission electron microscopy (HR-TEM) images were obtained with FEI Tecnai G2 microscope with 100 kV acceleration voltage. Scanning electron microscopy images (SEM) were done with FEI model Quanta microscope with accelerating voltages of 15–30 kV. X-ray diffraction patterns were obtained with Rigaku D/MAX 2400 with Cu source (λ = 1.54 Å, K_{α}). Raman spectra were measured with a DeltaNu apparatus using laser line of 512.5 nm. Diffuse reflectance spectra were obtained with Shimadzu UV–vis 2101 spectrometer. The Brunauer–Emmett–Teller (BET) specific surface areas (BET) were determined by a multipoint BET method using nitrogen adsorption measurements were done using an Autosorb equipment of Quantachrome Corporation. EPR spectra were measured with a custom-build spectrometer working at X-band with commercial cylindrical Bruker cavity and Varian klystron source and Varian magnet (0–800 mT). For low temperatures, an Oxford flux cryosystem was used (4–300 K). Magnetic field calibration was done by use of DPPH standard (g = 2.0037), frequency measurements with digital PTS frequency meter and as concentration standard Cu acetylacetonate powder (99.9% purity). Mass spectra with electrospray ionization source (ESI-MS) analysis were carried out on LCQ Fleet (Thermo Scientific) ion trap mass spectrometer.

2.4. Catalytic effect of titanate nanotubes: methylene blue oxidation

Tests for adsorption/oxidation of methylene blue were performed in a reactor at room temperature under magnetic stirring (100 rpm). The catalytic activity was evaluated by monitoring the intensity of the light absorbance peak of methylene blue at 665 nm. 10 mg of titanate nanotubes were dispersed in 50 mL of methylene blue aqueous solution with concentration of 50 mg L^{-1}. Then, dye oxidation was started by adding the appropriate amount of H_2O_2 10 M to give an initial concentration of 10, 20 and 100 mM of hydrogen peroxide into the suspension. For comparison, the same experimental procedure was applied in the absence of the catalyst and in the presence of TiO_2 anatase (Sigma–Aldrich) or TiO_2 P25 Degussa.

3. Results and discussions

3.1. Characterization of titanate nanotubes

Fig. 1 presents typical images of high-resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy (SEM) of the produced sodium titanate nanotubes (Na-TiNTs) and hydrogen titanate nanotubes (H-TiNTs) samples. From the SEM images (insert in Fig. 1), it can be observed that the products obtained by the hydrothermal treatment present morphology consisting exclusively of filaments, indicating a high efficiency in the synthesis. The tubular structure is revealed by the HR-TEM images. For both types of sample, the nanotubes present multiple wall structures (3–5 walls) having inner and outer diameter of about 6 and 10 nm, respectively, and length of more than 100 nm. Most of the tubes are open at both ends. In addition, the characteristic interlamellar spacing for titanate nanotubes are confirmed by the analysis of the high resolution images. For Na-TiNTs (Fig. 1a), the separation between successive concentric layers is 0.80 nm whereas this value is reduced to 0.78 nm for H-TiNTs [15]. The greater distance for Na-TiNTs is generally attributed to higher amount of interlamellar water. The produced sodium and hydrogen titanate nanotubes present surface areas of 165 m^2 g^{-1} e 220 m^2 g^{-1}, respectively, similar to values reported in literature [17].

The crystal structure of the synthesized products was evaluated by XRD as shown in Fig. 2. The XRD pattern of titanate nanotubes differs completely from its anatase TiO_2 precursor. The diffraction patterns of sodium and hydrogen titanates are similar to patterns of monoclinic trititanates crystals [18,19], but have very broad peaks, evidencing their nanoscale dimensions. The main diffraction peaks are assigned in Fig. 2. The exchange of Na^+ by H^+ in the titanate