



Synthesis of Nb₂O₅ nanoparticles through the oxidant peroxide method applied to organic pollutant photodegradation: A mechanistic study



Osmando F. Lopes^{a,b}, Elaine C. Paris^b, Caue Ribeiro^{b,*}

^a Departamento de Química - UFSCar, Rod. Washington Luiz, km 235, CEP: 13565-905 São Carlos, SP, Brazil

^b Embrapa Instrumentação, Rua XV de Novembro, 1452, CEP: 13560-970, SP, Brazil

ARTICLE INFO

Article history:

Received 1 June 2013

Received in revised form 6 August 2013

Accepted 16 August 2013

Available online 28 August 2013

Keywords:

Niobium pentoxide

Nanoparticles

Photocatalysis

Photodegradation mechanism

Water treatment

ABSTRACT

This paper evaluates the influence of the hydrothermal treatment temperature on the phase formation, structure and photocatalytic potential of Nb₂O₅ nanoparticles obtained by the oxidant-peroxo method (OPM). The materials were characterized by X-ray diffraction (XRD), Raman spectroscopy, UV–vis diffuse reflectance spectroscopy (DRS), scanning and transmission electron microscopy (SEM and TEM), thermogravimetry (TGA), Fourier transform infrared spectrometry (FTIR) and N₂ adsorption isotherms. The photocatalytic efficiency of the Nb₂O₅ nanoparticles and the mechanism of degradation were evaluated with respect to the degradation of the contaminants: rhodamine B (RhB) and atrazine under UV and visible radiation. The synthesized nanoparticles presented mixed phases of Nb₂O₅ orthorhombic and Nb₂O₅·nH₂O, with particle size ranging from 30 to 40 nm and specific surface area ranging from 129 to 199 m²/g. The results showed that the nanoparticles can be applied as catalysts for photoactivated reactions. The rate constant of RhB photodegradation in the reaction catalyzed by the Nb₂O₅ samples was approximately 5 times higher than the rate observed for RhB direct photolysis (RhB self-photolysis), and approximately 2 times higher than RhB photodegradation catalyzed by TiO₂ (reference). The surface hydroxylation and crystallinity were the most important parameters for the photoactivity per unit area of the Nb₂O₅ nanoparticles obtained at lower (100 and 125 °C) and higher (150 and 175 °C) hydrothermal temperatures, respectively. Furthermore, under UV radiation, the main photodegradation mechanism occurred by the attack of •OH radicals on the molecules (RhB and atrazine) and not by the direct oxidation of adsorbed molecules on the photocatalyst surface. Dye-sensitized photocatalysis was the main mechanism for RhB degradation under visible radiation.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Niobium pentoxide (Nb₂O₅) is a promising material for application in many fields due its properties, such as high specific surface area [1], high selectivity [2,3] and strength of surface acid sites [4,5]. It has been largely studied as a catalyst in several types of reactions including dehydration [6–8], hydration [9], esterification [10,11], hydrolysis [1], condensation [12], alkylation [13,14], dehydrogenation [15], and in many types of oxidation reactions [2,16]. Furthermore, Nb₂O₅ presents a band gap ranging from 3.1 to 4.0 eV and high absorption in the light spectrum [5,17–19]. These properties indicate the potential application of this material in photocatalysis, such as in advanced oxidative processes

(AOPs) for the degradation of organic contaminants. Several studies have shown that Nb₂O₅ presents photocatalytic properties, such as selective oxidation of organic contaminants [2,18,20], photodegradation of organic dyes [17,21] and hydrogen production [19].

However, studies employing Nb₂O₅ as a photocatalyst generally apply this material in the micrometric form, obtained by the simple calcination of commercial oxide or through treatment with reactants such as hydrogen peroxide, acids and bases [17,19,20]. This is a drawback for heterogeneous catalysis because it is a surface phenomenon that is strongly dependent on the catalyst surface area and adsorbed surface groups, such as OH[−], and is therefore dependent on the catalyst particle size. Despite the technological importance of nanoparticulated Nb₂O₅ [22], few preparation methods have been reported in the literature because Nb⁵⁺ ions are very unstable in aqueous solution [23–25]. Soft-chemistry methods may be suitable for the production of controlled surface areas and thus, the oxidant-peroxo method (OPM), through hydrothermal treatment, is a promising alternative because it is performed at low temperatures (100–200 °C). Because hydrothermal annealing

* Corresponding author. Tel.: +55 16 2107 2915; fax: +55 16 2107 2902.

E-mail addresses: osmando.iq@hotmail.com (O.F. Lopes), elaine.paris@embrapa.br (E.C. Paris), caue.ribeiro@embrapa.br, caue1977@gmail.com (C. Ribeiro).

allows the crystallization process to occur in mild conditions, this does not eliminate the hydroxyl groups in as-formed surfaces, which results in a material with high surface area and consequently greater number of acid sites [26]. This synthesis was previously reported by Leite et al., who obtained, through the OPM method, a pseudo-hexagonal Nb₂O₅ phase with different morphologies, presenting high surface areas and a large number of acid sites [22]. However, the potential of this route to produce Nb₂O₅ as an active photocatalyst was not properly investigated.

Therefore, the aim of this paper was to evaluate the photocatalytic potential of niobium oxide nanoparticles produced by the OPM method and to describe the dependence of the phase and structure on the hydrothermal treatment temperature and time. To study the photoactivity and the active mechanisms involved in the produced materials, rhodamine B (dye) and atrazine (pesticide) photodegradation under UV and visible radiation were used as probes, and a methodology for the detection of active oxidative species was investigated.

2. Materials and methods

2.1. Synthesis of Nb₂O₅

Nb₂O₅ nanoparticles were synthesized based on the procedure previously reported by Leite et al. [22]. Syntheses were performed by the OPM method using hydrothermal treatment for crystallization of the nanoparticles. The precursor ammonium niobium oxalate (NH₄[NbO(C₂O₄)₂(H₂O)₂]_n·H₂O – CBMM, Brazil) was dissolved in 100 mL of distilled water under vigorous stirring, resulting in a transparent solution after 15 min. To this solution, hydrogen peroxide (Synth, 30% v/v) was added at a 10:1 H₂O₂:Nb molar ratio, leading instantaneously to a transparent yellow solution, which indicates the formation of the niobium peroxo complex (NPC) [27]. NPC was crystallized by hydrothermal treatment, in a home-made stainless steel capsule with an internal covering of poly-tetrafluoroethylene, in which magnetic stirring could be applied to avoid agglomeration. The internal pressures were self-generated by water vapor pressure, according to the set temperature. The temperature of the hydrothermal treatment was studied by fixing the treatment time for 12 h and varying the temperature between 100, 125, 150 and 175 °C. These samples were identified as 100Nb12, 125Nb12, 150Nb12 and 175Nb12. The time of hydrothermal treatment was studied by fixing the treatment temperature at 125 °C and varying the time at 2, 12 and 24 h. These samples were identified such as 125Nb2, 125Nb12 and 125Nb24. After the specified reaction times, a white powder was formed in all cases. The powder was washed three times with distilled water and separated by centrifugation.

The hydrothermal treatment conditions, such as time and temperature, and the Nb precursor used in the synthesis have a strong effect on the final material properties, such as phase, morphology, particle size, and specific surface area and consequently, on the photocatalytic properties. In this way, niobium chloride (NbCl₅) was evaluated as a precursor to the Nb₂O₅ synthesis, to verify the effect of different Nb sources on the final material. Nb₂O₅ nanoparticles were synthesized based on the procedure previously reported method from Uekawa et al. [23]. NbCl₅ was fully dissolved in ethanol at a proportion of 50% weight. This solution was added to an NH₃ aqueous solution, leading to a final concentration of 0.5 mol L⁻¹. This procedure leads to a white precipitate of Nb₂O₅·nH₂O, which was washed repeatedly and separated by centrifugation. The precipitate was submitted to the same conditions for hydrothermal treatment, maintaining the molar ratio of Nb⁵⁺:H₂O₂ at 1:10, and treating the material at 175 °C for 12 h. However, in this synthesis, the phase did not change from the Nb₂O₅·nH₂O precursor, even at 175 °C/12 h (as observed in the

supplementary XRD data, Fig. 1S), which was sufficient for the crystallization of the material produced using the ammonium niobium oxalate.

2.2. Powder characterization

X-ray powder diffraction was conducted in a Shimadzu XRD 6000 at 30 kV and 30 mA with Cu K α radiation. In the analysis, the 2 θ range from 10 to 70° in a step-scanning mode was used with a step width of 0.02° and a fixed time of 4 s. The Raman spectroscopy analyses were performed in a Horiba Jobin-Yvon Raman spectrometer coupled to an Olympus TM BX41 microscope, which was used either for focusing the laser to the desired point of the sample or for gathering the scattered radiation. All spectra were gathered with the use of a 514.5 nm argon laser. Ultraviolet–visible (UV–vis) absorption was recorded using a Cary 5G spectrometer in total reflection mode with an integration cell.

A field emission gun-scanning electron microscope (FEG-SEM JEOL JSM 6701F) operating at 5.0 kV was used to verify the material morphology. High resolution transmission electron microscopy (HRTEM TECNAI F50) operating at 200 kV was used to verify the crystallographic orientations. TEM samples were prepared by wetting carbon-coated copper grids with a drop of the colloidal suspensions and drying in air.

The Fourier transform infrared spectra (FTIR) were collected in a PerkinElmer Spectrum 1000. These analyses were performed to detect the presence of species such as, OH groups and adsorbed water on the surface of the synthesized samples. For this analysis, the samples were first kept at a constant temperature of 100 °C for 12 h and were then placed in a desiccator to ensure the same atmospheric conditions for all samples prior to FTIR analysis. The analysis of N₂ adsorption at 77 K was conducted in a Micrometrics ASAP 2000, and the specific surface area was obtained by the application of BET modeling. Before the analyses were performed, the samples were pre-treated (degassing) by heating at 80 °C under vacuum until reaching a degassing pressure of less than 10 μ m Hg.

Thermal degradation was evaluated using a TA Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) under the following conditions: weight 10.00 \pm 0.50 mg; synthetic air flow 60 mL/min; heating rate 100 °C/min; and temperature range 100–900 °C.

2.3. Evaluation of photocatalytic activity

The photocatalytic potential of the synthesized samples was evaluated through the degradation of two different contaminants, rhodamine B dye (RhB) and atrazine. The photoactivities were studied under UV and visible radiation, to separate possible sensitization effects. These tests were performed in a thermostated photoreactor at 18 °C with a UVC radiation source (Lamps Phillips TUV, 15 W and maximum intensity at 254 nm) and a visible radiation source (Osram, maximum intensity at 440 nm).

To perform the photocatalytic tests, different samples with the same photocatalyst amount (150 mg L⁻¹) were prepared by dispersing 3 mg of photocatalyst in 20.0 mL of aqueous RhB (Aldrich, 5.0 mg L⁻¹) or atrazine (Merck, 10.0 mg L⁻¹). Because commercial TiO₂ (Aldrich nanopowder, 99.7%) is referred to in several papers as the most widely used photocatalyst [25], this material was tested under the same conditions as the reference. At regular time intervals, the samples were collected and analyzed in a UV–vis spectrophotometer (Shimadzu–1601PC) in the absorbance mode monitor the degradation kinetics at 554 nm and 222 nm for RhB and atrazine, respectively. The samples in dye or in pesticide solution were kept in the dark for approximately 12 h before the photocatalytic tests to evaluate possible adsorption effects were performed. None of the samples showed significant adsorption.

Download English Version:

<https://daneshyari.com/en/article/45420>

Download Persian Version:

<https://daneshyari.com/article/45420>

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