Applied Catalysis B: Environmental 205 (2017) 481–488

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Nanostructured niobium oxide synthetized by a new route using hydrothermal treatment: High efficiency in oxidation reactions

Nayara T. do Prado, Luiz C.A. Oliveira*

Departamento de Química, ICEx, Universidade Federal de Minas Gerais, Belo Horizonte, MG, CEP 31270-901, Brazil

ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form
13 December 2016
Accepted 28 December 2016
Available online 29 December 2016

Keywords:
Niobium oxide
Photocatalysis
Hydrothermal treatment
Oxidation

ABSTRACT

Nanostructured niobium oxides were synthesized by hydrothermal treatment using an amorphous Nb_2O_5 as precursor. The modification by hydrothermal treatment in the presence of oxalic acid or hydrogen peroxide resulted in versatile catalysts with many different properties verified by several characterization techniques. XRD analysis demonstrated the crystallinity increase. Significant morphological changes were observed by TEM, being possible to observe the presence of nanorods for the material treated with oxalic acid and nanospheres for the material treated in the presence of H_2O_2. Modifications in the porous structure were also observed, as well as the increase in BET specific area. This significant difference compared to precursor resulted in catalysts with higher performance than Nb_2O_5 in decomposition of methylene blue dye (MB) by heterogeneous fenton-like reactions and photocatalysis under UV light irradiation.

1. Introduction

In the context of heterogeneous catalysis, it is observed that systems based on niobium have played an important catalytic role in several reactions, acting as active phase, dopant and also as support. Special features such as redox property, high acidity and strong metal-support interaction has enabled these systems to present high catalytic performance in several reaction types [1].

In view of this, several niobium oxide synthesis methodologies have been described in the literature. However, significant advancements have been made in tailoring niobium nanoparticles with controlled structures and morphologies due to the superior properties of nano-sized materials. The obtention of nano-Nb_2O_5 using the sol-gel method followed by calcination or precipitation method in aqueous ammonia is widely described in the literature. However, the hydrothermal method has been presented as a good strategy to obtain metal oxide nanocrystals using milder temperatures and reaction conditions [2–5].

Recently, several studies have reported that the use of coordinating small organic molecules, such as oxalic acid, have enabled better control of nucleation and morphology in the hydrothermal synthesis of nanomaterials based on TiO_2 and WO_3 aiming their application in photocatalysis [6,7]. This same structure-directing agent was also employed in the hydrothermal synthesis of niobium oxide, allowing the obtention of nanocrystalline materials that showed a layered-type structure [8]. Moreover, there are several studies regarding the hydrothermal synthesis of Nb_2O_5 using alkaline solutions [9], but they mainly use niobic acid and niobium oxalate as the precursors.

In this work we report the synthesis of two catalysts obtained from the hydrothermal treatment, with oxalic acid or hydrogen peroxide, of a niobium oxide precursor in order to verify its influence on the morphology and porosity of the material. The advantage of using hydrogen peroxide lies in the fact that the only degradation products are water and oxygen. Therefore, it can be considered a clean synthesis method. Furthermore, hydrogen peroxide easily associates with transition metals such as Mo(VI), V(V), Nb(V) and W(VI), yielding metal-peroxo or metal-hydroperoxo species, which have received considerable attention due to their importance in a variety of industrial processes for showing the ability to release oxygen in active form [10]. Therefore, the proven catalytic properties of niobia and its availability justify the great interest in studying the behavior of this material in different processes.

The application of semiconductors in heterogeneous photocatalysis processes constitute an important research area. Currently, several studies have focused on developing new materials that are able to outperform TiO_2, one of the most widely used nanostructured semiconductors.

* Corresponding author.
E-mail address: luizoliveira@qui.ufmg.br (L.C.A. Oliveira).

http://dx.doi.org/10.1016/j.apcatb.2016.12.067
0926-3373/

Nb_2O_5 works under UV light irradiation as well as TiO_2. Comparatively, TiO_2 is regarded as a benchmark photocatalyst and it shows several great advantages, like chemical stability, non-toxicity and commercial availability, which are also observed for niobium oxide. However, the literature describes the fact that the recombination rate of photo-generated hole-electron pairs on TiO_2 is very high, which greatly reduces the photocatalytic efficiency and limits the industrial application of TiO_2 [11].

Despite this, TiO_2 has the ability to form hydrocolloids with high stability in water, which favors the catalytic activity. On the other hand, such stability does not favor the separation of the photocatalyst from the water, making it difficult to recover and reuse, which is extremely important both from an environmental and economic point of view [12]. As Nb_2O_5 does not present this drawback, its use as photocatalyst can be a new alternative for the degradation of contaminants.

The work of Prado et al. can be mentioned as an example of the effective recyclability of niobium oxide. The authors reported better catalytic activity of Nb_2O_5 in relation to TiO_2 and ZnO in indigo carmine degradation after 10 reaction cycles, confirming the easy recovery and long-term stability of Nb_2O_5 in photocatalysis [12].

The existence of few studies concerning the use of Nb_2O_5 for photocatalytic applications makes its use of considerable interest for a better understanding of its mechanism of action and advantages over already established photocatalysts [13].

It is worth mentioning that photocatalysts have been shown high effectiveness in degrading harmful organic substances and, therefore they can be an interesting approach for the treatment of water and wastewater [14]. In view of the above, it was decided to evaluate the catalytic potential of the synthesized materials in the photodegradation of organic compounds using methylene blue as a model molecule.

Other methods of chemical decomposition of organic contaminants are the Fenton-like systems, in which hydroxyl radicals can be generated by direct interaction of metal-hydroxyl species with H_2O_2 [15]. Despite the hydroxyl radicals belonging to the most reactive chemical species, metal peroxo and metal oxo-species also have been shown to be active intermediates in the oxidation of organic compounds [16]. Thus, the catalysts synthesized here were also assessed in Fenton-like systems since the possible generation of peroxo groups, after the hydrothermal treatment with H_2O_2, can confer good catalytic performance in the reaction mentioned type. In this way, the reactional systems reported here demonstrate the great potential and versatility possessed by niobium-based systems. However, their preparation, in the nanostructured form with high surface area, still represents a big challenge, evidencing the need for further studies in this area.

2. Experimental

2.1. Synthesis of the catalysts

Nb_2O_5 nanoparticles with different morphologies were synthetized by the hydrothermal method using a BERGHOF® BR-100 stainless steel autoclave containing a Teflon cup and magnetic stirrer set at 300 rpm. 1 g of Nb_2O_5 (supplied by CBMM) was dispersed in 40 mL of oxalic acid solution (OX) (0.2 mol L^{-1}) or 40 mL of distilled water and a subsequent addition of hydrogen peroxide (HP) (Synth, 50% v/v) in a 10:1 H_2O_2:Nb molar ratio. The suspension was placed in hydrothermal cell and the temperature adjusted to 220 °C for the treatment with OX or 150 °C for the treatment with HP under autogenous pressure in both cases. The times of the hydrothermal synthesis were 4 h for the OX treatment and 12 h for the treatment with HP, the materials identified as Nb_2O_5-OX, and Nb_2O_5-HP, respectively. These treatment times were chosen based on previous studies of our research group [17]. The solids obtained as final products were washed with distilled water until pH = 7, centrifuged and dried at 70 °C for 12 h.

2.2. Catalytic reactions

The photocatalytic activity of the synthesized materials was evaluated by the degradation of methylene blue dye (MB) under UV light irradiation. For this purpose, 10 mg of the catalyst was added to 10 mL of a MB aqueous solution (20 mg L^{-1}). Before irradiation, the photocatalyst was dispersed by magnetic stirring in absence of light for 60 min to achieve adsorption–desorption equilibrium between the photocatalyst and MB. Thereafter, the suspension was irradiated with UV light. The times of 30, 60, 120, 180, 240 and 300 min were evaluated. After centrifugation to separate the photocatalyst particles, the supernatants were analyzed at 664 nm using a UV-2600 Shimadzu spectrophotometer.

In Fenton-like systems, the oxidation of the methylene blue dye (50 mg L^{-1}) was carried out in the presence of 0.1 mL of H_2O_2 (Synth, 50% v/v), with a total volume of 10 mL and 10 mg of the catalyst during 5, 10, 30, 45, 60 and 120 min. As in the photocatalytic tests, the conversions were monitored by UV–vis measurements at 664 nm.

Total organic carbon content (TOC) was performed with a Shimadzu TOC-V_{CPH}, in order to evaluate the mineralization of the MB.

2.3. Characterization of the materials

UV–vis spectroscopy with diffuse reflectance geometry was performed with a UV-2600 Shimadzu from 200 to 800 nm. $BaSO_4$ powder was used as a reference (100% transmission), and the Kubelka–Munk equation was employed to manipulate the data.

X-ray diffraction data (XRD) was collected using a scan rate of 1° min^{-1} on a Shimadzu equipment, model XRD-7000 X-ray diffractometer, equipped with copper tube, 30 mA current and 30 kV voltage.

Transmission electron microscopy of the samples was carried out using Tecnai G2-20-SuperTwin FEI-200 kV at the Microscopy Center – UFMG.

The specific surface areas of the catalysts were calculated through the BET method in a low relative pressure region using the technique of adsorption/desorption of nitrogen at 77 K in a Quantachrome Autosorb iQ_2 equipment. The pore size distribution was calculated from the isotherm using the BJH model and the NLDFT method.

The acidity properties of the catalysts were characterized by the Temperature Programmed Desorption method (TPD) using NH_3 as probe molecule. A Quantachrome ChemBET-3000 equipment, containing TCD detector using a current of 150 mA and an attenuation of 32, was used. Approximately 0.2 g of catalyst was treated at 100 °C for 60 min in a continuous helium flow (80 mL min^{-1}) and NH_3 adsorption was then conducted at 50 °C. The TPD-NH_3 profiles were obtained at a heating rate of 10 °C min^{-1}.

The identification of acid sites of the samples was performed by adsorption of pyridine followed by infrared spectroscopy. Approximately 10 mg of sample was treated at 100 °C for 2 h under $N_{2(g)}$ flow (80–100 mL min^{-1}). Then the pyridine adsorption was carried out at a temperature of 55 °C for 1 h. Subsequently, the physisorbed pyridine was removed by heating the catalysts at 100 °C for 1 h. The samples were prepared as KBr pellets and analyzed by infrared spectroscopy in the 1800–1400 cm^{-1} region with resolution of 4 cm^{-1} and 16 scans.