



## Synthesis, characterization and catalytic activity of meso-niobium phosphate in the oxidation of benzyl alcohols

Michele C. Reis<sup>a</sup>, Suellen D.T. Barros<sup>a</sup>, Elizabeth R. Lachter<sup>a,\*</sup>, Rosane A.S. San Gil<sup>b</sup>, Jhonny H. Flores<sup>c</sup>, Maria I. Pais da Silva<sup>c</sup>, Thomas Onfroy<sup>d</sup>

<sup>a</sup> Universidade Federal do Rio de Janeiro – UFRJ, Laboratório de Polímeros e Catálise, Instituto de Química, CEP 21949-900 Rio de Janeiro, Brazil

<sup>b</sup> Universidade Federal do Rio de Janeiro – UFRJ, Laboratório Multiusuário de RMN de Sólidos, Instituto de Química, Rio de Janeiro, Brazil

<sup>c</sup> Departamento de Química, PUC-RIO, Rio de Janeiro, Brazil

<sup>d</sup> UPMC Univ Paris 06, Laboratoire de Réactivité de Surface, CNRS-UMR 7197, Ivry sur Seine, France

### ARTICLE INFO

#### Article history:

Received 14 November 2011

Received in revised form 2 April 2012

Accepted 7 May 2012

Available online 28 July 2012

#### Keywords:

Oxidation

Niobium phosphate

Niobia

Mesoporous materials

Benzyl alcohol

### ABSTRACT

In this work mesoporous niobium phosphate was synthesized hydrothermally by using SDS as the structure directing agent. The catalysts were characterized by N<sub>2</sub> adsorption, DRX, <sup>31</sup>P MAS NMR and FTIR. The activity of commercial and synthesized niobium phosphate catalysts were evaluated through the oxidation of benzyl alcohol and 1-phenylethanol in the presence of hydrogen peroxide. Good conversion and selectivity to oxidation products were obtained in mild conditions.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

The selective oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis. The oxidation products are intermediates in perfumery, pharmaceutical and agrochemical industries [1–4]. Non-catalytic oxidation involves the use of stoichiometric quantities of high oxidation state Cr, Mn or Os reagents that are often toxic, corrosive and expensive [5,6]. Furthermore, benzaldehyde can be obtained by hydrolysis of benzyl dichloride, although traces of chlorine are present in the product [7]. The liquid phase oxidation of toluene also produces benzaldehyde but the reaction is usually carried out in organic solvents which are environmentally unfriendly and whose selectivity is very poor [7]. Many efforts have been made in order to develop alternative environmentally friendly catalytic oxidations and also to reduce the volume of by-products formed in the overall synthetic route [1,8–10].

The use of hydrogen peroxide and heterogeneous catalytic systems in oxidation reactions has received some attention in the last years. Various heterogeneous catalysts have been employed in

oxidation reactions, such as TS-1, MO<sub>x</sub>–SiO<sub>2</sub> and metal phosphates [6,11].

The selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide was evaluated using heterogeneous catalysts such as Au/U<sub>3</sub>O<sub>8</sub> [12], hydrotalcite [13], Sn-MCM-48 [14] and ZSM-5 [15]. Recently vanadium phosphate has been evaluated in the oxidation of benzyl alcohol with molecular oxygen in water and the selectivity to benzaldehyde was 93.1% [4]. The synthesis of micro and mesoporous metal phosphates has attracted widespread attention from both academia and industry because of their high potential to various applications [16]. Efforts have also been made in developing new applications of niobium catalysts for chemical processes [17,18]. Mal et al. [19,20] evaluated niobium phosphate as catalyst in the oxidation reaction of naphthol and phenol with hydrogen peroxide. The authors found high selectivity in oxidation products in both reactions [19,20].

Our group has been evaluating niobium based catalysts in organic reactions such as oxidation of benzyl alcohol and benzylation of aromatic compounds. The results evidenced the high catalytic activity for these reactions [21–24]. However, to the best of our knowledge, the use of niobium phosphate as catalysts for alcohols oxidation has not been reported until now.

In this work the mesoporous niobium phosphate was synthesized hydrothermally by using SDS as the structure directing agent. Commercial and as-prepared niobium phosphate were

\* Corresponding author. Tel.: +55 2125627140; fax: +55 2125627256.  
E-mail address: [lachter@iq.ufrj.br](mailto:lachter@iq.ufrj.br) (E.R. Lachter).

characterized by N<sub>2</sub> adsorption, DRX, <sup>31</sup>P MAS NMR, FTIR and the activities toward the oxidation of benzyl alcohols in presence of hydrogen peroxide were evaluated.

## 2. Experimental

### 2.1. Materials

Benzyl alcohol, 1-phenylethanol, hydrogen peroxide 30%, niobium pentachloride, SDS and acetonitrile, commercial grade products, were used as received. Four niobium catalysts were studied: niobium phosphate (ADF/2043, named NbP-C), niobic acid (HY-340 named NbO) – supplied by CBMM (Araxá, Brazil), and mesoporous materials (NbP-S1 and NbP-S2) prepared by a surfactant method.

### 2.2. Synthesis of niobium phosphate

Initially 10 g NbCl<sub>5</sub> were solubilized in 200 mL of deionised water. After addition of 0.28 mol L<sup>-1</sup> phosphoric acid (H<sub>3</sub>PO<sub>4</sub> 85% aq.) the system was stirred for 30 min. After this time approximately 15 mL of NH<sub>4</sub>OH 28–30% aq. were added. The mixture was filtered and washed with deionised water to remove chloride ions. The white solid was transferred to a becher and 40 mL of an aqueous solution of sodium dodecyl sulfate (SDS) at 0.57 mol L<sup>-1</sup> were added. A white suspension was obtained under stirring for 30 min. 2 mL of H<sub>3</sub>PO<sub>4</sub> 85% aq. were added, the pH was adjusted by adding 2.8 mL of NH<sub>4</sub>OH to set pH = 4 and the mixture was stirred again for 30 min. The gel obtained was transferred to an autoclave for static hydrothermal treatment in an oven at 65 °C for 48 h. After this time, the material was filtered by using a Buchner system. The resulting gel was submitted to a soxhlet extraction by using HCl/EtOH 0.1 mol L<sup>-1</sup> in order to extract the surfactant (SDS). Finally the product (named NbP-S1) was oven-dried and calcined at 550 °C. Another material (named NbP-S2) was prepared as described above but in an open system.

### 2.3. Characterization

Specific surface area and adsorption isotherms of nitrogen at –196 °C were measured on an ASAP 2010 apparatus (Micromeritics). All samples were outgassed first at room temperature then at 300 °C to a pressure < 0.2 Pa. The surface areas were determined by the BET method, the pore size distributions by the BJH method and the total pore volume from the amount of N<sub>2</sub> adsorbed up to P/P<sub>0</sub> = 0.97.

X-ray diffraction (XRD) analyses were performed in a diffractometer model XRD Ultima IV Rigaku. Cu Kα radiation was used with 40 kV of voltage and current of 30 mA. The diffractograms were recorded in increasing Bragg angles (2θ), starting from 10 to 80°, with a 0.05° step for each 2 s.

<sup>31</sup>P MAS NMR spectra were obtained on a Bruker Avance III-400 spectrometer, operating at 162.05 MHz. H<sub>3</sub>PO<sub>4</sub> 85% was used for chemical shifts reference (δ = 0.0 ppm).

FTIR analysis of the structure of the samples were carried out in a Perkin Elmer Spectrum One spectrophotometer, between 4000 and 400 cm<sup>-1</sup>.

Analysis of the acidic properties of samples was performed by adsorption of pyridine followed by infrared spectroscopy. Samples were pressed at ~1 ton cm<sup>-2</sup> into thin wafers of ca. 8 mg cm<sup>-2</sup> and placed inside the IR cell. Before pyridine adsorption/desorption experiments, the wafers were thermally treated at 300 °C in static conditions: 1 h in O<sub>2</sub> (16 kPa) and 1 h under secondary vacuum. These wafers were contacted at room temperature with gaseous pyridine (200 Pa) via a separate cell containing liquid pyridine. The

**Table 1**

Textural properties of niobium phosphate samples and niobic acid.

| Catalyst | S <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> ) | V (cm <sup>3</sup> g <sup>-1</sup> ) | Dp <sup>b</sup> (nm) |
|----------|--|--------------------------------------|----------------------|
| NbO      | 132  | 0.15                                 | 4.5                  |
| NbP-C    | 165  | 0.29                                 | 6.2                  |
| NbP-S1   | 263  | 0.98                                 | 7.5                  |
| NbP-S2   | 110  | 0.56                                 | 9.5                  |

<sup>a</sup> Surface area determined by BET method.

<sup>b</sup> Average pore diameter.

spectra were then recorded following desorption from 150 °C with a Bruker Vector 22 spectrometer (resolution 2 cm<sup>-1</sup>, 128 scans). The reported spectra were obtained after subtraction of the spectrum recorded before pyridine adsorption. The amount of Brønsted and Lewis acid sites titrated by pyridine was obtained using a molar extinction coefficient value of ε = 1.67 cm μmol<sup>-1</sup> for the ν<sub>19b</sub> vibrations of protonated pyridine (Py-H<sup>+</sup>) at ~1540 cm<sup>-1</sup> and of ε = 2.22 cm μmol<sup>-1</sup> for the ν<sub>19b</sub> vibrations of coordinated pyridine (Py-L) at ~1455 cm<sup>-1</sup> [25].

### 2.4. Oxidation reactions

The oxidation reactions were carried out in a round-bottomed 50 mL two-necked flask provided with a reflux condenser and a septum for sample removal. The reaction mixture was magnetically stirred at atmospheric pressure and the temperature was kept at the mixture's reflux temperature by means of a constant-temperature bath. Samples of the reaction mixture were periodically withdrawn and analyzed by high-resolution gas chromatography. In a typical run 21 mmol of benzyl alcohol, 42 mmol of hydrogen peroxide 30% and 10% (w/w) of catalysts and 23.6 mL of acetonitrile were used as solvent. The variations of the substrate (benzyl alcohol or 1-phenylethanol) and product contents (benzaldehyde or acetophenone) were followed by using a VARIAN model 3800 gas-chromatograph equipped with a hydrogen flame ionization detector system and a capillary column (VA-5, 30 m, 0.32 mm ID, 1 μm df). The temperature was programmed from 50 °C to 180 °C with H<sub>2</sub> as the carrier gas at a rate of 2 mL min<sup>-1</sup>. Alcohol conversion was calculated taking into account the response factor which was determined experimentally.

The identification of the products obtained in the oxidation reaction was carried out by gas chromatography–mass spectrometry analysis (GC–MS) on an HP 6890, utilizing a DB-5 (30 m) fused silica column at the same temperature conditions with He as the carrier gas.

### 2.5. Acetalisation reactions

This reaction was studied to evaluate the relative acidity of the catalysts. The reaction was carried out in a 25 mL round-bottom two necked flask outfitted with a condenser and a septum for sample removal. In a typical run, hexanal (8 mmol, 0.8 g), ethylene glycol (16 mmol, 0.99 g) were added to the activated catalyst (0.05 g). The reaction mixture was magnetically stirred at atmospheric pressure and heated by means of a constant temperature bath (60 °C). The degree of hexanal conversion was analyzed periodically by gas chromatography (VARIAN, 3800). The product was also identified by GC/MS (HP5890 series II/HP5972 series, respectively).

## 3. Results and discussion

The textural properties of niobium catalysts are presented in Table 1.

Download English Version:

<https://daneshyari.com/en/article/55163>

Download Persian Version:

<https://daneshyari.com/article/55163>

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