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Modified niobia as a bifunctional catalyst for simultaneous dehydration and oxidation of glycerol

Luiz C.A. Oliveira[a,*], Marcio F. Portilho[b], Adilson C. Silva[a], Hosane A. Taroco[a], Patterson P. Souza[c]

[a] Departamento de Química, Universidade Federal de Minas Gerais, Av. Antônio Carlos 6627, Campus Pampulha, 31270-901, BH-MG, Brazil
[b] CENPES-Petrobras, Cidade Universitária, Q7. Ilha do Fundão, 21949-900, Rio de Janeiro-RJ, Brazil
[c] Centro Federal de Educação Tecnológica de Minas Gerais, CEFET-MG, Av. Amazonas 5253, 30421-169, BH-MG, Brazil

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ABSTRACT

The niobia (Nb_2O_5) obtained in this study was modified by pretreatment with hydrogen peroxide to produce a bifunctional catalyst ($Nb_2O_5//H_2O_2$) with both acidic and oxidizing properties. The oxidizing properties of niobia were obtained by the generation of peroxo groups on the catalyst surface. The catalytic conversion of glycerin showed high activity using H_2O_2 as the oxidant. The catalytic tests monitored by mass spectrometry (ESI-MS) suggested the formation of ethers obtained by the condensation of glycerol (m/z = 167, 223, 240). Furthermore, it was observed that the modification of the catalyst directs the formation of larger molecules such as triglycerol compared to niobia without pretreatment with H_2O_2.

1. Introduction

Compared to diesel fuel derived from petroleum, biodiesel can reduce approximately 78% of carbon dioxide emissions, considering the absorption of this small molecule by plants [1,2]. It also reduces smoke emissions by 90% and virtually eliminates emissions of sulfur oxides and can be used in any diesel engine cycle, with little or no adaptation [1–4]. In this context, biodiesel appears as a promising energy source that would cause less environmental impact, especially in reducing emissions of gases like CO_2, carbon monoxide, sulfur oxides (SOx), total hydrocarbons and most toxic hydrocarbons, which present risks to public health because of their potential carcinogenic properties [3]. Biodiesel production from various sources has been stimulated in many countries, especially in Europe. In 2008, the Brazilian government promoted a national program for the production and use of biodiesel, which provides a mixture of 2% biodiesel in diesel fuels (B2) as of 2008, and up to 10% (B5) by 2013 [3]. On the other hand, the production of this fuel has some limitations, such as the generation of large amounts of glycerol as a byproduct. Currently, the Brazilian market consumes about 40,000 tons/year of glycerol, while production has risen to about 150,000 tons/year [1]. This scenario seems to indicate that the viability of the biodiesel program is directly related to the production of new economically viable products from biodiesel byproducts, especially glycerol.

Although the use of biodiesel has many environmental benefits, the production of biodiesel results in a significant waste product, glycerol. The goal of this study is to obtain products such as di and triglycerols from glycerol using catalysts based on modified niobia. The motivation is to provide value-added products from biodiesel by-products, such as di- and tri- glycerols, which can be used as fuel additives [1].

The scientific literature presents several studies aimed at producing new compounds from glycerol [5–8]. Some researchers have studied the production of fuel additives [9], but the extreme conditions used and the difficult separation of homogeneous catalysts from the reaction medium make the process expensive. Studies of glycerol conversion have also implemented the use of heterogeneous catalysts, mainly using materials with acidic functionality such as zeolites, alumina silicates and niobium oxide [10]. Additional research has pursued the conversion of glycerol to polyglycerols and polyglycerol-esters that can be used as new materials for surfactants, lubricants, cosmetics, and food additives [6].

In recent years, niobium-based systems have received special attention due to their catalytic activity in several important chemical processes, particularly when high acidity and water tolerance are needed in the processes [11–13]. Nb_2O_5 has been widely used as a catalyst in reactions for dehydration, hydration, etherification, hydrolysis, condensation, dehydrogenation, alkylation,

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[*] Corresponding author. Tel.: +55 31 3409 6384; fax: +55 31 34095700.
E-mail address: luizoliveira@qui.ufmg.br (L.C.A. Oliveira).

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photochemical and electrochemical polymerization and oxidation [14–17]. In this study, Nb_2O_5 was synthesized and modified by treatment with hydrogen peroxide aiming to generate a bifunctional catalyst ($Nb_2O_5//H_2O_2$), *i.e.*, with both acidic and oxidizing properties. The catalysts were tested in the simultaneous dehydration and oxidation of glycerol to obtain ethers because these compounds can be employed as bio-additives for other fuels.

2. Materials and methods

2.1. Synthesis and characterizations

Nb_2O_5 (niobia) was prepared by treating 14 g of $NH_4[NbO(C_2O_4)_2(H_2O)]\cdot(H_2O)_n$ with NaOH (50 mL, 1 mol L^{-1}), followed by heating at 60 °C for 72 h [18]. This material was used as a precursor for the preparation of treated niobia ($Nb_2O_5//H_2O_2$), obtained by treating pure niobia (300 mg) with hydrogen peroxide 30% (4 mL) in water (80 mL) for 30 min at room temperature. The yellow solid was then filtered, washed with distilled water and dried at 60 °C for 12 h.

The particle diameter distribution and zeta potential variation of aqueous suspensions of the powder as a function of pH was measured by electrophoretic mobility using a Zetasizer 3000 (from M/s Malvern Instruments Ltd., UK) equipment. The Nb_2O_5 and $Nb_2O_5//H_2O_2$ aqueous solutions were prepared in Milli-Q water at a concentration of 0.33 g L^{-1}. Disintegration of particles was achieved using sonication for 20 min. The pH levels were adjusted using solutions of KOH and HCl, both at a concentration of 0.25 mol L^{-1}.

Nitrogen adsorption/desorption isotherms were obtained on a Micromeritics ASAP-2000 instrument. The specific surface area was calculated using the BET model. The pore size distribution was calculated based on the density functional theory (DFT).

The transmission electron microscopy (TEM) images were taken with a JEOL transmission electron microscope (model JEM 2000EXII).

The IR spectra were acquired with a Shimadzu FTIR (model IRPrestige-21) with IRsolution software. Accessories were used for attenuated total reflection (ATR-8200AH with ZnSe prism). The spectra were obtained from an average of 20 scans with a resolution of 4 cm^{-1}. The wavelength range measured was 4000–400 cm^{-1} using an IRPrestige-21 detector and a DLATGS Beam splitter (KBr/Ge).

2.2. Catalytic tests

Glycerol conversion was performed using H_2O_2 (30%, v/v) as the oxidizing agent. The catalytic tests were performed at 200 °C, using 10 mL of glycerol (1.15 mol L^{-1}) and 10 mg of catalyst in the presence of H_2O_2 (0.10 mL) in a batch reactor for 3 h at pH 6. The products of the reaction were analyzed by GC–MS (Shimadzu) and electrospray ionization mass spectrometry (ESI-MS) (Agilent). The percent conversion of glycerol was investigated by integrating the peak of glycerol to the total ion content (TIC), obtained before and after the reaction with the catalyst. The parameters for the GC–MS analysis were as follows: injector temperature 200 °C, injection volume 1 mL, flow 1.3 mL min^{-1} and Column HP-5 (5% polimetilfenil siloxane). A heating curve was established at 3 °C min^{-1}, from 90 °C to 150 °C. The glycerol reaction progress was monitored with electrospray ESI-MS (Agilent-1100), allowing for the identification of intermediates formed during this reaction. ESI-MS/MS experiments were performed in the positive ion mode. The glycerol decomposition was monitored using ESI-MS in an attempt to identify molecular intermediates. The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 mL min^{-1}. The spectral data obtained were averaged for 50 scans at 0.2 s each. Typical ESI-MS conditions were as follows: heated capillary temperature 150 °C, dry gas (N_2) at a flow rate of 5 L min^{-1}, spray voltage 4 kV, capillary voltage 25 V and tube lens offset voltage 25 V.

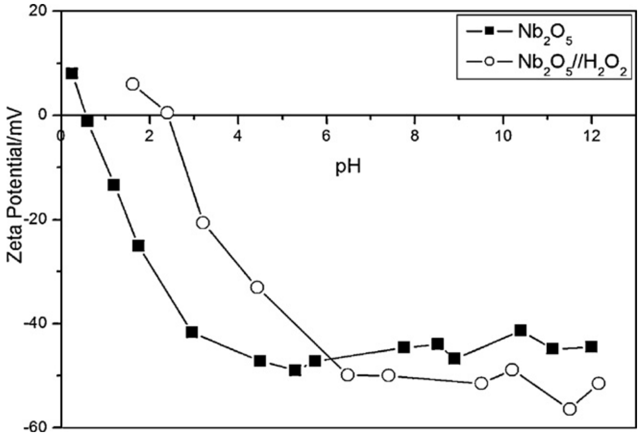

Fig. 1. The pH dependence of zeta potentials for Nb_2O_5 and $Nb_2O_5//H_2O_2$.

3. Results and discussion

3.1. Characterization of the materials

The $Nb_2O_5//H_2O_2$ produced by the method described in this paper had a yellowish (after H_2O_2 treatment) color due to the presence of peroxide groups on the surface of the niobia. These groups, which have oxidizing properties, were generated by treatment of niobia with H_2O_2. The surface changes of the materials were studied by zeta potential measurements. The variation of zeta potential with pH for the aqueous suspensions is shown in Fig. 1. The numerical value of zeta potential was found to vary with preparation conditions of the material and the medium. The zeta potential variation at pH > 6 was less than at pH < 6 in both samples. The $Nb_2O_5//H_2O_2$ suspension was more stable in alkaline medium because of its high zeta potential compared with the untreated niobia. The zeta potential was found to be approximately pH 0.57 and pH 2.40 for Nb_2O_5 and $Nb_2O_5//H_2O_2$, respectively. It is likely that there are more negative ions at the Nb_2O_5 particle surface compared to $Nb_2O_5//H_2O_2$. The treatment of Nb_2O_5 with hydrogen peroxide causes great changes in the surface of the material. The

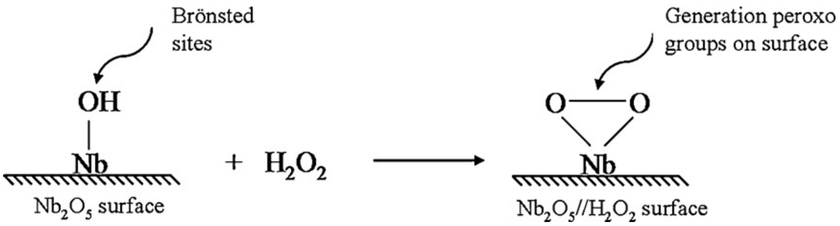

Fig. 2. Scheme of peroxo group formation on the niobia surface.