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# V- or Mo-modified niobium catalysts for glycerin conversion reactions in the presence of $H_2 O_2$

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#### ABSTRACT

In the present work, amorphous niobium oxides with 5% (w/w) vanadium or molybdenum isomorphically substituted into the material structure were synthesized. The materials were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The results show that vanadium and molybdenum were incorporated into the niobium oxide structure with concomitant changes in the morphologic and catalytic properties. Catalytic studies on the conversion of residual glycerin generated during biodiesel production in the presence of  $H_2O_2$  showed enhanced efficiency of ether formation with the vanadium-containing material. The NbV/ethanol/glycerin/250 °C system was found to convert 80% of glycerin. Experimentplanning studies in conjunction with the analysis of the surface response via gas chromatography–mass spectrometry (GC–MS) aided in the determination of the optimal conditions. The catalytic tests monitored by GC–MS showed the formation a mixture of ethers obtained by the condensation of glycerol. Furthermore, it was observed that the modification of the catalyst directs the formation of larger molecules such as ketone mainly in the catalyst containing vanadium.

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# 1. Introduction

Biodiesel is defined as a mono-alkyl-ester-based fuel derived from long-chain fatty acids obtained from renewable sources such as vegetable oils [1]. Transesterification is the most commonly utilized method for the conversion of oils and fat from vegetable sources into biodiesel. The transesterification reaction can be performed using different catalytic systems (acid, alkaline, or enzymatic), different alcohol/vegetable oil ratios, and different temperatures [2]. Biodiesel has been garnering considerable interest in the past few years as a sustainable alternative to petroleum-based diesel with less impact on the environment [1-3]. The production of biodiesel in an alkaline medium generates glycerin as one of the main by-products, which, as the worldwide production of biodiesel increases, may lead to a drastic reduction in the market price of this product [3,4]. One alternative to this problem consists of transforming residual glycerin into synthetic gas compounds, methane, or other products, such as acrolein, ethers, and alcohols [5.6]. In this context, the use of niobium oxide catalysts is an alternative heterogeneous catalyst for the conversion of glycerin into ethers and esters, which are in great demand in the oil industry [7]. Our group has recently published a study in which synthetic niobium oxides were modified to bear oxidizing groups on their surface; the modified niobium oxides were subsequently used as catalysts in the conversion of glycerin into ethers with C6–C9 length chains [8]. The isomorphic incorporation of transition elements into the niobium oxide structure was found to increase its catalytic properties [9]. The association of the niobium oxide with other metals, such as vanadium or molybdenum, may generate materials with high catalytic activity toward the oxidation of organic compounds [7,10]. In fact, some transition elements with high oxidation states, such as niobium, vanadium, and molybdenum, can form strongly oxidizing species upon reaction with  $H_2O_2$ . The highly reactive oxidative species formed - commonly referred to as peroxometalates - are effective in transferring oxygen in oxidation reactions [11].

The present work was aimed at the synthesis of vanadium- and molybdenum-doped niobium oxides and at the evaluation, through experiment planning, of the influence of the presence of a doping metal, the influence of different solvents (H<sub>2</sub>O, *tert*-butyl alcohol,

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Table 1	
Contrasts coefficients, factors, leve	ls, and responses.

Issues	Mean	Contrast coefficients								Responses % conversion	
		$X_1$	<i>X</i> <sub>2</sub>	<i>X</i> <sub>3</sub>	$X_{1}^{2}$	$X_{2}^{2}$	$X_{3}^{2}$	$X_1X_2$	$X_1X_3$	$X_2X_3$	
1	1	-1	-1	0	1	1	0	1	0	0	16
2	1	1	$^{-1}$	0	1	1	0	-1	0	0	19
3	1	$^{-1}$	1	0	1	1	0	-1	0	0	13
4	1	1	1	0	1	1	0	1	0	0	16
5	1	$^{-1}$	0	-1	1	0	1	0	1	0	12
6	1	1	0	-1	1	0	1	0	-1	0	22
7	1	$^{-1}$	0	1	1	0	1	0	-1	0	64
8	1	1	0	1	1	0	1	0	1	0	80
9	1	0	$^{-1}$	-1	0	1	1	0	0	1	14
10	1	0	1	-1	0	1	1	0	0	-1	23
11	1	0	$^{-1}$	1	0	1	1	0	0	-1	56
12	1	0	1	1	0	1	1	0	0	1	68
13	1	0	0	0	0	0	0	0	0	0	19
14	1	0	0	0	0	0	0	0	0	0	19
15	1	0	0	0	0	0	0	0	0	0	21

*X*<sup>1</sup> − Solvent (%, v/v): (−1) *tert*-butyl alcohol 10%; (0) water 10%; (+1) ethanol 10%.

 $X_2$  – Catalysts: (-1) pure Nb; (0) NbV; (+1) NbMo.

X<sub>3</sub> – Temperature (°C): (-1) 150; (0) 200; (+1) 250.

or EtOH), and the influence of temperature in the conversion of residual glycerin from biodiesel production. The conversion of glycerin and the formation of its products were detected using gas chromatography-mass spectrometry (GC-MS).

#### 2. Materials and methods

## 2.1. Preparation and characterization of the catalysts

Niobia (Pure Nb) was prepared by slow dropping of an 1 mol L<sup>-1</sup> NaOH solution in a 500 mL Teflon beaker containing 100 mL 0.26 mol  $L^{-1}$  solution of NH<sub>4</sub>[NbO(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)](H<sub>2</sub>O)n, kindly donated by CBMM - Companhia Brasileira de Metalurgia e Mineração (Araxá, state of Minas Gerais, Brazil) at 70 °C under vigorous stirring. The solids obtained were washed with distilled water until neutral pH. The Mo (NbMo) and V (NbV) substituted niobia were prepared from NH<sub>4</sub>[NbO( $C_2O_4$ )–(H<sub>2</sub>O)](H<sub>2</sub>O)n (1.7 mol L<sup>-1</sup>) and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O or Na<sub>3</sub>VO<sub>4</sub> solutions (0.09 mol  $L^{-1}$ ) by precipitation with concentrated ammonium hydroxide. The precipitates were washed with water, dried at 70 °C for 12 h. The treatment with hydrogen peroxide was performed treating the previously synthesized niobium oxide (300 mg) with 8 mL of aqueous hydrogen peroxide 30% (v/v) and 80 mL of water for 60 min. After these contact times the solids were washed with distilled water and oven dried for 12 h at 70 °C. Spectra were recorded in a Digilab(Excalibur, FTS 3000) FTIR spectrometer and processed with IRDM (IR data manager) software using the KBr pellet technique. The powder XRD data were obtained in a Rigaku model Geigerflex using Cu K $\alpha$  radiation scanning from 2 to 75° at a scan rate of 4° min<sup>-1</sup>. A scanning electron microscope (SEM) manufactured by JEOL Ltd., was used. SEM was coupled with EDS/INCA 350 (energy dispersive X-ray analyzer) manufactured by Oxford Instruments. The transmission electron microscope (TEM) images of all samples were taken with a JEOL transmission electron microscope model JEM 2000EXII.

## 2.2. Catalytic tests

The catalytic tests were performed at 150, 200 and 250 °C, using 20 mL of glycerol (1.15 mol L<sup>-1</sup>) and 10 mg of catalyst in the presence of  $H_2O_2$  (1.00 mL) in a batch reactor for 4 h at pH=6. The products of the reaction were analyzed by GC–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 mLmin<sup>-1</sup> and Column HP-5 (5% polimetilfenil siloxane). A heating curve was established at 3 °C min<sup>-1</sup>, from 90 °C to 150 °C. Table 1 presents all details about the experimental conditions of the catalytic tests.



Fig. 1. X-ray diffractograms (a) and FTIR spectra (b) of pure Nb, NbMo and NbV catalysts.



Fig. 2. XPS analyses of pure Nb, NbMo and NbV catalysts.



NbMo

Fig. 3. SEM images of pure Nb, NbV and NbMo catalysts.

## 2.3. Design of experiment (DOE) approach

In order to understand the hole of each relevant variable in doped niobia as catalyst  $3^3$  Box–Behnken designs was performed [12]. Thus, an experimental design set containing three factors (solvent percentage, catalyze and temperature) and three levels, that is low (-1), central (0) and high (+1) with triplicate in central point was carried out. In the present case were studied two variables quantitative (solvent percentage and temperature) and one qualitative (catalyze). Other variables such as reaction time were maintained fixed. Table 1 shows the contrast coefficients, factors, levels, and responses obtained. The statistical analysis involving DOE were performed in Microsoft Office<sup>®</sup> Excel 2007 software.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

The results obtained by X-ray diffraction (XRD) indicate the formation of an amorphous material, and no reflections consistent with the formation of crystalline phases were observed. Additionally, the presence of molybdenum and vanadium was not observed, which suggests the incorporation of these elements into the niobium oxide structure. These results were somewhat expected because the co-precipitation method used in the synthesis (without material calcination) does not induce long-range structural organization, which is a characteristic of crystalline materials [13].

The FTIR spectra of V- and Mo-doped niobium oxides (Fig. 1b) exhibit the characteristic bands of amorphous niobium oxide [14]. The O–H bond stretching bands are evident, especially the one centered at  $3160 \text{ cm}^{-1}$ , which is assigned to the stretching of Nb–OH internal hydroxyl bonds. The band centered at  $1696 \text{ cm}^{-1}$  is characteristic of the angular deformation of water molecules adsorbed onto the surface of the catalyst. Absorption bands centered at  $1402 \text{ and } 1272 \text{ cm}^{-1}$  are associated with the vibration modes of the niobium precursor. The bands located between  $500 \text{ cm}^{-1}$  and  $950 \text{ cm}^{-1}$  are consistent with angular vibrations of the O–Nb–O, O–V–O and O–Mo–O bonds; a broad band centered at approx.  $645 \text{ cm}^{-1}$  with a shoulder at  $895 \text{ cm}^{-1}$  is characteristic of an amorphous material, the presence of which is in agreement with the XRD results.

The catalysts were further characterized using X-ray photoelectron spectroscopy (XPS) (Fig. 2). Fig. 2A, which shows the general spectrum of the catalysts, exhibits signals assigned to Nb3d, Nb3p1, and Nb3p3, plus typical O1s signals assigned to niobium oxides [15]. In the figure inset, the zoomed-in section details the Mo3d (NbMo) signal, but not the V (NbV) one, which might be due to a low concentration of vanadium at the surface (less than 1%). Furthermore, all of the doped material spectra contained signals for sodium, an impurity. Fig. 2B shows an interesting result: the zoomed-in portion of the O1s region reveals, in addition to the typical oxide ( $O^{2-}$ ) signal centered at 530 eV, a shoulder at approximately 533 eV, which is attributed to the peroxometalate group formed at the surface of H<sub>2</sub>O<sub>2</sub>-treated catalysts [15]. These signals are most evident in the spectra of the NbV-doped materials, but also appear in those of the pure Nb materials.

The morphology of the materials (Fig. 3) was characterized using scanning electron microscopy (SEM). EDS chemical analyses were performed in conjunction with the SEM micrographs (Fig. 4). The morphologies of the pure Nb and NbMo, as shown in the SEM images, are similar: both are characterized by a smooth surface with few rough spots. By contrast, the vanadium-modified sample (NbV) exhibited a different morphology, where particle aggregation led to a rougher surface.



Fig. 4. EDS microanalyses of pure Nb, NbV and NbMo catalysts.

EDS analyses (Fig. 4) confirm the presence of vanadium and molybdenum in concentrations of 0.4% and 0.6% (m/m), respectively. Some impurities were detected, mostly sodium and carbon, which had also been observed in the XPS spectra.

#### 3.2. Glycerin conversion: kinetics study

An early kinetic study of glycerin conversion was performed using the catalysts in the presence of  $H_2O_2$ . The profiles of the kinetics curves are shown in Fig. 5.

The vanadium-containing catalyst, NbV, showed the largest conversion of glycerin in the time interval of the study. After 360 min, the NbV, NbMo, and pure Nb catalysts had converted 92, 90, and 69% of the glycerin, respectively. The result obtained for the NbV catalyst is attributed to the presence of a large number of highly oxidative groups at the surface, i.e., peroxo groups, as observed in the XPS spectra. In fact, other authors have already noted that vanadium compounds react more readily with H<sub>2</sub>O<sub>2</sub> to form reactive species that can transfer oxygen to organic substrates [10]. Fig. 5b shows a schematic representation of the entire process involving



**Fig. 5.** Glycerin conversion kinetics using the Mo- and V-modified catalysts at  $250 \degree$ C. Glycerin 90% (v/v); solvent: H<sub>2</sub>O (a). Schematic representation of the peroxo group generation and glycerin conversion (b).

the reaction with  $H_2O_2$  that leads to the formation of a peroxovanadate reactive group at the surface of the catalyst and to the conversion of glycerin. We emphasize that, for studies where solvent and temperature were varied, a reaction time of 4 h was chosen because conversion rates are suitably high in this time period, as demonstrated during the kinetics study (Fig. 5a).

## 3.3. Factorial design analysis

Factorial design is a very useful tool to obtain deeper information about the relationships among the studied variables and to establish the optimum experimental conditions presenting more comprehensive understanding of the investigated system through simultaneous evaluation of variables combined with a reduced number of experiments. In the present case, for the  $3^3$  Box–Behnken design with triplicate in central point, the variables considered were solvent percentage added in glycerin, catalyst and temperature according to shown in Table 1. Analyzing Table 1 under a general optical, it is observed that high response (glycerin conversion) was obtained through experiment 8 (1,0,1), that is, in condition containing ethanol 10%, NbV and 250 °C, while the lower response was obtained in experiment 5 (-1,0,-1), that is, *tert*-butyl 10%, NbV and 150 °C. After the calculations the following model was obtained:

$$\begin{split} \hat{y} &= \underbrace{19.7}_{(\pm 0.67)} + \underbrace{4.00x_1}_{(\pm 0.41)} + \underbrace{1.88x_2}_{(\pm 0.41)} + \underbrace{24.63x_3}_{(\pm 0.41)} + \underbrace{0.29x_1^2}_{(\pm 0.60)} - \underbrace{3.96x_2^2}_{(\pm 0.60)} \\ &+ \underbrace{24.54x_3^2}_{(\pm 0.60)} + \underbrace{0.00x_1x_2}_{(\pm 0.58)} + \underbrace{1.50x_1x_3}_{(\pm 0.58)} + \underbrace{0.75x_2x_3}_{(\pm 0.58)} \end{split}$$



Fig. 6. Surface response to the 3<sup>3</sup> Box–Behnken design studies: A, pure Nb oxide; B, NbV; C, NbMo.

Analyzing the coefficient model within 99% confidence interval, just the coefficient  $X_3$  (temperature) was significant. On other hand, the factors solvent and catalyst in average did not present relevant effects within interval investigated. Since the model did not present lack of fit for 99% significant interval, three surface responses considering variable  $X_2$  fixed in levels -1 (A, pure Nb), 0 (B, NbV) and +1 (C, NbMo) were considered in order to observe the effect of the different catalyst in relation to temperature and solvent in different levels. Through the surfaces it is possible to observer that in average the response tends to increase when temperature is fixed in high level for glycerin added to ethanol 10%, independently to the catalyst used. However, by surfaces was possible also to see that pure niobia presents lower glycerin conversion in comparison with niobia doped with metal. Nevertheless, the higher response obtained was achieved



**Fig. 7.** Glycerol chromatograms (A), detailed pure glycerol (B) and detailed cyclic ethers (C). Evaluation of the influence of solvents: EtOH (black line) and t-But alcohol (blue line). Amount of ether formed at different reaction times (D). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

when NbV was used as catalyst. Finally, the surface response (Fig. 6) modeling study indicates that the increases of temperature will improve the response. Thus, the results suggesting the possibility of the increases in the glycerin conversion taking into account experiment containing as conditions: ethanol 10%, NbV and temperature above to 250 °C. However, it is necessary to know to what extent the temperature increases will be chemical significance, that is, will be practicable to glycerin conversion process. The reactions with higher rates of conversion under the experimental conditions were analyzed in further detail. For this purpose, chromatograms for the products of the conversion reactions with the highest rates were obtained and are summarized in Table 1.

The chromatogram in Fig. 7A–C describes the NbV-catalyzed conversion reactions using ethanol and *tert*-butyl alcohol as solvents. As evident from the results in Table 1, the conversion rate is higher when ethanol is used, probably because of a more



Fig. 8. Glycerol chromatogram – treatment with pure Nb (solid line) and NbMo doped (dash line); solvent: H<sub>2</sub>O.



Fig. 9. Scheme showing the products obtained after glycerol conversion.

favorable reaction with the shorter-chain alcohol. However, the branched-chain alcohol showed a higher selectivity for ethers. Ether production from the large volume of residual glycerin from biodiesel production is considered an added-value product as the worldwide production of this biofuel increases [5]. The detail in Fig. 7B shows the difference in conversion capacity of glycerin and to further product formation in the form of cyclic ethers. In fact, the reaction may involve dehydration steps and a similar process like Mars Van Krevelen mechanism [8] that takes place in two steps: a reaction between the niobia surface and the glycerol, in which the latter is oxidized and the former reduced, followed by the reaction of the reduced oxide with added H<sub>2</sub>O<sub>2</sub> to restore the initial state (Fig. 5b). The presence of vanadium seems to facilitate the formation of groups peroxos by the decomposition of H<sub>2</sub>O<sub>2</sub> compared with pure niobia and Mo-doped catalyst. Based on peak area on the chromatogram the mixtures of cyclic ether correspond to approximately 35% from glycerol conversion in the presence of ethanol as solvent after 1 h of reaction (Fig. 7D).

In addition, multidimensional NMR spectroscopy (do not shown here) and CG-MS confirmed that the while the condensed phase is composed of ethers, esters among other classes of organic compounds, the carbonyl compounds found in the volatile phase are mostly ketones.

The chromatograms in Fig. 8, which characterize the products of the reactions catalyzed by pure Nb and NbMo using water as solvent (the other reactions with higher conversion rates), show different rates for each material: 56 and 68% for Nb and NbMo, respectively. Both reactions produced cyclical ethers as the main product. The structures of such compounds are shown in Fig. 8. Fig. 9 displays a general scheme showing the products formed by glycerol conversion.

## 4. Conclusion

In the present work, niobium compounds that contain Mo and V as doping elements in the niobium oxide structure were synthesized. The insertion of these elements induced significant structural and morphological changes to the catalysts. Their treatment with  $H_2O_2$  appears to promote the formation of highly reactive groups at the surface, which are most prevalent on the vanadium-containing material, and these reaction groups generated the peroxovanadate species.

Based on experiment planning in conjunction with GC–MS analysis, neither the presence of the doping metals nor the use of different solvents influenced the glycerin conversion rate. An increase in temperature was found to aid in the oxidation of residual glycerol to cyclic ethers, which can be used in the oil industry as fuel additives.

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