FULL PAPER

Niobium Compounds in Transesterification Reactions of Soybean Oil: A Promising Use of NbCl$_5$

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Abstract:

In heterogeneous catalysis, many transition metals and its derivatives, such as titanium and iron, have been vastly studied as nanoscale catalysts, but little is known about the use of niobium compounds. Being biodegradable and renewable, biodiesel contribute to the independence from oil and environment protection. In this work we have used different niobium compounds NbCl$_5$, C$_4$H$_4$NNbO$_9$.xH$_2$O, NbPO$_4$ and Nb$_2$O$_5$ synthetized by sol-gel technique with high surface area and with different crystalline structures (amorphous and nano crystalline), as a heterogeneous catalyst in biodiesel synthesis from commercial soybean oil. The commercial and the synthesized niobium oxide were used checking the effect of morphology and acidity presented in the yield of biodiesel synthesis. The results obtained were compared these results with the use of amorphous niobium oxide and another oxide catalyst. The biodiesel obtained was characterized by gas chromatography system equipped with a FID detector. NbCl$_5$ has presented the best yields of conversion among the other niobium derivatives and potential application in Biodiesel synthesis.

Keywords: biodiesel; heterogeneous catalyst; niobium compounds; transesterification

1. Introduction

Biodiesel is a clean, safe and renewable fuel, and have it performance analogous to the diesel obtained from oil [1]. It is made from several natural biological sources, from vegetable and animal feedstock to even algae and waste cooking oil. It is biodegradable, non-toxic, better lubricant and with lower index of gas emission and sulphur content than ordinary diesel [1-3]. The main sources of vegetable oils used worldwide in the biodiesel production are: the palm, soybean, sunflower, coconut, rapeseed and tung [1-4]. This feedstock is mostly reacted with methanol in a transesterification reaction to yield a range of different long-chain methyl esters. The reaction can be catalyzed by bases (NaOH, KOH, carbonates and corresponding alkoxides), mineral acids (sulfuric, hydrochloric and sulphonic), solid acid oxides (TiO$_2$, SnO$_2$, ZnO,

Li$_4$SiO$_4$, Li$_2$SiO$_3$, LiAlO$_2$ and Li$_2$TiO$_3$) and either enzymes like lipases [4-12]. Due to the reversibility of the reaction an excess of alcohol is normally used to shift the equilibrium towards the products (Scheme 1) [3].

The transesterification reaction is the mainly industrial route to the biodiesel production, followed by esterification [2]. The alkaline transesterification is faster than the acidic and for this reason is the most used [13]. However, the use of alkaline or acid catalysts in the biodiesel production have disadvantages such as corrosion and emulsification [14]. To minimize these problems, metallic Lewis catalysts, homo- and heterogeneous, have been used for the esterification and/or transesterification reactions of fatty acids and triglycerides [2, 15]. Heterogeneous systems are active for alcohols with longer carbonic chain, reaching conversions higher than 95%, where neither acid or alkaline

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catalysts are effective, without producing corrosion or emulsion. In addition, the use of

Lewis acid facilitates reuse and recovering the catalys. [16-17].
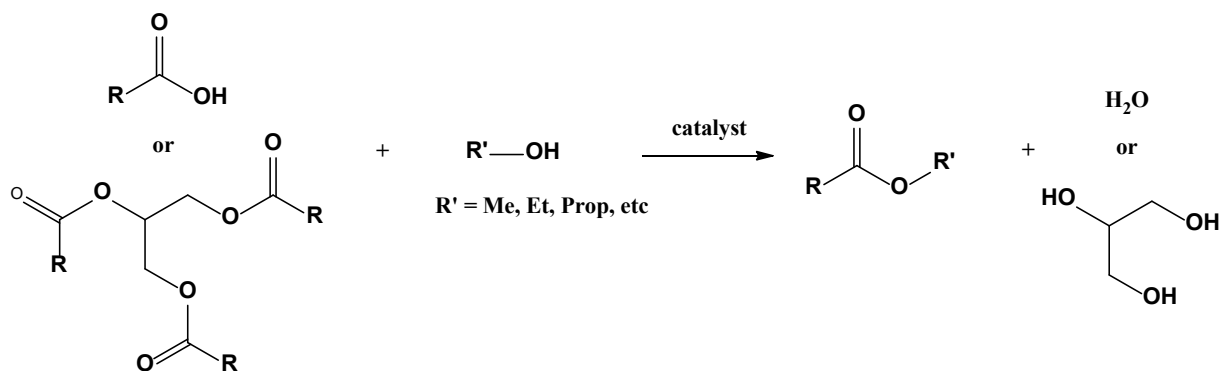
Scheme 1. Biodiesel production reaction.

The heterogeneous catalysts exhibit stability (chemical and thermal) and good availability. The anchoring of the organic groups in their active sites can evidence the porosity property. [18] The use of transition metal oxides exhibited great efficiency of conversion. Misono and co-workers, for instance, have used TiO_2 in different sulfated functionalized structures such as $TiO_2/SO_4^{2-}/(NH_4)_2SO_4$ and TiO_2/SO_4^{2-} resulting in a methyl ester yield of 58.7 and 82.2 %, respectively [19]. In addition, Karmee *et al*. used pure ZnO as heterogeneous catalyst to obtain biodiesel from *Pongamia pinnata* oil in 24 h resulting in a yield of 83 % [20].

Niobium oxides and their derivatives have been described as a compatible heterogeneous catalyst for various organic reactions [21-23]. Recently, Brandão *et al.* described the use of amorphous niobium oxide in the esterification reaction of soybean oil obtaining a maximum yield of 36% after 60 minutes of reaction, and a yield of 3% for the transesterification reaction of the same oil [24]. Srilatha *et al.* detailed a procedure for esterification and transesterification of used cooking oil using niobium oxide impregnated with 12-tungstophosphoric acid resulting in an optimized yield of 90% [25]. Also, Sairre *et al.* reported a method for transesterification of beta-keto esters using Nb_2O_5 on different alcohols giving moderate to good isolated yields (33-98 %) [26]. However, although the number of studies of heterogeneous based catalyst in biodiesel production have increased recently, a few researchers have investigated the use of nano-solid acids and the use of niobium compounds.

Brazil having the largest worldwide known niobium reserve has the great challenge of creating pioneering technologies. Niobium is highly oxophilic and can easily accommodate a number of ligands presenting different coordination numbers. For this reason, its organometallic chemistry is very rich, and a large number of niobium complexes have been reported [27]. Thus, the development of newest niobium compounds nanostructured and amorphous catalysts emerges as sustainable solution. Nano-structured particles can achieve large surface area, increasing the exposure of the reagents in the active sites, producing higher yields in mild reactional situations [18].

In this work we have investigated the catalytic activity of various niobium-based compounds on the transesterification of soybean oil using methanol. The niobium compounds tested were $NbCl_5$, $C_4H_4NNbO_9 \cdot xH_2O$, $NbPO_4$ and Nb_2O_5 synthetized by sol-gel technique with high surface area and with different crystalline structures (amorphous and nano crystalline). The product was characterized and quantified by gas chromatography.

2. Results and Discussion

Synthesis of Nb_2O_5

White powders were obtained for both precursor resins that were calcined at 300 to 700 °C for 1h. This suggests the complete decomposition of organic residues derived from alkoxide formation, as shown at Scheme 2.

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Subsequently, the newly catalyst was pulverized using mortar and pestle and stored for posterior

XRD characterization.

$$NbCl_5 + BuOH \longrightarrow NbCl_{5-x}(OBu)_x + x\ HCl \xrightarrow{\Delta} Nb_2O_5 + CO_y + x\ H_2O$$
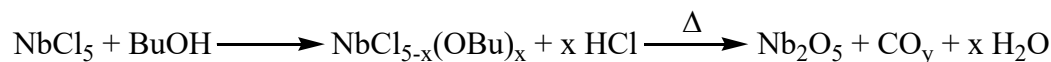
Scheme 2. Niobium oxide structures reaction.

XRD characterization

The diffractograms for the commercial niobium pentoxide showed a characteristic halo diffraction of amorphous materials. However, when the samples were treated at 400 and 500 °C, the diffractograms indicated characteristic peaks of the hexagonal crystalline phase (JCPDS 28-0317), Figure 1. From the sample treated at 500 °C and more evidently in the treated samples above 600 °C the growth of a second crystalline phase, denoted by the symbol * in Figure 1, is observed according to the orthorhombic crystalline phase (JCPDS 30-0873 – Figure S1 in the Supplementary Material).
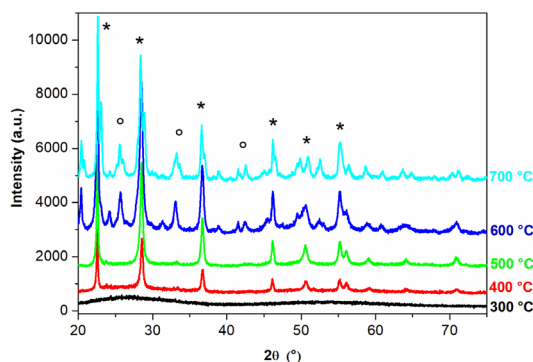

Figure 1. XRD data for the sintered powders at 300, 400, 500, 600 and 700 °C.

The increment in temperature from 600 to 700 °C does not appear to increase the intensity of the orthorhombic peaks. By the analysis of the diffractograms, it is also verified that the relative intensity of the diffraction peaks increases with the temperature elevation from 300 °C, presenting high crystallinity starting from 500 °C. This suggests that in the temperature range studied increasing the heat treatment temperature improves the crystallinity of the material [28]. It is evident, therefore, a correlation between the processes of phase crystallization and elimination of the organic components.

The SEM images are used to analyze the evolution of the morphology of the powders synthesized at 300, 400, 500 and 700 °C, presented in the Figure 2. It is possible to observe in lower temperatures (300 and 400 °C) the particles present more squared shape with size of 200 nm to 1 μm, while increasing the sintering temperature (500 and 700 °C), probably due to the coalescence process, the particles are bigger 200 nm to 2 μm and with more round shape at 700 °C.

In addition, the samples were analyzed according their surface area using the BET technique, as shown in the Table 1. It was possible to observe that the surface area decreases with the increase of the sintering temperature used, where the highest surface area obtained was for the amorphous sample, sintered at 300 °C.

Table 1. Surface area data from synthesized niobium oxides.

| Sintering temperature	Surface area (m^2/g)
300	30.82
400	16.42
600	18.67
700	8.98

Analysis and quantification of fatty acid methyl esters of transesterification reactions

Figure 3 shows the optimized chromatogram with the retention times of the 1.0 μL injection of the methyl esters mixture (standard-primary) of the fatty acids at the concentration of 100mg/L. The elution order and their respective detection times were identified by first injecting each methyl ester. Preliminary analyzes of the soy oil such as saponification, acid index, ester value and all the reactions chromatograms with different niobium catalysts are presented in the supporting information.
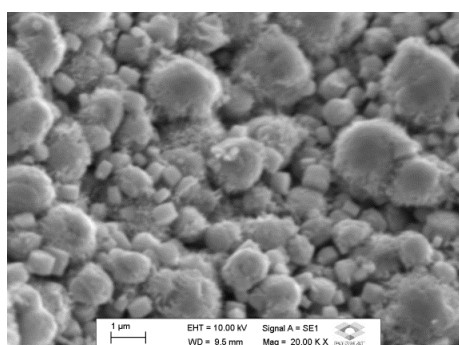
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300 °C
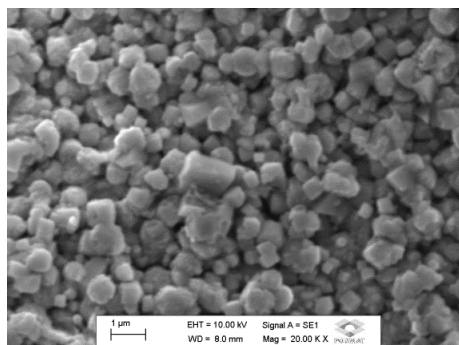
400 °C
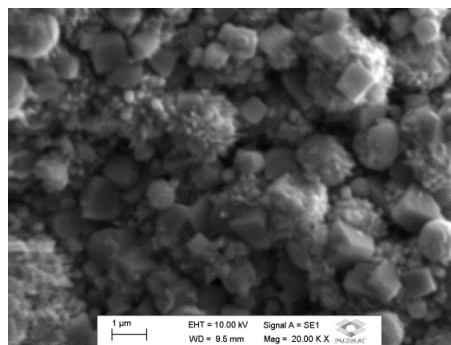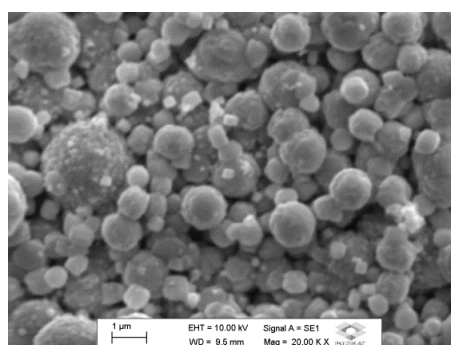

500 °C

700 °C

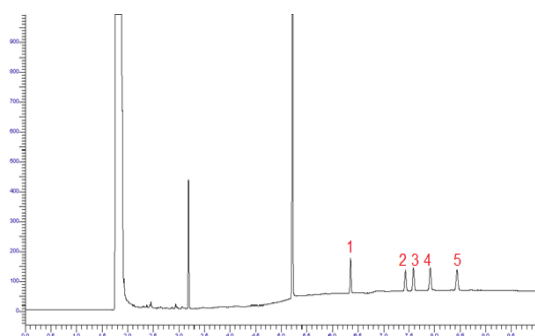**Figure 2**. SEM images of synthetized niobium oxides at different temperatures.

Figure 3. Chromatogram obtained after the injection of 1.0 µL of standard stock solution containing the palmitate esters of methyl (1), methyl stearate (2), methyl oleate (3), methyl linoleate (4) and methyl linolenate (5).

The not referenced peaks on the Figure 3 chromatogram correspond from left to right to heptane (solvent), methyl octanoate and 4-methyl-phenol, respectively. These substances were not quantified in this work. The chromatograms and their quantitative data for the 1.0 µL injections of the transesterification reactions of soybean oil using $NbCl_5$ and the different synthesized niobium pentoxide catalysts (amorphous Nb_2O_5, SG400, SG500, SG600, SG700, SG800) are shown in the SI Figure S3 to S10. Here, we present the chromatogram for the best catalytic performance, $NbCl_5$, Figure 4 and in Table 2 the data obtained by injecting 1.0 µL of the transesterification reaction diluted in heptane (1:1000) using $NbCl_5$ as catalyst.
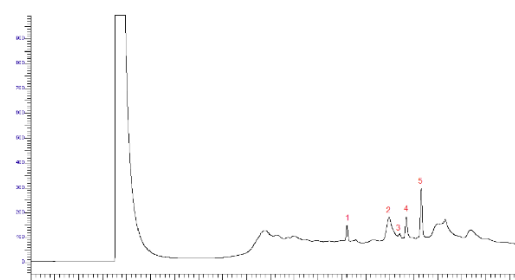

Figure 4. Chromatogram obtained after the injection of 1.0 µL of the transesterification reaction diluted in heptane (1:1000) using $NbCl_5$ as a catalyst containing methyl palmitate, (1), methyl stearate (2), methyl oleate (3), methyl linoleate (4) and methyl linolenate (5).

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Table 2. Data obtained by injecting 1.0 µL of the transesterification reaction diluted in heptane (1:1000) using $NbCl_5$ as catalyst.

Index	Component	Time (min)	Area	Concentration ($\mu g.L^{-1}$)
1	methyl palmitate	6.602	114674.15	72.8
2	methyl stearate	7.498	26422.05	12.9
3	methyl oleate	7.682	238930.49	107.2
4	methyl linoleate	7.886	542520.93	233.4
5	methyl linolenate	8.220	111001.33	46.4

From the obtained concentrations and using Equation (1) it was possible to determine the yields of the transesterification reactions for all the conditions of different catalysts used.

$$\text{Equation (1)} \quad \% \, yield \; = \; \frac{\sum \frac{m_{ME}}{MM_{ME}}}{\frac{m_{TG}}{MM_{TG}} \, x \, 3} \; x \; 100$$

The data for the performance of the others niobium catalysts are summarized in Table 3. The data are presented in descending order of yield.

Table 3. Transesterification reaction of soybean oil using different niobium based catalysts.

Entry[a]	Catalyst	Conversion[b,c] (%)
1	$NbCl_5$	41.6
2	$Nb_2O_5 \cdot xH_2O$	< 1
3	$NbPO_4$	< 1
4	SG700	< 1
5	SG500	< 1
6	SG600	< 1
7	SG400	< 1
8	Nb_2O_5 (amorphous)	< 1
9	$C_4H_4NNbO_9 \cdot xH_2O$	< 1

[a]Reaction conditions: 10 g of soybean oil, 4.5 mL of MeOH, 4h, reflux. [b]Conversion determined by gas chromatography (GC) of the crude methyl esters from the reaction mixture. [c]Entries displayed in descending order of conversion.

The $NbCl_5$ presented the best performance as catalyst in transesterification reaction. $Nb_2O_5 \cdot xH_2O$ (niobic acid), $NbPO_4$, Nb_2O_5 (amorphous), $C_4H_4NNbO_9 \cdot xH_2O$ and the various niobium oxides synthetized in this work (SG400, SG500, SG600 SG700) were inactive and presented very poor yields. Niobium pentachloride is highly electrophilic, making possible act as a Lewis acid, have a low-cost commercial, and has been used by our group and other researchers as an effective catalyst in synthetic methodologies in a variety of reactions, obtaining excellent results [23, 29-30]. Thus, $NbCl_5$ emerge with a good catalyst to transesterification reaction between soybean oil and methanol, in a very efficient manner with good yields, short reaction time and under mild reaction conditions.

3. Material and Methods

The various niobium compounds were used as received: $NbCl_5$ (CBMM), $C_4H_4NNbO_9.xH_2O$ (CBMM), $NbPO_4$ (CBMM) and $Nb_2O_5.xH_2O$ (CBMM). The Nb_2O_5 powders were synthetized by sol-gel (amorphous and two different crystalline structures (hexagonal and hexagonal + orthorhombic).

Preparation of nanostructured Nb_2O_5

The Nb_2O_5 powders were prepared by sol-gel technique using $NbCl_5$ as starting material, following the work of Schmitt *et al.* [31]. Niobium chloride was added to n-butyl alcohol and acetic acid. The clear, viscous solution was allowed to stir until homogenized and sonicated (132 W and 40 Hz) for 60 min. Prior to calcination, the reaction was concentrated to approximately ¼ of its volume. The final resin obtained, viscous and yellowish, were calcined for 1 h in different temperatures (400 to 800 °C) in order to obtain different crystalline phases. The powders were characterized by XRD (Rigaku RINT2000 CuKα, 40 kV and 20 mA), MEV (EVOLS15 – Zeiss. Equipament) and Brunauer–Emmett–Teller (BET) adsorption of nitrogen at 77K in a Micromeritics ASAP 2010).

Biodiesel synthesis

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The niobium based catalyst of each compounds was prepared adding 5% mol of the desired niobium compound in 4.5 mL in anhydrous methanol in 50 mL round flask with 10 g of soybean oil pre heated at 65 - 70 °C and stirred for 15 min. After the catalyst addition, the solution was refluxed for 4 h. The product was washed 3 times with water and brine, extracted in hexane and dried in Na_2SO_4.

The methyl ester content of the product was characterized and quantified by a Clarus 600 PerkinElmer (Waltham, MA, USA) Gas Chromatography (GC) system located at the Laboratory of Organic Synthesis and Processes (LSOP, Unesp, Bauru, SP, Brazil). The GC is equipped with an autosampler, flame ionization detector (FID), an Elite-Wax chromatographic column (30 m x 0.25 mm ID x 0.25 µm) of PEG (polyethylene glycols, polar stationary phase), connected to a protective column of 5m x 0.53mm DI, injection syringe with a capacity of 5.0 µL with a 0.47 mm DI and a liner temperature of 250 °C. The standardized method used a 2.0 µL injection with a POC (Programmable on-column) injection type, 1:20 split ratio, N_2 flow at 450 mL/min. The programmed furnace temperature started at 100 ºC, with a hold of 1.5 min, then heating to 220 °C, with an increase rate of 30 °C/min and hold of 1.5 min, ending with heating up to 223 ºC, with a 30 ºC/min ratio and hold of 3.5 min.

4. Conclusions

The results show that $NbCl_5$ is a promising option to promote the transesterification reaction of soybean, being very active with 41% of conversion, in short reactional time and mild reaction conditions. The synthesized Nb_2O_5 catalysts and commercial niobium compounds show a low Lewis Acid acidity, incapables of active effectively the carbonylic active site on the fatty acid to promote the transesterification reaction of soybean oil with methanol. This work demonstrates that the developing simple and efficient reagents for transesterification reaction become increasingly important in the field of biodiesel synthesis.

Supporting Information

Supplementary information (XRD characterization, chromatograms) is available free of charge at link as PDF file.

Acknowledgments

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