



Optimization of esterification reaction over niobium phosphate in a packed bed tubular reactor

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ABSTRACT

The aim of this work was to investigate the effect of the calcination temperature on the textural properties, structure and acidity of niobium phosphate and the relationship between those properties and the catalytic activity for the continuous esterification reaction using oleic acid and ethanol. For this purpose, samples of niobium phosphate were prepared by calcination at 300, 350, 400, 450, 500 and 600 °C. Despite the good thermal stability presented by niobium phosphate, best results were achieved for samples pretreated at 300 °C, which presented higher acidity, surface area and catalytic activity. For this sample, the experimental conditions of temperature (from 220 to 290 °C), amount of catalyst (from 0 to 0.8 g) and ethanol:oleic acid molar ratio (from 2:1 to 14:1) were studied using design of experiments (DOE) and optimized with canonical analysis. The esterification reaction of oleic acid led to yields of esters up to 70% and conversion up to 90% at optimized conditions.

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1. Introduction

Niobium materials have been shown very promising in heterogeneous catalysis as catalyst components or when they are added in small amounts to catalysts [1]. These materials exhibit special properties that are very important for a good quality catalyst such as stability and strong metal support interaction [2]. In addition to these features, niobium-containing catalysts also have strong acid properties that are preserved in polar liquids [3]. The vast majority of acid solids used as catalysts cannot maintain the desirable activity and stability without deactivation of the acid sites in water or very highly protic medium. In this context, the development of insoluble water-tolerant solid acids, as niobium phosphate, are expected to give great benefits in industrial applications [3].

Niobium phosphate ($\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$) is an amorphous solid acid catalyst ($H_0 \leq -8.2$) with a high ratio of Lewis/Bronsted acidity. This compound shows a very high activity in acid-catalyzed reactions in which water molecules participate or are liberated [3]. Niobium

phosphate shows textural, acidic, and catalytic properties similar to niobic acid and conserves these properties at higher pretreatment temperatures [1]. According to Florentino et al. [4], the BET area of niobic acid becomes practically zero after a pretreatment at 500 °C. However, for niobium phosphate, the BET area remains very high at this temperature, with a surface area of approximately 140 m²/g. Besides that, niobium phosphate maintains higher amount of strong acid sites with increasing pretreatment temperatures than niobium oxide.

Considering the urgency to develop alternatives to petroleum-based fuels, esterification reaction is a very promising route to synthesize biodiesel. Esterification consists in an acid-catalyzed reaction, which produces long-alkyl chain fatty acid alkyl esters that can be used as biofuel [5]. In this reaction, the alcohol in contact with the free fatty acid generates esters as a main product (biodiesel) and water as a byproduct. The advantage presented by esterification reaction is that this route accepts low quality feedstock with high concentration of free fatty acids (FFA) and no formation of glycerin. The vast majority of low cost feedstocks available for biodiesel production present a very high percentage of FFA, making the conventional alkali-catalyzed transesterification impracticable [6]. Because of that, a previous free fatty acids esterification reaction is an alternative process to

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transesterification reaction when low-quality oils and fats are used as feedstock [7].

Considering that esterification reaction involves water as product, niobium-containing materials can be a good option as catalysts for this process. Bassan et al. [5] evaluated two niobium based catalysts (niobic acid, niobium phosphate) in the esterification reaction of fatty acids (C12–C18) with different alcohols (methanol, ethanol, butanol). The results showed that niobium phosphate was the most active in esterification of lauric acid with butanol, at a temperature of 120 °C, molar ratio butanol:acid of 10:1, and reaction time of 4 h. In those conditions, niobium phosphate presented a conversion of 81%, while niobic acid presented a conversion of 41%. According to the characterizations carried out with both catalysts, niobium phosphate showed a surface area and pore volume higher than niobic acid. Besides that, the acid sites quantification indicated that niobium phosphate presented higher concentration of Brønsted acid sites (BAS) than the other catalyst.

Based on the advantages showed for the use of niobium phosphate in the esterification reaction and accounting for the fact that there are much less studies in the literature devoted to biodiesel production using this catalyst, especially in continuous reactor, the objective of this work was to investigate the use of niobium phosphate as a solid acid catalysts in the continuous esterification of oleic acid and ethanol. Our group has already researched this reaction using niobic acid as solid catalyst [8]. Aiming at comparing the materials, we applied the same methodology used in the previous work. Thus, different temperatures of calcination were evaluated. After selecting the best calcination temperature, the experimental conditions of temperature (from 220 to 290 °C), amount of catalyst (from 0 to 0.8 g) and ethanol:oleic acid molar ratio (from 2:1 to 14:1) were evaluated using design of experiments (DOE). It is known that when many parameters affect the biodiesel production, the application of a statistical experimental design is recommended, as this type of approach allows analyzing the influence of the process variables on the response with a smaller number of experiments, which reduces reagent consumption and laboratory work [9]. The effect of each parameter as well as of their interactions on the yield of esters was studied using a central composite design (CCD) coupled with response surface method (RSM) and optimized by canonical analysis technique. The central composite design (CCD), developed by Box and Wilson [10], has been the most accepted experimental design for second-order models and is considered the best alternative to the full factorial three-level design, because this technique presents lower experimental costs. The CCD consists in a first order factorial design (2^k) with additional points (center points and axial points). Those additional points allow the estimation of the coefficients of a second order surface. The response surface methodology (RSM) is an efficient mathematical and statistical approach, which has been successfully employed in process optimization. By using this technique, a lot of information can be obtained: i) the functional relationship between the dependent and independent variables by regression analysis, which also explains the significance of each variable of the experimental design (CCD, in this case), ii) the determination of the levels of independent variables that produce the best response and iii) the suitable function to be used for predicting future response. Besides that, the RSM enables the researcher to identify new operating conditions that produce desired improvements. However, it is necessary to write the second order response surface function in an easier form to be interpreted by the researcher. Thus, the reduction of the response to the canonical form, which is called canonical analysis, allows the determination of the stationary point nature (maximum, minimum or saddle point) and the analysis of the entire response system, by observing the sign and magnitude of the characteristic roots of the

quadratic coefficients matrix.

2. Experimental section

2.1. Materials

Oleic acid (Synth) and ethanol (Synth 99.5%) were used as substrates in the esterification reactions. Solvent n-heptane (Química Moderna, 99.9%) was used for the gas chromatography analysis. For the titration of samples, ethanol (Synth 99.5%), ethyl ether (Dinâmica 98%), sodium hydroxide (Impex 99%), and phenolphthalein indicator (Dinâmica) were used.

The niobia based catalyst used in this work was niobium phosphate, $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ (AD-5970), supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM). The catalyst was prepared by heating $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ at different calcination temperatures, under air flow of 20 mL/min for 2 h. The calcination temperatures tested were 300, 350, 400, 450, 500 and 600 °C.

2.2. Catalyst characterization

The catalysts were analyzed by nitrogen adsorption, thermogravimetric analysis (TGA-DSC), X-ray diffraction in-situ (XRD) and temperature-programmed desorption of ammonia (TPD of ammonia).

BET surface areas were determined on a Quantachrome Nova-1200 apparatus, from nitrogen adsorption measurements at 77 K. The pore volume was estimated using BJH method.

The combined thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis were carried out using Q600 SDT differential analyzer (TA instruments) coupled to a thermo-balance. Niobium phosphate (weight of 12 mg) was placed inside an alumina vessel and heated from 25 °C to 800 °C at a temperature rate of 20 °C/min and air flow rate of 100 mL/min.

X-ray diffraction in-situ was obtained at the XPD-10B beamline, at Brazilian Synchrotron Light Laboratory (LNLS). Samples were sieved (20 mesh) and heated to the desired temperature of calcination, at a rate of 10 °C/min and synthetic air flow rate of 20 mL/min. Then, they were maintained at this temperature for 2 h. Scans were obtained from 20° to 47°, with a step size of 0.003 and a counting time of 1 s, using a wavelength of 1.54056 Å and a resolution of 8 keV.

Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out to evaluate the total acidity of the catalysts. The analyses were obtained using a ChemBET-3000 equipment. Samples (weight \pm 0.18 g) were treated at 300 °C for 1 h, under nitrogen flow rate of 20 mL/min. Then, the adsorption of ammonia was performed at 100 °C for 30 min. After that, the removal of physically adsorbed ammonia was purged for 2 h at 100 °C, under nitrogen flow rate of 20 mL/min. Finally, desorption of chemisorbed ammonia was performed by heating the samples from 100 to 700 °C under nitrogen flow and temperature rate of 10 °C/min.

2.3. Experimental procedure

The continuous esterification reactions were performed using an experimental apparatus, which is composed of: i) a mechanical stirring (Ika, RW 20), ii) a high pressure liquid pump (LabAlliance, Series III), iii) pre-heating zone (made of stainless steel tubing, 218 cm, 1/16 in OD inner diameter 0.79 mm) and fixed bed reactor (made of stainless steel tubing, 29.5 cm, 3/8 in OD inner diameter 6.8 mm) placed in furnaces (heating power of 2000 W) connected to temperature controllers (Novus N1100) and iv) a cooling system. The experimental apparatus is illustrated in Fig. 1.

For the experiments, the substrate composed by ethanol and

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