Fuel Processing Technology 106 (2013) 619–624

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Esterification of fatty acids with alcohols over niobium phosphate

Iria A.L. Bassan [a], Danielle R. Nascimento [a], Rosane A.S. San Gil [b], Maria I. Pais da Silva [c], Carla R. Moreira [c], Wilma A. Gonzalez [d], Arnaldo C. Faro Jr. [a], Thomas Onfroy [e], Elizabeth R. Lachter [a,]*

[a] *Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de Polímeros e Catalise, 21941-900, Rio de Janeiro, Brazil*
[b] *Universidade Federal do Rio de Janeiro, Instituto de Quimica, Laboratório Multiusuário de RMN de Sólidos, Rio de Janeiro, Brazil*
[c] *Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, Rua Marques de São Vicente 225, Gávea, CEP: 22453-900, Rio de Janeiro, RJ, Brazil*
[d] *Instituto Militar de Engenharia, Rio de Janeiro, Brazil*
[e] *UPMC Univ Paris 06, Laboratoire de Réactivité de Surface, CNRS-UMR 7197, Ivry sur Seine, France*

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 20 June 2012
Accepted 6 September 2012
Available online 2 November 2012

Keywords:
Esterification
Niobium phosphate
Niobium
Fatty acids

ABSTRACT

The aim of this study is the evaluation of niobium catalysts (niobic acid, niobium phosphate) in the esterification reactions of fatty acids (C12–C18) with alcohols (methanol, ethanol, butanol). The catalysts were characterized by different techniques (N_2 adsorption/desorption, XRD, FTIR, FTIR of adsorbed pyridine). The niobium phosphate was the most active in esterification of lauric acid with butanol and can be reutilized three times without loss of activity.

1. Introduction

Esterification of carboxylic acids with alcohols is a liquid phase reaction very important in industry due to the application of organic ester products. Recently, the acid-catalyzed esterification of long-alkyl-chain fatty acids has been of great interest because long-alkyl chain fatty acid alkyl esters can be used as biofuel [1,2].

Biodiesel can be produced either by transesterification reaction of vegetable oils and fats and esterification reaction of fatty acids [1,3]. In the transesterification of vegetable oils, a triglyceride (TG) reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acid alkyl esters and glycerol.

The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of alcohol. Transesterification is a an equilibrium reaction, therefore, to obtaining the desired product in high yield, it is necessary to use an excess of alcohol so as to allow its phase separation from the glycerol formed in the reaction medium [4]. The transesterification of vegetable oils using basic catalysts is more studied but it present some disadvantages such as the presence of free fatty acids producing soap and difficulty in the separation of biodiesel [1,3].

Esterification reactions are commonly catalyzed using mineral liquid acids such as sulfuric acid, hydrochloric acid and organic acids like p-toluenesulfonic acid (p-TsOH). Homogeneous catalysts, though effective, lead to serious contamination problems, since they are toxic, corrosive and produce by-products which are difficult to separate from the reaction medium, which results in higher production costs.

The esterification of carboxylic acids by solid acid catalysts is very important, considering the low cost of feedstocks with high concentration of free fatty acids (FFA) and no formation of glycerin [1,3,5]. Moreover, it is expected that a good solid acid catalyst can simultaneously carry out esterification of FFA and transesterification of vegetable oils [1,3,6–8].

The removal, handling and disposal of corrosive waste have motivated a large number of studies concerning the development and applications of heterogeneous catalyst systems. The most used solid acid catalysts for the esterification reaction are the ion-exchange organic resins, such as Amberlyst 15 [8,9], zeolites [10], silica-supported heteropolyacids (HPA/silica) [11] and ZrO_2 [12]. These catalysts exhibit limitations in applicability for catalyzing esterifications due to low thermal stability (Amberlyst 15, <140 °C), mass transfer resistance (zeolite) or loss of active acid sites in the presence of a polar medium [11]. The effect of carbon chain length on esterification of carboxylic acids with methanol using silica-supported Nafion (SAC-13) was studied. A continuous inhibitory effect on activity and in the reusability caused by increasing the chain length of the carboxylic acid was observed [13].

Efforts have also been made in developing new applications of niobium catalysts for chemical processes including esterification [14,15]. The catalytic activity of commercial niobium phosphate was evaluated in the esterification of acetic acid with various alcohols. Conversion higher than 90% of alcohol to ester was obtained in the reaction of n-butyl alcohol with acetic acid. In the reaction of acetic acid with 1-decanol the conversion of the alcohol after 2 h was 27.1% and

---

* Corresponding author.
E-mail address: lachter@iq.ufrj.br (E.R. Lachter).

http://dx.doi.org/10.1016/j.fuproc.2012.09.054

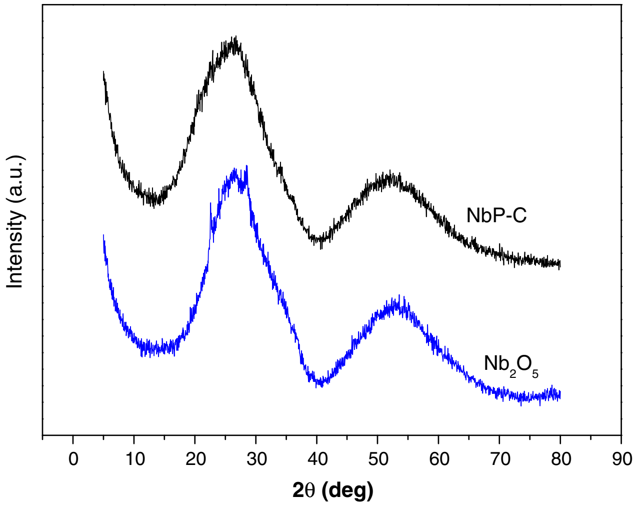

Fig. 1. X-ray diffraction patterns obtained for samples NbP-C and $Nb_2O_5 \cdot nH_2O$.

24.1% with the catalyst calcined at 300 °C and 500 °C, respectively [16]. The esterification of oleic acid with methanol catalyzed by niobic acid was studied and yields 9% of methyl oleate after 5 h [16]. With the niobic acid treated with phosphoric acid the yield of methyl oleate increases to 35%. The authors suggested that the introduction of phosphate group on the niobic acid forms a niobium phosphate that acts as active catalytic sites [17]. Antonelli et al. [18] reported the introduction of strong Brønsted acid sites onto the amorphous niobic acid by treatment of the material with diluted H_2SO_4 or H_3PO_4 solution. They evaluated these materials for acid catalysis reactions and verified that, despite the higher activity after the treatment with mineral acids, deactivation occurs due to leaching of sulfur species [18]. Information about the use of niobium phosphate for the esterification of fatty acids is almost inexistent in the available literature. Continuing our interest in the catalytic activity of niobium compounds in organic reactions [19–25], in this work we present the results about the esterification of fatty acids (C12–C18) with alcohols catalyzed by niobic acid and niobium phosphate.

2. Experimental

2.1. Reactants and catalysts

Fatty acids (lauric, oleic, stearic, from Vetec, Brazil), methanol (Vetec), ethanol (Tedia, Brazil) and 1-butanol (Vetec) were used without further purification. Niobium phosphate (NbP) and niobic acid ($Nb_2O_5 \cdot nH_2O$) were supplied by CBMM and were calcined at 300 °C before use.

2.2. Catalysts characterization

Nitrogen adsorption isotherms at −196 °C were measured in an ASAP 2010 apparatus (Micromeritics). All samples were outgassed first at room temperature then at 300 °C to a pressure of <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_2 adsorbed up to $P/P_0 = 0.97$.

Table 1
Properties of niobium catalysts.

Catalyst	S[a] (m^2g^{-1})	Vp[b] (cm^3g^{-1})	Dp (nm)
NbP	165	0.16	5
$Nb_2O_5 \cdot nH_2O$	152	0.29	6

[a] Surface area determined by BET method.
[b] Pore volume determined around saturation pressure.

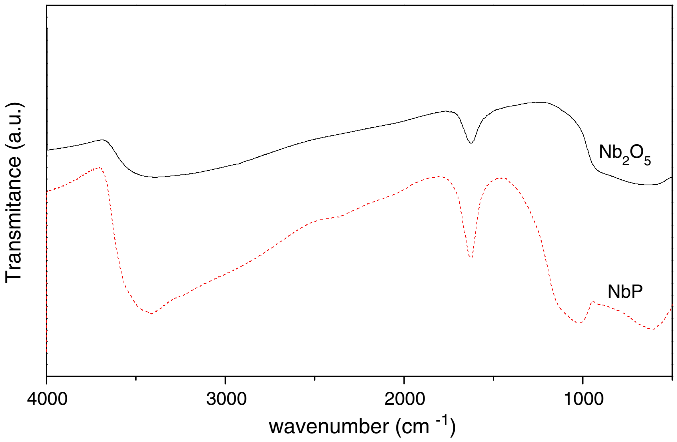

Fig. 2. Structural FTIR obtained for samples NbP and $Nb_2O_5 \cdot nH_2O$.

The catalysts were characterized by X-ray Powder Diffraction collected in a Miniflex Rigaku instrument using Cu Kα radiation. The samples were scanned over the angular range 5–80° (2θ), with a step size of 0.040° and a scan rate of 1 s per step.

Analysis of the acidic properties of the samples was performed by adsorption of pyridine followed by infrared spectroscopy. Before analysis, samples were pressed at ~1 ton cm^{-2} into thin wafers of ca. 10 mg cm^{-2} and placed inside the IR cell.

Before the pyridine adsorption/desorption experiments, the wafers were thermally treated at 300 °C in static conditions: 1 h in O_2 (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 spectra were then recorded following desorption at 150 °C with a Bruker Vector 22 spectrometer (resolution 2 cm^{-1}, 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 by using a molar extinction coefficient value of $\varepsilon = 1.67$ cm μmol^{-1} for the ν_{19b} vibrations of protonated pyridine

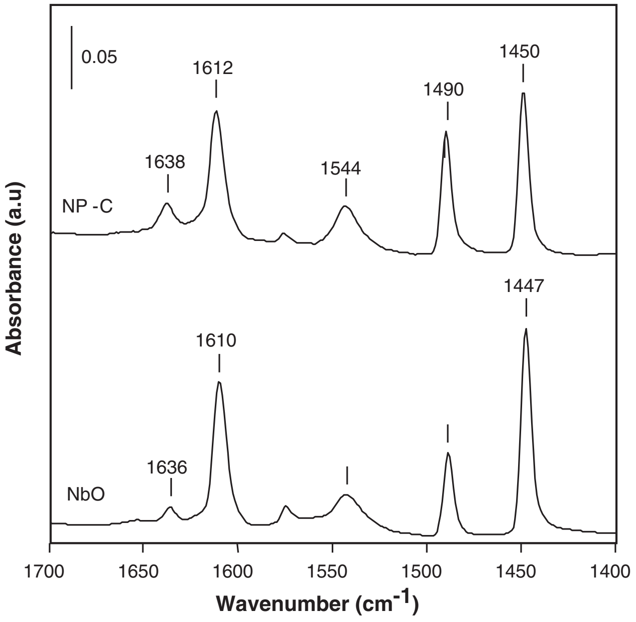

Fig. 3. FTIR spectra of pyridine adsorbed and evacuated at 150 °C on the catalysts.