



Editor's choice paper

Influence of pore size and loading for Nb₂O₅/SBA-15 catalysts on synthetic ester production from free fatty acids of castor oil

C. García-Sancho^a, R.M.A. Saboya^b, J.A. Cecilia^c, A.V. Sales^b, F.M.T. Luna^b,
E. Rodríguez-Castellón^{c,*}, C.L. Cavalcante Jr.^{b,*}

^a Grupo de Energía y Química Sostenibles (EQS), Instituto de Catálisis y Petroleoquímica (CSIC) C/Marie Curie 2, 28049 Madrid, Spain

^b Universidade Federal do Ceará, Depto. de Engenharia Química, Grupo de Pesquisa em Separações por Adsorção, Núcleo de Pesquisas em Lubrificantes, Campus do Pici, Bl. 1010, Fortaleza, CE, Brazil

^c Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Campus de Teatinos, 29071 Málaga, Spain

ARTICLE INFO

Article history:

Received 5 April 2017

Accepted 29 April 2017

Available online 6 May 2017

Keywords:

Niobium oxide
Mesoporous silica
Esterification
Ricinoleic acid
Biolubricant

ABSTRACT

In this study, the influence of the pore size in mesoporous silica (SBA-15) and the loading of niobium oxide species (Nb₂O₅) have been evaluated on the esterification reaction of free fatty acids from castor oil to obtain products that can be used as bio-based lubricant feedstocks. Characterization techniques such as XRD, N₂ sorption, Raman spectroscopy, NH₃-TPD, XPS and TEM have been employed to characterize the synthesized catalysts, demonstrating the high dispersion of the niobia species. The catalytic results showed that the SBA-15 support with an average pore size of 8.5 nm and a loading of 12 wt.% of Nb₂O₅ was the best catalyst to obtain higher conversion values in the esterification reaction of ricinoleic acid. This fact was probably due to the pore diameter of this catalyst was the most suitable for the diffusion of reagents and products. The textural properties were more relevant than the acidic properties for Nb₂O₅ supported on silica catalysts. The reuse data indicated that the conversion values decrease after each cycle probably due to the formation of carbonaceous deposits in the active sites, discarding the niobium leaching which is negligible. The catalytic activity could be almost thoroughly recovered by using a thermal regeneration treatment.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the use of renewable resources and raw materials has attracted considerable attention towards a sustainable development to counteract the drawbacks of traditional fossil fuels such as their unsteady prices or their contribution to greenhouse effect due to CO₂ emissions. Currently more than 60% of lubricants utilized are considered as harmful for the environment and most of them come from mineral oils for which biodegradability is only around 20%. Thus, the development of vegetable oil-based lubricants to replace petroleum-based materials possesses great interest for the scientific community considering that vegetable oils show a high biodegradation degree, up to 99% [1,2]. As the direct use of conventional vegetable oils is limited due to some properties such as their oxidation and polymerization, the formation of branched and

monounsaturated esters produces lubricants with more applications, since they display acceptable oxidative stability and melting points [1,3,4]. Therefore, the free fatty acids (FFA) from biomass are considered as sustainable and alternative candidates for bio-based lubricant production by using an esterification reaction [5,6].

The utilization of different vegetable oils (sunflower, soybean, palm, coconut, etc.) and lineal or branched alcohols also affects the physicochemical properties and applications of biolubricants [6,7]. However, the use of agricultural areas for growing of these plants competes with the production of food and animal feedstocks, being more suitable the non-edible oil crops [8–10]. Castor oil is an abundant non-edible vegetable oil whose worldwide production is of 1.14 Mt cultivated on 12,600 km² and an average seed yield of 902 kg ha⁻¹. Moreover, this plant has low cost, it grows on lands which are not suitable for food crops and tolerates diverse weather conditions, so it is an interesting alternative feedstock [11,12]. Castor oil is different from other vegetable oils being its most abundant fatty acid the ricinoleic acid (nearly 90%) which possesses a hydroxyl group in position 12, providing additional natural chemical functionality so the pertinent esters exhibit inter-

* Corresponding authors.

E-mail addresses: castellon@uma.es (E. Rodríguez-Castellón), celio@gpsa.ufc.br (C.L. Cavalcante Jr.).

esting properties, including high viscosity, improved lubricity and favorably high flash point [12–14].

The classic preparation method of synthetic esters is the esterification reaction between FFA and alcohol in presence of homogeneous acid catalyst, such as H_2SO_4 , HCl , H_3PO_4 or RSO_3H [15,16]. Nevertheless, the conventional mineral acids are corrosive and harmful, being more advisable the use of solid acid catalysts because they minimize environmental damages, they are more easily separated from the reaction medium and they can be reused [17–20]. Several solid acid catalysts have been tested for the esterification of ricinoleic acid by using different alcohols: polyaniline-sulfate [21], organo-sulfonic acids doped polyaniline [22,23], WO_3 supported on porous clay heterostructure with Si-Zr pillars [24] and ion-exchange resins [25]. On the other hand, the synthetic esters produced from 2-ethyl hexanol are attractive for their applications in the cosmetic, pharmaceutical, food and chemical industries and also as components of oil bases and lubricants; thus, the esterification of FFA, such as oleic or palmitic acid, and 2-ethylhexanol has been reported in the literature by employing sulfonic acids or enzymes, as catalysts [15,16,26].

Niobium oxide (Nb_2O_5) has been demonstrated to have interesting acidic properties and to be highly insoluble in water [27–30], which is a key factor considering that H_2O molecules are produced for esterification reaction. Hence, different Nb_2O_5 containing catalysts have been tested for esterification reactions of other fatty acids [31–34]. However, niobium oxide possesses a low specific surface area, being recommendable to employ high-surface supports to improve the dispersion and enhance the number of available active sites. Therefore, the use of mesoporous supports as MCM-41 or SBA-15, which exhibit high surface area and suitable chemical and thermal stabilities, favors the dispersion of the active phase, increasing the available sites of niobium oxide, as previously reported [35–39]. Moreover, the pore size of these materials can be modified by varying the synthesis conditions and using organic swelling agents such as trimethylbenzene [40–42], which could be of great interest due to the large size of the FFA molecules.

The main objective of this study was the synthesis of niobium oxide supported on SBA-15 as acid catalysts, modulating the pore size of the support and the loading of Nb_2O_5 in order to optimize the esterification of ricinoleic acid with 2-ethylhexanol. The influence of the reaction time and temperature on the catalytic reaction was evaluated and the catalysts were characterized to determine their structure–activity relationships. Likewise the reusability of the catalysts was also assessed.

2. Experimental

2.1. Preparation of catalysts

Different mesoporous SBA-15 silica were synthesized following a procedure based on the method previously described by Vilarrasa-García et al. [42]. Firstly, 4 g of Pluronic (P-123, $M = 5800 \text{ g mol}^{-1}$, Aldrich) were dissolved in 144 mL of 1.7 M hydrochloric acid solution under magnetic stirring at 40 °C. Right after, 8.75 mL of the source of silica (tetraethyl orthosilicate, TEOS, Aldrich, 98%) were added dropwise. The final molar composition of the synthesis gel was $\text{P123/SiO}_2/\text{HCl}/\text{H}_2\text{O} = 1/55/350/11100$. The resulting suspension was stirred at room temperature for 72 h for the synthesis at room temperature and 24 h for hydrothermal synthesis. In the latter case, the gel was transferred to a teflon lined reactor and placed in an autoclave, aging the gel at 120 °C for 48 h. Moreover, a third synthesis procedure was carried out using 1,3,5-trimethylbenzene (TMB, Aldrich, 95%) as swelling agent, which was added after the surfactant solution and before adding TEOS. Thus, 4.75 mL of TMB were incorporated dropwise and TEOS was

added 30 min later, following the same procedure than hydrothermal synthesis. In all cases, the solid was recovered by filtration, washed and dried at 60 °C, and then calcined in air at 550 °C for 6 h with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ in order to remove the surfactant. The supports were denoted as SBA_{RT} , SBA_{HT} and SBA_{TMB} for the room temperature, hydrothermal and hydrothermal with swelling agent synthesis, respectively. Likewise, a commercial silica sample (Merck, 40–63 μm), denominated as Si, was employed to compare with the obtained mesoporous silica materials.

Different amounts of niobium oxide were incorporated to the supports by using the incipient wetness impregnation with niobium oxalate (Alfa-Aesar). Thus, aqueous solutions of niobium oxalate in 0.1 M oxalic acid were used to incorporate different amounts of Nb_2O_5 on the supports (2, 4, 8, 12 and 16 wt%). The materials were dried in air at 60 °C after impregnation and calcined at 400 °C for 4 h (heating rate of $2 \text{ }^\circ\text{C min}^{-1}$). These catalysts were named as X-yNb, where X indicated the support (SBA_{RT} , SBA_{HT} , SBA_{TMB} and Si) and y represented the weight percentage of Nb_2O_5 in each catalyst.

2.2. Characterization of catalysts

Powder diffraction patterns were collected on a PANalytical automated diffractometer, EMPYREAN model, using $\text{Cu-K}\alpha$ 1,2 (1.5406 Å) radiation and a last generation PIXcel detector. The database employed were ICSD, PDF 2-2004 and COD of High Score-Plus programme of PANalytical.

The textural parameters were determined from nitrogen adsorption–desorption isotherms at $-196 \text{ }^\circ\text{C}$, obtained using an automatic gas adsorption analyser from Micromeritics (ASAP 2020). Prior to N_2 adsorption, the samples were outgassed at 200 °C and 10^{-4} mbar for 10 h. Surface areas were determined by using the Brunauer–Emmet–Teller (BET) equation and a nitrogen molecule cross section of 16.2 \AA^2 . The Density Functional Theory method (DFT) was employed to determine the pore size distributions.

Raman spectra were recorded on a FT-Raman spectrometer, using a Nd:YAG laser as the excitation source at 1064 nm and the laser power was set to 100 mW. Raman spectroscopy was performed on powder samples without any previous treatment.

The morphology of the catalysts was studied by transmission electron microscopy (TEM), by using a FEI Talos F200X equipment which combined outstanding high-resolution S/TEM and TEM imaging with energy dispersive x-ray spectroscopy (EDS) signal detection, and 3D chemical characterization with compositional mapping.

X-ray photoelectron spectra were obtained with a PHI Versaprobe II with high flux x-ray source providing a focused monochromatic x-ray Al $\text{K}\alpha$ beam of 100 micrometers that is scanned 1400 micrometers (large area) in the sample surface (100 W, 15 kV, 1486.6 eV). High-resolution spectra were recorded at a given take-off angle of 45° by concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV. Each spectral region was scanned several sweeps until a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 1.5×10^{-6} Pa. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine the binding energies of the different element core levels more accurately.

The temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out to evaluate the total surface acidity of the catalysts. After cleaning of the catalysts (80 mg) with helium and subsequent adsorption of ammonia at 100 °C, the NH_3 -TPD was performed by raising the temperature from 100 to 550 °C, under a helium flow of 40 mL min^{-1} , with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$

Download English Version:

<https://daneshyari.com/en/article/4751892>

Download Persian Version:

<https://daneshyari.com/article/4751892>

[Daneshyari.com](https://daneshyari.com)