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Mixed oxides tuned with alkaline metals to improve glycerolysis for sustainable biodiesel production

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ABSTRACT

In this study, monoglycerides were produced as glycerol value-added products via transesterification reaction of methyl stearate. This green and selective process involved catalysis from hydrotalcite-like compounds with different metals incorporated (Li, K or Cs) to improve their basic properties. Layered double hydroxides were obtained by two different methods and activated by calcination. All samples were examined by X-ray diffraction, specific surface area determined by the BET method, temperature-programmed desorption of CO₂ and infrared absorption spectroscopy with Fourier transform for basic sites measurement. Metal content was determined by inductively coupled plasma optical emission spectroscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The hydrotalcite-like compounds modified with monovalent metal ions (Li, K or Cs) with the lamellar structure were synthesized. The metal percentage incorporated was higher for materials modified with Li than for those modified with K and Cs. This fact can be attributed to the lower size of their ionic radii. All mixed oxides presented basic properties. The products were analyzed by gas chromatography. The correlation between the basic properties of the solid catalysts and the activity in the transesterification reaction was investigated. The highest activity was found for the catalyst with Li incorporated by the co-precipitation method with yield values around 78% for monoglycerides. Which also showed the greatest Lewis medium basic sites density, a 31% more than the rest of the materials.

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1. Introduction

A growing interest in the preparation of biofuels from biomass is emerging due to the increased concern about environmental issue [1,2]. In this context, biodiesel has gained considerable attention as a nontoxic, biodegradable and renewable alternative to petroleum-derived fuels. Biodiesel is usually manufactured by transesterification of plant and animal oils with methanol or ethanol, with glycerol as a coproduct [2]. The increase in biodiesel production is generating high amounts of glycerol. Consequently, the price of glycerol has dropped dramatically [3]. Thus, it is desirable to convert low-cost glycerol into value-added chemicals or materials. In addition, glycerol is an environmentally friendly com-

pound containing a highly multifunctional structure, making it a versatile building block for the synthesis of a broad family of valuable derivatives by several catalytic processes involving oxidation [4,5], hydrogenolysis [6–8], dehydration [9], etherification [10], etc. The cost of biodiesel production is still an important aspect. In a first stage, glycerol can be used to reduce the acidity content of the feedstock by the esterification reaction, as Felizardo reported.

One of the promising routes to glycerol valuation is its catalytic esterification to produce monoglycerides, which are important fine chemicals for food, detergent, plasticizer, pharmaceutical and cosmetic formulations [11].

Monoglycerides, the glycerol monoesters, can be obtained by the transesterification (glycerolysis) of fatty methyl esters with glycerol or by the direct esterification of glycerol with fatty acids. However, the three hydroxyl groups in glycerol are not very different in reactivity, thus the product of the direct esterification or transesterification of glycerol with acid and/or base catalysts is a

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mixture of mono-, di-, and sometimes triglycerides depending on the catalyst performed, plus the glycerol that has not reacted.

Heterogeneous catalysis has gained importance in the field of basic catalysis, and different materials such as oxides [12–16], hydroxides [17] and organic modified mesoporous materials [18] have been studied. For this purpose, layered double hydroxides (LDH) have probably been the most studied materials as basic catalysts in the last few years, and there is a vast literature concerning catalysis with this kind of material [19]. Nowadays, hydrotalcite-like compounds have gained special relevance in the transesterification of oils for biodiesel synthesis [20].

LDH are bidimensional anionic clays with an alternating layered structure with positively charged brucite-type layers, where Mg^{2+} cations are substituted by Al^{3+} cations and the interlayers contain the charge balancing anions and water molecules. These compounds are represented by the formula $(M_{(1-x)}^{2+}M_x^{3+}(OH)_2)^{x+}(A_{x/n}^{n-}mH_2O)^{x-}$, where the divalent ion may be Mg^{2+} or monovalent ions such as Li^+ , K^+ , Cs^+ , and the trivalent ion Al^{3+} , Fe^{3+} or Cr^{3+} . The compensating anion (A^{n-}) may be CO_3^{2-} , NO_3^- , Cl^- , SO_4^{2-} , and x can take values between 0.25 and 0.33.

Conventional hydrotalcites generally show low catalytic activity in their original form, but through controlled thermal decomposition, LDH are converted to mixed oxides with high specific surface areas and strong basic sites [21,22]. The basicity can be tuned, and other catalytic properties can be imparted through the incorporation of a range of catalytically active metals in the brucite lattice structure [23–25].

In this paper, the influence of alkaline metals on the structural and catalytic properties of the samples has been studied. These materials were used in the transesterification (glycerolysis) of methyl stearate with glycerol. The precursors and mixed oxides were characterized by different physicochemical methods, such as X-ray powdered diffraction (XRD), specific surface determined by the BET method. The chemical composition of mixed oxides was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), energy dispersive analysis (EDS) and X-ray photoelectron spectroscopy (XPS) for the lithium samples. The density and strength of basic sites of mixed oxides were determined by CO_2 probe molecule, which is one of the most widely used to characterize basic surfaces by infrared absorption spectroscopy with Fourier transform (FT-IR) [26] and temperature-programmed desorption (TPD) [27]. Moreover, the products of transesterification were analyzed by gas chromatography.

2. Material and methods

2.1. Synthesis

The preparative methods adopted in this study were direct co-precipitation and impregnation. In the direct co-precipitation method, the samples were prepared by the low supersaturation method at constant pH (10 ± 0.2), with M^{2+}/M^{3+} constant molar ratio of 3, according to the procedure reported by us elsewhere [22]. Two solutions were prepared. One of them contained $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and the nitrate of the alkaline metal to incorporate them dissolved together in distilled water and the other, 0.085 M of Na_2CO_3 in distilled water. Both solutions were dropped simultaneously into 50 mL of distilled water at 60 mL h^{-1} . The pH was kept constant by adding a 2 M NaOH solution. The co-precipitation was carried out at room temperature, and the gel was continuously stirred magnetically. The mixture was kept under magnetic stirring for 4 h. The precipitate was aged in the mother liquor overnight at room temperature, and then the precipitate was separated and washed with distilled water, by centrifugation at

2800 rpm, until pH 7. The resulting material was dried overnight at 90°C in the open air. Finally, the solids were calcined in open air at 450°C for 9 h [22].

In the impregnation method, a salt aqueous solution of the metal ions was added to the Mg-Al mixed oxide obtained by co-precipitation. The theoretical metal loading was 10 wt%. The suspension was kept under stirring at room temperature for 20 min and then, it was dried in a vacuum rotary evaporator. The resulting solid was dried at 90°C overnight, then it was calcined in air flow at 350°C for 2 h and finally, at 500°C for 8 h [23].

LDH samples and mixed metal oxide (MMO) samples were named by the symbol of the third metal incorporated followed by Mg-Al, and the symbol used as subindex corresponds to the synthesis method: co-precipitation (C) and impregnation (I). Thus, in the case of the sample with lithium incorporated: (Li-Mg-Al)_i, (Li-Mg-Al)_c.

2.2. Characterization

All samples were examined by XRD on a Philips PW 3838 diffractometer, using monochromatic Cu K radiation ($\lambda = 1.54 \text{ \AA}$) at a scan speed/rate of $\frac{1}{4}^\circ \text{ min}^{-1}$ in a range between 10° and 80° and a step size of 0.02° .

The specific surface areas were measured using a Micromeritics ASAP 2000 instrument by single point at $P/P_0 = 0.3$ through the BET method. The precursors were degassed at 200°C and the calcined materials at 390°C , both for 50 min.

The scanning electron microscopy (SEM) studies of the MMO were performed with a JEOL JSM-6380 LV, coupled with an energy dispersion analyzer (EDX) Oxford Instruments model 7582. The specimens were Au coated (sputtering) to make them conductive. The SEM acceleration voltage was 20 kV.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a multitechnique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV and a Mg anode operated at 100W. The working pressure in the analyzing chamber was less than 2.0×10^{-8} mbar. Samples were supported on double-sided Cu tape and previously evacuated for 12 h.

The MMO chemical composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The equipment was a VISTA-MPX CCD Simultaneous ICP-OESVARIAN.

The catalyst basic properties were measured by temperature-programmed desorption (TPD) and Fourier transform infrared spectroscopy (FTIR) of CO_2 . Typically, about 100 mg of the sample is placed in a quartz reactor and pretreated in argon at 100°C for 60 min prior to the adsorption of CO_2 at the same temperature. After the adsorption of carbon dioxide (3 wt% CO_2 in He; $20 \text{ cm}^3 \text{ min}^{-1}$) for 60 min, the catalyst was treated with a flow of helium ($20 \text{ cm}^3 \text{ min}^{-1}$) for 45 min at 100°C in order to remove physically adsorbed CO_2 . The CO_2 -TPD desorption was measured by heating the sample from room temperature to 900°C at a heating rate of $10^\circ\text{C min}^{-1}$. The CO_2 uptake was determined by integrating the detected peaks using the software of the equipment previously calibrated with different amounts of Na_2CO_3 . The CO_2 desorbed was analyzed and quantified by an on-line gas chromatograph (Shimadzu GC-14A) equipped with a TCD.

The structure of CO_2 chemisorbed on the sample was determined by infrared spectroscopy (IR). Data were obtained using a Shimadzu FTIR-8101 M spectrophotometer after CO_2 adsorption at room temperature and sequential evacuation at 25, 100, 200, 300, and 400°C . Spectra were taken at room temperature. An inverted T-shaped Pyrex cell containing the sample pellet was used. The two ends of the short arm of the T were fitted with CaF_2 windows. Finally, the difference spectrum for each sample was obtained by

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