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Zinc glycerolate as a novel heterogeneous catalyst for the synthesis of fatty acid methyl esters

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ABSTRACT

In this work, zinc glycerolate (ZnGly) is studied as a new catalyst for an environmentally friendly production of biodiesel. The solid was prepared by a simple procedure, characterized and studied in the transesterification of soybean oil with methanol.

ZnGly was able to convert soybean oil into fatty acid methyl esters with 66–76% yield and up to 95–97% triglyceride (TG) conversion in the 100–140 °C reaction temperature range studied. The catalyst showed a long life and could be reused for five catalytic cycles without deactivation or selectivity loss.

The catalyst exhibited good tolerance toward 0.5 wt.% water, without important changes in the TG conversion, but with a 23% decrease in FAME yield.

In the presence of 10 wt.% fatty acids, ZnGly showed an almost complete TG conversion with an increase in FAME yield of 51% (93% FAME selectivity at 50 min reaction time). At 140 °C and in acid oil, ZnGly can be easily transformed into Zn carboxylate and partially re-generated in the presence of glycerol.

1. Introduction

Biodiesel is a liquid biofuel produced from animal fats and vegetable oils, of which rapeseed, sunflower and soybean oils are the most commonly used raw materials.

Biodiesel production can be considered an environmentally friendly activity, by contributing to reduce pollution caused by used oils and fats. Biodiesel is a "clean" fuel because it helps to reduce global CO_2 emissions compared to petroleum-derived diesel, it produces less pollutant gases, its combustion generates less SO_2 emissions, it is biodegradable and non-toxic, and has a high level of lubricity.

Biodiesel is used as a source of energy, for example blended with petrodiesel for the mass market (in Argentina a 7% biodiesel blend is currently used) or in small and medium-size agro-industrial activities.

Industrially, biodiesel is produced by transesterification of triglycerides with an alcohol (usually methanol or ethanol) by homogeneous base catalysis (sodium or potassium hydroxide or alkoxide). Small factories with different feed qualities (using refined and reused oils at the same time) generally use batch processing. Continuous processes, however, are more adequate for larger factories that can afford larger staffs and require a more uniform feed.

Homogeneous base catalysts present some disadvantages, such as the formation of soap due to the neutralization of free fatty acids (FFA) present in low-quality oils, or the saponification of triglycerides in the presence of water.

The use of a heterogeneous catalyst would simplify the separation and purification steps. There is a growing interest in finding a solid catalyst that is active in the transesterification of triglycerides, while it is selective with raw materials of low quality, that is to say a catalyst that is stable in the presence of FFA and water. Given that it will be used in "green" processes, it should also be non-pollutant and non-toxic.

In previous works [1,2] on soybean oil transesterification catalyzed by zinc carboxylate salts at 140 °C, the formation of zinc glycerolate (ZnGly) was observed in the reaction medium (for zinc laurate, palmitate and stearate). Zn acetate was less stable, and the transformation started at 100 °C. Similar results were found using zinc hydroxide acetate and zinc hydroxide nitrate salts as heterogeneous catalysts. The former solid transformed into ZnGly in the reaction medium at 100 °C, and the latter at 140 °C.

In view of these results, zinc glycerolate was synthesized, and preliminary experiments at 140 °C [1] showed an oil conversion of 80.2% with a FAME yield of 50.9% in the transesterification of soybean oil with methanol. No reports on the use of Zn monoglycerolate as catalyst in the synthesis of biodiesel were found in the literature. The most similar reference is the use of calcium diglyceroxide as the active phase in the transesterification of triglycerides

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[4–7]. This solid has a similar structure, the same anion, and they are also similar in the sense that both can be formed in the reaction medium if the cation is present.

Zinc glycerolate is classified as non-irritant, and it is widely used in pharmaceutical formulations with therapeutic or prophylactic properties, in cosmetic industries, veterinary product and as a lubricant and as a polymer stabilizer [8–10]. The synthesis of ZnGly is an economical and simple procedure [11]. ZnGly has potential as a new clean catalyst for an environmentally-friendly biodiesel production.

The goal of the present work was to investigate ZnGly as a novel and green catalyst in the transesterification of soybean oil with methanol. Its stability in consecutive reuses, and the effect of water and fatty acid were studied.

2. Experimental

2.1. Catalyst preparation

The zinc glycerolate solid was synthesized according to the procedure reported by Dong and Feldman [11] with slight modifications. The salt preparation was carried out in a Parr reactor under N_2 atmosphere (30 psi). An amount of 0.05 mol zinc acetate dihydrate (99% Sigma–Aldrich) and 3.4 mol of glycerol with 2% of water was fed into the reactor and heated up to 160 °C for 1 h at 500 rpm. The resulting precipitate was filtered, washed with ethanol and dried for 1 h at 40 °C.

2.2. Catalyst characterization

The catalyst structure (synthesized and recovered after reaction) was validated by X-ray diffraction (Philips PW1710, using Cu Kα radiation scan in the 2θ range 2°–60°) and by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Nicolet 6700FT-IR spectrometer).

The morphological properties of the solids were obtained from the N_2 adsorption isotherm at 77 K by the BET method using a Nova 1200e Quantachrome instrument, and the pore size distribution was calculated by the BJH method. The catalyst particle size distribution was evaluated using a Partica LA-950 V2 Laser Diffraction Particle Size Distribution Analyzer (HORIBA), and the morphology of the powder catalysts was analyzed by SEM (JEOL 35 CF scanning electron microscope).

The thermal stability of the catalysts was determined using a thermogravimetric analyzer (Discovery TGA) under N_2 flow from room temperature to 800 °C (at a heating rate of 20 °C/min).

The amount of Zn in the catalysts (before and after reaction) was determined by atomic adsorption spectrometry (AAS, Perkin Elmer Analyst 700).

The acidity of the solid was analyzed by potentiometric titration. The catalyst was dispersed in acetonitrile and titrated with a 0.1 N *n*-butylamine solution dissolved in the same solvent [12].

The basicity of the solid was estimated by the benzoic acid titration method using indicators. A slurry with 100 mg of ZnGly and the indicators (bromothymol blue and phenolphthalein) was titrated with a 0.01 M solution of benzoic acid in methanol [13].

2.3. Catalytic tests

The catalytic tests were carried out in a 600 cm^3 Parr reactor (internal diameter: 64 mm) operated in batch mode, equipped with a 4-angled blade stirrer.

The reaction was studied at 100 and 140 °C, with an agitation rate of 500 rpm, and a reaction time of 2, 4 and 6 h. The raw materials and the catalyst were fed into the reactor and then the system was heated up until reaction temperature was reached. At that moment, the agitation was started and a zero time sample was taken.

For the reaction, soybean oil (Argentinian commercial brand) without any special pretreatment and methanol (UVE HPLC) were used. The methanol/oil molar ratio was 30:1, and the catalyst loading was 3 wt.% (with respect to oil).

Additional experiments were conducted in order to quantify the influence of external mass transfer: the catalytic tests were performed at different agitation rates (from 300 to 1000 rpm). In order to study the reusability of the samples, five consecutive tests were performed at 140 °C (the solids were washed with hexane and ethyl ether/ethyl alcohol solution (50/50)). The effect of water and free fatty acid content on the transesterification reaction was investigated (in separate experiments) by adding 0.5 wt.% of water (with respect to oil) or 10 wt.% of saturated fatty acid [14] (stearic acid, Sigma–Aldrich ≤99%, with respect to oil) into the reaction medium under the conditions described above.

Reaction samples were centrifuged to improve the separation of methanol from the oil phase. A ~50 mg sample was taken from the oil phase and prepared for chromatographic analysis. The chromatography of the reactants and products was carried out in a Perkin Elmer AutoSystem XL equipment with a DB-17HT capillary column and a FID detector (according to the standard UNE-EN 14105 norm).

In addition, fatty acid content of each reaction sample (polar and non-polar phases) was determined by titration according to norm UNE-EN 14104.

The triglyceride (TG) conversion (X) and FAME yield (Y) were calculated using the following equations:

$$X_{TG} = \frac{\text{mol TG}_{t_0} - \text{mol TG}_{t_f}}{\text{mol TG}_{t_0}} \quad (1)$$

$$Y_{FAME} = \frac{\text{mol FAME}_{t_f}/3}{\text{mol TGE}_{t_0}} \quad (2)$$

where TGE is the triglyceride molar equivalent,

$$\text{mol TGE} = \text{mol TG}_{t_0} + \frac{2}{3}\text{mol DG}_{t_0} + \frac{1}{3}\text{mol MG}_{t_0} + \frac{1}{3}\text{mol FFA}_{t_0} \quad (3)$$

Five independent transesterification reactions were carried out (under the above specified operating conditions) to review the variability and repeatability of the results and determine the overall experimental error (of the catalytic test and chromatographic determination). The overall standard error calculated was ±0.7% for TG conversion and ±1.6% for FAME yield.

For the esterification reaction, oleic acid (OA, Anedra 61.5%) was used. The molar ratio of alcohol to OA was 30:1, and the catalyst loading was 3 wt.% (with respect to OA). OA concentration was measured according to norm UNE-EN 14104.

3. Results and discussion

3.1. Characterization of the synthesized Zn glycerolate

The morphological properties of synthesized Zn glycerolate are shown in Table 1. The solid presented a low surface area, 1.3 m^2/g, with a pore radius of 21.7 nm.

Table 1
Morphological properties of the zinc glycerolate.

Properties	ZnGly
Specific surface area (m^2/g)	1.3
Pore volume (cm^3/g)	0.01
Pore radius (Å)	21.7
Particle size (μm)	26.6