



Calcium zincate derived heterogeneous catalyst for biodiesel production by ethanolysis

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HIGHLIGHTS

- ▶ Calcium zincate treated at 400 °C is active in the ethanolysis of sunflower oil.
- ▶ By using a 3 wt.% of catalyst at 78 °C, FAEE yields higher than 95 wt.% are reached after 3 h.
- ▶ The catalytic activity is maintained even in the presence of free fatty acids (until 1.1° acidity) in the sunflower oil.
- ▶ The addition of Na₂CO₃ to the catalyst allows removing Ca and Na from biodiesel (<5 ppm).

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ABSTRACT

The transesterification reaction of sunflower oil with ethanol to produce fatty acid ethyl esters (FAEEs) was studied by using calcined calcium zincate as solid base catalyst. The effect of experimental parameters, such as catalyst loading, ethanol:oil molar ratio, free fatty acid and water contents, and stability in the ethanolysis of sunflower oil in the presence of calcium zincate thermally treated at temperatures as low as 400 °C are reported. Thus, by using a 3 wt.% of catalyst at 78 °C, FAEE yields higher than 95 wt.% after 3 h of reaction time, can be reached. The addition of FFA (until 1.1° of acidity) does not affect the catalytic activity, with yields values higher than 95 wt.%, but water brings about a negative effect. However, the catalyst has demonstrated to be less resistant to the reutilization in the ethanolysis process due to the leaching of calcium species, but addition of sodium carbonate to the catalyst before the catalytic process allows obtaining, after washing with water, a biodiesel with concentrations of Ca and Na lower than 5 ppm.

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1. Introduction

The petroleum fuels are limited and depleting day by day due to the increasing of the consumption and the society is really concerned about the environmental issues related to their outrageous consumption during the last century. For ecological and economic reasons, biofuels obtained from biomass are considered as a feasible alternative since they can be integrated into the existing industrial plants. Biodiesel is one of the most world-wide used biofuels, and it is derived from vegetable oils, animal fats, and used waste cooking oil. Its combustion emits fewer pollutants over the whole range of air–fuel ratio in comparison with diesel. Transesterification of vegetable oils and animal fats is the most common industrial method for producing biodiesel. Many studies have been carried out using different vegetable oils, such as those derived

from cotton [1], soybean [2,3], rapeseed [4–6], sunflower [7] and winter rape [8], as well as frying oils [9–11]; different alcohols such as methanol [12], ethanol [13] and butanol [14], and different catalytic systems, mainly homogeneous ones such as alkaline hydroxides [13,15,16], sulfuric acid [17], and supercritical fluids or enzymes such as lipases [2,18,19]. However, biodiesel production, under heterogeneous conditions, in the presence of solid catalysts instead of homogeneous ones, has emerged as an attractive route which could potentially lead to decrease the overall cost production, because of the recovery and reuse of catalysts [20] and the possibility of carrying out simultaneously both transesterification and esterification reactions [21], if acid solids are employed. The use of heterogeneous catalysts for biodiesel production has been reviewed by different authors [22–25], and mechanistic and kinetic aspects have been also discussed. Among the different types of solid catalysts, much attention has been paid to calcium oxide since it possesses relatively high basic strength, a less environmental impact due to its low solubility in methanol and it can be obtained

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from cheap natural sources, like limestone or eggshells. López-Granados et al. [26] used an activated calcium oxide as a solid base catalyst in the methanolysis of sunflower oil, finding that CaO is rapidly hydrated and carbonated in air. Moreover, leaching of active species was observed in the reaction media when the catalyst was activated at high temperature. In order to stabilize this basic oxide against atmospheric agents, we have recently reported the use of calcium zincate dihydrate as precursor of solid base catalyst, which activation at 400 °C gives rise to very active solid base catalysts for the methanolysis of sunflower oil [27].

On the other hand, in the synthesis of biodiesel, there is an increasing tendency to use ethanol instead methanol, because of its renewable production from biomass [13,28]. However, the choice of ethanol to obtain the corresponding mixture of fatty acid ethyl esters (FAEEs) also presents some drawbacks, such as the formation of stable emulsion during ethanolysis and the price of ethanol which is currently more expensive than methanol. Many different solid catalysts have shown to be effective for methanolysis of vegetable oils, but the number of studies dealing with the heterogeneously-catalyzed ethanolysis is limited, although it has been increased in the last years, as Stamenković et al. [29] have pointed out. In this sense, CaO has been used in five cycles of sunflower ethanolysis with FAEE yields higher than 97% [30]. Watcharathamrongkul et al. [31] have demonstrated, in the transesterification of soybean oil with ethanol catalyzed by calcium oxide prepared from the calcination of CaO, Ca(OH)₂, limestone, and Ca(OH)₂/CaO, that catalytic activity depends on the basic strength and textural properties of the resulting CaO. Moreover, the production of FAEE can be also accomplished by using supercritical ethanol [32,33], enzymatic systems [34] or assisted by ultrasounds [35].

Bearing in mind these considerations, and as a continuation of a previous work [27] where calcium zincate dihydrate was shown to be an excellent precursor of a base catalyst for the transesterification of sunflower oil with methanol, the present work deals with its catalytic behaviour in the ethanolysis of sunflower oil and the influence of several experimental variables, such as ethanol:oil molar ratio, catalyst weight, temperature and reaction time, reutilization and influence of adding different amounts of free fatty acids and water, on the catalytic performance.

2. Experimental

2.1. Catalyst preparation and characterization

Calcium zincate dihydrate was synthesized according to the procedure proposed by Ziegler and Johnson [36], and explained in a previous paper [27]. The calcium zincate precursor was thermally treated *in situ* prior the catalytic tests, in a tubular furnace at 400 °C (heating rate 20 °C min⁻¹), for 1 h under a helium flow. The characterization was performed by using the techniques described in Ref. [27].

2.2. Transesterification procedure

The ethanolysis of edible sunflower oil was performed in a glass batch reactor with a water-cooled condenser, controlled temperature and inert atmosphere (N₂). Before the reaction, the catalysts were activated at 400 °C for 1 h (heating rate, 20 °C min⁻¹) under a helium flow. Once the catalyst reached the room temperature, 15 g of oil was added, and the mixture was heated under strong stirring (600 rpm) up to the reaction temperature. Then, ethanol ultrapure (CH₃CH₂OH, 99.8% Reagent Sigma Aldrich) was added to the oil–catalyst mixture by using the dropping funnel. The initial experimental conditions were: ethanol/oil molar ratio = 20/1, stir-

ring rate = 600 rpm and a reaction temperature of 78 °C (at 65 °C, there was no significant production of biodiesel). Aliquots (ca. 1 mL) were taken at different reaction times and then were quenched by adding 1 mL of H₂O and agitating for few minutes. Later, 1.5 mL of dichloromethane was added, and this mixture was again agitated and set aside to develop two phases: the ester phase containing dichloromethane, FAEE, mono-, di and triglycerides (and traces of ethanol and glycerol) and the polar phase containing glycerol and ethanol (and traces of esters). The dichloromethane was then removed from the organic phase by evaporation at 90 °C. The composition of the transesterification products derived from the ethanolysis of sunflower oil was determined by high performance liquid chromatography (HPLC) using a JASCO chromatograph equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055) and column oven (co-2065) using a PHENOMENEX LUNA C18 reversed-phase column (250 mm × 4.6 mm, 5 mm). The solvents were filtered through a 0.45 mm filter prior use and degassed with helium. A linear gradient from 100% methanol to 50% methanol + 50% 2-propanol–hexane (5:4, v/v) in 5 min was employed. Injection volumes of 15 µL and a flow-rate of 1 mL min⁻¹ were used. The column temperature was held constant at 40 °C. All samples were dissolved in 2-propanol/hexane (5:4, v/v). The weight content in FAEE determined by HPLC was considered to represent the wt.% yield in FAEE of the catalytic process assuming that, during the neutralization and the rinsing process of the ester phase, only traces of esters were transferred to the polar phase and that only the extraction of methanol and glycerol takes place.

3. Results and discussion

3.1. Catalyst characterization

The structural and textural characterization of the precursor and calcined materials has been reported elsewhere [27], and the main data are compiled in Table 1. The XRD and TG-DTA techniques have demonstrated that calcium zincate dihydrate, CaZn₂(OH)₆·2H₂O, is transformed at 400 °C into a mixture of CaO and ZnO, although the formation of well-crystallised CaO phase was not observed, because it would require temperatures higher than 500 °C. XPS analysis has also corroborated the presence of these two inorganic phases, although CaCO₃ and Ca(OH)₂, stemming from the contact of the activated phase with air during the sample transfer from the oven to the XPS chamber, have been also detected. However, this calcium carbonate is almost absent in the precursor, even after remaining in contact with air for two weeks.

The BET surface area (76.7 m² g⁻¹) and pore volume (0.144 cm³ g⁻¹) values, as determined from adsorption–desorption of nitrogen at –196 °C, are higher than those reported for bulk CaO and ZnO [37]. It is noteworthy that the pore size distribution was relatively narrow and centred around 4.3 nm with a FWHM of 3 nm.

3.2. Catalytic activity

The base catalyst obtained after thermal treatment of calcium zincate dihydrate at 400 °C has previously shown to be very active in the methanolysis of sunflower oil, reaching FAME yields higher than 90 wt.%, after 45 min of reaction at 60 °C, by using a methanol:sunflower oil molar ratio of 12 and 0.75 wt.% of catalyst respect to the oil weight [27]. By taking into account that less attention has been paid to the ethanolysis of vegetable oils, it was considered of interest to evaluate the catalytic behaviour of this base catalyst in this reaction. For this reason, the influence of several experimental parameters, such as ethanol/oil molar ratio, catalyst loading, reac-

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