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Issues concerning the use of renewable Ca-based solids as transesterification catalysts

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ABSTRACT

The purpose of this work is to discuss some relevant issues that affect the catalytic performance of renewable-based $CaCO_3$/CaO solids in the transesterification of triglycerides for producing biodiesel. Particularly, this study analyses the catalytic performance of the renewable catalysts obtained from calcined eggshells focusing on the calcination step, handling of the activated catalysts, and on the ageing when exposed to the atmosphere. Only severe calcination conditions ensure a complete decomposition of $CaCO_3$ based precursors into CaO, which, on the other hand, result in quite uniform catalyst properties. Neither the source of the eggshells nor the preparation procedure before calcination influenced the catalytic performance of the calcined solids, which remained essentially unaltered through five reaction/recovery cycles. Exposure to atmospheric air negatively affects the catalytic performance of the solids, causing a significant loss of activity in samples aged for 30 days, though most of their initial fresh catalytic activity could be recovered by washing them with methanol.

1. Introduction

Nowadays, biodiesel manufacture at industrial scale is at a crossroads situation in countries like Spain. The significant efforts and investments made in the past decade for increasing the installed manufacturing capacity led to a boom in the development of industrial installations for producing quality biodiesel from various oily raw materials, such as rapeseed or soy, to cite just two examples. The conventional methods for producing this biofuel typically comprise transesterification of triglycerides by methanolysis in the presence of a homogeneous catalyst (usually strong bases) [1]. In such industrial processes, typically around 90% of the manufacturing costs are allocated to the purchase of the raw material acting as source for the triglycerides. However, there are many other associated costs to the manufacturing process, which are minor but not negligible. In industrial operation units, a series of conditioning, separation and purification steps are required in order to manufacture a quality product and, at the same time, to recover reagents and catalysts, which are usually energy intensive and are inevitably associated to an increase in the manufacturing costs.

In this sense, heterogeneous catalysts can contribute to simplifying the biodiesel manufacturing process, especially in the stages of purification of the final reaction products. This fact has led to numerous research efforts by many authors in the quest for developing suitable solids with good catalytic activity, selectivity to fatty-acid esters and adequate reusability, the latter meaning that the catalysts do not suffer a significant loss of activity upon regeneration. Between the most studied basic solid catalysts, calcium oxide (CaO) can be highlighted, because of its availability, low cost and high catalytic activity [1].

One of the possible routes for obtaining CaO is the thermal decomposition of calcium carbonate ($CaCO_3$) present in minerals such as calcite or animal products like egg shells or shells of molluscs and crustaceans. CaO of very high purity could be obtained from renewable sources by waste valorisation from other industries such as the food industry [2]. A plethora of works have been published regarding the use of different Ca renewable sources for producing catalysts; however, there has not been a comprehensive and systematic analysis of catalyst conditioning and experimental

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Abbreviations: C, commercial fresh eggs; F, farm eggs; Q, quail fresh eggs; BCA, boiled commercial hen eggshells milled in an agate mortar (BCA) and with a particle size distribution comprised between 200 and 300 μm; BCA_50, boiled commercial hen eggshells milled in an agate mortar (BCA) and with a particle size distribution below 50 μm; RCA, raw commercial (RC) hen eggshells milled in an agate mortar with a particle size distribution comprised between 200 and 300 μm; RCG, raw commercial (RC) hen eggshells milled using a blade grinder with a particle size distribution comprised between 200 and 300 μm; FA, catalyst precursors obtained from farm hen eggshells milled in an agate mortar; QA, catalyst precursors obtained from quail eggshells milled in an agate mortar.

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reaction procedures for evaluating the catalytic performance that could bias the conclusions established.

In the field of the heterogeneously-catalysed transesterification reaction for biodiesel production, there are recent studies where other authors have previously studied the production of CaO from eggshells for biodiesel production [3–6] and recent reviews of the state-of-the-art can be found in the literature [2,7,8]. All these works studied different calcination temperatures to achieve a proper decomposition of the $CaCO_3$, for which temperatures above 700 °C are needed.

However, the process of synthesis and activation of CaO is critical when it comes to achieving good catalytic activity and good reproducibility. Thus, it is important to have a precise control of the variables involved in the process of eggshells calcination. Furthermore, as a result of carbonation and rehydration phenomena that lead to the formation of $CaCO_3$ when the solids are exposed to CO_2 [9,10] and moisture naturally present in the ambient air, CaO catalysts are aged rapidly, losing the catalytic activity. This issue clearly indicates that it is crucial to minimize the exposition of the catalyst samples to air after calcination and, in order to correctly assess the catalytic activity of the catalysts prepared, it is necessary to develop adequate protocols for handling the catalyst samples after the calcination process and prior to the start-up of the reaction.

Although most of the works include several cycles of catalysts recovery and reuse, the literature concerning the catalyst stability of Ca-containing solids obtained from eggshell is scarce so far [11,12]. In addition to this, a careful analysis of the formation of new compounds in the proper reaction that could act also as catalysts, such as calcium glyceroxide, has not been discussed in depth except for a few works [9,13,14]. In a previous study performed using eggshells as catalysts precursors, achieving good reproducibility in the results was found to be difficult [12]. This could probably be due to a poor control of the conditions during calcination and handling of the Ca-containing solids. The present work aims at discussing in depth some relevant issues that affect the catalytic performance of renewable-sourced CaO that could serve as heterogeneous catalyst in the transesterification reaction of fatty acids triglycerides for biodiesel production. Particularly, focus has been made on the possible transformations that could take place on the catalyst surface due to factors such as the starting raw materials or the experimental procedures followed during the catalyst preparation and testing, among others.

2. Materials and methods

2.1. Raw materials and chemicals for biodiesel production

Biodiesel was prepared by means of transesterification using refined sunflower oil (Urzante, Spain) as raw material. Methanol (99.9% min) was selected as alcoholic reactant for the transesterification (methanolysis). Tetrahydrofuran (THF, 99.7% min) was used as solvent in the analysis of the reaction samples collected over time from the setup. Three varieties of eggshell were studied: (i) from laying hens bred in hatcheries, labelled as commercial eggs, C; (ii) from farm hens bred in open air pastures, F; and (iii) from quails eggs, Q. Hen and quail eggs were purchased in a commercial store located in Pamplona.

2.2. Experimental setup for biodiesel synthesis

The biodiesel was produced in a laboratory scale setup consisting of various batch reactors in parallel. Each of the reactors is composed of a 0.25 L double-walled glass vessel with a closed external heating jacket using a hot water flow for providing heat and temperature control externally by means of a thermostatic water bath. Reactors are equipped with a magnetic stirrer, a sampling device for extracting reaction samples, and a K-type thermocouple which is in contact with the liquid reaction medium for monitoring the reaction temperature. The product samples could be collected by means of direct extraction from the reactor with a syringe. These samples were subsequently centrifuged to remove the catalyst and diluted with tetrahydrofuran (THF, Scharlau, HPLC grade). Once filtered with Acrodisc® filters with 0.2 μm PTFE membrane, the samples were analysed by size exclusion chromatography (SEC) with differential refractive index detector at room temperature, as described elsewhere [15].

Along this work the reference reaction conditions were 60 °C, a molar methanol-to-oil ratio of 12:1 with a catalyst load of 2 wt.% with respect to the total amount of oil. Nonetheless, some of the experiments have been carried out varying these operating conditions in order to study their influence on the transesterification reaction. Particularly, some experiments were done using methanol-to-oil molar ratios of 6:1 and 24:1, whilst catalyst loads of 0.25, 0.5, 1 and 4 wt.% have also been studied.

In order to prevent the catalyst samples from ageing, the solid is rapidly transferred into the reaction setup containing the alcohol reagent right after finishing the calcination step, when the calcined catalyst is still hot, extracting it from the muffle furnace when the temperature inside the furnace is about 350 °C. Such temperature could be set from preliminary tests for tuning the experimental protocol. The reaction was immediately initiated after the addition of the oil into the reactor, by rapid mixing of the liquid reactants. Additionally, different procedures have been studied by varying the liquid medium in which the solid is placed before the reaction: either in pure alcohol or in pure sunflower oil, which will be discussed in Section 3.3.

Furthermore, an ageing and regeneration study was conducted by assessing the catalytic performance of fresh catalyst samples tested immediately after their calcination, and also at different ageing times after their exposure to ambient air. The regeneration of the aged catalyst samples was developed by direct contact with methanol at 25 °C for 1 h under stirring using a magnetic stirrer.

On the other hand, spent samples after their use in transesterification were recovered from the reaction medium by filtration. Afterwards, the samples were abundantly washed with THF and further dried at 65 °C under vacuum overnight.

2.3. Catalysts preparation and characterisation

The eggshells were obtained by direct emptying of the as-received raw eggs (R) or by peeling off from eggs boiled for 30 min in deionized water (B). The eggshell chips were preconditioned in the laboratory by washing them abundantly using deionized water and further dried for 24 h at 100 °C. Afterwards the eggshell chips were crushed and milled, manually in an agate mortar (A) or mechanically in a small grinding mill (G). The resulting milled catalyst precursors were then sieved in order to get a particle size distribution comprised between 200 and 300 μm. In addition, another catalyst was prepared using fine powder, below 50 μm, from boiled eggs.

The calcination of the different solid precursors was carried out in a Nabertherm B180 muffle furnace under air atmosphere. In order to optimize the calcination conditions, a design of experiments was conducted by varying the final calcination temperature and the idle time at that temperature. These parameters were studied in the ranges comprised between 500 and 850 °C and between 3 and 12 h, respectively. The surface area of the calcined solids (S_{BET}) and the mass loss in the calcination process were analysed. The latter is directly related to the efficiency of the