



Full Length Article

Metallic monolithic catalysts based on calcium and cerium for the production of biodiesel



Inés Reyero^a, Ainara Moral^a, Fernando Bimbela^{a,b}, Jelena Radosevic^c, Oihane Sanz^c, Mario Montes^c, Luis M. Gandía^{a,b,*}

^a Grupo de Reactores Químicos y Biorreactores, Departamento de Química Aplicada, Universidad Pública de Navarra, Edificio de los Acebos, Campus de Arrosadía, 31006 Pamplona, Spain

^b Institute for Advanced Materials (InaMat), Universidad Pública de Navarra, Campus de Arrosadía, 31006 Pamplona, Spain

^c Departamento de Química Aplicada, UFI 11/65, Facultad de Ciencias Químicas de San Sebastián, UPV/EHU, Paseo Manuel de Lardizábal 3, 20018 San Sebastián, Spain

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ABSTRACT

The present work reports the preparation, characterization and testing of Ca/Ce oxides as heterogeneous catalysts for the transesterification of sunflower oil with methanol (methanolysis), both in powder and structured forms, to produce biodiesel. A series of Ca-based catalysts in powder form were prepared on four different supports (commercial Al₂O₃, SiO₂ and CeO₂, along with in-house prepared CeO₂) following different techniques. The best catalyst formulation in terms of activity and stability was a Ca/Ce mixed oxide (20 wt% CaO) catalyst prepared under the metallic citrates decomposition technique. Different suspensions could be formulated using this catalyst for further washcoating Fecralloy[®] monoliths. The effect of the solvent (water or alcohols) and of the use of additives (polyvinyl alcohol, polyvinylpyrrolidone, and colloidal Al₂O₃ and CeO₂) on the catalytic performance of the catalysts in the transesterification reaction was studied. The best results could be obtained for the structured catalysts prepared using suspensions having isopropanol as solvent medium and 1% of polyvinylpyrrolidone. The monoliths prepared using this formulation yielded the best oil conversions after a second reaction cycle reported so far in the literature concerning the use of structured catalysts for biodiesel production, with oil conversion values of 70% after 6 h of reaction at 60 °C using recovered and thermally regenerated monoliths. The thermal reactivation of the catalysts has been proven to be crucial in order to partially recover the catalyst activity, though significant leaching of the active catalytic layer was found to occur during the first reaction cycle. The results presented here are remarkably superior to the best ones previously reported in the literature concerning the use in a second reaction cycle of structured methanolysis catalysts at atmospheric pressure.

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1. Introduction

Certain scientific topics suffer from a sudden outburst of research interest by a wide part of the scientific community. Biodiesel production via heterogeneous catalytic transesterification of triglycerides is one of the exemplifying cases. In spite of the very abundant literature concerned with this topic that has appeared in the recent years [1,2], there is still a lack of systematic research studies focusing on the main challenges to be faced such as e.g. the issue of the poor chemical stability of the catalysts proposed

for the production of biodiesel which complicates their reutilization [3–8].

In a recent review by Mittelbach the challenges that the biodiesel industry has to face nowadays have been clearly exposed [9], and definitely process intensification has to be addressed in order to achieve the necessary technology improvement mentioned therein [10,11], an improvement capable of granting lower energy input, higher overall yields and less waste material in the process. As accurately pointed out by Mittelbach, biodiesel is still the cheapest alternative to fossil diesel fuel, and it must be borne in mind that the transition period from fossil-derived energy sources to a 100% non-fossil energy mix scenario is neither going to be easy nor imminent.

Structured catalytic reactors such as those based on monolithic catalysts constitute an interesting approach in terms of process

* Corresponding author at: Institute for Advanced Materials (InaMat), Universidad Pública de Navarra, Campus de Arrosadía, 31006 Pamplona, Spain.

E-mail address: lgandia@unavarra.es (L.M. Gandía).

intensification of biodiesel production via transesterification with methanol (methanolysis) of triglycerides. Such catalytic reactors are hydrodynamically superior compared to those based on particulate catalyst formulations, and certain basic operation units, namely catalyst separation when using slurry reactors, can be avoided. This could reduce the production costs and improve the quality of both biodiesel and glycerol in industrial operation, yet only a few studies can be found in the literature on the use of structured methanolysis catalysts [12–19].

For structured catalysts to reach a successful implementation in biodiesel production, some challenges still need to be tackled and given proper solutions. Particularly, adherence of the active phase onto the support or substrate is a key issue where there is still a long path to be covered before the problem is finally solved. In this regard, leaching phenomena have been discussed in some studies using Ca-based heterogeneous catalysts in powder form. However, little is still known on the performance of structured catalytic systems containing CaO as active phase. It should be noted that CaO exhibits an outstanding activity in alcoholysis reactions with triglycerides which, along with other advantages such as wide availability, low cost and even “renewable” origin justify the interest in further investigations.

In a previous work, the use of Mg–Al hydrotalcites deposited on Fecralloy[®] metallic monoliths by the washcoating method was studied for the methanolysis of sunflower oil [12]. Adherence of the active phase onto the substrate was found to be challenging even though some works in the literature have astonishingly achieved CaO adherences on cordierite monoliths up to 99% [16] in spite of the stability problems exhibited by this active phase related to the formation during reaction of calcium glyceroxide [7,8,20]. Our previous study revealed that adding small amounts (5–10 wt%) of sepiolite as additive into the slurries during catalyst preparation was positive for enhancing adherence. Up to 77% oil conversion could be attained after 10 h of reaction at usual methanolysis conditions, though catalyst stability remained unsolved because the catalyst could not be reutilised after its recovery [12].

Calcium oxide from a variety of both mineral and organic sources is very likely the most investigated solid as methanolysis catalyst [7,8,20–22]. As far as we know, this compound has always been used as methanolysis catalyst in powder form. Only Kwon et al. describe the use of CaO supported over γ -alumina wash-coated cordierite honeycomb monoliths for fatty acid methyl esters production [15]. However, CaO has poor chemical stability under transesterification reaction conditions, resulting in the leaching of calcium species into the reaction mixture [7,8,20,23]. Several approaches have been followed in order to improve the stability of calcium such as the modification of CaO with metals and the use of perovskites containing Ca. Significant enhancement on the catalyst reusability has been achieved with CaO–CeO₂ mixed oxides [24,25] and CaO supported on Ce-based materials [26].

In this work, a series of CaO-containing solids in powder form were prepared under different techniques aiming at achieving catalytic formulation that could eventually be capable of yielding both high catalytic activity and stability. Thus, the first part of the study aimed to identify those catalysts prepared under different techniques that presented promising results in the methanolysis of sunflower oil. Only those samples yielding superior catalytic performances were further studied in the preparation of the structured catalysts. To overcome the adherence and stability issues, different strategies such as using different solvents during the stage of catalyst deposition onto the monoliths, the use of different additives and regeneration by means of thermal reactivation have been studied.

2. Materials and methods

2.1. Catalysts preparation

Different catalysts were prepared, both in powder form and structured on monolithic substrates. All the samples considered in this study together with the nomenclature used and relevant information regarding their preparation and catalytic testing are compiled in Table 1.

A series of calcium catalysts was prepared on four different supports following the incipient wetness impregnation technique; the Ca content in this series was fixed at 10wt%. Calcium nitrate (Ca(NO₃)₂·4H₂O, Sigma Aldrich, 99.0% min.) was selected as Ca precursor. Commercial Al₂O₃ (Spheralite 505, Procatalse), SiO₂ (Aerolyst 350, Degussa) and CeO₂ (99.995% min., Sigma-Aldrich) were directly used as supports. Another ceria support was synthesized in the laboratory from cerium nitrate (Ce(NO₃)₃·6H₂O, Merck, 98.5% min.) by precipitation of cerium hydroxide at 90 °C using NH₄OH solution (Merck) as precipitating reagent until a final pH of 8.5 was attained, followed by ageing at 90 °C for 4 h, drying at 100 °C for 12 h and calcination at 700 °C for 5 h in a muffle furnace.

On the other hand, a series of Ca–Ce oxides could be prepared by the method of metallic citrates decomposition, based on the reaction of cerium nitrate with citric acid (anhydrous, Panreac, 99.5% min.), following a procedure similar to that described in Samantaray et al. [27]. Four different solids having different calcium contents (0, 5, 10 and 20 wt%) and an additional CaO solid could be prepared following this procedure.

Ca–Ce oxides could also be prepared by direct physical mixing of the corresponding nitrate salts and further calcination, following two different procedures. In the first case, the necessary amounts of the metallic nitrate salts were dissolved in aqueous medium and maintained under vigorous stirring for 5 h. Afterwards, the water from the solution was evaporated and the resulting solids were dried at 100 °C for 12 h and subsequently calcined at 700 °C for 5 h. The solids were prepared so as to have a nominal content of CaO in the final solid of 10 wt%. In the other case, the necessary amounts of both nitrate salts were mechanically mixed in a mortar and were directly calcined at 1050 °C for 4 h.

Regarding the structured catalysts, a commercial metallic alloy (Fecralloy[®], FeCr22Al5, 50 μ m, Goodfellow) served for the preparation of the monoliths as described in Reyero et al. [12]. A washcoating technique was selected for depositing Ca and Ce from a suspension prepared with a mixed Ca–Ce oxide prepared again by the method of metallic citrates decomposition. In this case, the mixed oxide was formulated in order to have a CaO content of 20 wt%. Different suspensions were prepared using this mixed Ca–Ce oxide (20Ca/Ce-cit), both in aqueous and in alcoholic media. The alcohols used for preparing the suspensions were methanol, ethanol, and isopropanol of high purity (Scharlau, anhydrous, 99.8% min.). The solids from these suspensions (slurried catalyst) were also tested after solvent evaporation to compare their activity to that from the original solid precursor (20Ca/Ce-cit).

Furthermore, in various formulations different additives were added into the suspensions in order to enhance their adherence properties. Different combinations were tested using 1% polyvinyl alcohol (PvOH, Sigma-Aldrich, 99% min.) or 1% polyvinylpyrrolidone (PVP, average molecular weight of 40,000 g/mol, Sigma-Aldrich) and/or 20% colloidal ceria (NYACOL[®]). Additional formulations were prepared using 20% colloidal alumina (NYACOL[®]) together with 1% PvOH, and with two other PVP contents in isopropanol (0.5 and 2%). After washcoating, the slurry excess was eliminated by centrifugation and then the solids were dried at 120 °C for 30 min and calcined at 700 °C for 5 h.

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