



# Biodiesel production over thermal activated cerium modified Mg–Al hydrotalcites

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## ABSTRACT

Heterogeneous basic catalysts can be used for biodiesel production. The performances of several types of such materials are described in the literature but small attention is given to its deactivation in reaction medium. This paper put in evidence that catalysts are not static identities in the reaction medium, and relates the physical characteristics of fresh and post reaction samples with deactivation mechanisms.

Catalysts, tested during the methanolysis of soybean oil, were prepared by thermal activation of Ce modified Mg–Al hydrotalcites (Mg/Al = 3, Ce/Mg < 0.1 atomic ratios). Calcination at 575 °C allows to nanostructured samples with main XRD lines belonging to periclase and cerianite. Additionally, calcined samples containing 3% and 5% of Ce showed hydrotalcite patterns pointed out that cerium promotes the fast rehydration and restructuring. All the prepared samples showed contamination with sodium aluminate which masks the Ce effect on the catalysts basicity due to its strong basicity. In the tested conditions, the catalysts with Ce/Mg > 0.03 (atomic ratio) presented FAME yields higher than 90%. Thermogravimetry analysis of post reaction catalysts evidenced that cerium influences the reaction mechanism. The post reaction catalysts evidenced that surface restructuring occurs during reaction with sizeable change of the elements distribution which as beneficial effect on the catalytic performances.

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## 1. Introduction

Transport and energy are key components of the modern life and the foundation of economy [1].

Energy exists in various forms and come from sources qualified as renewable and non-renewable. The concept of renewability is based upon the scale of human events and if the source can be replaced during that period. Renewable technologies are considered as clean sources of energy [2]. In this context biodiesel is pointed out as a renewable, sustainable alternative fuel for compression ignition engines [3–6]. Also biodiesel is viewed as a solution for the CO<sub>2</sub> abatement [7,8] since the combustion of fossil fuel is the major source of this environment harmful compound.

In 2020 the member states of the European Union are supposed to have cut their greenhouse gas emissions by 20%, raised the share of total energy consumption met from renewable sources to 20%, and increased energy efficiency by 20% [9]. This EU directive will prompt the production of biodiesel but recent estimated data from EIA for 2030 (Fig. 1) preview that non-renewable fossil oil and coal will dominate the world energy mix and thus the use of biofuels

will be inexpressive in the near future. Even in this world scenario, unfavorable to renewable energy sources, environmental skeptics pointed out that the existent technology for biodiesel is a factor in raising world hunger [10]. In fact biodiesel, a mixture of fatty acids esters, is produced by catalyzed alcoholysis of vegetable oils or animals fats, and using vegetable oil, even non-edible, creates a competition between oil for food and oil for fuel [11].

The fuel versus food dilemma its an important topic for large scale production of biodiesel using vegetable oils. The role of bio-fuels in the future energy supply mix strongly depends on the development of more proficient technology for biofuels production that avoids or lowers foods versus fuels competition [12].

The alcoholysis reaction occurs in the presence of acid or basic catalysts. Homogeneous catalysts nowadays in use, although effective, lead to serious contamination problems that make essential the implementation of good separation and product purification protocols increasing the production costs. The cost of biodiesel is 1.5–3 times the price of conventional diesel [13] and the selection of an appropriate catalyst is crucial for the design of a sustainable and competitive transesterification process [14]. Many types of solid catalysts have been tested in transesterification reactions and it is possible to group them in three general categories: metal, alkaline and acid catalysts [15]. Enzymes can also be used to produce biodiesel [16].

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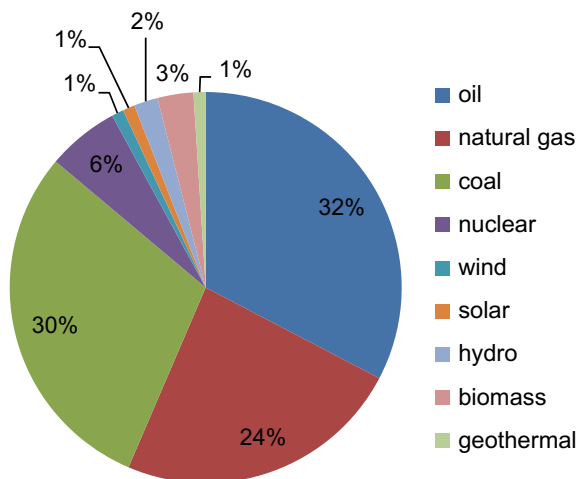


Fig. 1. World energy mix in 2030 (source Energy International Agency – EIA).

Several materials with basic character have been used to catalyze the synthesis of biodiesel. Sharma et al. [17] present an interesting discussion for catalysts such as oxides (Mg, Ca, Sr), hydrotalcites (Mg–Al based), alumina loaded with various compounds and zeolites. The authors focus their discussion on the preparation of the catalysts, catalytic behavior (methyl esters yield), reaction mechanisms and deactivation processes. Other reviews on the catalysts for biodiesel production are available in the literature. The latest emphasizes the fact that a well design heterogeneous catalyst can yield high throughput of biodiesel thus making this renewable fuel more competitive [18].

Magnesium–aluminum layered double hydroxides (LDHs), or hydrotalcites, have been extensively studied as catalysts or catalysts precursors for biodiesel production. In fact, since calcination of LDHs yields mixed oxides with basic properties [19], LDHs have found application in many organic reactions considered to be catalyzed by bases [20,21] namely for methanolysis of vegetable oils [22–24]. Hydrotalcites are anionic clays with general formula  $[M_1^{2+}_x M_2^{3+}_y (\text{OH})_2]^{x+y} [A^{n-}]_{x/n} \cdot y\text{H}_2\text{O}$  where  $M_1^{2+}$  and  $M_2^{3+}$  are di and trivalent cations in octahedral positions [25]. For Mg–Al hydrotalcites some  $\text{Mg}^{2+}$  ions, in brucite layers, are replaced by  $\text{Al}^{3+}$  and the charge balancing anions are usually  $\text{CO}_3^{2-}$  ions [23], which are incorporated in the interlayer region, together with water molecules [26]. Taking into account that the hydrotalcites and subsequent mixed oxides properties can be tailored introducing dopant elements during or after the hydrotalcite preparation step [22], in the present work cerium doped Mg–Al hydrotalcites have been prepared and tested for soybean oil methanolysis. Cerium was selected as dopant element taking into account the results of H. Abimanyu et al. [27] and Daza et al. [28]. Indeed these authors reported a beneficial effect on the catalysts basicity using cerium as dopant element. Additionally Sajith et al. [29] reported an improve of combustion biodiesel performances when nanoparticles of cerium oxides were added. Daza et al. [30] also reported beneficial effect of adding  $\text{CeO}_2$  to Al–Mg hydrotalcites in  $\text{CO}_2$  reforming of methane.

## 2. Experimental

### 2.1. Preparation of the catalysts

Several methods can be used to prepare Mg–Al hydrotalcites [31–33]. The most common preparation method is the coprecipitation at constant pH. The incorporation of guest elements in the

Mg–Al double layered hydroxides can be achieved by coprecipitation [34]. Thus the Mg–Al and Ce modified hydrotalcites were prepared by coprecipitation according to the procedure schematized in Fig. 2. More details on the preparation procedure are given elsewhere [35]. This preparation procedure was recently adopted by Gomes et al. [36]. All the samples were prepared with Mg/Al = 3 atomic ratio and with Ce/Mg atomic ratios 0, 0.03, 0.05 and 0.10. The samples will be referred in the text as 0Ce, 3Ce, 5Ce and 10Ce. A strongly basic solution (100 mL) containing  $\text{Na}_2\text{CO}_3$  and NaOH was slowly added to a solution (300 mL) containing the adequate amounts of Al, Mg and Ce nitrates. For each sample (20 g) the coprecipitation took around 2 h and was carried out under vigorous stirring and pH roughly 8. The used reagents, except for NaOH (purity  $\approx$  99%), were *p.a.* grade acquired from Fluka. After coprecipitation the solids were repined in contact with mother liquors during 3 h at room temperature. Then the precipitates were filtrated and washed with abundant water. The washing procedure was repeated until the pH of the washing water reach 7. The dried solids (overnight at 120 °C), with different yellow shades (from chalky to yellow), were calcined 5 h at 575 °C in a muffle. The calcination temperature was chosen considering the thermogravimetry profiles obtained for dried samples.

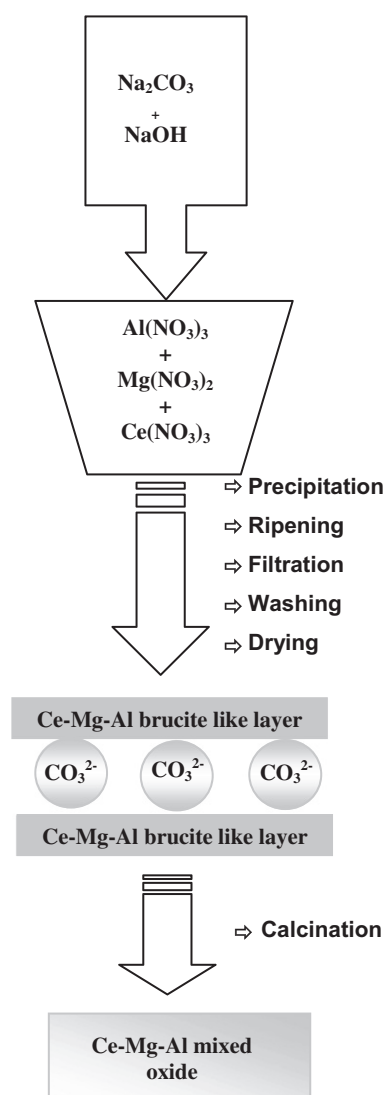


Fig. 2. Catalysts preparation procedure.

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