



## MgM (M = Al and Ca) oxides as basic catalysts in transesterification processes

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### ABSTRACT

This work investigates the use of MgAl and MgCa oxides as catalysts for transesterification processes, in order to evaluate their potential as heterogeneous catalysts for biodiesel production. The catalysts were characterized by XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy), SEM (Scanning electron microscopy), CO<sub>2</sub>-TPD and N<sub>2</sub> adsorption. MgCa oxides were more active than MgAl in the transesterification of ethyl butyrate with methanol at 60 °C and atmospheric pressure. The highest activity was found for a bulk Mg:Ca molar ratio of 3.8, with a conversion of 45%, whereas MgO was inactive. Moreover, lixiviation of the active phase was not observed, thus excluding the contribution of the homogeneous catalysis to the studied transesterification process. In the methanolysis of sunflower oil, the activity follows the same tendency observed in the transesterification of ethyl butyrate with methanol. A FAME (fatty acid methyl esters) yield of 92% has been reached with a methanol:oil molar ratio of 12, a reaction temperature of 333 K and a 2.5 wt.% of the Mg:Ca(3.8) catalyst.

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## 1. Introduction

Biodiesel, a nonpetroleum-based fuel, is known as a clean and renewable fuel that consists of fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), derived from the transesterification of triglycerides with methanol or ethanol, respectively, in the presence of the suitable catalyst [1–3]. At the present day, the cost of biodiesel is not competitive with petroleum diesel without subsidies or tax incentives due to the cost of raw materials and processing. The process is mainly carried out by homogeneous catalysis in the presence of basic species, including sodium or potassium hydroxides, their carbonates or alkoxides. The use of heterogeneous catalyst systems in alcoholysis of triglycerides could contribute to minimize homogeneous process problems, such as the production of soaps, separation and purification of biodiesel. The cost of biodiesel could certainly be reduced by the use of a heterogeneous catalyst, greatly simplifying the post-treatment of the products (separation and purification) and not producing soaps through free fatty acid neutralization or

triglyceride saponification. In contrast, processes using heterogeneous catalysts need higher temperatures to be effective in a reasonable time.

Different solid catalysts for biodiesel production have been proposed, mainly based on basic alkaline and alkaline-earth compounds [4–13], acid solids [14–16] and enzymes [3,17]. Moreover, the transesterification of vegetable oils can also be accomplished in supercritical methanol without catalyst [18,19]. However, in spite of the numerous research papers already reported, much work is still necessary to extend the use of heterogeneous catalysis. Although some of these catalysts show an excellent catalytic behaviour, they do so at the expense of high temperatures and pressures. This is the case of the EsterFIP process already used in commercial biodiesel production plants [20–23]. Some solid bases, showing good catalytic activity, are most probably catalyzing transesterification reactions through a homogeneous molecular pathway rather than a truly heterogeneous one, due to their non-negligible solubility in alcohols. Nevertheless, studies on the reusability and regeneration of the catalysts are necessary to estimate the potential of a specific catalyst for commercial application.

Among the basic metal oxides, those derived from layered double hydroxides (LDH) have been extensively studied due to their tuneable properties which have allowed them to find potential

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applications in different catalytic fields [24,25–28]. In this sense, the basic sites of calcined Mg–Al hydrotalcites exhibit enough strength to be used in transesterification reactions [6,8,9,29]. Thus, Di Serio et al. [6] have reported the use of MgO and calcined hydrotalcites as catalysts for the transesterification of soybean oil with methanol, finding that catalytic results are well correlated with the basicity and textural properties of the catalysts, which depend on both the nature of the precursor and the preparation method. Cantrell et al. [8] have demonstrated that calcined Mg–Al LDHs are effective catalysts in the methanolysis of glyceryl tributyrates, increasing the rate with Mg content, whereas Xie et al. [9] found an oil conversion of 67% when a soybean oil:methanol molar ratio of 15:1, a reaction time of 9 h and a catalyst amount of 7.5 wt.% were used at the temperature of methanol reflux, for a calcined hydrotalcites with an intermediate Mg/Al ratio.

It is generally assumed that the basicity of simple oxides is determined, in a first approximation, by the metal electronegativity [30]. The basic character increases as the metal becomes less electronegative. However, the more basic metal oxides, such as those formed with alkaline and alkaline earth metals are usually carbonated in air, and hence inert. Strong basicity only appears after a high temperature treatment to obtain a carbonate-free metal oxide surface [31]. The possibilities offered by solid base catalysts can be markedly enhanced with respect to conventional homogenous catalysts, such as alkaline hydroxides and methoxides, if new synthesis methods to prepare well structured, high-surface area basic materials are optimized. This has been pointed out by Corma and Iborra [32] in their review about the optimization of alkaline earth metal oxide and hydroxide catalysts for base-catalyzed reactions.

The aim of our research was to investigate the behaviour of different MgM (M = Al and Ca) oxides in two transesterification processes: a simple model reaction between ethyl butyrate and methanol, and the methanolysis of sunflower oil for biodiesel production. All precursors were synthesized by using the co-precipitation method, and after calcination the corresponding metal oxides were obtained. The structural, textural and acid–base characteristics of catalysts were determined by different techniques.

## 2. Experimental

### 2.1. Synthesis of the samples

MgAl and MgCa oxides with different Mg/M (M = Al or Ca) molar ratios were prepared by the co-precipitation method, and subsequent calcination of the precursors. These were obtained by slowly adding a 2 M aqueous solution of the corresponding metal nitrates to an aqueous solution containing  $\text{Na}_2\text{CO}_3$  and NaOH ( $\text{OH}^-/(\text{Mg} + \text{M})$  molar ratio of 0.3). The precipitation was performed under vigorous stirring at 333 K, for 1 day. Finally, the solids were filtered, washed with deionized water and dried at 333 K. MgAl samples were calcined at 773 K for 6 h (heating rate of  $1 \text{ K min}^{-1}$ ), whereas MgCa precursors, due to the higher stability of calcium carbonate, were treated at 1073 K. The samples were labeled as Mg:M(x), being x the bulk Mg/M molar ratio, as determined by ICP-AES. A commercial hydrotalcite (HTcom) supplied by Aldrich was also used for comparison.

### 2.2. Characterization methods

The Mg, Al and Ca contents have been determined by ICP-AES by using a PerkinElmer (model ELAN DRC-e) spectrometer. Powder X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer using  $\text{Cu K}\alpha$  radiation and a graphite monochromator.

Scanning electron micrographs were obtained by using a JEOL SM 840. Samples were placed over an aluminium drum and covered with a gold film using a JEOL Ion Sputter JFC 1100.

X-ray photoelectron spectra were obtained with a Physical Electronics PHI-750 spectrometer, equipped with a X-ray radiation source of Mg  $\text{K}\alpha$  (1253.6 eV). In order to measure binding energies (BE) ( $\pm 0.1 \text{ eV}$ ), the C 1s signal of the adventitious carbon at 284.8 eV was used as reference. Prior to the analysis, all samples were outgassed for 12 h under ultra-high vacuum ( $< 1.3 \times 10^{-6} \text{ Pa}$ ).

Nitrogen adsorption–desorption isotherms at 77 K were obtained using an automatic Micromeritics ASAP 2020, after outgassing the samples at 473 K and  $1 \times 10^{-2} \text{ Pa}$  overnight.

The basicity of the catalysts was studied by temperature-programmed desorption using  $\text{CO}_2$  as probe molecule. Catalysts (100 mg) were pretreated under a helium stream at 1073 K for 1 h ( $20 \text{ K min}^{-1}$ ,  $100 \text{ mL min}^{-1}$ ). Then, the temperature was decreased to 373 K, and a flow of pure  $\text{CO}_2$  ( $50 \text{ mL min}^{-1}$ ) was subsequently introduced into the reactor during 1 h. The TPD of  $\text{CO}_2$  was carried out between 373 and 1073 K under a helium flow ( $10 \text{ K min}^{-1}$ ,  $30 \text{ mL min}^{-1}$ ), and  $\text{CO}_2$  was detected by an on-line gas chromatograph (Shimadzu GC-14A) provided with a TCD, after passing by an ice-NaCl trap to eliminate any trace of water.

The catalytic decomposition of 2-propanol at 623 K was used as a test reaction for the study of the effective basicity of catalysts. A fixed-bed tubular glass reactor working at atmospheric pressure was loaded with 30 mg of catalyst without dilution (0.2–0.3 mm particle size). MgAl and MgCa oxides were thermally activated under helium flow for 3 h ( $60 \text{ mL min}^{-1}$ ) at 873 and 1073 K, respectively. Isopropanol was fed into the reactor by flowing He (dried through a molecular sieve, flow rate  $25 \text{ mL min}^{-1}$ ) through a saturator-condenser at 303 K, which gave a constant isopropanol flow of 7.5 vol.%. The reaction products were analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a FID and a fused silica capillary column SPB1.

### 2.3. Catalytic activity

The catalytic activity was evaluated in the transesterification of ethyl butyrate (Aldrich) with methanol (ultra pure, Alfa Aesar), and the methanolysis of a commercial edible grade sunflower oil. The transesterification was performed in a glass batch reactor with a water-cooled condenser, controlled temperature (333 K) and inert atmosphere ( $\text{N}_2$ ). Before the reaction, the catalysts were activated at different temperatures for 1 h (heating rate,  $10 \text{ K min}^{-1}$ ) under a helium flow. After cooling, the catalyst was added to the reaction mixture under helium. To minimize mass-transfer limitations, in a previous paper [13] we have studied the influence of the stirring rate on the catalytic activity in similar transesterification processes, and a value of 1250 rpm was found to be necessary in order to get a suitable contact between the ester and alcohol phases. The reaction was stopped by submerging the reactor in an ice bath. The catalyst was separated by filtration, and the reaction products were analyzed, in the case of ethyl butyrate and methanol, in a gas chromatograph (Shimadzu GC model 14A) equipped with FID and a capillary silica fused SPB1 column.

In the triglycerides transesterification process, aliquots (ca. 1 mL) were taken from the agitating reaction mixtures at different reaction times. The reaction was quenched by adding 1 mL of 0.1 M HCl aqueous solution and agitating for few minutes. Then, 1 mL of dichloromethane was added, and this mixture was again agitated and set aside to develop two layers: the ester layer containing dichloromethane, mono, di and triglycerides and FAME (and traces of methanol and glycerine) and the polar layer containing glycerine, methanol, water dissolved HCl and metal chlorides

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