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## Base Catalysts Derived from Hydrocalumite for the Transesterification of Sunflower Oil

María José Campos-Molina,<sup>†</sup> José Santamaría-González,<sup>†</sup> Josefa Mérida-Robles,<sup>†</sup> Ramón Moreno-Tost,<sup>†</sup> Monica C.G. Albuquerque,<sup>‡</sup> Sebastián Bruque-Gámez,<sup>†</sup> Enrique Rodríguez-Castellón,<sup>†</sup> Antonio Jiménez-López,<sup>†</sup> and Pedro Maireles-Torres<sup>\*,†</sup>

<sup>†</sup>Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain and <sup>‡</sup>Grupo de Pesquisa em Separações por Adsorção (GPSA) Departamento de Eng. Química, Universidade Federal do Ceará (UFC) Campus do Pici, blc. 709 60455-760 Fortaleza-CE Brazil

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This work investigates the use of a layered Ca–Al double hydroxide (hydrocalumite) as precursor, after its thermal activation, of base catalysts for the methanolysis of sunflower oil. Above 750 °C, hydrocalumite is transformed into a mixture of CaO and mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>). Another Ca–Al material obtained under similar experimental conditions was also studied, but using the Ca/Al molar ratio of the mayenite, 12:14. A sunflower oil conversion of 97% has been reached with a methanol/oil molar ratio of 12:1, a reaction temperature of 60 °C, and 1 wt % of the CaAl-2:1 catalyst. This catalyst needs to be previously activated at 500 °C in helium atmosphere, which is an activation temperature at least 200 °C lower than that required to revert the CO<sub>2</sub> poisoning in bulk and supported CaO catalysts.

### 1. Introduction

Currently, our oil dependence is responsible for many of the greatest environmental, health, and security problems the world is facing today. Finding a way to ease our dependence on oil presents one of the paramount challenges of our age. Biodiesel, which is a relatively clean-burning, renewable fuel produced from vegetable oils and animal fats, could be used to replace at least partially the diesel fuel obtained from fossil resources. Biodiesel has many advantages over petrodiesel, among them the significant reduction of harmful emissions (CO, SO<sub>x</sub>, particulates); it can be used in almost any normal internal combustion diesel engine with few special modifications; and it can be stored and transported using existing infrastructure and equipment already used for regular petroleum diesel.

Biodiesel generally consists of fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), derived from the transesterification of triglycerides with methanol or ethanol, respectively. Normally, most biodiesel is prepared using homogeneous basic catalysts, such as potassium hydroxide, sodium hydroxide, as well as potassium and sodium alkoxides.<sup>1</sup> Base catalysts are preferred to acid ones such as sulphuric or sulfonic acids, given the corrosive character and lower activity of the latter. However, removal of the base catalyst after reaction is problematic, since the current practice of aqueous quenching with acid results in some degree of saponification (i.e., hydrolysis of the ester and formation of the corresponding sodium carboxylate), as well as the formation of emulsions rendering difficult separation steps of the ester phase.<sup>2,3</sup> Further, an alkaline wastewater stream

is generated. To circumvent these problems, the use of heterogeneous catalysts is of interest, thus rendering the process more environmentally friendly. Very recently, several reviews about the use of heterogeneous catalysts, acid or base solids, for biodiesel production have been published in literature.<sup>4–9</sup>

Most of base solids studied for the transesterification process of vegetable oils have been metal oxides, including alkaline earth metal oxides and transition metal oxides. Among alkaline earth oxides, calcium oxide has attracted much attention in biodiesel production due to its high basicity, low solubility, and low price.<sup>10–15</sup> However, to increase the transesterification reaction rate it requires thermal activation at temperatures as high as 700 °C in order to remove the surface carbonate and hydroxyl groups. Moreover, an important drawback for the use of many base solids is the leaching of the active phase in the reaction medium, thus the

\*To whom correspondence should be addressed. Telephone: +34 952131873. Fax: +34 952137534. E-mail: maireles@uma.es.

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process operating in the transesterification reaction would be mixed, with contribution of both homogeneous and heterogeneous catalysis. An alternative to stabilize these basic oxides against leaching is the use of supports that facilitate their dispersion and in which the interaction support–active phase could prevent its leaching into the reaction medium. Recently, Albuquerque et al.<sup>16</sup> have stabilized CaO on a siliceous SBA-15 for the transesterification of sunflower oil with methanol, reaching a conversion of 95% of triglycerides after 5 h of reaction, without contribution of the homogeneous process associated to leached calcium oxide.

Basic metal oxides derived from layered double hydroxides (LDH) have been extensively studied due to their tunable properties that have allowed them to find potential applications in different catalytic fields.<sup>17–20</sup> Most LDHs adhere to the general chemical formula:  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ , where  $M^{II}$  represents any divalent metal cation,  $M^{III}$  any trivalent metal cation, and  $A^{n-}$  an anion (inorganic or organic). An alternative to stabilize soluble metal oxides against leaching could be the use of hydrotalcites as precursors, where thermal decomposition yields high surface area mixed oxides that presumably expose strong Lewis base sites.<sup>21</sup> In this sense, calcined hydrotalcites exhibit enough strength, which has allowed it to be largely used in the transesterification of triglycerides.<sup>22–31</sup> For instance, Di Serio et al.<sup>23</sup> have reported that the catalytic activity of calcined hydrotalcites in the transesterification of soybean oil with methanol is well correlated with their basicity and textural properties, which depend on both the nature of the precursor and the preparation method. Cantrell et al.<sup>24</sup> have demonstrated that calcined Mg–Al LDHs are effective catalysts in the methanolysis of glyceryl tributyrate, increasing the rate with Mg content, whereas Xie et al.<sup>25</sup> found that calcined hydrotalcites with a intermediate Mg/Al ratio reached 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.

On the other hand, the Friedel's salt  $[Ca_2Al(OH)_6]Cl_2 \cdot H_2O$ , also called hydrocalumite, where  $Ca^{2+}$  and  $Al^{3+}$  ions are ordered in the hydroxide layers and the interlayer water molecules are coordinated to Ca atoms, creating 7-fold-coordinated Ca sites. Above 750 °C the structure is transformed into a mixture of CaO and mayenite  $Ca_{12}Al_{14}O_{33}$ .<sup>32</sup> The decomposition of calcium-containing hydrotalcite-like materials could probably incorporate new properties (particle size, basicity, less solubility, etc.) that would allow these materials to be successfully used in transesterification of triglycerides.

The present work was aimed at the use of hydrocalumite as precursor to obtain base catalysts effective in the methanolysis of sunflower oil for biodiesel production. Two precursors were synthesized by using the coprecipitation method, with different Ca/Al molar ratio and, after calcination, the corresponding metal oxides were obtained. The catalysts were characterized by using different techniques.

## 2. Experimental Section

**2.1. Catalysts Preparation.** Hydrocalumite was prepared according to the method proposed by Vieille et al.<sup>32</sup> The synthesis was carried out at 60 °C under vigorous magnetic stirring using deionized decarbonated water in inert atmosphere (He) to prevent incorporation of atmospheric CO<sub>2</sub>. 100 mL of a  $CaCl_2$  and  $AlCl_3 \cdot 6H_2O$  aqueous solution (Ca/Al molar ratio = 2:1) was added dropwise to 250 mL of a water–ethanol solution (2:3, v:v). The pH was kept constant at 11.5 by the simultaneous addition of a 2.0 M NaOH solution. After complete addition of the metallic salts, the precipitate was aged in the mother solution for 24 h, and then centrifuged, washed with water, and dried at 60 °C. A material with a Ca/Al molar ratio of 12:14 was also obtained by the same procedure. These materials were heated in air at 750 °C (heating rate of 1 °C·min<sup>−1</sup>) for 13 h. The samples were labeled as CaAl-2:1 and CaAl-12:14, according to the Ca/Al molar ratio in the starting solution.

**2.2. Characterization Methods.** Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer using Cu K $\alpha$  radiation and a graphite monochromator. Scanning electron micrographs (SEM) were obtained by using a JEOL SM 840. Samples were placed over an aluminum drum and covered with a gold film using a JEOL Ion Sputter JFC 1100.

X-ray photoelectron spectra (XPS) were obtained with a Physical Electronics PHI-5700 spectrometer, equipped with a X-ray radiation source of Mg K $\alpha$  (1253.6 eV) and of Al K $\alpha$  (1483.6 eV). In order to measure binding energies ( $\pm 0.1$  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 ultrahigh vacuum ( $< 1.3 \times 10^{-6}$  Pa). N<sub>2</sub> adsorption–desorption isotherms at −196 °C were obtained using an automatic Micromeritics ASAP 2020, after outgassing at 200 °C and  $1 \times 10^{-2}$  Pa overnight.

In situ surface infrared spectra of calcined materials were collected by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Varian 3100 FTIR spectrometer. A Harrick Scientific Praying Mantis supplied with a high temperature reaction chamber mounted inside the spectrometer can provide temperature-controlled flow through atmospheres attaining up to 450 °C. The background spectrum was recorded with KBr purged with a 50 mL min<sup>−1</sup> He flow. The DRIFTS spectra of adsorbed species were measured under a He flow in the 4000–400 cm<sup>−1</sup> interval with a resolution of 4 cm<sup>−1</sup>, collected by adding 124 scans.

Evolved gas analysis at programmed temperature by mass spectrometry (EGA-MS) was carried out. The main molecules,

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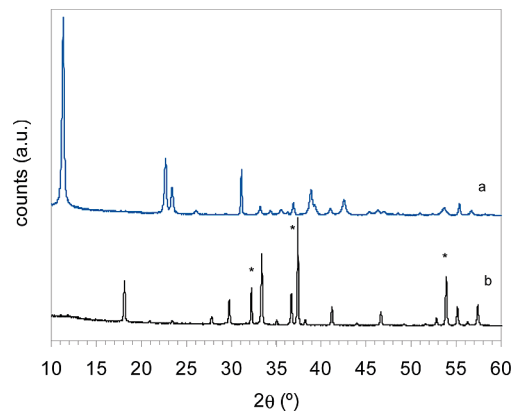
H<sub>2</sub>O and CO<sub>2</sub>, arising from the decomposition of the materials were monitored by recording the  $m/z = 18$  and 44 signals, respectively. 80 mg of the sample was loaded in quartz micro-reactor, and 50 mL (STP) min<sup>-1</sup> of He were passed through the container while the sample was heated at 10 °C min<sup>-1</sup>. A quadrupole mass spectrometer, model BALZERS Prisma QMS 200 controlled by BALTZER Quadstar™ 422 software, was connected online to the reactor outlet for the analysis of gases generated.

**2.3. Transesterification of Sunflower Oil.** The catalytic activity was evaluated in the transesterification of edible grade sunflower oil (acidity  $\leq 0.2^\circ$ ) with methanol (ultra pure, Alfa Aesar). The transesterification was performed in a glass batch reactor with a water-cooled condenser, controlled temperature (60 °C), atmospheric pressure, and inert atmosphere (N<sub>2</sub>). Before the reaction, the catalysts were activated at different temperatures for 1 h (heating rate, 20 °C min<sup>-1</sup>) under a helium flow. After cooling, the catalyst was added to the reaction mixture under helium atmosphere. The catalyst was separated by filtration, and the reaction products were analyzed by high performance liquid chromatography (HPLC) using a JASCO liquid chromatograph equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055), and column oven (co-2065) using a PHENOMENEX LUNA C<sub>18</sub> reversed-phase column (250 mm × 4.6 mm, 5  $\mu$ m). The solvents were filtered through a 0.45  $\mu$ m 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 15 min was employed. Injection volumes of 15  $\mu$ L and a flow-rate of 1 mL min<sup>-1</sup> were used. The column temperature was held constant at 40 °C. All samples were dissolved in 2-propanol–hexane (5:4, v/v).

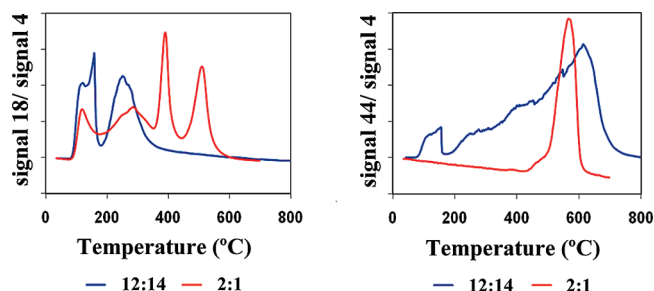
The standard reaction conditions were: molar ratio methanol/oil 12:1, 1 wt % catalyst in relation to the oil amount, reaction temperature = 60 °C, stirring rate = 1000 rpm, 16.5 mL of methanol, and inert atmosphere.

### 3. Results and Discussion

**3.1. Characterization of Catalysts.** Two catalysts with Ca/Al molar ratio of 12:14 and 2:1, corresponding to the Ca/Al ratios in the mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) and hydrocalumite ([Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O), respectively, were prepared. The powder X-ray diffraction pattern (XRD) of the synthesized CaAl-2:1 precursor is typical of layered compounds with maximum intensity for the (001) reflections at low  $2\theta$  values: 11.3° (003) and 22.7° (006), which appear together with other characteristic peaks at 31.2° (110) and 28.9° (116) (Figure 1). This XRD pattern can be indexed in a hexagonal lattice with an  $R\bar{3}$  rhombohedral symmetry where layers of Ca(OH)<sub>6</sub>H<sub>2</sub>O and Al(OH)<sub>4</sub> are alternated and the Cl<sup>-</sup> ions are placed between these layers.<sup>33</sup> After calcination at 750 °C, new phases are observed in the corresponding XRD pattern, which can be assigned to mayenite<sup>34</sup> ( $2\theta$ : 18.2, 29.8, 33.5, 36.7, 41.3, 46.7, 55.3, and 55.6°) and cubic CaO ( $2\theta$ : 32.3, 37.3, and 54.0°) phases, the latter resulting from the different Ca/Al molar ratios in hydrocalumite and mayenite. The diffractogram of the CaAl-12:14, calcined under similar conditions, only shows evidence of peaks corresponding to a pure mayenite phase. The presence of different phases in the calcined CaAl materials could influence the catalytic performance, as will be discussed below.



**Figure 1.** XRD of (a) CaAl-2:1 precursor and (b) after calcination at 750 °C.



**Figure 2.** Mass-spectral analysis of the evolved gases (EGA-MS) of the two calcined samples.

The results from the mass-spectral analysis of the evolved gases (EGA-MS) obtained in the course of the thermal treatment of the two CaAl catalysts, between room temperature (rt) and 800 °C taken as reference the He signal are illustrated in Figure 2. The behavior of the two samples is different. The CaAl-12:14 sample is completely dehydrated at about 400 °C, whereas CaAl-2:1 needs temperatures of about 600 °C. Taking into account the XRD results, we can conclude that the water molecules eliminated below 400 °C are mainly associated with the mayenite phase, because this is the only phase present in the CaAl-12:14 material, whereas, at higher temperature, water molecules could be mainly associated to CaO phase, as Ca(OH)<sub>2</sub>, which is present in the CaAl-2:1 material. The signal of CO<sub>2</sub> evolved is also different for the two materials. Thus, CaAl-12:14 shows a first CO<sub>2</sub> desorption at low temperature (below 200 °C) due to the physisorbed CO<sub>2</sub> and a broadband between 200 and 700 °C; CaAl-2:1 only presents a defined desorption peak centered at 550 °C. The higher CO<sub>2</sub> evolved in CaAl-12:14 could be related with its higher surface area (vide infra). From these results, we can conclude that the CaAl-2:1 material suffers dehydration and decarbonation processes below 550 °C, and the CaAl-12:14 catalyst at temperatures higher than 700 °C.

IR spectrum of the calcined CaAl-2:1 shows broad absorptions associated with the presence of water molecules and carbonate anions (Figure 3). The absorption bands at 3646 and 3487 cm<sup>-1</sup> can be assigned to superficial OH groups associated to Ca(OH)<sub>2</sub> which is present in the material, as previously shown by EGA-MS. The broad band, below 3000 cm<sup>-1</sup>, also displays a contribution of OH stretching due to adsorbed H<sub>2</sub>O, which is confirmed by the presence of the bending vibration band at 1620 cm<sup>-1</sup>. The presence of

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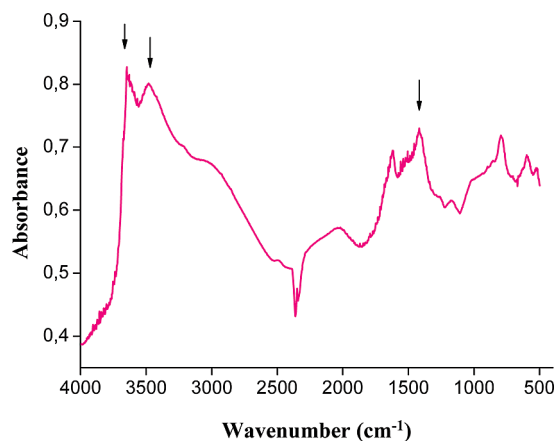


Figure 3. IR spectra of the calcined CaAl-2:1 material.

physisorbed  $\text{CO}_2$  is reflected by the relative broad and weak peak at  $1400\text{ cm}^{-1}$  typical of  $\text{O}-\text{C}-\text{O}$  vibrations ( $\nu_3$ ) for adsorbed (non interlayer) carbonate anions that are present on the outer surface of the crystallites.<sup>35</sup> The well-defined infrared bands at  $1445$  and  $875\text{ cm}^{-1}$  are characteristic of the  $\text{C}-\text{O}$  stretching and bending modes of calcium carbonate, associated with the formation of superficial calcite.<sup>36</sup>

Figure 4 shows the scanning electron micrographs (SEM) of the two fresh and calcined materials. The micrograph of hydrocalumite shows the presence of platelets of homogeneous size lower than  $1\text{ }\mu\text{m}$ , which is typical of well-crystallized hydrotalcite-type compounds as previously shown by XRD patterns. By comparing the micrographs of the two calcined materials it is clear that the composition of the samples has a significant influence on the morphology of the resulting oxides. Thus, although the two samples present particles of different morphologies and sizes, in the CaAl-2:1 calcined material there are also particles with rod form which could be  $\text{CaO}$ .

Regarding the textural characteristics of the two catalysts (Table 1), CaAl-12:14 possesses a slightly larger BET surface area and pore volume. This is in agreement with XRD and SEM results that revealed a lower crystallinity and particle size for CaAl-12:14. The nitrogen adsorption/desorption isotherms obtained for the two catalysts are Type III in the IUPAC classification, typical of solids with weak gas/solid interactions.<sup>37</sup>

To get insights into the surface composition, XPS analysis was also employed in this study. Table 2 shows the BE values obtained for Ca 2p, Al 2p, C 1s, and O 1s, and the Ca/Al atomic ratios determined by XPS analysis and the theoretical Ca/Al atomic ratios for calcined materials. The surface Ca/Al atomic ratio for the CaAl-2:1 catalyst, 4.47, is higher than 2, the theoretical value present in the hydrocalumite precursor, and much higher than the corresponding theoretical value of the mayenite (0.86). This agrees well with the presence of  $\text{CaO}$  on the surface of the CaAl-2:1 catalyst, as previously detected by XRD. On the other hand, the CaAl-12:14 catalyst presents a deficit of superficial calcium ( $\text{Ca}/\text{Al} = 0.53$ ) with respect to the theoretical value (0.86), thus pointing out a surface enriched with aluminum with respect to CaAl-2:1 catalyst. It can be thought that an

aluminum hydroxide could coprecipitate during the synthesis process that is then converted into a superficial amorphous alumina after calcination, giving rise to a low superficial Ca/Al atomic ratio for the CaAl-12:14 catalyst. The binding energies of the different elements are very similar in both catalysts.

**3.2. Catalytic Activity in Transesterification of Sunflower Oil with Methanol.** Methanolysis of sunflower oil was performed at  $60\text{ }^\circ\text{C}$ , as described in the Experimental section, and the influence of different reaction parameters was studied to optimize the FAME yield.

First, the optimal activation temperature of the CaAl catalysts was determined because the active surface sites of catalysts based on  $\text{CaO}$  are unavoidably poisoned by atmospheric  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . López-Granados et al.<sup>14</sup> have demonstrated that  $\text{CO}_2$  is the main deactivating agent, whereas the negative effect of water is less important. In agreement with the EGA-MS data, a temperature of  $500\text{ }^\circ\text{C}$  has been chosen to activate the two CaAl catalysts. The evolution of the FAME yield as a function of the reaction time (Figure 5) reveals that, after 3 h, a yield of 98% is reached with the CaAl-2:1 catalyst, whereas the CaAl-12:14 barely reaches a conversion of 10%. It is obvious that, in the latter case, the activation temperature is insufficient to obtain an active catalyst, and the presence of a low surface Ca/Al molar ratio, as revealed by XPS analysis, impedes having a high proportion of active sites on the surface of this catalyst, thus evidencing that aluminum oxide centers do not play a key role in the catalytic activity. It is usually necessary to employ temperatures higher than  $700\text{ }^\circ\text{C}$  to revert the  $\text{CO}_2$  poisoning when  $\text{CaO}$ -based catalysts are employed, and therefore an activation temperature of  $500\text{ }^\circ\text{C}$  for the CaAl-2:1 catalyst implies a reduction of  $200\text{ }^\circ\text{C}$  respect to the temperature needed to activate bulk  $\text{CaO}$  or supported on SBA-15.<sup>14,16</sup>

The effect of the catalyst loading was investigated by using 1, 2, and 5 wt % catalyst with respect to the oil weight. The other reaction parameters were maintained unchanged: activation temperature =  $500\text{ }^\circ\text{C}$ , methanol/oil molar ratio = 12/1, reaction temperature =  $60\text{ }^\circ\text{C}$ , and stirring rate = 1000 rpm. The results compiled in the bar diagram of Figure 5 indicate that the conversion of sunflower oil, at low reaction time, was increased with the catalyst amount, in such a way that with 5 wt % of catalyst a FAME yield close to 100% was attained after 2 h. Moreover, this yield increased steadily with reaction time for each catalyst loading. After 3 h, the FAME yields were higher than 90% in all cases.

The study of the influence of the methanol/oil molar ratio has revealed that values higher than the stoichiometric one (3:1) favor the production of methyl esters (Figure 5). The maximum value of FAME yields, after 3 h of reaction, is achieved when a methanol/oil molar ratio of 12/1 is used. This excess of methanol promotes the transesterification reaction and extracts products from the catalyst surface renewing the catalytic sites.<sup>38</sup>

Another experiment was designed to compare the catalytic activity of  $\text{CaO}$  and CaAl-2:1 catalyst. Thus, the amount of  $\text{CaO}$  loaded in the reactor was chosen to be the same as that present in CaAl-2:1 catalyst, which contains 10.5 wt % of  $\text{CaO}$ . The  $\text{CaO}$  was activated at  $500\text{ }^\circ\text{C}$  under the same experimental conditions described in the Experimental section of the paper. The catalytic results show that  $\text{CaO}$  is

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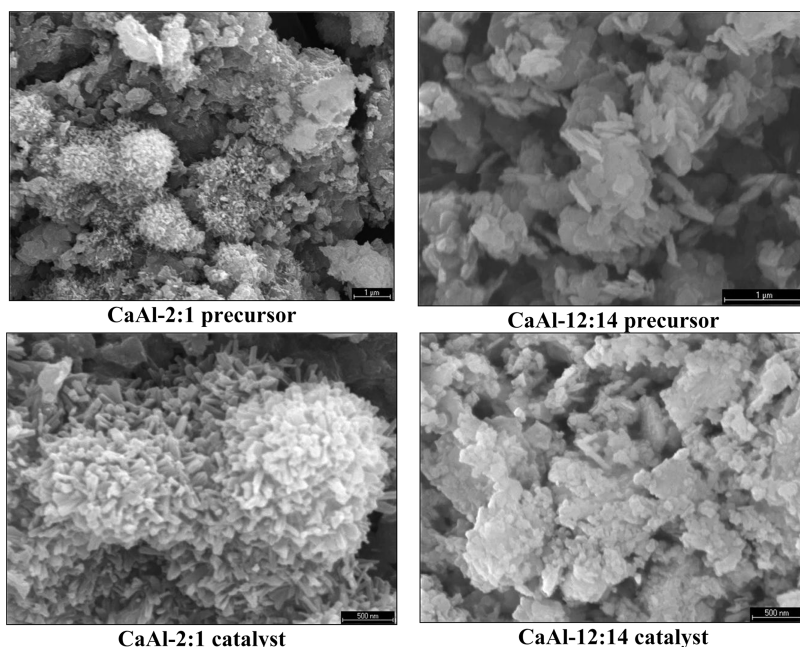


Figure 4. Scanning electron micrographs (SEM) of the two fresh and calcined materials.

Table 1. Textural Properties of Catalysts

sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p^a$ ( $\text{cm}^3 \text{g}^{-1}$ )	$d_{\text{av}}$ (nm)
CaAl-12:14	16.7	0.062	11.2
CaAl-2:1	2.1	0.023	21.6

<sup>a</sup>  $V_p$  at  $P/P_0 = 0.95$ .

Table 2. Binding Energies (eV) and Ca/Al Atomic Ratios of the Catalysts

catalyst	BE (eV)					Ca/Al theor.
	Ca 2p <sub>3/2</sub>	Al 2p	C 1s	O 1s	Ca/Al from XPS	
CaAl-2:1	347.0	73.9	290.1, 284.8	531.0	4.47	2
CaAl-12:14	347.0	74.0	289.4, 284.6	531.2	0.53	0.86

Table 3. FAME Yield (%) for CaO and CaAl-2:1 Catalyst<sup>a</sup>

reaction time (h)	FAME yield (%) CaO	FAME yield (%) CaAl-2:1
1	3.8	51
2	24.5	88
3	62.7	98

<sup>a</sup> Activation temperature = 500 °C, 1 wt % CaAl-2:1 catalyst, 26.2 mg CaO, methanol/sunflower oil molar ratio = 12, reaction temperature = 60 °C.

less effective than the CaAl-2:1 material in the transesterification of sunflower oil (Table 3). After 3 h of reaction, the FAME yield by using CaO was of 62.7%, whereas the CaAl-2:1 catalyst gives rise to a value of 89%. These results point out some kind of synergism between the mayenite and CaO phases obtained by thermal treatment of the hydrocalumite.

An important aspect to be taken into account in the developing of solid catalysts for biodiesel production is the possibility to reutilize the catalyst. Catalyst stability was tested by recovering the solid after a catalytic run by decantation, without further activation and maintaining the catalyst inside the reactor covered by a film of reaction products to avoid contact with the atmosphere, and placing it in contact with new fresh portions of methanol and sunflower oil. The catalytic results of a second run reveal that conversion is maintained higher than 95%. However, after two runs, the separation of the catalyst from the reaction medium became difficult, probably due to the decrease in the particle size that makes more difficult their separation, and the catalytic activity strongly decays. This sharp decrease could be also attributed to the leaching of active species. The lixiviation of active species could lead to a contribution of the homogeneous process to the overall catalytic activity, as previously found for bulk CaO.<sup>14</sup> In order to evaluate this assumption, the activated CaAl-2:1 catalyst was placed in contact with methanol for 1 h at 60 °C, under inert atmosphere. Then, the catalyst was withdrawn by filtration and the oil was added to the methanol under the same conditions described in the Experimental section.

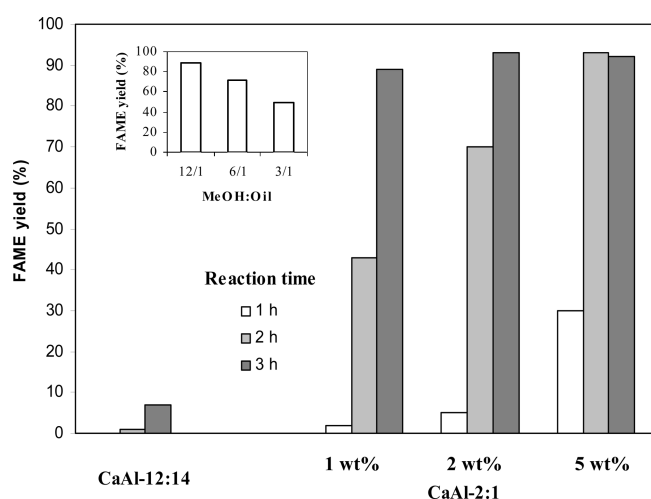
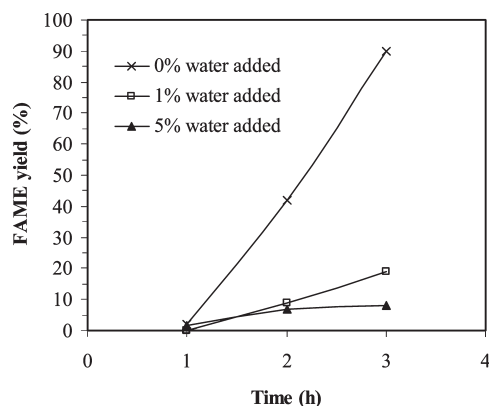


Figure 5. FAME yield as a function of the reaction time for the two catalysts (methanol/oil = 12). Influence of the catalyst percentage in the FAME yield for the CaAl-2:1 catalyst. Inset: influence of the methanol/oil molar ratio in the FAME yield versus reaction time for the CaAl-2:1 catalyst (1 wt %). Activation temperature = 500 °C, reaction temperature = 60 °C.



**Figure 6.** Effect of water addition on the FAME yield for the CaAl-2:1 catalyst (activation temperature = 500 °C, 1 wt % catalyst, methanol/sunflower oil molar ratio = 12, reaction temperature = 60 °C).

Thus, whether a fraction of the active phase is dissolved into the methanol, catalytic activity should be observed when it is put in contact with oil. However, the conversion values found was null, thus confirming the stability of the active phase against lixiviation. Thus, the decrease in the conversion could be attributed to the deactivation of the active sites due to the occlusion or irreversible adsorption of reactants or reaction products.

On the other hand, water and free fatty acids (FFA) are considered as poisons in biodiesel production processes if base catalysts are used. Bearing in mind that using low quality oils, i.e., fried oils or nonedible oils with high FFA content, is mandatory to reduce the final price of biodiesel, base catalysts must be active in the presence of these poisons. To study the effect of water and FFA on the activity of CaAl-2:1 catalyst, two water loading (1 and 5 wt %) were used, and a sunflower oil with an acid value of 15.6 mgKOH/g was prepared by adding octanoic acid (refined oil has a value of 3.9 mg KOH/g). The results indicate that the presence of water greatly affects the FAME yield (Figure 6), since the addition of low water percentage (1 wt % with respect to the oil) is sufficient to provoke a drastic decrease in the catalytic

activity. Similarly, the increase of the oil acidity exerts a negative effect on the FAME yield, and, after 3 h, the yield decreased from 92% for 3.9 mg KOH/g to 36% for 15.6 mg KOH/g.

Therefore, it can be concluded that layered inorganic phases based on double metal hydroxides can be used as precursors of mixed metal oxides after calcination. Thus, synthesis gels containing different Ca/Al molar ratios lead, after calcination at 750 °C, to a CaAl-2:1 catalyst with two phases: CaO and mayenite, whereas only a crystalline phase, mayenite, was detected for CaAl-12:14. It has been found that this latter catalyst was almost inactive, after activation at 500 °C, which can be explained by considering the presence of superficial aluminum species masking the active sites associated to mayenite, as well as the need of higher activation temperatures, as deduced from EGA-MS studies. However, a catalyst containing CaO and mayenite is very active in the methanolysis of sunflower oil, requiring activation temperatures lower than that needed to decarbonate bulk and supported CaO.

#### 4. Conclusions

A new precursor of base catalysts for biodiesel production under heterogeneous conditions is proposed. Thus, a layered Ca–Al double hydroxide (hydrocalumite) is transformed by calcination at 750 °C in a mixture of CaO and mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ), which is a base catalyst active in the methanolysis of sunflower oil. A sunflower oil conversion of 97% has been reached with a methanol/oil molar ratio of 12:1, a reaction temperature of 60 °C, and 1 wt % of calcined hydrocalumite. This catalyst was previously activated at 500 °C in helium atmosphere, which is an activation temperature at least 200 °C lower than that needed to revert the  $\text{CO}_2$  poisoning in bulk and supported CaO catalysts.

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