

Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel

Alberto Navajas^{a,b}, Idoia Campo^a, Ainara Moral^{a,b}, Javier Echave^c, Oihane Sanz^c, Mario Montes^c, José A. Odriozola^d, Gurutze Arzamendi^{a,b}, Luis M. Gandía^{a,b,*}

a Departamento de Química Aplicada, Edificio de los Acebos, Universidad Pública de Navarra, Campus de Arrosadía s/n, E-31006 Pamplona, Spain

b Institute for Advanced Materials (InaMat), Universidad Pública de Navarra, E-31006 Pamplona, Spain

c Departamento de Química Aplicada, Facultad de Ciencias Químicas de San Sebastián, Universidad del País Vasco, P. Manuel de Lardizábal 3, E-20018 San Sebastián, Spain

d Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, Avda. Américo Vespucio 49, 41092 Sevilla, Spain

* Corresponding author: L.M. Gandía (lgandia@unavarra.es)

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Abstract

There is still a need for active, selective and stable heterogeneous catalysts for the synthesis of biodiesel. In this work, magnesium-aluminium hydrotalcites with Mg/Al molar ratios within the 1.5–5 range were synthesized by coprecipitation and used as transesterification catalysts for the synthesis of biodiesel. The mixed oxides obtained after calcination recovered the hydrotalcite structure in the form of meixnerite after rehydration in boiling water. The solids were characterized by XRD, TGA, N₂ adsorption-desorption, and SEM. Basic properties were assessed by means of Hammett indicators and CO₂-TPD. Rehydrated materials with the highest Mg/Al ratios showed some distinctive features: low surface area, well defined flake-like crystals, high basicity and strong basic sites with H₊ values above 11. They were also the most active catalysts allowing to achieve 51–75% sunflower oil methanolysis conversion after 8 h of reaction under mild conditions (60 °C, 1 atm), methanol/oil molar ratio of 12 using between 2 and 6 wt% of catalyst. The conversion increased up to 96% (92% fatty acid methyl esters yield) using 2 wt% catalyst and methanol/oil molar ratio of 48. Catalyst leaching was not a serious problem with these solids that could be reutilized maintaining very good activities. A general accordance between solids basic properties and their catalytic performance has been observed. These results are among the best reported in the literature for heterogeneous methanolysis catalysts and have been attributed to the high basicity of the rehydrated solids and the presence of strong and accessible basic sites probably consisting in interlayer hydroxide anions at the edges of the crystals.

Keywords: Biodiesel; Hydrotalcites; Methanolysis; Rehydration; Transesterification.

1. Introduction

Transesterification with methanol (methanolysis) of the triglycerides present in vegetable oils catalyzed by homogeneous Na or K hydroxides or methoxides in batch or flow reactors is the most common method for the industrial production of biodiesel [1]. This process suffers from several drawbacks mainly because the catalyst cannot be reutilized and it is required the neutralization and washing of the produced biodiesel and glycerol which generates large volumes of wastewater. With the aim of helping to overcome these problems, great efforts are currently being devoted to develop active and stable heterogeneous catalysts for biodiesel production. A variety of basic and acid solids have been considered for the transesterification of triglycerides and the esterification of free fatty acids (FFA) with variable degrees of success [2]. As concerns the methanolysis of vegetable oils, it can be mentioned the use of alkaline-earth metals oxides and hydroxides [3,4], supported alkaline and alkaline-earth metals compounds [5,6], and hydrotalcites [7–10]. In spite of the great effort devoted to this task there is still a need for active, selective and stable catalysts for improving the synthesis of biodiesel through the heterogenization of the catalyst.

Due to their tunable properties and promising performance, hydrotalcites are among the materials that have attracted more attention in the recent years as transesterification catalysts. Hydrotalcites belong to the layered double hydroxides (LDHs) family. These minerals are described by the formula $[M^{2+}_n M^{3+}_m (OH)^{2(n+m)}]^{m+} [A^{x-}]_{m/x} \cdot y H_2O$, where M^{2+} is a divalent metal (e.g. Ca^{2+} , Mg^{2+} , Zn^{2+}), M^{3+} is very frequently Al^{3+} , A^{x-} an anion (e.g. CO_3^{2-} , NO_3^- , Cl^-) and x is within the 0.1–0.5 range. More specifically, hydrotalcites are Mg-Al-LDHs that can be viewed as brucite, $Mg(OH)_2$, with partial substitution of Mg^{2+} by Al^{3+} . This results in net positive charge in the layers that is balanced by anions located, together with water molecules, in the interlayer space [11–14].

It is well-known that the oxides obtained after the calcination of hydrotalcites at moderate temperatures can recover the original layered structure when exposed to water [15]. These reconstructed Mg-Al LDHs (meixnerite) contain hydroxyde anions in the interlayer space and Brønsted basic sites active in a variety of base-catalyzed reactions. However, there are very few reports on the use of rehydrated hydrotalcites in methanolysis reactions. Xi and Davis [16,17] studied the methanolysis of tributyrin, a model triglyceride, catalyzed by hydrotalcites with Mg/Al molar ratios of 2 and 4. These authors found that the rehydrated solids were significantly more active than the calcined ones. Kim et al. showed a positive effect of rehydration on the activity of a hydrotalcite with Mg/Al molar ratio of 2.8 in the methanolysis of soybean oil [10].

In previous studies by our group with commercial Mg-Al hydrotalcites it was found that the original solids were inactive for methanolysis of sunflower oil. Among the calcined solids only one mainly consisting of MgO was active whereas rehydration significantly improved the activity of the solids with the highest Mg/Al ratios [7]. In this work, the investigation is extended to a series of Mg-Al hydrotalcites synthesized considering different Mg/Al ratios that were characterized by means of several techniques. The performance as transesterification catalysts of the calcined and rehydrated materials was tested in the methanolysis of sunflower oil. Takehira has reviewed the recent developments of LDH-derived catalysts, with emphasis on the performance of rehydrated hydrotalcites [18]. In spite of the abundant literature existing, to our knowledge, there is no a study equivalent to this one reporting on the results of a systematic investigation on the combined effects of the rehydration and composition of Mg-Al hydrotalcites on their performance as methanolysis catalysts.

2. Experimental

2.1. Catalysts preparation

The hydrotalcites were prepared by coprecipitation from two aqueous solutions, one of them containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich) and the other NaOH 2.3 M (Scharlau) and Na_2CO_3 0.6 M (Aldrich). The concentrations of the metallic solutions were adjusted to obtain Mg/Al nominal molar ratios of 2, 3, 4, 5, 6 and 7 with aluminum concentrations in the range between 0.27 and 0.5 M. Both solutions were simultaneously added dropwise into a jacketed glass flask of 500 cm³ at room temperature under vigorous stirring. The addition rate was controlled to maintain the pH between 10 and 11 until putting out the metallic solution after about 3 h. The resulting suspension was stirred for 20 h at 65 °C, and then filtered to recover a white precipitate that was thoroughly washed with deionized water until achieving a pH of 7 to remove sodium ions. The solids were dried at 100 °C for 24 h to give the as-synthesized hydrotalcites (HT) that will be denoted as HTx-as, where x is the nominal Mg/Al molar ratio employed for the synthesis.

The solids were calcined at 500 °C (1.3 °C/min) for 6 h to give the calcined materials that will be referred to as HTx-ca. To obtain the rehydrated hydrotalcites, calcined samples were immersed into boiling deionized water until total liquid evaporation after about 15 min. The resulting solids were rapidly removed from the hot vessel and dried under vacuum at 65 °C for 5 h to give the rehydrated hydrotalcites that are denoted as HTx-rh. The degree of rehydration of the several solids was similar, resulting in a weight increase of about 36 wt%. Solids with other percentages of rehydration were prepared varying the immersion time (1-30 min) of the calcined hydrotalcites into boiling deionized water.

2.2. Catalysts characterization

Elemental analyses were performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a VISTA-MPX (VARIAN) spectrophotometer. The catalysts were characterized by N₂ adsorption-desorption at -196 °C with a static volumetric apparatus (Micromeritics ASAP 2000 adsorption analyzer). Prior to the measurements, samples were degassed for 5 h at 80 °C. Specific surface areas (S_{BET}) were calculated using the BET method from the nitrogen adsorption isotherms taking a value of 0.162 nm² for the cross-sectional area of the adsorbed N₂ molecule. Specific total pore volumes were assessed from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at -196 °C (1.547 g/cm³). X ray powder diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using Cu K α (40 mA, 40 kV) radiation ($\lambda = 1.5418 \text{ \AA}$) and a range of 2θ angles between 20 and 80° (scan step size of 0.05°). Thermogravimetric analyses (TGA) were performed in a Seiko Exstar 6000 thermobalance under oxygen flow and heating rate of 5 °C/min. The morphology of the samples was examined with a scanning high-resolution field-emission electron microscope (HITACHI S-5200).

The basic properties of the solids were determined through temperature programmed desorption of CO₂ (CO₂-TPD) and tests with Hammett indicators. CO₂-TPD experiments were carried out using a Micromeritics AutoChem II apparatus equipped with a TCD detector and a programmable furnace with temperature control. Typically, 50 mg of the sample were placed in a quartz tube over quartz wool and pretreated at 50 °C for 30 min under flowing Ar. Afterwards the sample was saturated at room temperature with a CO₂ stream (10 vol. % CO₂ in Ar). CO₂ desorption was registered from room temperature to 1000 °C at a heating rate of 10 °C/min. In order to calculate the basicity (basic sites density) it was assumed that one CO₂ molecule is adsorbed on one surface basic site.

The basic strength (H_-) was determined according to the method based on the color change of Hammett indicators [15]. The value of H_- is approximately given by the pK_a of the acid indicator showing upon adsorption a color intermediate between those of the acidic and basic forms. The indicators employed in this work were (pK_a values are given between parentheses): bromothymol blue (7.2), phenolphthalein (9.3), thimolphthalein (9.9), alizarine yellow (11.0) and indigo carmine (12.2). The determination of H_- was carried out placing about 100 mg of the solid in a test tube, adding about 2 cm³ of a solution of the indicator in toluene and shaking vigorously. After equilibration, the suspension was examined for color change.

2.3. Transesterification reactions

Transesterification reactions were carried out in a Radleys Carousel Tornado IS6 system with capacity for carrying out simultaneously up to 6 catalytic tests. Each reaction was performed in a 100 cm³ round bottomed flask closed hermetically and with mechanical stirring to obtain a good suspension of the catalysts particles. The flasks are directly heated by the hotplate where they lean which allows a temperature control within ± 0.5 °C. The sidearm of the flasks was adapted to fit a type K thermocouple and the inlet and outlet sides of a recirculation loop made of 1/8" Teflon tubing and comprising a diaphragm-type metering pump (ProMinent Gugal type G) and a stainless steel three-way ball valve for sampling purposes. Reactions were carried out with HPLC grade methanol (Scharlau) and refined sunflower oil (Urzante, Navarra, Spain; acid value of 0.07 mg KOH/g); a molecular weight of 879.5 g/mol was assumed for the oil. Reference reaction conditions were 1 atm, 60 °C, 2 wt% of catalyst referred to the oil loaded into the reactor, and methanol/oil molar ratio of 12. When using the calcined samples as catalysts, the solids were used immediately after calcination, being weighted and transferred still hot into the reaction flask containing the oil to minimize the interaction with ambient water and CO₂. In the case of the reactions catalyzed by the rehydrated

solids, they were used immediately after the final drying at 65 °C under vacuum. In a typical catalytic run, 30 g of sunflower oil and the required amount of solid catalyst were placed in a round bottomed flask and heated in the Radleys Carousel system under vigorous stirring. When the reaction temperature (60 °C) was attained and stabilized, 13.0 g of methanol (methanol/oil molar ratio of 12) were rapidly added and the recirculation pump switched on. Samples (about 0.5 g) were taken at various intervals through the three-way valve and stored in 30 cm³ sealed glass flasks. The reaction was short-stopped by addition in each flask of some drops of a glacial acetic acid (Scharlau, HPLC grade) solution (0.6 N) in tetrahydrofuran (THF, Scharlau, HPLC grade) to neutralize the catalyst. Samples were further diluted with about 14 g of additional THF. Once filtered with Acrodisc[®] syringe filters with 0.2 µm nylon membrane, samples were analyzed by size exclusion chromatography (SEC) with a differential refractive index detector at room temperature as described elsewhere [19].

2.4. Catalysts stability

The chemical stability of the catalysts has been investigated analysing the possible presence of leached Mg and Al in the reaction mixture. Some of the samples taken from the reaction system were diluted in THF and then carefully filtered and introduced in a rotary evaporator at room temperature. After evaporation, the dry fraction was treated with 50 cm³ of HCl 0.1 N. The resulting solution was analysed by ICP-AES to determine the Mg²⁺ and Al³⁺ concentrations. Leached compounds were referred to the total metal in the sample withdrawn from the reactor assuming that all components in the reactor are perfectly mixed.

Another experiment was done after removing by centrifugation the catalyst HT5-rh from two solutions of methanol that contained this solid for 1 or 4 h, respectively, at the reaction conditions (60 °C, 2 wt% of catalyst). Then, the recovered methanol (without the solid catalyst) was added to the required amount of oil to perform an ordinary methanolysis activity test under

12:1 methanol/oil molar ratio. Some samples were taken at different times and analyzed by SEC. The purpose of this experiment is to check if there is some activity that could be linked to the presence in the methanol of leached components of the hydrotalcite and/or dissolved residual Na ions. Na ions can remain in the rehydrated solids if the as-synthesized hydrotalcites have not been washed carefully after the coprecipitation process.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. Composition, structure and texture

The Mg/Al molar ratios of the as-synthesized hydrotalcites determined from the ICP-AES elemental analyses are included in Table 1.

Table 1

Mg/Al molar ratios and lattice parameters of the as-synthesized hydrotalcites.

Sample	Mg/Al (nominal)	Mg/Al (ICP-AES)	a (Å)	c (Å)
HT2-as	2	1.5	3.05	22.86
HT3-as	3	2.3	3.07	23.44
HT4-as	4	3.1	3.07	23.79
HT5-as	5	4.1	3.07	23.37
HT6-as	6	5.0	3.09	24.00
HT7-as	7	4.0	3.08	22.90

For all the samples, but especially for the Mg-rich formulations, the Mg/Al ratio of the solid was lower than the nominal one and varied from 1.5 for HT2-as to 5.0 for HT6-as. There is the possibility that the precipitation of the Mg^{2+} and Al^{3+} cations was not complete and/or that some compounds precipitated as segregated phases were selectively removed through washing. In our case, due to the high pH values (10–11) prevailing during the coprecipitation,

non-hydrotalcite segregated phases and their re-dissolution during washing are more likely than incomplete precipitation because of the increased solubility of aluminium hydroxide compared to $\text{Mg}(\text{OH})_2$ under these synthesis conditions [8]. Similar discrepancies between the nominal and actual compositions of Mg-Al hydrotalcites have been reported by Cantrell et al. [20]; although in this case the cause was attributed to the low pH during precipitation (7.6–8). Nevertheless, it should be noted that the Mg/Al ratio obtained from the elemental analysis is the mean resulting from the contribution of the several chemical compounds present in the sample.

The XRD patterns of the as-synthesized and rehydrated solids are shown in Fig. 1.

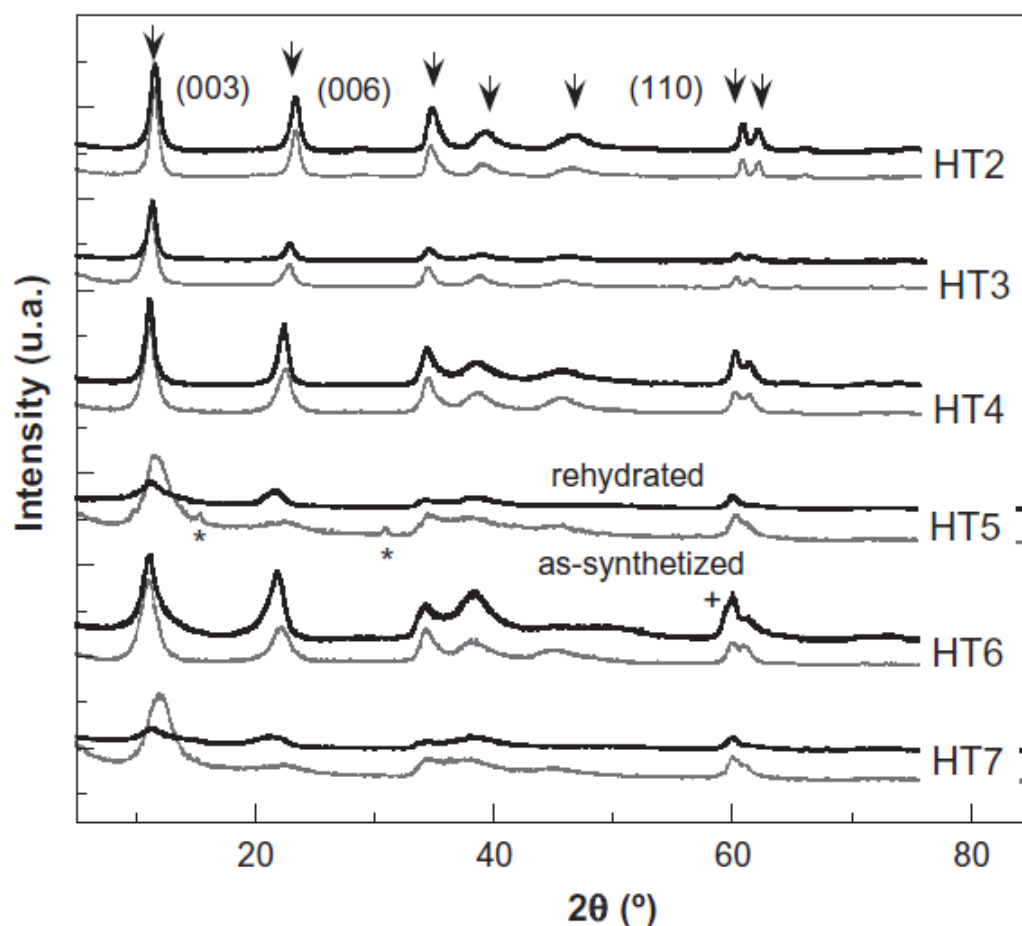


Fig. 1. XRD patterns of the samples indicated. In each case the pattern on top correspond to the rehydrated sample whereas that on the bottom corresponds to the as-synthesized material. (↓) Hydrotalcite; (*) $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$; (+) $\text{Al}(\text{OH})_3$.

The solids obtained after calcination in air at 500 °C (XRD patterns not shown) consisted in Mg and Al oxides. The characteristic diffraction peaks of the hydrotalcite phase [20] were visible in all the patterns included in Fig. 1 although there are differences in crystallinity among samples, which were much higher for the solids with actual Mg/Al molar ratios equal or lower than 3 (HT2-as, HT3-as and HT4-as). The crystallinity of the hydrotalcites synthesized by coprecipitation has been related to the supersaturation of the synthesis solution [12]. In this regard, high supersaturations give rise to less crystalline materials due to the high number of crystallization nuclei. Although all the solids were synthesized according to the same procedure, it seems reasonable that the higher concentrations used to prepare the materials with relatively high ratios led to supersaturation conditions less favourable for obtaining crystalline solids. Furthermore, in the case of HT5-as, two weak peaks that can be attributed to hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) were present in the XRD pattern. This suggests that the true Mg/Al ratio of the hydrotalcite phase in this sample should be lower than the value of 4.1 obtained by ICP-AES. The formation of hydromagnesite in samples with high Mg content (Mg/Al ratio ≥ 4) has been reported by Miyata [11]. No diffraction peaks corresponding to other phases such as $\text{MgAl}_2(\text{OH})_8$, boehmite ($\alpha\text{-AlOOH}$), brucite ($\text{Mg}(\text{OH})_2$), $\text{Al}(\text{OH})_3$ or sodium carbonate could be detected in the XRD patterns of the as-synthesized materials.

The lattice parameters (a and c) for the several samples have been calculated from the spacings of the (1 1 0), (0 0 3) and (0 0 6) crystallographic planes [20]; the results have been included in Table 1. The values of the parameters indicated that all samples crystallized with the three-layer (rhombohedral) stacking sequence characteristic of hydrotalcite. Al^{3+} substitution for Mg^{2+} gives rise to a decrease of the lattice parameter a from 3.141 Å for brucite to 3.043 Å for hydrotalcites with Mg/Al molar ratios below 2 [11,21]. In our case, there is a qualitative accordance with this trend because the highest value of a (3.09 Å) was for HT6-as, a sample that also exhibited the highest Mg/Al ratio (5) according to the ICP-AES analyses.

As concerns the rehydrated samples, the XRD patterns included in Fig. 1 show that the solids recovered the original hydrotalcite structure through meixnerite formation, meaning that hydroxide anions are intercalated between the layers. As in the case of the as-synthesized samples, the rehydrated solids with Mg/Al molar ratios equal or lower than 3 showed well-ordered structures which could be attributed to the retro-topotactical transformation also known as “memory effect” characteristic of these materials [7,14,18]. Solids with Mg/Al ratios above 3 showed less crystalline structure, whereas in the XRD pattern of HT6-rh diffraction peaks of $\text{Al}(\text{OH})_3$ were detected suggesting that hydrotalcite was not the only phase present in the starting material.

Fig. 2 shows the TGA results for selected (HT2, HT3, and HT5) as-synthesized (Fig. 2A) and rehydrated (Fig. 2B) hydrotalcites.

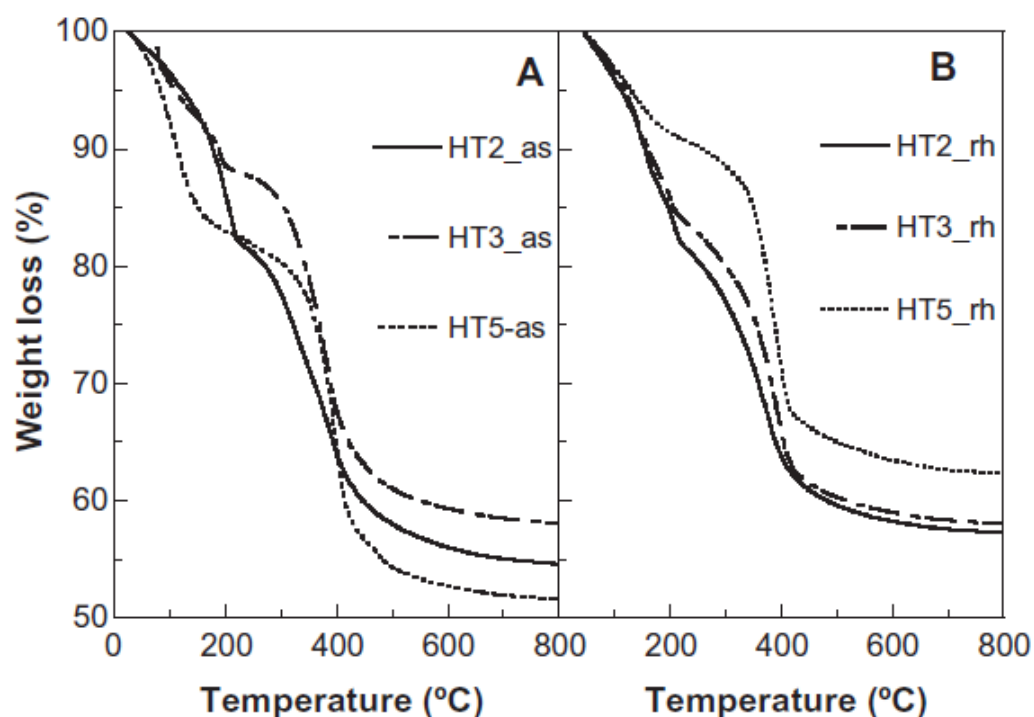


Fig. 2. TGA results of the HT2, HT3 and HT5 materials. A: as-synthesized samples; B: rehydrated samples.

The total weight loss is around 42–48% showing two steps: the first one below 200 °C associated with water physically adsorbed and water in the interlayer space, and the second step

between 200 °C and 500 °C due to the dehydroxylation of the brucite-like sheets and the decomposition of the carbonates in the interlayer region. In the case of the rehydrated materials, the solids show similar weight losses of 40–43% in two steps which are in good agreement with results reported in the literature [2]. In this case, the second step corresponds to the dehydroxylation of the brucite-like sheets and the loss as water of the hydroxide ions present in the interlayer space of the rehydrated solids which explains the lower total weight loss compared with the original solids that contained carbonates.

The BET specific surface areas of the several solids in the as-synthesized, calcined, and rehydrated forms are included in Table 2.

Table 2

Specific surface areas of the samples indicated.

	S_{BET} (m ² /g)		
	As-synthesized (as)	Calcined (ca)	Rehydrated (rh)
HT2	103	248	66
HT3	82	247	12
HT4	108	201	3
HT5	32	179	1
HT6	88	232	2
HT7	32	172	6

As expected, the specific surface areas clearly increase for the calcined solids, particularly for the materials with the lowest Mg/Al ratios (HT2- ca and HT3-ca) that show S_{BET} values of 248 m²/g order. High total specific volumes (0.58–0.95 cm³) are also exhibited by these samples. Similar trends have been found by Link Shumaker et al. for hydrotalcites with Mg/Al molar ratios of 1.9 and 2.7 [9]. The decomposition of the LDH structure by dehydroxylation of the layers and the evolution as CO₂ of the carbonate anions present in the interlayer region

creates the porosity responsible for the increase of the specific surface area. After rehydration of the calcined solids the LDH structure is restored but in a more compact manner due to the presence of hydroxide instead of carbonate ions in the interlayer region with the result of a dramatic decrease of the specific surface areas [8]. Only the HT2-rh and HT3-rh samples show appreciable S_{BET} values of 66 and 12 m^2/g , respectively.

In Fig. 3 the N_2 adsorption-desorption isotherms of the HT5-as, HT5-ca and HT5-rh samples are depicted as representative examples. The results clearly reveal the very different textural properties of these materials. New mesoporosity is developed in the calcined sample with pore sizes mainly comprised between 3 and 8 nm and a maximum at about 5 nm. After rehydration the solid becomes essentially non-porous probably due to the formation of agglomerated hydrotalcite platelets by the presence of interlayer hydroxide anions.

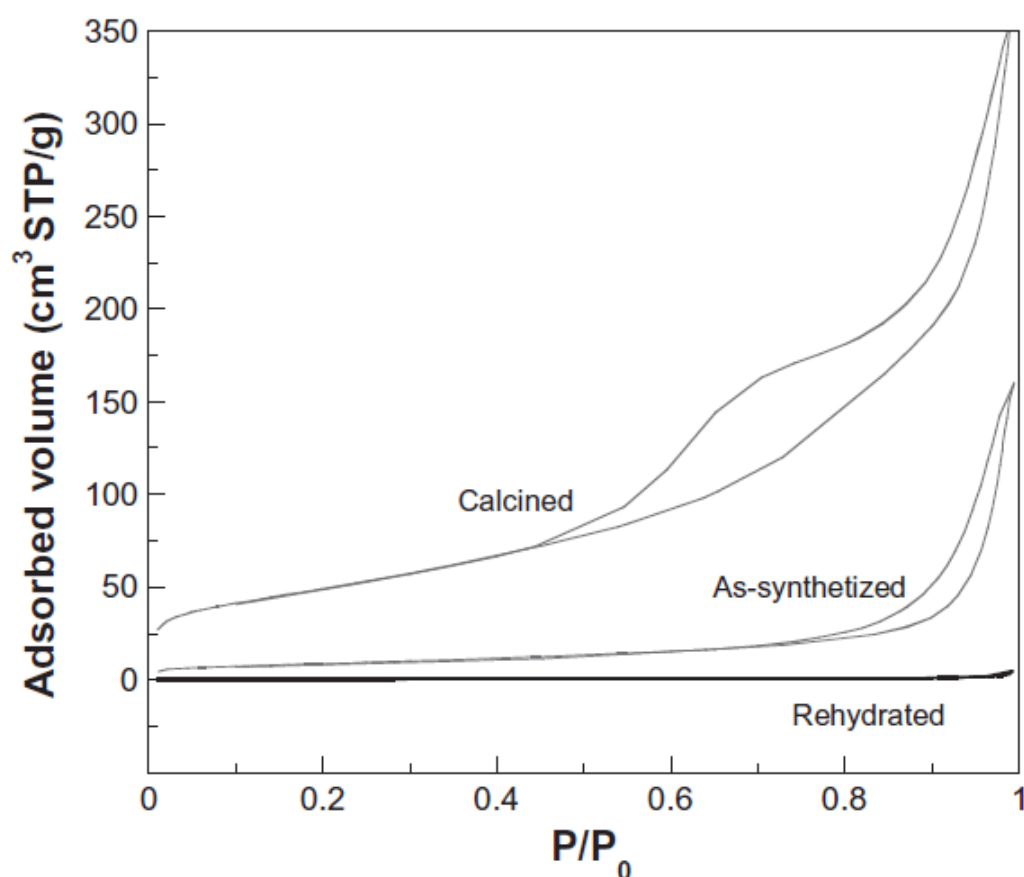


Fig. 3. Nitrogen adsorption-desorption isotherms at 77 K of the as-synthesized, calcined and rehydrated HT5 solids.

Fig. 4 shows representative SEM photographs of the HT5-as, HT5-ca, HT5-rh and HT3-rh samples. The image of the as-synthesized solid is typical of the lamellar hydrotalcite structure whereas the calcined solid shows a spongy appearance in accordance with its porous nature. In the case of the rehydrated samples, an aggregation of platelets seems to take place giving rise to well-defined flake-like crystals which is in agreement with the marked loss of textural properties exhibited by these hydrotalcites.

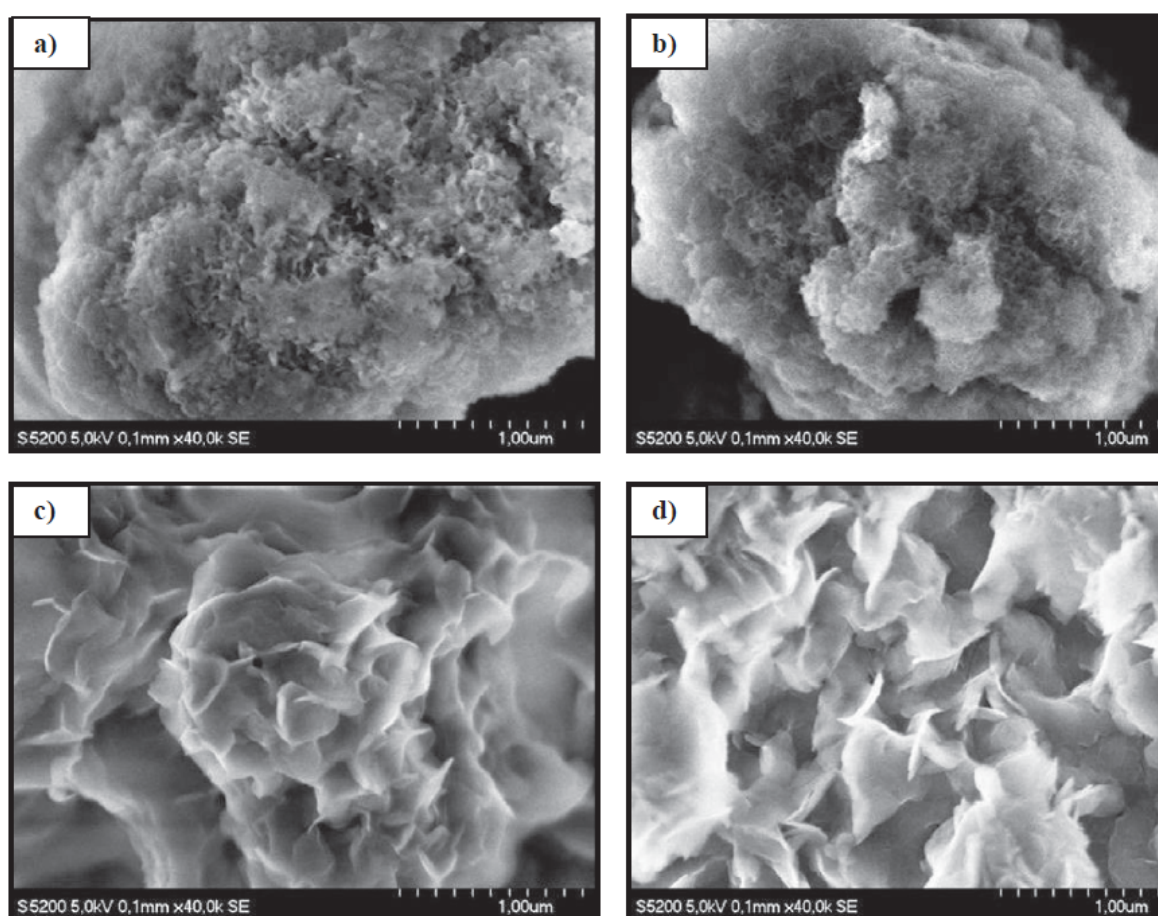


Fig. 4. SEM images of HT5: a) as-synthesized, b) calcined, c) rehydrated; and d) HT3 rehydrated.

3.1.2. Basic properties

The basic strength (H_{b}) of the several samples was investigated by using different acid-base Hammett indicators [21]. In accordance with previous results obtained with commercial

Mg-Al hydrotalcites [7], the rehydrated solids were the only ones having basic sites as strong ($H_{\text{ind}} \geq 11.0$) as to change the colour of alizarine yellow ($pK_a = 11.0$) and indigo carmine ($pK_a = 12.2$). Calcined solids showed lower basic strengths changing the colour of thimolphthalein ($H_{\text{ind}} \geq 9.9$) whereas the as-synthesized hydrotalcites showed the lowest basic strength as they only changed the colour of bromothymol blue ($H_{\text{ind}} \geq 7.2$). The high basic strength of the rehydrated solids is attributed to the presence of hydroxide anions (Brønsted sites) in the interlayer space, mainly located at the edges and defects of the platelets [12,16,18,20,22,23].

The basicity of the rehydrated solids was measured by CO₂-TPD. It has been reported that during calcination of Mg-Al hydrotalcites strong Lewis basic sites (oxide anions), medium-strength sites (Mg^{2+} - O^{2-} and Al^{3+} - O^{2-} pairs) and also weak sites are generated [24]. In our case, calcined solids exhibited low basicity with a broad distribution of weak sites showing CO₂ desorption at relatively low temperatures (below 350 °C). In contrast, the rehydrated samples were significantly more basic. Fig. 5 shows the CO₂-TPD results for some of the rehydrated hydrotalcites (HT2-rh, HT3-rh and HT5-rh). It can be seen that CO₂ desorbs at higher temperatures (above 350 °C) compared with the calcined samples indicating the presence of stronger basic sites. The temperatures corresponding to the maxima of the desorption peaks in the CO₂-TPD patterns increase as the Mg/Al molar ratio also increases: about 405 °C for HT2-rh, 410 °C for HT3-rh and 430 °C for HT5-rh. The basicity follows the same trend; in this regard, HT5-rh showed the highest basicity (346 $\mu\text{mol/g}_{\text{catalyst}}$) followed by HT3-rh (182 $\mu\text{mol/g}_{\text{catalyst}}$) and HT2-rh (46 $\mu\text{mol/g}_{\text{catalyst}}$). If one assumes that the basicity of the rehydrated samples is due to the compensating OH⁻ ions present in the interlayer region, and that these ions are proportional to the number of Al³⁺ ions [14,22] the basicity should be higher for the hydrotalcites with lower Mg/Al ratios. However, the results included in Fig. 5 show the opposite trend. It should be noted that in order to be measured the basic sites have to be accessible to the CO₂ molecule. However, it has been shown previously that the rehydrated samples exhibit poor

porosity and that as the Mg/Al molar ratio increased big flake-like crystals were formed suggesting that CO₂ accessibility could be limited to the compensating anions present in the edges of the platelets. As a matter of fact, Roelofs et al. [22] found that only 1–5% of the total basic sites of a rehydrated hydrotalcite with Mg/Al molar ratio of 2 participated in a condensation reaction. On the other hand, Winter et al. [23] demonstrated that only a minor fraction (less than 10%) of the OH⁻ ions present in hydrotalcite samples could be titrated by CO₂-TPD.

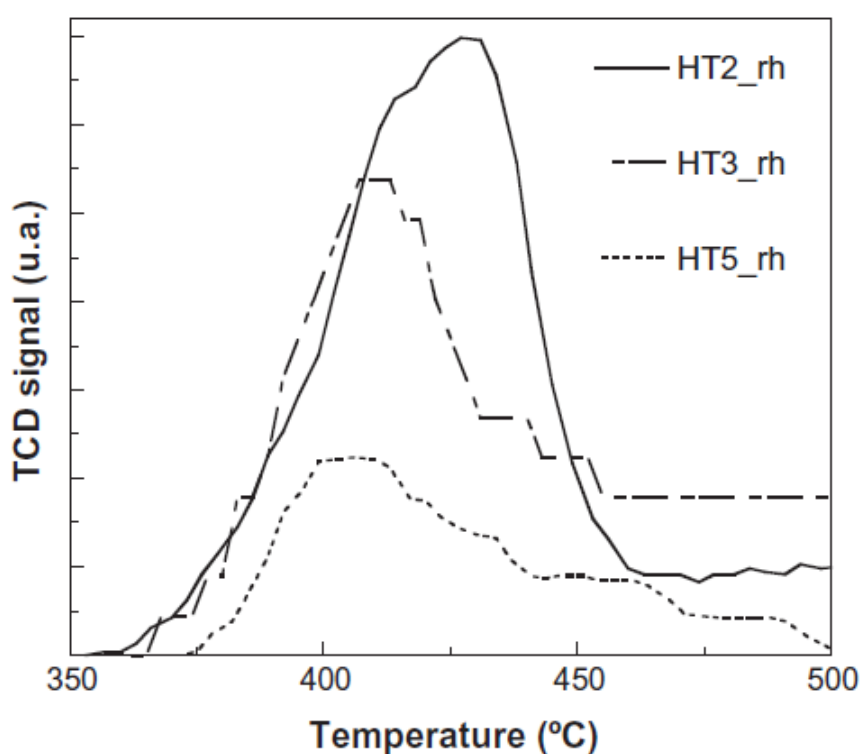


Fig. 5. CO₂-TPD profiles of the samples indicated.

3.2. Catalytic performance

3.2.1. Transesterification conversion

The main objective of this study was to investigate the catalytic performance of rehydrated Mg-Al hydrotalcites with different Mg/Al ratios in the transesterification reaction of sunflower oil with methanol. The as-synthesized hydrotalcites and the mixed oxides obtained after calcination were inactive under the reference conditions considered in this work (60 °C, 1 atm,

methanol/oil molar ratio of 12, and 2 wt% of catalyst referred to the oil). This indicates that, in spite of the good textural properties of these solids, their basic sites, characterized by H_{-} values below 11.0, are not strong enough to catalyze the methanolysis reaction. Although there is no general agreement on this regard, this finding is in accordance with previous results by our group [7] and results by other researchers [9,16]. Studies in which calcined hydrotalcites are reported to show significant methanolysis activities were carried out under much more favourable reaction conditions compared to the ones in the present work: very high methanol/oil molar ratios (up to 55:1), catalyst concentrations (up to 20 wt%) or reaction temperatures (up to 210 °C) [25–28].

As shown in Fig. 6, most of the rehydrated hydrotalcites presented significant methanolysis activities giving rise to sunflower oil conversions after 8 h of reaction that ranged between 10% for HT2-rh and 50–53% for HT5-rh, HT6-rh and HT7-rh. Catalysts HT3-rh and HT4-rh gave intermediate final conversion values of 37% and 46%, respectively, thus showing that there is a positive effect of the Mg/Al molar ratio on the methanolysis activity of the rehydrated hydrotalcites that could be related with the basicity of these solids that also increases with the Mg/Al molar ratio, as evidenced by the CO₂-TPD results. Furthermore, the results of the analysis performed with the Hammett indicators showed that, in contrast with the as-synthesized and calcined solids, the rehydrated materials were the only ones that contained strong basic sites with H_{-} above 11 and even 12.2 that seem to be necessary to catalyze the methanolysis reaction at the mild conditions considered in this work. Abelló et al. [13] also observed that calcined hydrotalcites become active in aldol condensation reactions after rehydration. Xi and Davis [17] found that hydrotalcites reconstructed after rehydration were significantly more active catalysts in the transesterification of tributyrin with methanol than the mixed oxides resulting upon calcination. Wang et al. [15] had recently obtained very good results in the aldol condensation of acetone catalyzed by rehydrated hydrotalcites.

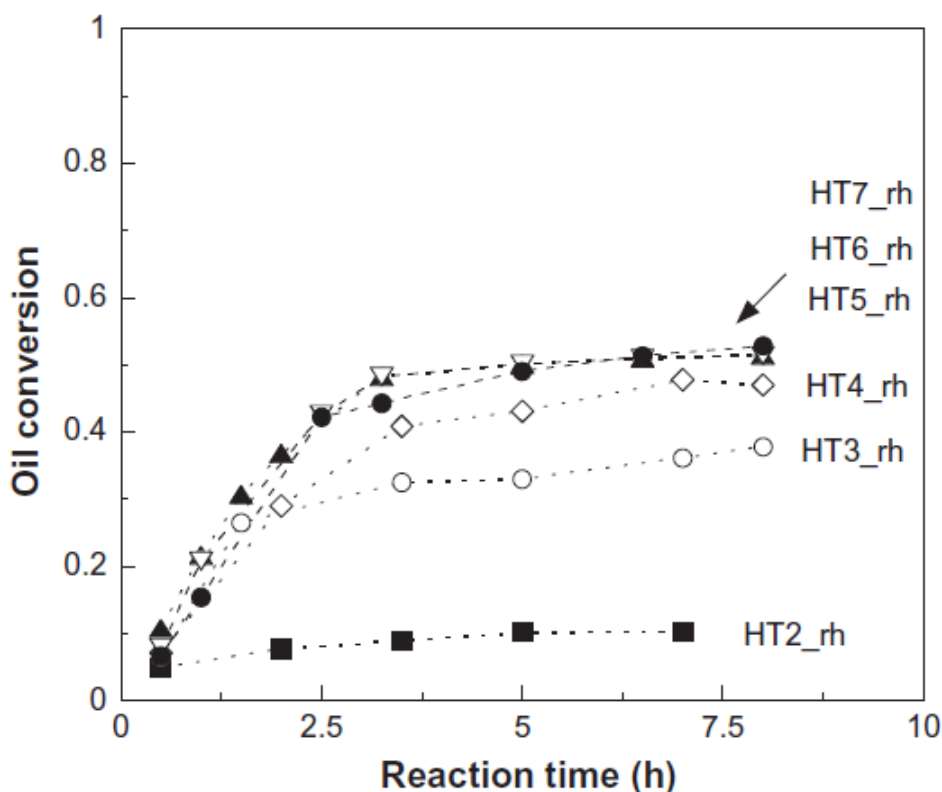


Fig. 6. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 60 °C, methanol/oil molar ratio of 12:1 and catalyst concentration of 2 wt%. Catalysts: HT2-rh (■), HT3-rh (○), HT4-rh (◇), HT5-rh (▲), HT6-rh (▼) and HT7-rh (●).

These observations reinforce the idea that OH⁻ ions, most likely those present on the edges of the platelets, behave as strong basic sites thus making rehydrated Mg-Al hydrotalcites active methanolysis catalysts. Other authors have also invoked the possible contribution of an easier migration of methanol in the solids containing water to explain the activity of rehydrated Mg-Al hydrotalcites [10]. Clearly, these solids are interesting heterogeneous catalysts with great potential to be considered as substitutes for the homogeneous alkaline compounds used in a variety of chemical processes. In the recent review by Takehira [18] the interested reader can look up for the variety of reactions in which these materials have shown promising activities.

In order to assess the possible influence of the degree of rehydration on the methanolysis activity, samples HT2-ca and HT3-ca were immersed in boiling water during different time periods. The rehydration degree, defined as the weight increase after drying under vacuum at

65 °C, could be varied between 18 and 36 wt% for HT2-rh and between 24 and 36 wt% for HT3-rh. In the case of HT2-rh the sample with a rehydration degree of 18 wt% was almost inactive whereas the solid rehydrated up to 36 wt% gave 10% oil conversion after 8 h of reaction, as shown in Fig. 6. As for the HT3-rh sample, the oil conversion increased from 28% for the solid with the lowest rehydration degree (24 wt%) to 37% (Fig. 6) for the solid with 36 wt% of rehydration. It can be concluded that the activity increases with the degree of rehydration which seems to be limited to values around 35 wt% at which the best activity is obtained [22,29,30]. This behaviour could be related to an increased basicity (number of interlayer OH⁻) ions as the rehydration degree increases [31] as well as to structural aspects [32]. Kim et al. rehydrated a calcined hydrotalcite with Mg/Al molar ratio of 2.8 in a constant humidity chamber at 25 °C [10]. Several samples were generated by treating the original rehydrated solid under N₂ flow at temperatures up to 500° C. The soybean oil methanolysis conversion at 70 °C, 2.2 wt% of catalyst and methanol/oil molar ratio of 15:1 was within the 10–20% range for the samples treated from 100 °C to 400 °C compared to about 57% for the rehydrated solid, meaning that the loss of water decreased the catalytic activity. Unfortunately, the degrees of rehydration of the solids were not reported in that study. Xi and Davis [16] found that the activity of rehydrated hydrotalcites decreased as interlayer water molecules were lost and suggested a possible interaction of the interlayer hydroxide anions with the brucite-like layers. Yu and Schmidt [33] also proposed that the presence of interlayer water molecules solvate and stabilize the interlayer hydroxide anions. These authors suggested that non-stabilized interlayer hydroxide anions can deprotonate their neighbouring structural hydroxyl groups resulting in a significant loss of Brønsted basicity. Nevertheless, it has been reported that water in excess could contribute also to an inactivation of the basic sites [16,17,29].

3.2.2. Influence of the catalyst load and methanol concentration

One of the most active catalysts, HT5-rh, was selected for performing a study of the influence of the reaction conditions on the methanolysis performance. In this series of experiments the temperature was maintained at 60 °C, a value close to the maximum temperature that can be attained at 1 atm which corresponds to the methanol normal boiling point. Fig. 7 shows the evolution with reaction time of the sunflower oil conversion in a series of methanolysis reactions performed with a methanol/oil molar ratio of 12 and different loads of the HT5-rh sample. As expected, the oil conversion at any reaction time increases with the catalyst load.

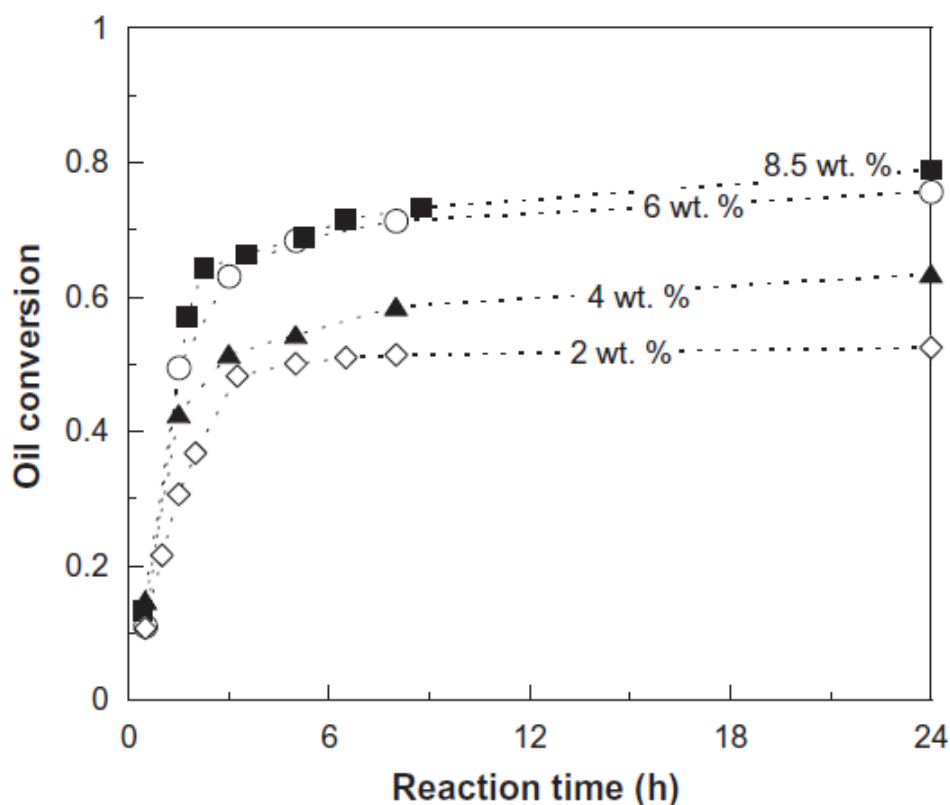


Fig. 7. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 60 °C, methanol/oil molar ratio of 12:1 and the following concentrations of the HT5-rh catalyst: 2 wt% (◇), 4 wt% (▲), 6 wt% (○) and 8.5 wt% (■).

The oil conversions after 24 h of reaction increased from 51% to 62% and 75% when the catalyst load increased from 2 wt% to 4 wt% and 6 wt%, respectively. A further increase of the

catalyst load up to 8.5 wt% gave rise to a final oil conversion of 78% which is significantly lower than the one that could be expected thus suggesting that the catalyst load has surpassed the limit that can be maintained in homogeneous suspension in our experimental setup. Xie et al. also observed an oil conversion increase with the catalyst load within the 1–7 wt% range, and a conversion decrease for higher loads that was related to mixing problems [34].

Some authors have suggested that glycerol and glycerides can be adsorbed on the polar surface of rehydrated hydrotalcites deactivating them [25,28]. In this context, and with the aim of reducing this possible effect, a series of transesterification experiments was performed with 2 wt% of HT5-rh and different methanol/oil molar ratios (12:1, 24:1, 48:1). Fig. 8 shows the results obtained which are very interesting because the excess of methanol is remarkably positive regarding the final oil conversion which after 24 h of reaction increases from 51% to 72% and 96% when the methanol/oil molar ratio used increases from 12:1 to 24:1 and 48:1, respectively. The latter value is close to thermodynamic limit. However, the influence of the methanol/oil molar ratio on the oil conversion is almost inexistent during the first 2 h of reaction. Being glycerol one of the reaction products and given its ability to be adsorbed on the hydrotalcites surface, the behaviour shown in Fig. 8 is indeed compatible with a positive effect of the excess of methanol that dilutes the glycerol (and glycerides) formed reducing the influence of adsorption phenomena. The results obtained with a methanol/oil molar ratio of 48:1 and only 2 wt% of catalyst (96% oil conversion and 92% fatty acid methyl esters yield) are among the best reported in the literature on biodiesel synthesis with heterogeneous catalysts. This further supports the interest of rehydrated Mg/Al hydrotalcites as heterogeneous methanolysis catalysts although it should be taken into account that a large excess of methanol is not desirable due to its negative effect on equipment size and separation and recovery costs.

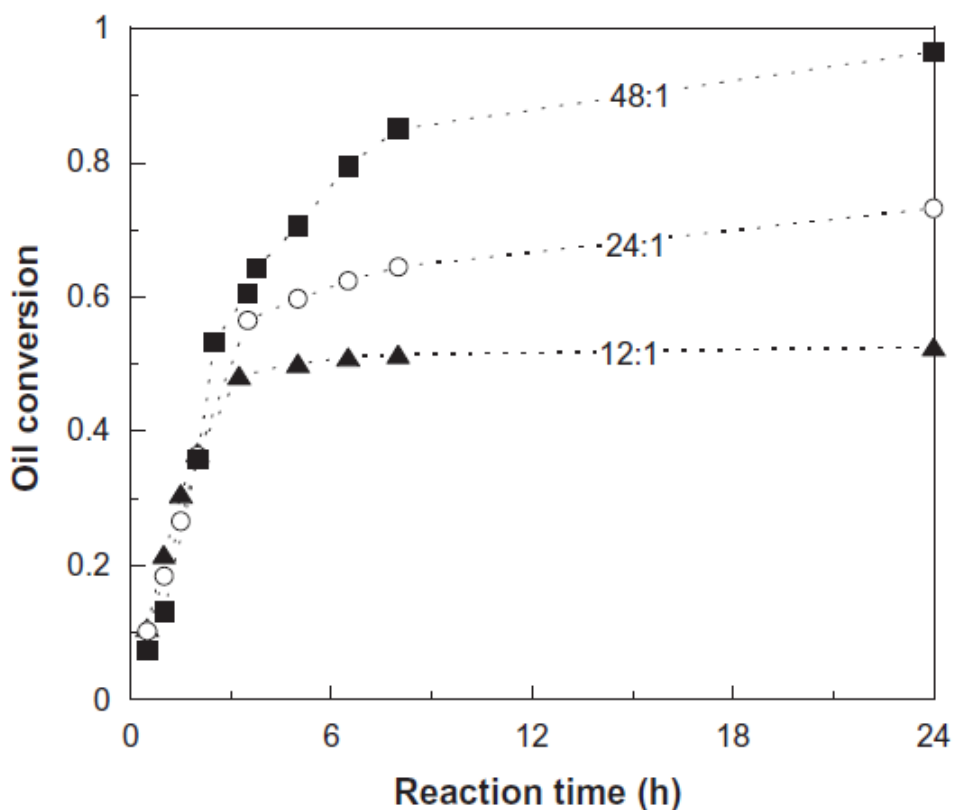


Fig. 8. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 60 °C, 2 wt% HT5-rh and the following methanol/oil molar ratios: 12:1 (▲), 24:1 (○) and 48:1 (■).

3.2.3. Intermediate transesterification products formation

Monoglycerides and diglycerides are intermediate products of the methanolysis reaction which involves 3 reversible steps in series, where glycerol and biodiesel are obtained as the final products [19]. Due to their negative effect on the fuel quality, biodiesel standards establish strict limits to the contents of monoglycerides and diglycerides [35]. This fact makes necessary to investigate the formation of these products, which is not very frequent in the literature on biodiesel synthesis catalysts. Fig. 9 shows the yields of diglycerides and monoglycerides obtained with the different rehydrated hydrotalcites as a function of the oil conversion (60 °C, methanol/oil molar ratio of 12 and 2 wt% of catalyst). It can be seen that very similar results were obtained with the different catalysts so their properties are not different enough as to affect the methanolysis selectivity. The degree of rehydration neither affected the products

distribution. The catalysts are very selective towards biodiesel formation. For example, at an intermediate level of oil conversion of 50% the yields of fatty acid methyl esters (biodiesel), diglycerides and monoglycerides were about 44%, 4% and 2%, respectively.

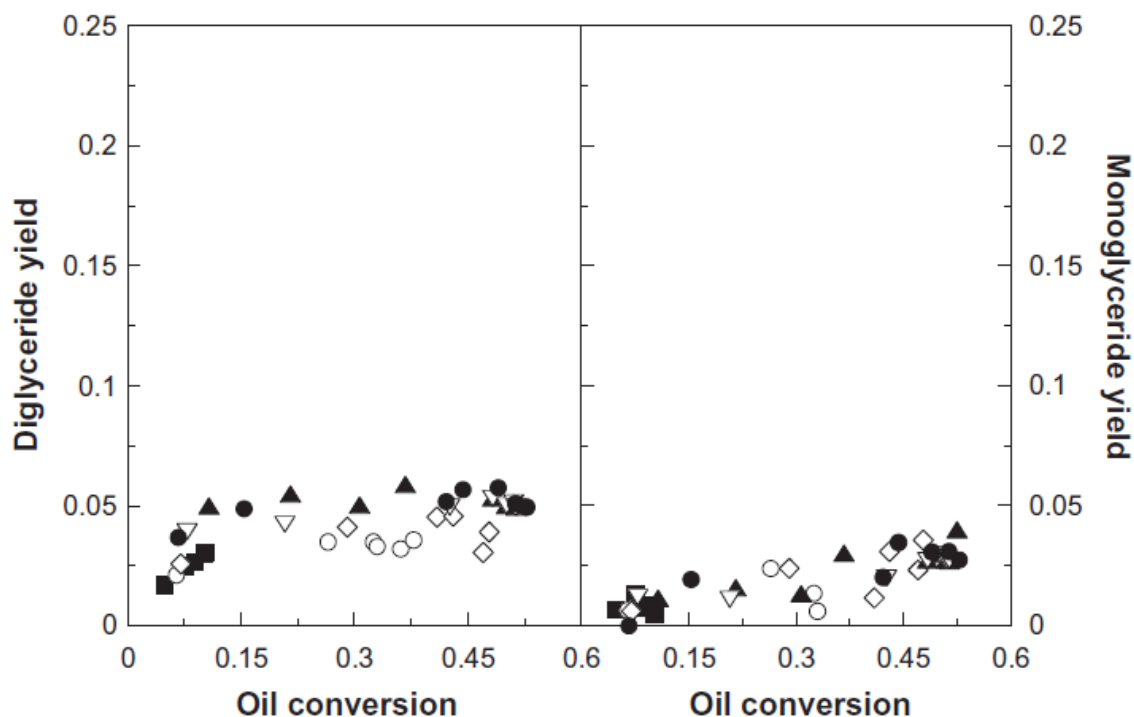


Fig. 9. Evolution with the sunflower oil conversion of the diglycerides and monoglycerides for a series of transesterification reactions carried out at 60 °C, methanol/oil molar ratio of 12:1, and 2 wt% of the catalysts: HT2-rh (■), HT3-rh (○), HT4-rh (◇), HT5-rh (▲), HT6-rh (▽) and HT7-rh (●).

On the other hand, whereas the glycerides yields remained almost constant, that of biodiesel increased linearly with the oil conversion. These results are slightly better than those reported using NaOH supported on γ -alumina [5] catalysts. This is in contrast with Cabased methanolysis catalysts which at intermediate oil conversions give much higher monoglycerides and diglycerides yields which are within the 15–25% range, although the glycerides yields greatly decrease as the oil conversion increases [3]. The catalytic behaviour of the rehydrated hydrotalcites suggests that the reaction at the Brønsted basic sites could occur through very active methoxi species [36].

As concerns the influence of the methanol/oil molar ratio on the yields of the transesterification products, there is almost no influence within the range of values considered in this work. This means that the molar ratio of 12:1 represents an excess of methanol high enough as to favour the formation of the fatty acid methyl esters. Methanol/oil molar ratios above this value have a positive effect on the final oil conversion likely due to an increased dilution of glycerol and intermediate products thus reducing the driving force for the adsorption of that compounds on the catalysts surface that can lead to deactivation. However, using a very high excess of methanol is not justified from the point of view of the methanolysis selectivity.

3.2.4. Catalysts stability and reutilization

A key issue when considering a catalyst for a process is the possibility of its reutilization. In this work, the presence of the metallic components of the hydrotalcites used (Mg and Al) in the reaction products was investigated through elemental analyses. Under the reference reaction conditions (60 °C, methanol/oil molar ratio of 12, 2 wt% of catalyst) it has been found that leaching of the catalysts was lower than 1% after 5 h of reaction. On the other hand, when the methanol recovered after putting it into contact for up to 4 h with the catalysts (see Section 2.4.) was used to perform the transesterification reaction no activity was found. These results indicate that rehydrated hydrotalcites are relatively resistant towards leaching under typical transesterification reaction conditions at 1 atm. Therefore, the activity exhibited by these solids is not due to the presence of leached Mg^{2+} or Al^{3+} [16,25], neither to residual Na from the coprecipitation process provided that a correct washing has been performed during the synthesis. The chemical stability of these materials is significantly superior to that of Ca-based compounds which have been profusely proposed as effective methanolysis catalysts for biodiesel synthesis [3,4]. It has been found that CaO is transformed under reaction conditions to form calcium diglyceroxide which is significantly soluble in the reaction mixture.

Modification of CaO with alkali metals, particularly Li, has been proposed to improve the catalytic performance of CaO but, according to Puna et al. [37], this strategy seems to lead to an enhanced calcium diglyceroxide formation.

The results obtained under methanol/oil molar ratio of 48:1 were very promising as they are very close to the limits proposed by the UNE EN 14214:2003 standard requiring a minimal methyl esters content of 96.5% in biodiesel [35]. However, leached Mg^{2+} and Al^{3+} increased remarkably up to 2.3% and 4.5%, respectively, when using a methanol/ oil ratio of 48:1. This fact together with the problems associated to handling high volumes of methanol limit the feasibility of using very high methanol/oil ratios for improving the final biodiesel yield in heterogeneously-catalyzed transesterification reactions using rehydrated hydrotalcites.

Although leaching is not a serious problem with rehydrated hydrotalcites it is necessary to investigate their reusability capacity to assess suitably their stability as methanolysis catalysts. HT4-rh and HT5-rh samples were recovered from the reaction medium after being used and they were cleaned by washing with acetone and ethanol, and then calcined and rehydrated as proposed by Corma et al. [29]; these samples were denoted as HT4-rh2 and HT5-rh2, respectively. The results of the methanolysis reactions performed under reference conditions with the original catalysts and the recovered, cleaned and reconditioned ones are shown in Fig. 10. As can be seen, in the case of the HT4 solid there is no significant change of activity whereas for the other catalyst the oil conversions achieved with the HT5-rh2 sample were about 27% lower than the ones obtained with HT5-rh. The final oil conversion achieved after 8 h of reaction decreased from 51% to 37% upon reutilization. Corma et al. found that 87.5% of the original conversion was maintained when reutilizing a hydrotalcite [29]. In the work of Kim et al. the reutilization of the rehydrated hydrotalcites was apparently not investigated [10]. In our case, it is not possible to explain at present the different behaviour exhibited by the HT4-rh2 and HT5-rh2 samples.

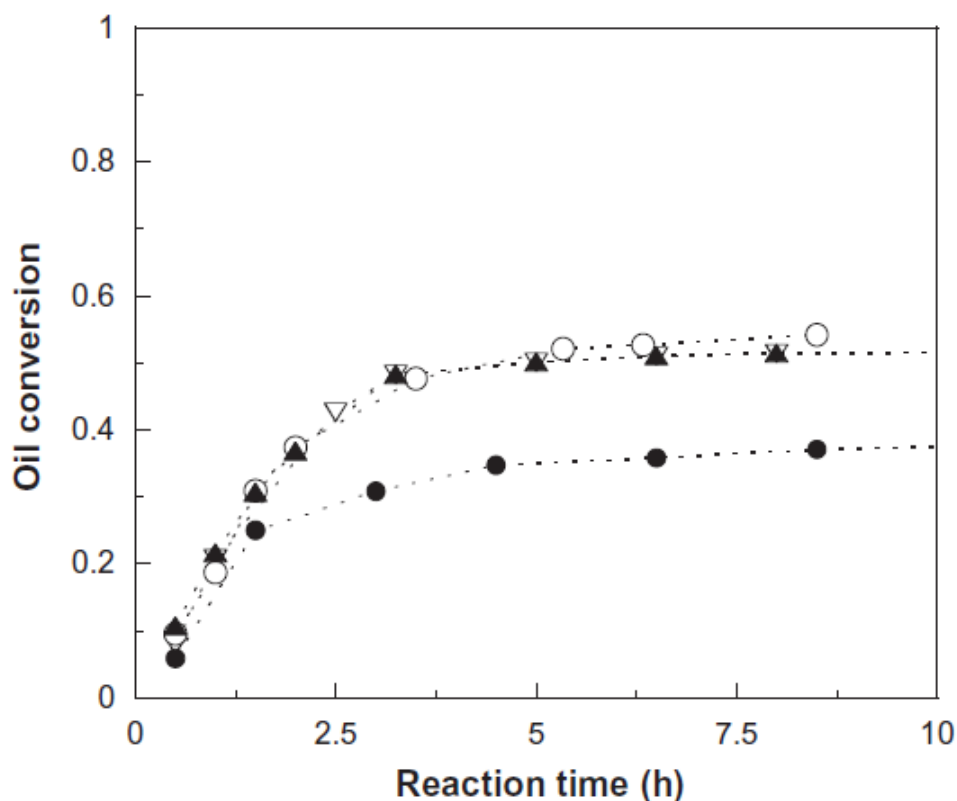


Fig. 10. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 60 °C, methanol/oil molar ratio of 12:1 and 2 wt% of the catalysts: HT4-rh (▽), HT4-rh2 (○), HT5-rh (▲) and HT5-rh2 (●).

XRD analyses indicated that both solids kept the hydrotalcite structure although HT5-rh2 was less crystalline. As the active sites seem to be associated to hydroxide anions at the edges of the platelets in well-defined crystals it can be speculated that the loss of activity could be related to loss of crystallinity during the reconditioning process that includes additional steps of washing, calcination and rehydration.

4. Summary and conclusions

A series of hydrotalcites synthesized by coprecipitation with different Mg/Al molar ratios has been considered as catalysts for the synthesis of biodiesel. Calcined oxides recovered the hydrotalcite structure in the form of meixnerite after rehydration in boiling water. Rehydrated hydrotalcites showed poor textural properties compared to the as-synthesized ones although

they exhibited good crystallinity. As for the basic properties, the basic strength was much higher for the rehydrated solids that were the only ones with H_{L} values higher than 11. Strong basic sites were associated to Brønsted-type interlayer hydroxide anions that were absent in the as-synthesized and the calcined solids. The basicity of the rehydrated materials increased with the Mg/Al molar ratio. A general accordancy between the basic properties of the catalysts and their activity for the sunflower oil methanolysis was found. In this regard, only the rehydrated hydrotalcites were significantly active. Furthermore, the activity increased with the Mg/Al ratio and with the degree of rehydration. Under reference transesterification conditions (60 °C, 1 atm, methanol/oil ratio of 12 and 2 wt% of catalyst) about 50% oil conversion could be achieved after 8 h of reaction with the most active samples. This conversion could be increased up to 75% after 24 h when using 6 wt% of catalyst and up to 96% when the methanol/oil molar ratio was increased to 48:1. Biodiesel yield achieved 92% after 24 h under these conditions. This is among the best results reported in the literature for heterogeneous methanolysis catalysts taking into account the mild reaction conditions used. Although the level of catalyst leaching was low in general, it increased when using a large excess of methanol. This fact together with the difficulties associated to handling large volumes of methanol limit the feasibility of utilizing very high methanol/oil molar ratios for improving the performance of these catalysts. Nevertheless, the stability of the rehydrated hydrotalcites are quite good compared to that of wellknown methanolysis catalysts such as CaO. Rehydrated hydrotalcites recovered after use and subjected to washing, calcination and rehydratation maintained very good activities thus confirming their effectivity as heterogeneous catalysts for biodiesel synthesis.

Acknowledgements

The authors thank the Spanish Ministerio de Economía y Competitividad (MINECO), the former Ministerio de Ciencia e Innovación (TRA2009_0265 and ENE2015-66975-C3-1-R) and the European Regional Development Fund (ERDF/FEDER) for the financial support. Spanish MINECO and FEDER are also acknowledged for the pre-doctoral aid awarded to Ainara Moral (BES-2013-062799) funded under the ENE2015-66975-C3-1-R project (“Structured Catalytic Systems for Biofuels Production”). J.E., O.S. and M.M. acknowledge the Basque Government (IT1069-16) and the Spanish MINECO/FEDER (ENE2015-66975-C3-3-R and CTQ2015-73901-JIN) for the financial support.

References

- [1] Busca G. Bases and basic materials in industrial and environmental chemistry: a review of commercial processes. *Ind. Eng. Chem. Res.* 2009;48:6486–511.
- [2] Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: a review. *Fuel Process. Technol.* 2009;90:770–7.
- [3] Reyero I, Arzamendi G, Gandía LM. Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts. *Chem. Eng. Res. Des.* 2014;92:1519–20.
- [4] Reyero I, Bimbela F, Navajas A, Arzamendi G, Gandía LM. Issues concerning the use of renewable Ca-based solids as transesterification catalysts. *Fuel* 2015;158:558–64.
- [5] Arzamendi G, Campo I, Arguiñarena E, Sánchez M, Montes M, Gandía LM. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts. Comparison with homogeneous NaOH. *Chem. Eng. J.* 2007;134:123–30.
- [6] Degirmenbasi N, Boz N, Kalyon DM. Biofuel production via transesterification using sepiolite-supported alkaline catalysts. *Appl. Catal. B: Environ.* 2014;150–151:147–56.
- [7] Navajas A, Campo I, Arzamendi G, Hernández WY, Bobadilla LF, Centeno MA, Odriozola JA, Gandía LM. Synthesis of biodiesel from the methanolysis of sunflower oil

- using PURAL® Mg-Al hydrotalcites as catalyst precursors. *Appl. Catal. B: Environ.* 2010;100:299–309.
- [8] Gomes JFP, Puna JFB, Gonçalves LM, Bordado JCM. Study on the use of MgAl hydrotalcites as solid heterogeneous catalysts for biodiesel production. *Energy* 2011;36:6770–8.
- [9] Link Shumaker J, Crofcheck C, Tackett SA, Santillan-Jimenez E, Morgan T, Ji Y, Crocker M, Toops TJ. Biodiesel synthesis using calcined layered double hydroxide catalysts. *Appl. Catal. B: Environ.* 2008;82:120–30.
- [10] Kim MJ, Park SM, Chang DR, Seo G. Transesterification of triacetin, tributyrin, and soybean oil with methanol over hydrotalcites with different water contents. *Fuel Process. Technol.* 2010;91:618–24.
- [11] Miyata S. Physico-chemical properties of synthetic hydrotalcites in relation to composition. *Clays Clay. Min.* 1980;28:50–6.
- [12] Cavani F, Trifirò F, Vaccari A. Hydrotalcite-type anionic clays: preparation, properties and applications. *Catal. Today* 1991;11:173–301.
- [13] Abelló S, Medina F, Tichit D, Pérez-Ramírez J, Groen JC, Sueiras JE, Salagre P, Cesteros Y. Aldol condensations over reconstructed Mg-Al hydrotalcites: structureactivity relationships related to the rehydration method. *Chem. Eur. J.* 2005;11:728–39.
- [14] Debecker DP, Gaigneaux EM, Busca G. Exploring, tuning, and exploiting the basicity of hydrotalcites for applications in heterogeneous catalysis. *Chem. Eur. J.* 2009;15:3920–35.
- [15] Wang Z, Fongarland P, Lu G, Essayem N. Reconstructed La-, Y-, Ce-modified MgAlhydrotalcite as a solid base catalyst for aldol condensation: Investigation of water tolerance. *J. Catal.* 2014;318:108–18.
- [16] Xi Y, Davis RJ. Influence of water on the activity and stability of activated Mg-Al hydrotalcites for the transesterification of tributyrin with metanol. *J. Catal.* 2008;254:190–7.
- [17] Xi Y, Davis RJ. Influence of textural properties and trace water on the reactivity and deactivation of reconstructed layered hydroxide catalysts for transesterification. *J. Catal.* 2009;268:307–17.

- [18] Takehira K. Recent development of layered double hydroxide-derived catalysts-Rehydration, reconstitution, and supporting, aiming at commercial application. *Appl. Clay Sci.* 2017;136:112–41.
- [19] Arzamendi G, Arguiñarena E, Campo I, Gandía LM. Monitoring of biodiesel production: simultaneous analysis of the transesterification products using size-exclusion chromatography. *Chem. Eng. J.* 2006;122:31–40.
- [20] Cantrell DG, Gillie LJ, Lee AF, Wilson K. Structure-reactivity correlations in MgAl hydrotalcite catalyst for biodiesel synthesis. *Appl Catal A: Gen* 2005;287:183–90.
- [21] Misra C, Perrotta AJ. Composition and properties of synthetic hydrotalcites. *Clays Clay Miner.* 1992;40:145–50.
- [22] Roelofs JCAA, van Dillen AJ, de Jong KP. Base-catalyzed condensation of citral and acetone at low temperature using modified hydrotalcite catalysts. *Catal. Today* 2000;60:297–303.
- [23] Winter F, Xia X, Hereijgers BPC, Bitter JH, van Dillen AJ, Muhler M, de Jong KP. On the nature and accessibility of the brønsted-base sites in activated hydrotalcite catalysts. *J. Phys. Chem.* 2006;110:9211–8.
- [24] Di Cosimo JI, Díez VK, Xu M, Iglesia E, Apesteguía CR. Structure and surface and catalytic properties of Mg-Al basic oxides. *J. Catal.* 1998;178:499–510.
- [25] Liu Y, Lotero E, Goodwin Jr JG, Mo X. Transesterification of poultry fat with methanol using Mg-Al hydrotalcite derived catalysts. *Appl. Catal. A: Gen.* 2007;331:138–48.
- [26] Antunes WM, de Oliveira Veloso C, Henriques CA. Transesterification of soybean oil with methanol catalyzed by basic solids. *Catal. Today* 2008;133–135:548–54.
- [27] Georgogianni KG, Katsoulidis AP, Pomonis PJ, Kontominas MG. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. *Fuel Process. Technol.* 2009;90:671–6.
- [28] Silva CCCM, Ribeiro NFP, Souza MMVM, Aranda DAG. Biodiesel production from soybean oil and methanol using hydrotalcites as catalyst. *Fuel Process. Technol.* 2010;91:205–10.
- [29] Corma A, Hamid SBA, Iborra S, Velty A. Lewis and Brønsted basic active sites on solid catalysts and their role in the synthesis of monoglycerides. *J. Catal.* 2005;234:340–7.

- [30] Di Serio M, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Ind. Eng. Chem. Res.* 2006;45:3009–14.
- [31] Climent MJ, Corma A, Iborra S, Epping K, Velty A. Increasing the basicity and catalytic activity of hydrotalcites by different synthesis procedures. *J. Catal.* 2004;225:316–26.
- [32] Abelló S, Medina F, Tichit D, Pérez-Ramírez J, Sueiras JE, Salagre P, Cesteros Y. Aldol condensation of campholenic aldehyde and MEK over activated hydrotalcites. *Appl. Catal. B: Environ* 2007;70:577–84.
- [33] Yu K, Schmidt JR. Elucidating the crystal face- and hydration-dependent catalytic activity of hydrotalcites in biodiesel production. *J. Phys. Chem. C* 2011;115:1887–98.
- [34] Xie W, Peng H, Chen L. Calcined Mg-Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. *J. Mol. Catal. A: Chem.* 2006;246:24–32.
- [35] European Committee for Standardization, Automotive fuels. Fatty methyl esters (FAME) for diesel engines. Requirements and test methods, European Standard EN14214:2003; 2013.
- [36] Lotero E, Goodwin Jr JG, Bruce DA, Suwannakarn K, Liu Y, López DE. The Catalysis of Biodiesel Synthesis. Spivey JJ, Dooley KM, editors. *Specialist Periodical Reports-Catalysis*, vol 19. Cambridge, UK: The Royal Society of Chemistry; 2006. p. 41–8.
- [37] Puna JF, Gomes JF, Bordado JC, Neiva Correia MJJE, Soares Dias AP. Biodiesel production over lithium modified lime catalysts: activity and deactivation. *Appl Catal A: Gen* 2014;470:451–7.