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LDHs Instability in Esterification Reactions and Their Conversion to Catalytically Active Layered Carboxylates

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Abstract Layered double hydroxides (LDH) containing Zn/Al and Mg/Al with different counter-ions and M^{2+}/M^{3+} ratios were synthesized and used as catalysts in the esterification of fatty acids with methanol. High conversion rates were obtained depending on the reaction conditions. However, LDHs were also converted in situ into layered carboxylates and this new material was responsible for the observed catalytic activity, which was preserved even after several consecutive reuse cycles.

Keywords Layered double hydroxides · Layered carboxylates · Catalysis · Esterification · Methyl esters

1 Introduction

Biodiesel is defined as a renewable substitute of mineral diesel, which can be produced by alcoholysis of vegetable oils and/or animals fats or by esterification of fatty acids in the presence of short monohydroxylated alcohols and a catalyst either homogeneous or heterogeneous [1–3].

Biodiesel production technologies evolved a lot in the last few years but the majority of the currently available industrial facilities are still based on the alcoholysis of low acid number feedstocks in alkaline media. For biodiesel production using homogeneous basic catalysts, low acid number fatty materials are crucial to avoid soap formation, which decreases the catalyst availability and promotes emulsification. For this reason, low cost feedstocks such as acid oils, rendered materials, soapstocks and used cooking oils must be pretreated before use in such processes [1, 2, 4].

In general, alkyl esters produced by homogeneous base catalysts must be purified in order to meet the current biodiesel standards through a series of washings stages, starting with a dilute acid solution that is usually needed to breakdown the soap [2]. On the other hand, glycerin is obtained as a co-product with glycerol contents typically in the range of 80–85 %. Besides a low acid number, ideal feedstocks must present a suitable chemical composition for biodiesel production and these are independent of the method used for synthesis. For instance, feedstock chemical composition has a direct influence on the viscosity, oxidative stability, and cold flow properties of the resulting biofuel, among others. Several studies have discussed these aspects in detail [5–7].

With the aim of minimizing the generation of effluents, reducing the production costs and facilitating the use of low cost fatty materials, heterogeneous catalysts have been proposed as alternative methods to produce biodiesel [1, 4, 8, 9]. Different solid catalysts have been used for this purpose, such as zeolites, metal oxides, inorganic salts, coordination compounds, ionic liquids, organic acids, and organic bases, as well as layered compounds including layered hydroxide salts (LHSs), layered carboxylates and layered double hydroxides (LDHs) [10].

The use of LDHs as precursors of nanostructured oxides that are catalytically active in the transesterification of vegetable oils was reviewed recently [11]. However, most of the studies carried out so far have been addressed to the use of vegetable oils of low acid number and to the discussion of the observed catalytic activity in relation to

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different aspects of the catalysts, such as the method of preparation, the M^{2+}/M^{3+} ratio, the metals used in the composition, the pore and crystals sizes, their basicity and the presence of different intercalated species and dopants. On the other hand, only one article was found in which nanostructured oxides, produced by calcination of quintinite (a natural occurring LDH, with the formula $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$) at 500 °C, are described as catalysts for the esterification of fatty acids (octanoic acid) and for the simultaneous transesterification/esterification of feedstocks containing 15–30 % of fatty acids. These reactions were carried out at 25–100 °C and recycling experiments were performed in which 95 % of the original catalytic activity was preserved after five recycling cycles, along with the M^{2+}/M^{3+} ratio and the original structure of the LDH catalyst [12].

Regarding layered hydroxide salts, Cordeiro et al. [3] showed that zinc hydroxide nitrate [ZHN, $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$] can be used as an heterogeneous catalyst for the esterification of fatty acids and for the transesterification of vegetable oils. In addition, these authors have shown that ZHN turned into zinc laurate ($C_{24}H_{26}O_4Zn$) when used in the catalytic conversion of lauric acid to methyl laurate and this layered material was held responsible for the observed catalytic activity.

Other layered metal carboxylates were also tested as catalysts for the esterification of fatty acids. Layered lanthanum and copper(II) laurates were used for the esterification of lauric acid with methanol at 140 °C with 10 % catalyst and a MR of 6:1. Lanthanum laurate produced conversions of 90.5 % while copper(II) laurate converted 81.5 % of the fatty acids into alkyl esters [13]. The catalytic activity of both manganese and nickel carboxylates was also demonstrated in the synthesis of methyl laurate, with conversions of 90 and 77 wt% being obtained at 140 °C with 10 wt% of catalyst and a MR of 6:1 [14].

In order to investigate why layered hydroxide salts are converted to layered carboxylates while layered double hydroxides have preserved their original structure as described by Kondamudi et al. [12], we have performed a systematic study whereby a variety of LDHs were evaluated as catalysts in the esterification of fatty acids with the aim of demonstrating their performance as well characterizing the influence of the M^{2+}/M^{3+} ratio and the type of intercalated anion in the observed catalytic activity.

2 Experimental

Lauric acid and one fatty acid mixture, identified as FFA, were used in this study. The FFA mixture was rich in oleic acid and its chemical composition was determined using the AOCS Ce1 F-96 method. In this method, esterification of fatty acids is carried out using methanol and boron trifluoride as the reaction catalyst and resulting methyl esters are subsequently analyzed by quantitative capillary gas chromatography.

All LDHs were synthesized by the co-precipitation method [15]. Typically, a 0.1 mol/L solution containing di and trivalent metals was slowly added in a solution containing sodium hydroxide and the final pH of the reaction media was adjusted at 8.0. After completing the reaction, the suspension containing the LDH was centrifuged and the supernatant was removed from the reaction medium. The solid was washed with five portions of distilled water and oven-dried at 50 °C for 48 h. A series of LDH was obtained by varying the ratio between the di and trivalent cations. The following LDH materials were tentatively synthesized: Zn/AlCl with Zn/Al ratio of 1:1–5:1 and $ZnAlNO_3$ with Zn/Al ratio of 1:1, as well as Mg_2AlNO_3 and Zn_2AlCO_3.

Powder X-ray diffraction (XRD) patterns were recorded in a Shimadzu XDR-6000 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) and a dwell time of 1° min^{-1}. The FTIR spectra were recorded in a Bio-Rad FTS 3500GX instrument using 1 % of sample in 100 mg of spectroscopic grade KBr. Measurements were performed in the transmission mode with accumulation of 32 scans and a nominal resolution of 2 cm^{-1}.

Esterification reactions were carried out with 2–6 wt% of HDL in relation to the amount of fatty acid in a Büchiglass Miniclave Drive pressure vessel at different temperatures and alcohol:fatty acid molar ratios (MR). The reaction vessel was sealed but not pressurized, so that the internal pressure corresponded to the vapor pressure of the most volatile component of the reaction mixture (alcohol). In all experiments, the system was stirred at 500 rpm, after which the catalyst was recovered by filtration and the excess of alcohol was evaporated at low pressure. Based on preliminary optimization experiments, the reaction time for all experiments was fixed in 2 h [3].

The total amount of alkyl esters was determined in the final product by high-performance liquid chromatography (HPLC) in a Shimadzu LC10AD workstation (Shimadzu Scientifics Inc., Kyoto, Japan) fit with a SIL10A autoinjector and a RID10A refractive index detector. A Waters Spherisorb C18 column (4.6 × 250 mm, 5 mm) was used at 35 °C in isocratic elution with 9:1 (vol/vol) acetonitrile:acetone at 0.9 mL min^{-1}. External calibration was based on standard solutions of alkyl esters and fatty acids in the 0.05–2 mg mL^{-1} concentration range.

Two strategies were used to quantify the conversion of fatty acids to alkyl esters. One was based on HPLC whereby the resulting amount of alkyl esters was expressed in relation to the amount of fatty acids present in the original material. The other was based on the AOCS Ca 5a-40

method, which was used to measure the acid number before and after esterification. Fatty acid conversion was calculated by expressing the final acid number in relation to the acid number of the starting material and these results were compared to those obtained by HPLC.

3 Results

3.1 Characterization of Fatty Acids and Esters

The batch of lauric acid used in this study was 98 % pure and was used without any further purification. On the other hand, the FFA mixture contained 62.4 wt% of oleic acid, 7.5 wt% of linoleic acid, 6.0 wt% of palmitic acid, 5.4 wt% of myristic acid, 5.1 wt% of palmitoleic acid, 2.3 wt% of elaidic acid, 2.0 wt% of stearic acid, 1.5 wt% of myristoleic, and 7.8 wt% of other FFA minor components at concentrations lower than 0.5 wt%.

The reliability of the AOCS Ca 5a-40 method to quantify the extent of fatty acid esterification was first verified with three experiments carried out under the same experimental conditions. Such observation was demonstrated by analyzing their esterification products by HPLC. The HPLC results were then compared to the ester conversion calculated by the AOCS titration method. The HPLC method gave ester conversions of 96.7, 47.1, and 69.5 %, while the AOCS method indicated 97.0, 48.7, and 70.4 % for the samples 7, 10, and 11 (Table 1), respectively. Therefore, due to its simplicity and relatively low cost, the titration method was selected to measure the catalytic conversions.

3.2 Characterization of Layered Double Hydroxides (LDHs)

LDHs were characterized by XRD and the patterns obtained had a typical profile of well crystallized layered compounds whose basal reflections were very intense (Fig. 1a). The LDH with the lowest Zn/Al molar ratio had a relatively low crystallinity and this property was due to the presence of increased amounts of Al^{3+} in its structure, causing an apparent distortion in the hydroxide layer network. The corresponding basal distances, calculated with the Bragg equation, had specific values for each anion allocated in the interlayer space, regardless the type of M^{2+} cation or the M^{2+}/M^{3+} ratio found in the layered structure. For instance, LDHs containing chloride ions presented a basal distance of 7.7 Å, which is similar to the distance reported for other LDH systems containing chloride [16]. Also, the basal distance did not change with changes in the Zn/Al ratio, indicating that chloride ions are the only species responsible to keep the layers separated from each other. On the other hand, LDHs prepared with nitrate or carbonate ions presented a basal distance of 8.9 and 7.4 Å, respectively, which were also in good agreement with the presence of these ions in the interlayer space [17–19]. This included the LDH of the Mg/Al series (Mg_2AlNO_3, Fig. 1a), which displayed a basal spacing of 8.8 Å. However, the XRD profile of this LDH was typical of layered

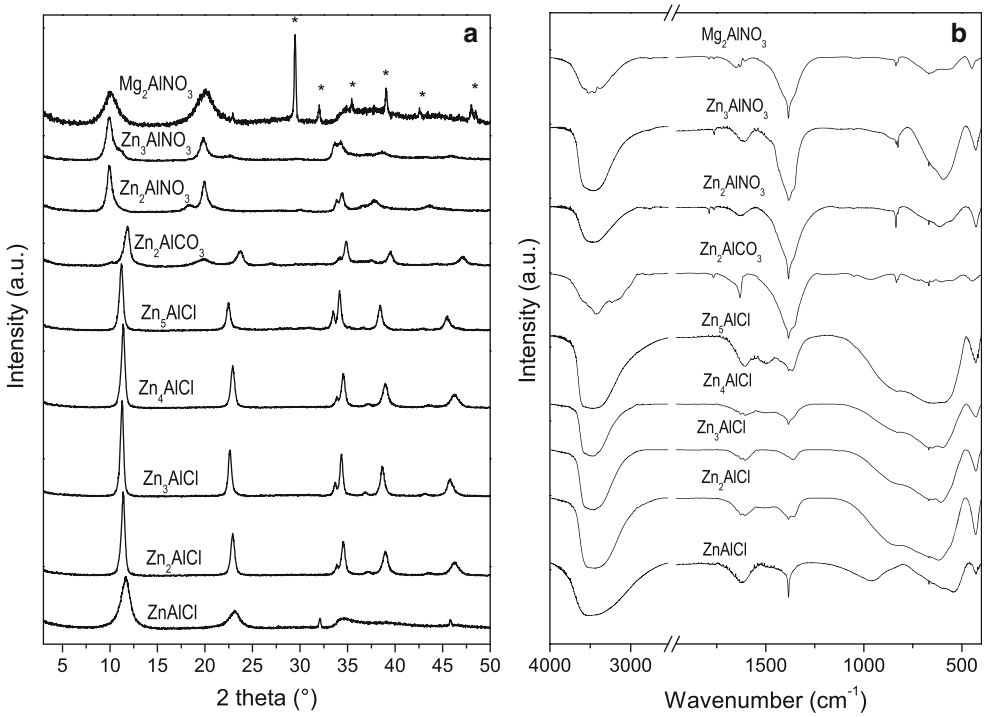

Fig. 1 XRD patterns (**a**) and FTIR spectra (**b**) of synthetic LDHs

materials with a low structural order and some degree of contamination by magnesium and/or aluminum oxides/hydroxides was also observed in its structure, as indicated by asterisks in Fig. 1a.

The FTIR spectra of LDHs presented a strong and broad band around 3,472 cm^{-1}, which was attributed to the O–H stretching mode of either physisorbed and/or intercalated water molecules or hydrogen-bonded hydroxyls groups of the interlayer spaces (Fig. 1b). The band at 429 cm^{-1} can be interpreted as lattice vibration modes (M–O stretching), while the band observed at 1,620 cm^{-1} is attributed to the O–H bending vibration of water molecules.

A common band at 1,370 cm^{-1} is present in all spectra, regardless the anion that was used for synthesis (chloride, carbonate or nitrate). This band can be attributed to carbonate vibrations and it is commonly found in LDHs due to their ability to retain carbonate from CO_2 present in the atmosphere [20, 21]. This band is weak for the LDH prepared with chloride because only a small amount of carbonate was adsorbed during sample preparation and storage [22]. Although the LDH synthesis was performed in inert atmosphere, such contamination may have occurred in solid state when the samples were exposed to the air. On the other hand, this same band became more intense in the FTIR spectra of LDHs prepared with carbonate and nitrate ions but, in this latter case, this was partially due to both ions presenting an intense band at similar wavenumbers [20].

3.3 Catalytic Performance of the LDHs

LDHs of the Zn/Al and Mg/Al system were tested as solid catalysts in the esterification of fatty acids with methanol and the obtained results are collectively shown in Table 1. When Zn_2AlNO_3 was used in experiments 1 and 10, samples containing 49.0 and 48.7 % of methyl esters were obtained from lauric acid and the free fatty acid mixture FFA, respectively. This means that the catalytic performance of the LDH was literally the same, regardless of the type of fatty acids used for esterification.

The effect of temperature on reaction conversion was initially evaluated with the LDH Zn_5AlCl. The catalytic response of this LDH increased dramatically when the reaction temperature was increased from 100 to 140 °C with all other reaction variables maintained unchanged (experiments 6 and 7 in Table 1). Such improvement in the catalytic performance was also observed when lauric acid was replaced by a complex mixture of free fatty acids (FFAs). Likewise, for reactions in which Zn_2AlNO_3 was used as the esterification catalyst, the conversion of FFAs into methyl esters increased steadily when the reaction temperature was increased from 100 to 120 and 140 °C (experiments 10, 11, and 12), regardless of the lower LDH concentration in the latter experiment. These results gave additional evidence that higher temperatures led LDHs of the Zn/Al series to higher conversion rates.

Table 1 Esterification of lauric acid and the fatty acid mixtures FFA with methanol

Experiment[a]	Acid	MR[b]	CAT[b]	CAT (wt %)	T[b] (°C)	Conversion (wt %)
1	Lauric	6:1	Zn_2AlNO_3	2	100	49.0
2	Lauric	6:1	ZnAlCl	2	100	42.1
3	Lauric	6:1	Zn_2AlCl	2	100	42.1
4	Lauric	6:1	Zn_3AlCl	2	100	42.2
5	Lauric	6:1	Zn_4AlCl	2	100	42.8
6	Lauric	6:1	Zn_5AlCl	2	100	43.3
7	Lauric	6:1	Zn_5AlCl	2	140	97.0
8	Lauric	6:1	Zn_2AlCO_3	2	100	42.4
9	Lauric	6:1	Mg_2AlNO_3	2	100	24.7
10	FFA mix	6:1	Zn_2AlNO_3	5	100	48.7
11	FFA mix	6:1	Zn_2AlNO_3	5	120	70.4
12	FFA mix	6:1	Zn_2AlNO_3	2	140	90.1
13[c]	Lauric	6:1	Without catalyst	–	100	23.0
14	Lauric	6:1	Magnesium laurate	2	100	28.0
15	Lauric	6:1	Aluminum laurate	2	100	30.0
16	Lauric	6:1	Zinc laurate	2	100	42.2

[a] All experiments were carried out for 2 h

[b] *MR* Methanol:fatty acid molar ratio, *CAT* Catalyst, *T* reaction temperature

[c] Withdrawn from reference 13

Under the same experimental conditions, Zn_2AlNO_3, Zn_2AlCl and Zn_2AlCO_3 (experiment 3, 8, and 10, respectively) had similar catalytic performances in the esterification of lauric acid with methanol. Nominal conversions of 49.0, 42.1, and 42.4 wt% were obtained at 100 °C with a molar ratio of 6:1, respectively. Hence, the anion used for intercalation seemed to have little influence over the reaction conversion, even though Zn_2AlNO_3 had a performance slightly higher than that of the other two LDH catalysts. Unfortunately, these results cannot be directly compared because several factors may have interfered with the catalytic response.

The effect of varying the amount of the added catalyst was also assessed for Zn_2AlNO_3 (experiments 1 and 10) under otherwise identical reaction conditions. An increase in the LDH concentration from 2 to 5 wt% maintained the final reaction conversion almost unchanged. However, a complex substrate (FFA mixture) was used in the latter experiment and this may partially explain the reasons why both reaction conversions were so similar. Assuming that different fatty acids may have different reactivities, the FFA mixture may have required higher catalyst concentrations to match the same catalytic performance of experiment 1, which was carried out with lauric acid exclusively.

For reactions carried out at 100 °C, all LDH catalysts were shown to be catalytically active because they resulted in conversions higher than that of thermal conversion (experiment 13 in Table 1), which was obtained by others in the absence of an added catalyst [13]. However, the catalytic response of Mg_2AlNO_3 (experiment 9, Table 1) was very close to the thermal conversion of the reaction system. On the other hand, Zn_2AlNO_3 was more active than Mg_2AlNO_3 in the esterification of lauric acid, showing that the type of metal has an influence in the catalytic performance of the LDHs (experiments 1 and 9), even though the latter LDH was partially contaminated (Fig. 1a). Table 1 also shows that all ZnAl LDHs displayed rather similar catalytic performances at 100 °C and this was probably due to the incorporation of a similar proportion of Zn in all layered materials, independently of the molar ratio used for synthesis.

3.4 Characterization of the LDH Catalysts After Use

As already described elsewhere [3], layered hydroxide salts (LHSs) are converted to layered carboxylates when used as solid catalysts for the esterification of fatty acids. Based on this, it seemed plausible to assume that LDHs could be amenable to the same structural modification as did layered hydroxide salts under similar reaction conditions. The confirmation of this hypothesis would also have a critical influence on the discussion of the catalytic performance of LDHs. For this reason, the solids that remained insoluble after the esterification of fatty acids with methanol were recovered, characterized by XRD and FTIR and compared with the structure of the original layered materials.

After reaction completion, the LDH catalysts were recovered by filtration, washed with ethanol:hexane solution 1:1 (vol/vol) and dried at 50 °C until constant weight. Soon afterwards, the solids were analyzed by XRD and FTIR to verify modifications that might have occurred in their layered structure as a result of esterification. Figure 2 displays the XRD and FTIR profiles of some representative solids that were obtained after use in the esterification of both lauric acid and the FFA mixture. All solids recovered after esterification of lauric acid had similar XRD and FTIR patterns but the solids obtained after esterification of FFA were very difficult to isolate in a single phase. Such behavior was attributed to the complex composition of FFA, which included both linear and non linear molecules (saturated and unsaturated fatty acids, respectively).

The XRD of Zn_2AlNO_3 before (Fig. 1a) and after (Fig. 2a) use in the esterification of lauric acid revealed drastic changes in the XRD pattern of the original solid, with its basal distance raising from 8.9 to 29.2 Å after one esterification stage. Also, the recovered solids displayed FTIR spectra that are specific of long chain fatty acids (Fig. 2b). The bands observed at 2,952 and 2,848 cm^{-1} corresponds to the asymmetrical stretching of C–H in methyl and methylene groups, whereas the symmetrical stretching of this bond was only observed at 2,920 cm^{-1} because this vibration is strongly affected by the conformational arrangement of the alkyl groups, moving towards higher frequencies with the increase of the conformational disorder of the carbon chains [23]. The asymmetrical and symmetrical stretching of carboxylate anions were observed at 1,540 and 1,397 cm^{-1}, respectively, while the bands centered at 1,461 and 742 cm^{-1} were attributed to the angular deformations of C–H in CH_2.

These results indicated that the LDH catalysts underwent a structural/chemical modification whereby fatty acid anions were incorporated into the layered structure. According to both XRD and FTIR data, the LDHs were transformed into layered carboxylates as zinc hydroxide nitrate did under similar experimental conditions [3]. Additionally, the layered carboxylates were recovered by filtration and their catalytic performance was tested in five consecutive reaction cycles in which the conversion of fatty acids to methyl esters was maintained almost unaltered. Figure 2 shows the XRD and FTIR analyses of the remaining Zn_2AlNO_3 solids after five reaction cycles. The basal spacing was shown to be the same as that of the solids recovered after one reaction cycle and the FTIR spectra of both solids had the same vibrational modes that were already attributed to the axial deformations of C–H in

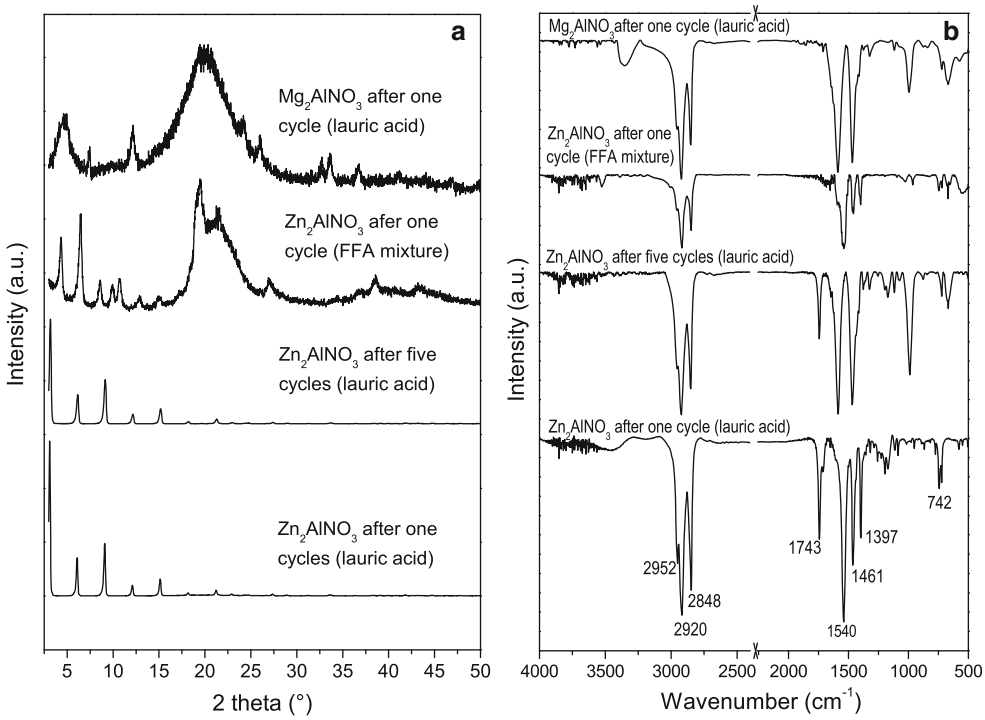

Fig. 2 XRD patterns (**a**) and FTIR spectra (**b**) of the solids recovered after one and five cycles of the LDH catalysed esterification of fatty acids with methanol

methylic and methylenic carbon atoms and C=O in carboxylate anions. However, other authors have shown that this catalytic system is structurally stable in other reaction systems, such as the transesterification of raw materials with low acid number and the esterification of acid oils at temperatures lower than those used in the present study [12, 24–28].

To the best of our knowledge, the conversion of LDHs into layered carboxylates has not been reported earlier by other research groups. Here we infer that if all of the LDHs were transformed into zinc, aluminum or magnesium laurates after the first reaction cycle and if these laurates were amenable to reuse in several consecutive reaction cycles without any loss of their catalytic performance, then the catalytic activity was due to the metal carboxylates rather than to the LDHs. Also, the catalytic effect of metal carboxylates is more important than that induced by the OH groups present in the pristine LDH, since there was no evidence for contaminating water molecules in the FTIR spectra of the solids recovered after each reaction cycle.

The solids recovered after esterification of the FFA mixture with Zn_2AlNO_3 had FTIR profiles similar to those of the solids recovered from the esterification of lauric acid. This fact demonstrated that LDHs are able to form Zn/Al carboxylates with fatty acids of different degrees of unsaturation and chain lengths. Indeed, these solids revealed XRD diffraction patterns that are typical of layered carboxylates with basal distances of 41.4 and 41.2 Å, which are characteristic of carboxylates with 18 carbons atoms such as those found in the FFA admixture (oleic acid and stearic acid, respectively) [29].

Figure 2 also shows the XRD and FTIR data of Mg_2AlNO_3 after its use in the esterification of lauric acid. The XRD of the recovered solids showed a mixture of crystalline materials with a basal distance of 29.3 Å, compatible with the structure of the Mg/Al laurate. However, these recovered solids were less crystalline and more difficult to recover after reaction completion. The intense peak at 20° in 2θ was attributed once again to the structural disorder of the carbon chains and the FTIR spectra showed the same bands discussed earlier for the stretching of C–H in methyl and methylene groups, as well as the angular deformation of these at 1,461 cm^{-1} [23]. The antisymmetric and symmetric vibrational modes of carboxylate anions were visible at 1,540 and 1,390 cm^{-1}, respectively.

The chemical nature of the metal carboxylates that were recovered after esterification of fatty acids with methanol depended on the type of LDH used in the beginning of the first reaction cycle. LDHs of the Zn/Al series would produce zinc and aluminum carboxylates, whereas those of the Mg/Al series would produce magnesium and aluminum carboxylates. Hence, to evaluate the catalytic activity of these metal carboxylates individually, zinc, magnesium, and aluminum laurates were synthesized and tested in the esterification of lauric acid with methanol. These results are shown in Table 1, where experiment 13 corresponds to the thermal conversion of lauric acid into methyl laurate under that specific reaction condition [14].

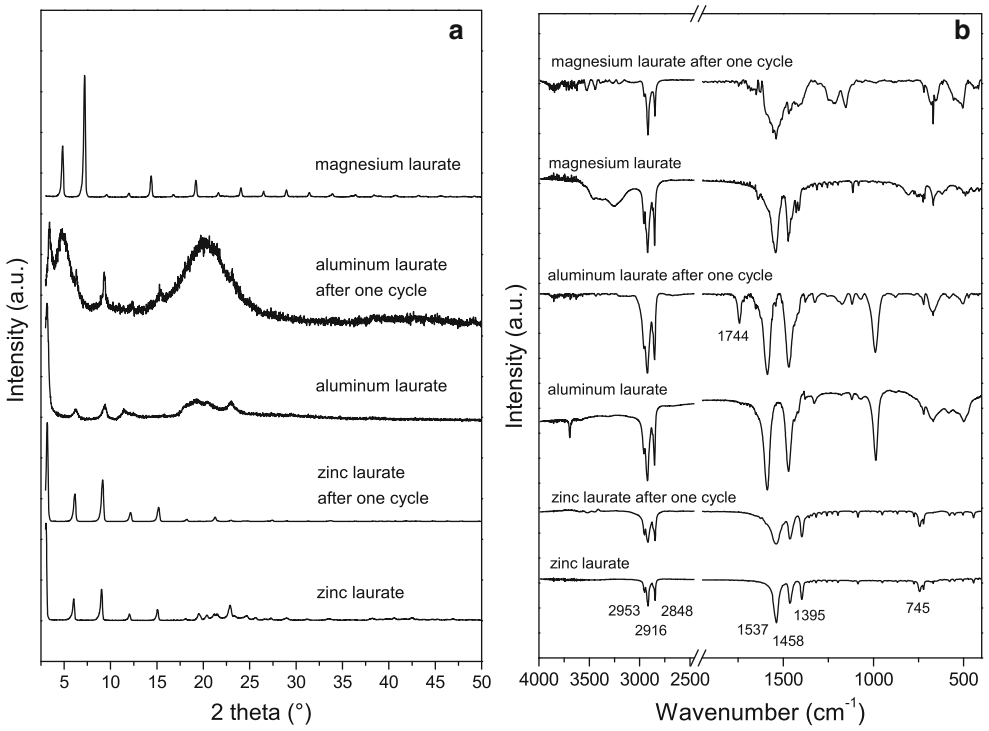

Fig. 3 XRD patterns (**a**) and FTIR spectra (**b**) of magnesium, aluminum, and zinc carboxylates before and after the esterification of lauric acid with methanol (one reaction cycle)

The abilities of zinc, magnesium, and aluminum laurates to catalyze the conversion of lauric acid into methyl laurate are shown in Table 1 (experiments 14 to 16). Both magnesium and aluminum laurates were shown to be catalytically active (experiments 14 and 15, Table 1) in relation to the corresponding thermal conversion (experiment 13 in Table 1). However, under otherwise identical experimental conditions, zinc laurate had the best catalytic performance (42.2 wt%) while the other two led to lower conversions of 28–30 %. Based on the same strategy used for LDHs, the solids that remained insoluble after reaction completion were recovered and analyzed by XRD and FTIR to see whether the structure of the metal carboxylate had survived after one reaction cycle.

Figure 3a shows the XRD patterns of different metal carboxylates before and after use in the esterification of lauric acid with methanol. Magnesium laurate revealed to be highly crystalline by XRD, with a characteristic basal spacing of 29.4 Å (Fig. 3a). However, this solid catalyst was hardly recoverable after one reaction cycle because most of it remained partially dissolved in the reaction medium after cooling. As not enough solids could be recovered by recrystallization, it was not possible to generate their corresponding diffraction pattern. Freshly synthesized aluminum laurate had a layered structure with a basal spacing of 28.4 Å that remained almost unchanged after one single use in the esterification of lauric acid (28.6 Å). The X-ray diffraction pattern of the recovered solids was also quite similar to that of the freshly synthesized material, indicating that the layered structure of aluminum laurate withstood its application in the catalytic conversion of lauric acid to methyl laurate. The basal spacing of zinc laurate also remained unchanged after one reaction cycle under similar reaction conditions (29.1 Å) and the XRD pattern of the recovered solids confirmed its stability in such reaction system.

The FTIR spectra of magnesium, aluminum, and zinc laurates, before and after use in the lauric acid esterification with methanol, are collectively shown in Fig. 3b. All of these layered materials and their corresponding recovered solids displayed the same typical vibration modes of metal carboxylates, including the axial deformation of C–H in CH_2 and CH_3 and the symmetric and antisymmetic stretching of carboxylate anions. In the FTIR of the aluminum laurate recovered solids, the appearance of a band at 1,744 cm^{-1} indicated that lauric acid was only partially converted to methyl laurate as some of the unreacted material could be observed by FTIR.

Based on the results shown above, it is clear that metal carboxylates are catalytic active in the esterification of fatty acids and that their layered structure is kept almost unchanged after at least one reaction cycle, therefore

reinforcing the current hypothesis that LDHs are converted to layered metal carboxylates when subjected to the experimental conditions used in this work.

4 Discussion About the Catalytic Performance

As discussed above, LDHs are converted to metal carboxylates when exposed to methanol and free fatty acids at temperatures above 100 °C. Such transformation results from the attack of carboxylic acids, forming metal carboxylates that reorganized themselves as a new layered material with different properties. In general, metal carboxylates have a relatively low melting point around 85 °C, meaning that, at the conditions used in this work, most if not all of their layered structure was disassembled during the reaction course and subsequently reassembled as crystalline compounds when the reaction mixture was cooled down to room temperature.

The catalytic activity of different metal carboxylates can be explained by the Person's Hard Soft [Lewis] Acid Base (HSAB) principle. As Al^{3+} and Mg^{2+} have similar electronic configurations and hard Lewis acid character, these metals form stable compounds with the carboxylate anions. As zinc is in the border between hard and soft Lewis acids, the carboxylates formed with this metal are more labile and this may partially explain their better catalytic performance in the esterification of fatty acids with methanol.

5 Conclusions

In this work, several LDHs of the Zn/Al and Mg/Al systems were used as catalysts for the esterification of fatty acids. All LDHs were characterized by XRD and FTIR before and after use. These techniques demonstrated that LDHs changed in situ into metal carboxylates, which were responsible for the observed catalytic activity. Among the different metal carboxylates involved in this study, zinc carboxylates had the highest catalytic activity and this was attributed to the Lewis acid character of the transition metal.

It is also important to mention that some of the layered double hydroxides evaluated in this work were also calcined until total dehydroxylation and the resulting nanostructured oxides were subsequently used as catalysts in the esterification of fatty acids. As in the case of fresh LDHs, the calcined LDHs were isolated in the form of crystalline layered carboxylates after one reaction cycle, showing that the observations made in this work are also valid for mixed oxides derived from LDHs.

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