J. Braz. Chem. Soc., Vol. 23, No. 1, 46-56, 2012.
Printed in Brazil - ©2012 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Layered Metal Laurates as Active Catalysts in the Methyl/Ethyl Esterification Reactions of Lauric Acid

Fábio da Silva Lisboa,[a] José Eduardo F. da Costa Gardolinski,[b] Claudiney S. Cordeiro[a] and Fernando Wypych*,[a]

[a]Centro de Pesquisas em Química Aplicada (CEPESQ), Departamento de Química, CP 19081 and
[b]Laboratório de Análise de Minerais e Rochas (LAMIR), Departamento de Geologia, CP 19062,
Universidade Federal do Paraná, 81531-980 Curitiba-PR, Brazil

No presente trabalho são reportadas as sínteses, caracterizações e investigações das atividades catalíticas de lauratos lamelares de cobre(II), manganês(II), lantânio(III) e níquel(II) nas reações de esterificação metílica e etílica do ácido láurico. Nas reações de esterificação metílica, conversões entre 80 e 90% foram observadas para todos os catalisadores, ao passo que, para a esterificação etílica, somente o laurato de manganês mostrou atividade catalítica razoável, com conversões próximas de 75%. Reações de reuso dos lauratos de cobre e lantânio em três ciclos de reação foram investigadas; nelas, ambos os catalisadores preservaram a sua estrutura e mantiveram a atividade catalítica próxima daquela observada para o primeiro ciclo de reação.

In this work we report the synthesis, characterization and investigation of the catalytic activity of layered copper(II), manganese(II), lanthanum(III) and nickel(II) laurates in the methyl and ethyl esterification reactions of lauric acid. In the methyl esterification, conversions between 80 and 90% were observed for all catalysts, while for the ethyl esterification only manganese laurate showed reasonable catalytic activity, with conversions close to 75%. Reuse of copper and lanthanum laurates in three cycles of reaction was also investigated and both catalysts preserved the structure and retained catalytic activity close to that observed for the first reaction cycle.

Keywords: metal carboxylates, layered laurates, biodiesel, lauric acid esterification

Introduction

There has been much recent discussion regarding alternative sources of energy to replace fossil fuels derived from petroleum. One such alternative is the biodiesel,[1] which is usually obtained through transesterification of vegetable oils and animal fats or esterification of free fatty acids (FFA).[2] In both processes, a catalyst needs to be used. Sodium or potassium methoxide or their precursors (sodium or potassium hydroxide) are currently used for the transesterification reactions and inorganic acids are used for the esterification process.[3]

In transesterification reactions, sodium hydroxide is one of the most common homogeneous catalytic precursors due to its low cost. During homogeneous catalysis, many steps are necessary to produce biodiesel and, as a consequence, the price of the final product increases. This process has many disadvantages, both from economic and ecological standpoints, which can be briefly summarized as: (*i*) it is conducted in batch reactors that limit the large scale production; (*ii*) the catalyst needs to be neutralized and cannot be recovered for reuse; (*iii*) inorganic salts are formed and need to be washed out from the fatty acid methyl esters; (*iv*) soaps are formed when the raw material has some acidity, lowering the reaction yield and inhibiting the separation of the esters from glycerol (a byproduct of the transesterification reaction); (*v*) contaminated glycerine is obtained; (*vi*) the water formed during the saponification reaction retards the transesterification reaction by hydrolysis; (*vii*) the alkaline medium is very aggressive to the equipment, just to cite some drawbacks.

A way to minimize the costs of these processes is to use catalysts that can operate in heterogeneous media, such as transition metal oxides, zeolites and ionic exchange resins, among others. The biodiesel market is expected to grow rapidly due to the environmental benefits and

---

*e-mail: wypych@ufpr.br

government directives that will come into effect in the near future. Increasing biodiesel consumption requires optimized production processes, simplified operations, high reaction yields and high purity products. Low-cost solid heterogeneous catalysts can help solving some of these problems.

When zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$) was used as catalyst in the methyl/ethyl transterification reaction of soybean or palm oil and esterification of commercial lauric acid, zinc hydroxide nitrate was transformed into zinc carboxylate.[4] This was observed during isolation of the solid after the esterification reactions. Zinc carboxylate was then synthesized and tested, showing to be very active in the production of alkyl monoesters, which were obtained by the esterification reactions of fatty acids and/or transesterification of triacylglycerols (triglycerides).

Similar results were obtained when layered double hydroxides (LDH), also known as hydrotalcite-like compounds, were employed as catalysts in esterification reactions. The use of LDHs or their nanostructured oxides (obtained from the calcination of different LDHs under mild conditions) in esterification reactions only led to the isolation of metal carboxylates after the reactions.[5]

Since in previous studies only zinc laurates were synthesized and evaluated, the objective of the present work was to synthesize and characterize layered copper, manganese, lanthanum and nickel laurates as well as to evaluate their catalytic activity in the methyl and ethyl esterification reactions of commercial lauric acid. Tests of reuse of the copper and lanthanum laurates were performed, in which the structures and respective catalytic activities were investigated up to the third use cycle.

Experimental

Catalysts synthesis

Layered metal laurates were synthesized through precipitation or metathesis in alcoholic medium,[4] starting by neutralization of lauric acid with sodium hydroxide and followed by precipitation of each compound through slow addition of an aqueous solution containing the metal ions of interest.

It the first step, 4.33 g (21.6 mmol) of lauric acid P.A. (Vetec, 98%) were totally dissolved in 20 mL of methanol P.A. (ACS, 99.8%) and neutralized by a stoichiometric amount of sodium hydroxide (Vetec, 98%). The white precipitate of sodium laurate obtained was then separated and dissolved in 30 mL of distilled water at room temperature and under vigorous stirring.

In the second step, metal salt solutions were added dropwise to the aqueous/alcoholic sodium laurate solution. After addition, each system was submitted to magnetic stirring for 1 h. The amounts used in the syntheses were: (*i*) for manganese(II) laurate, 10.8 mmol of $Mn(NO_3)_2{\cdot}4H_2O$ (Vetec, 97.0%) were dissolved in 100 mL of distilled water; (*ii*) for copper(II) laurate, 10.8 mmol of $Cu(NO_3)_2{\cdot}3H_2O$ (Synth, 98.0%) were dissolved in 100 mL of distilled water; (*iii*) for lanthanum(III) laurate, 15.0 mmol of La_2O_3 (Vetec, 99.5%) were dissolved in 50 mL of 10% HNO_3 (Quimex, 65%) in an ice bath and (*iv*) for nickel(II) laurate, 10.8 mmol of $NiCl_2{\cdot}6H_2O$ (Vetec, 97.0%) were dissolved in 100 mL of distilled water.

The washing of the solids was performed first with ethanol P.A. (ACS, 99.5%) to eliminate the possible presence of unreacted lauric acid and later with distilled water to eliminate the residues of the metal salt used in the precipitation, or even sodium laurate formed *in situ*.

The number of washing steps with the organic solvent was considered ideal when the supernatant after centrifugation was visually limpid. About three washing steps were sufficient and this number was also applied to the distilled water washing.

Esterification reactions

The catalytic activity of the layered metal laurates was investigated in the methyl (ethyl) esterification reaction of lauric acid. The experiments were performed in a 100 mL capacity steel reactor (Büchiglass miniclave drive) equipped with an internal magnetic type hurricane stirring system, applying a standard rotation of 500 rpm. The temperature was controlled with an external thermostated mineral oil bath (Julabo model HE-4).

For the tests in the reactor, the reaction conditions were established starting from a factorial design (2^3) with two levels and three variables,[6] in which the influence of temperature, molar ratio (M.R. = alcohol/acid) and catalyst amount were investigated. The high and low levels for each variable were respectively 140 and 100 ºC for temperature (central point of 120 ºC), 14:1 and 6:1 for molar ratio alcohol/acid (central point of 10:1) and 10 and 2% for catalyst percentage in relation to the mass of lauric acid used in the reaction (central point of 6%). Eleven experiments were performed for each catalyst, three of them at the central point.

The reactions were carried out as follows: the lauric acid, alcohol and catalyst were introduced into the reactor, which was tightly closed and heated, reaching the reaction temperature in approximately 15, 25 and 45 min for temperatures of 100, 120 and 140 ºC, respectively.

The reactions were conducted for 2 h[7] and, at the end of the programmed period, the content of the reactor was transferred to a 100 mL round bottom flask, from which the excess alcohol was removed by rotary evaporation with reduced pressure at 65 ºC for methanol and 80 ºC for ethanol. The pressure of the reactor was controlled by the vapor pressure of the most volatile component of the reaction medium, methanol or ethanol. For the reaction temperatures of 100, 120 and 140 ºC using methanol, the pressures registered by the barometer were respectively 4, 6 and 8×10^5 Pa, while for ethanol, whose experiments were only conducted at 140 ºC, the pressure was 6×10^5 Pa. The conversion of lauric acid to the respective ester was measured by quantification of free fatty acids, according to the method Ca-5a-40 of the American Oil Chemists' Society (AOCS).[8]

Since the reactions can also proceed due to the influence of temperature,[9] tests of thermal conversion were performed following a factorial design with two levels and two studied variables, temperature and molar ratio, in the absence of the catalyst. The catalytic activity of the tested solids was verified by comparing the results of methyl/ethyl esters conversion, obtained under each condition, for the catalyzed reactions and the respective thermal conversions without catalyst addition.

Catalyst reuse tests were performed to verify the possible maintenance of catalytic activity and structure after the first reaction cycle. Only copper and lanthanum laurates were evaluated. The reuse procedure was accomplished starting from the recovery of the solids, which were washed with acetone and dried in a vacuum stove at 60 ºC until constant mass. As the recovery was not complete, due mainly to physical losses (around 95%), the amount of the reagents (alcohol and lauric acid) and catalyst were adjusted to maintain the same proportions of the first reaction cycle. Based on the proportions and recoveries, the solids were tested in more reaction cycles, resulting in three experiments for each catalyst.

Characterizations

X-ray diffraction (XRD) patterns were recorded with a Shimadzu XDR-6000 instrument using CuK_α radiation ($\lambda = 1.5418$ Å), dwell time of 2° min^{-1}, current of 30 mA and tension of 40 kV. The samples were placed and oriented by hand pressing after filling top-loading aluminum or neutral glass sample holders.

The Fourier transform infrared (FTIR) spectra were recorded with a Bio-Rad FTS 3500GX instrument, using approximately 1% of sample in 100 mg of spectroscopic grade KBr, the pellets being pressed at 10 tonnes. The measurements were performed by transmission mode with accumulation of 32 scans and recorded with a nominal resolution of 4 cm^{-1}.

Thermal analysis (thermogravimetry (TGA) and differential thermal analysis (DTA)) measurements were performed in 150 µL alumina crucibles with a Mettler-Toledo TG/SDTA 851e thermoanalyzer under a 50 mL min^{-1} oxygen flow, at a heating rate of 10 °C min^{-1}, in the range of 30-1000 °C.

Results and Discussion

The X-ray powder diffraction patterns (Figure 1) show that the compounds have a layered structure, as can be seen from the typical basal peak sequence between 3 and 20° and absence of non-basal peaks due to the crystals orientation in the sample holder.

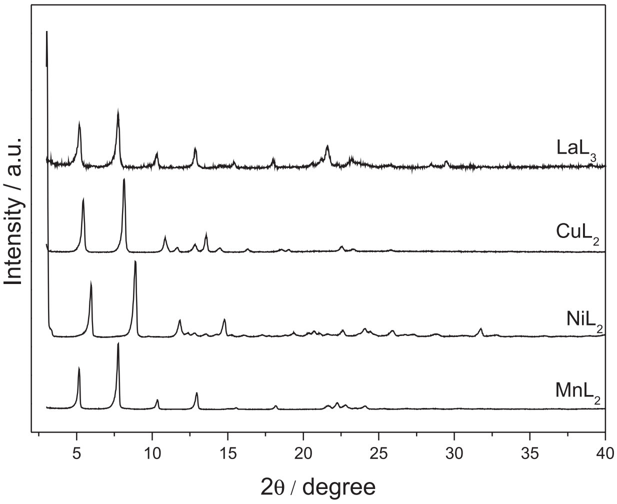

Figure 1. X-Ray powder diffraction patterns of the layered laurates.

The stacking direction is along the "a" axis (h00 direction) and the diffraction profile is very similar for all compounds, suggesting that probably all of them are isostructural with anhydrous zinc octanoate.[10] The basal spacings calculated for each of the synthesized laurates are consistent with the organic chains being arranged as tilted bilayers between the zinc layers (Figure 2).[10-12] The model used to represent the laurates structure is based on the structure of anhydrous zinc octanoate, due to the similarity of the XRD patterns with the above described layered metal laurates. The basal spacing values calculated by using the highest order basal peak possible were 29.97 Å, 32.63 Å, 34.16 Å and 34.53 Å for nickel, copper, manganese and lanthanum laurates, respectively. The basal distances for the laurates are coherent with an increase in the ionic radii of the metals present in the structures, Ni^{2+} (0.69 Å),

Cu^{2+} (0.72 Å), Mn^{2+} (0.91 Å) and La^{3+} (1.22 Å). However, the increased radius is not the only factor that contributes to this increase in basal distance. The organic chains are oriented with specific angles, and the coordination of the metal centers and the M–O distances can also influence the basal distance (Figure 2).[13]

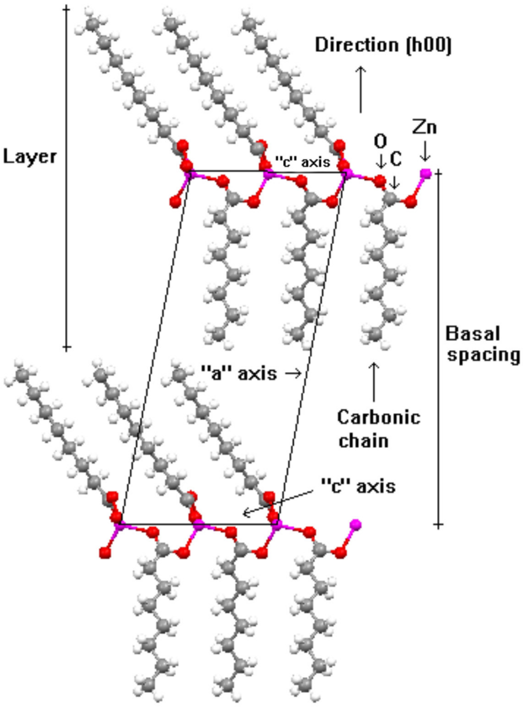

Figure 2. Schematic representation of the zinc octanoate structure: view along the "b" axis (adapted from references 10-12).

The FTIR spectra of the compounds (Figure 3) present vibration modes characteristic of saturated fatty acid salts and of the way the carboxylate groups are connected to the metals building the layers. The coordination of the laurate to the metals can be verified by the presence of stretching bands between 430 and 540 cm^{-1}, which can be attributed to M–O bonds.[14] All products present vibrations due to O–H bonds, indicating the presence of moisture or of structural water in the composition of the synthesized laurates. For the manganese and lanthanum laurates, the broad band of the O–H bond vibration was attributed to the presence of moisture. For the nickel compounds, on the other hand, there is a low intensity sharp peak, indicating the possibility that water is connected structurally to the inorganic layer. The vibrational groups that undergo the highest variations are those closest to the metal centers, as can be seen in Table 1, which shows the values for the vibrations of the most significant bands in each compound, supplying information about the structure of each layered laurate.

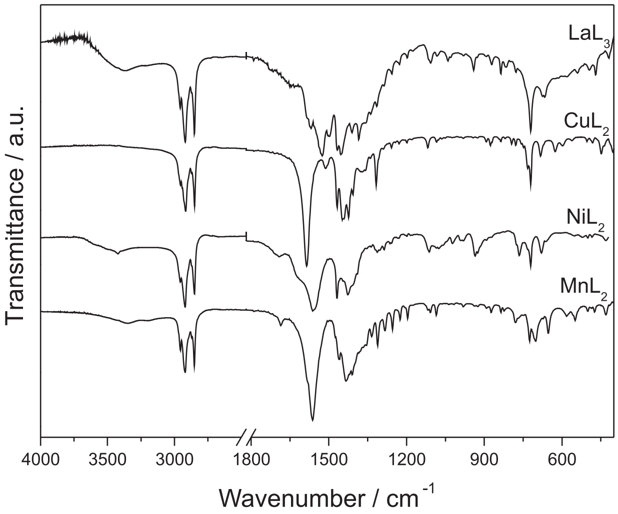

Figure 3. FTIR spectra of the layered laurates.

The asymmetric and symmetric stretchings of the methyl groups between 2956 and 2850 cm^{-1} and the angular deformation at 721 cm^{-1} of the methylenic groups have very close energy values for all compounds and are characteristic of saturated chain fatty acids. In many cases these vibrations are taken as a fingerprint of the class of compounds. In the region of 1200 and 1300 cm^{-1}, it was possible to verify the presence, in all compounds, of a group of CH_2 stretching bands related to the all-*trans* conformation of these groups in the layered carboxylate structure.[15] The weak bands in the region of 750 and 1350 cm^{-1} are attributed to coupling of scissoring, wagging and twisting modes.[13] The profile of the vibrational spectrum indicates that the compounds may really be isostructural, as seen from the XRD analysis. The splitting of the antisymmetric and symmetric vibrational modes of the carboxylate groups, with values of Δν between 137 and 164 cm^{-1}, is typical of compounds with two carboxylates bridging metal centers,[12,14,16] consistent

Table 1. Peak positions (in cm^{-1}) for the vibrational modes of the layered metal laurates

Compound	ν M–O	ν O–H	$\nu_{ass}CH_3$	$\nu_{(s)}CH_3$	δ CH_2	ν_{ass} COO^-	$\nu_{(s)}$ COO^-	$\Delta\nu_{(COO^-)}$
MnL_2	499	3344	2954	2850	725	1562	1409	153
CuL_2	449	-	2954	2848	721	1585	1421	164
NiL_2	430	3423	2956	2848	721	1562	1425	137
LaL_3	540	3375	2956	2850	721	1525	1384	141

Table 2. Thermal processes of layered metal laurates obtained from the TGA/DTA curves (in °C)

Compound	Melting point	Burning of the organic matter	Exothermic peak	Oxide formation
MnL_2	81	228-356	284	356
LaL_3	66	326-400	370	1000
NiL_2	81	318-440	365	834
CuL_2	113	221-378	285; 320	425

with the layered zinc octanoate structure (Figure 2). The thermal analysis curves (TGA/DTA) of the laurates show very characteristic organic carboxylate decomposition profiles (Figure 4).[17] Table 2 summarizes the processes attributed from the thermal analysis curves.

The compounds MnL_2, LaL_3, NiL_2 and CuL_2 presented endothermic melting events at temperatures of 81, 66, 81 and 113 °C, respectively. The melting process occurs in a single thermal event, as observed for zinc carboxylates with different chain lengths.[13] The proximity of the melting point

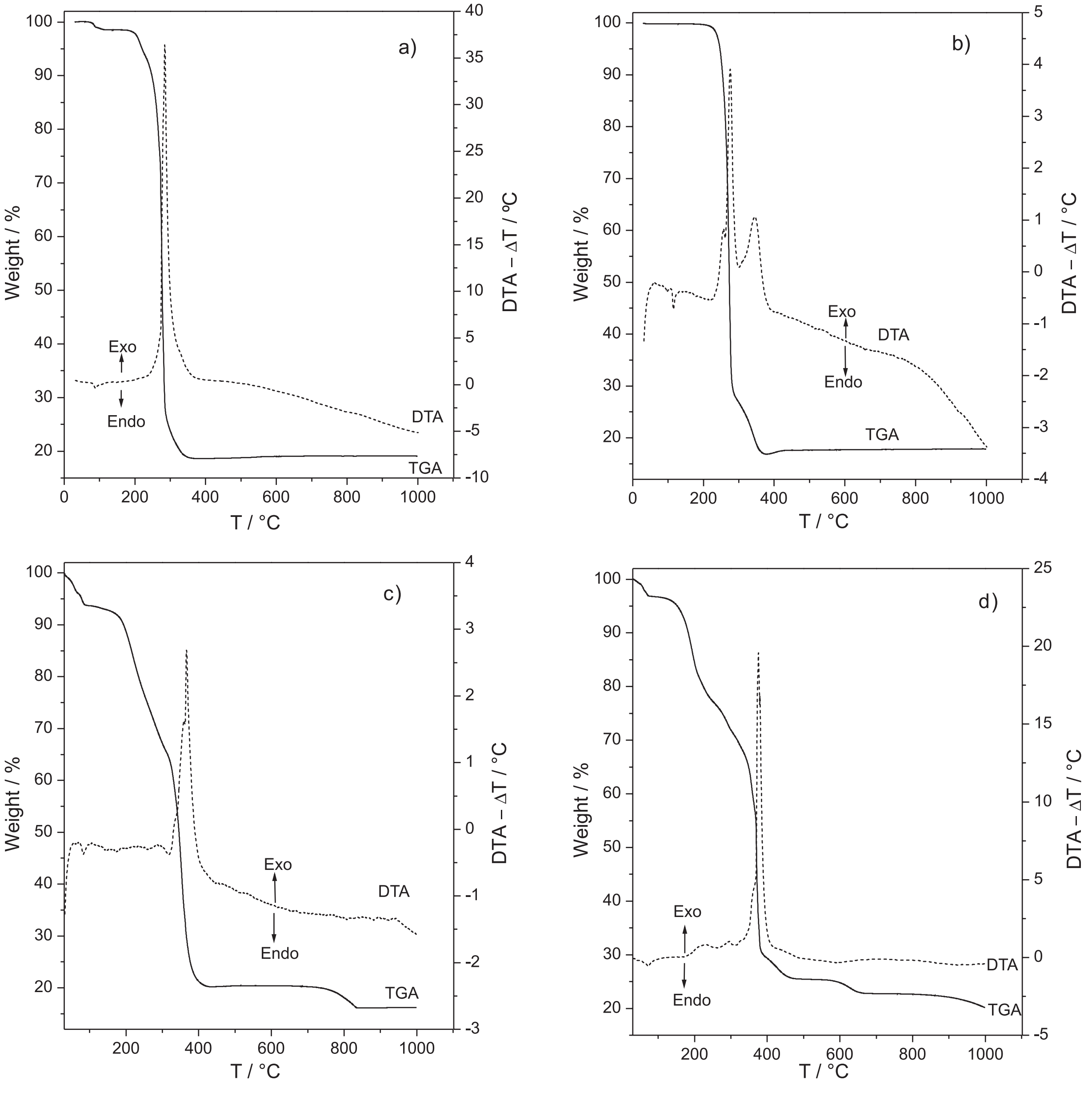

Figure 4. Thermal analysis curves (TGA/DTA) of the layered laureates: manganese (a), copper (b), nickel (c) and lanthanum (d).

values can also be another indication of the compounds similar structures. As reported in the literature,[13] in which the melting of the alkyl chains in the saturated fatty acid zinc carboxylates was investigated by XRD, FTIR and DSC, about 30% of the all-*trans* conformation of the methylenic groups present in the structure is lost during melting and a mixture of fragments of the structure is obtained, in which the carboxylate group is coordinated to the metal in the bridge bidentade and the monodentade modes. The laurates of manganese, nickel and lanthanum presented mass losses between 60 and 180 °C, attributed to the loss of physisorbed water in the first compound and structural water in the last two compounds. Even though the water removal temperature of the structure is low, the low melting point of the solids can facilitate removal of the molecules from the structure.

This class of compounds behaves like ionic liquids, especially during the melting observed in the catalytic reactions medium. The organic matter oxidation is accompanied by intense exothermic peaks in the region of 150 and 400 °C in the DTA curves and, after this, it is possible to see the start of formation of stable metal oxides. From the thermal analysis curves and the purity of the compounds, attested by the XRD and FTIR analysis, the compositions of the laurates could be estimated as follows: $Mn\{CH_3(CH_2)_{10}COO\}_2$, $Ni\{CH_3(CH_2)_{10}COO\}_2{\cdot}2H_2O$, $Cu\{CH_3(CH_2)_{10}COO\}_2$ and $La\{CH_3(CH_2)_{10}COO\}_3{\cdot}3H_2O$, where the oxide amounts obtained after the analysis are in agreement with the theoretical values, in the range of 1 to 5%.

Methyl esterification reactions of lauric acid

The results obtained for the thermal conversion of lauric acid to the respective ester, used as control for comparison with the reactions in which the catalyst was added, can be observed in Table 3. Only ester and water are formed in the reactions. All the tested catalysts melted in the reaction medium and were reconstructed as the temperature decreased, being recovered almost completely, with only small physical losses.

The largest conversion into ester was 67% at 140 ºC, using a molar ratio of 6:1, and the smallest was 12% at 100 ºC, using the molar ratio of 14:1. The results of the central point were very similar, close to 39%, indicating the reproducibility of the assays. The values obtained served as parameters to verify that the addition of the catalysts to the reaction medium increases the conversion of acid into ester. The final results were calculated by subtraction of the values obtained without catalysts (thermal conversion "T") from those where the catalysts were present (catalyzed reaction "C"). These data are compiled in the column "C – T" of Table 4 (and Supplementary Information - Tables S1 to S3) and are given as ester in percentage points (ester p.p.). The subtraction gave positive values for all the evaluated catalysts, except for experiment 8, indicating a contribution of the layered laurates to increase the conversion of lauric acid into ester, and attesting the catalytic activity of the evaluated compounds.

The highest conversions obtained with the catalyzed reactions were observed in experiments 9 (83%) and 14 (90%) for MnL_2 (Table 4); 20 (81%) and 25 (77%) for NiL_2 (Table S1); 31 (78%) and 36 (82%) for CuL_2 (Table S2); and 42 (79%) and 47 (90%) for LaL_3 (Table S3). These values represent the largest conversions of lauric acid into ester, but they do not reflect the largest increases in relation to the control. In experiment 15, for example, the conversion was 79%, the third largest conversion value. However, the gain in relation to the thermal conversion was 25 p.p., a larger value than the 16 p.p. of experiment 9. This was also observed for experiments 22, 24, 26, 30, 32 and 33.

Table 3. Methyl esterification due to thermal conversion

	Variable		Reaction conditions		Results	
Exp.	M.R.	T	M.R. (alcohol: acid)	T / ºC	Remaining lauric acid / %	Ester / %
1	–1	–1	6:1	100	77	23
2	–1	+1	6:1	140	33	67
3	+1	–1	14:1	100	88	12
4	+1	+1	14:1	140	46	54
5	0	0	10:1	120	60	40
6	0	0	10:1	120	61	39
7	0	0	10:1	120	61	39

Exp = experiment; M.R. = molar ratio; T = temperature. Standard deviation of the central point (Exp. 5, 6 and 7): ± 0.67.

Table 4. Methyl esterification using MnL_2 as catalyst

Exp	Variable			Reaction conditions			Results	
	M.R	CAT	T	M.R.	Catalyst / %	T / ºC	Ester / %	C – T (Ester p.p.)
8	–1	–1	–1	6:1	2	100	20	–3
9	–1	–1	+1	6:1	2	140	83	16
10	–1	+1	–1	6:1	10	100	24	1
11	+1	–1	–1	14:1	2	100	18	6
12	+1	–1	+1	14:1	2	140	69	15
13	+1	+1	–1	14:1	10	100	19	7
14	–1	+1	+1	6:1	10	140	90	23
15	+1	+1	+1	14:1	10	140	79	25
16	0	0	0	10:1	6	120	47	7
17	0	0	0	10:1	6	120	47	8
18	0	0	0	10:1	6	120	47	8

Exp = experiment; M.R. = molar ratio (alcohol:acid); CAT = catalyst; T = temperature; C – T = Catalyzed conversion – thermal conversion. Standard deviation of the central point (Exp. 16, 17 and 18): ± 1.62. Reaction time: 2 h.

In general, the factors that most influenced the conversion were temperature and molar ratio (alcohol:acid). The temperature increased positively the conversion and the increase in molar ratio had a negative influence (Table 5). Since the catalyzed path requires lower activation energy, more molecules have sufficient energy to react effectively than in the non-catalyzed path, and the reaction rate and conversion efficiency increase with increasing temperature. In the case of molar ratio (alcohol:acid), the greater amount of alcohol difficults the access of the substrate to the catalyst active site, reducing the reaction rate and consequently changing the equilibrium of the esterification reaction. In order to verify which catalyst had the best catalytic behavior, the percentage of conversion into ester *versus* results of experiments conducted under the same conditions was plotted in a graph (Figure 5). We grouped the experimental conditions in which the variables temperature, molar ratio and catalyst percentage were fixed and the experiments were varied from 1 to 11; then, we verified which catalyst behaved best under each condition. It was surprising that the same catalyst did not

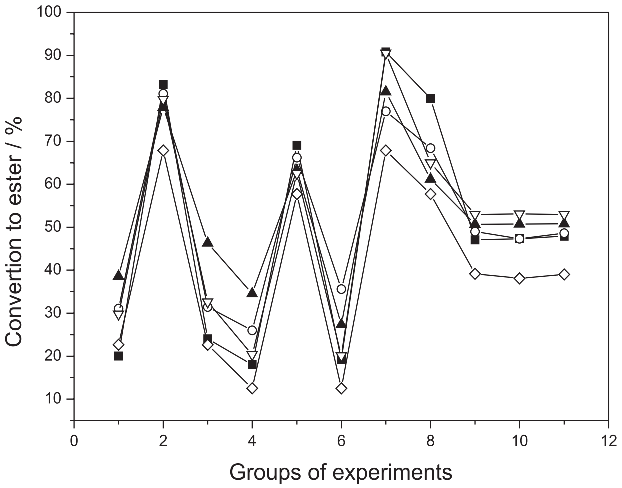

Figure 5. Comparison of the conversions to ester obtained in each experimental condition employed for the catalysts in the esterification of lauric acid. (◇) thermal conversion; (▽) LaL_3; (▲) CuL_2; (○) NiL_2; (■) MnL_2. Groups of experiments: 1 = 8, 19, 30, 41; 2 = 9, 20, 31, 42; 3 = 10, 21, 32, 43; 4 = 11, 22, 33, 44; 5 = 12, 23, 34, 45; 6 = 13, 24, 35, 46; 7 = 14, 25, 36, 47; 8 = 15, 26, 37, 48; 9* = 16, 27, 38, 49; 10* = 17, 28, 39, 50; 11* = 18, 29, 40, 51 (* = central point; experiments performed in triplicate).

Table 5. Variable influences in the methyl esterification reactions of lauric acid

Compound	1st order interactions			2nd order interactions		
	T / ºC	Catalyst	M.R.	Catalyst/M.R.	Catalyst/T	T/M.R.
MnL_2	60.42	5.93	–7.95	4.65	3.31	–4.54
NiL_2	44.94	4.83	–3.27	6.68	–0.16	–2.84
CuL_2	37.43	0.50	–11.37	–5.15	0.22	2.15
LaL_3	48.74	3.96	–16.19	–2.82	2.69	–5.21

M.R. = molar ratio (alcohol:acid). All values are expressed as percentage points (p.p.).

always provide the highest conversion under the different experimental conditions. In some cases the conversion was better at lower temperatures; in others, it was better at higher ones.

Since the catalyst percentage used in the reactions was always calculated in relation to the mass of lauric acid, there was a variation in the amount of metal centers present in the reaction medium, due to the different molar weights of each compound, as estimated by thermal analysis. To verify if the molar weight had an influence on the catalyst performance, we analyzed the conversion into ester in function of the metal sites in each case (turnover number - TN). However, this correlation was not observed. Different catalysts performed differently depending on the experimental conditions.

During the melting process, only part of the structure is fragmented and the resulting structural "clusters" (metal site connected to some organic carboxylates) are responsible for the catalytic behavior. To support that, manganese(II), copper(II) and nickel(II) nitrates were used as catalysts to verify the influence only of the cation, and the catalytic activities were similar to those given by thermal conversion (MR of 6:1; 2% of catalyst and 100 °C).

Ethyl esterification reactions of lauric acid

A factorial design for the ethyl esterification reactions of each laurate was also performed. The tests were based on the best results obtained with the methyl esterification, due to the lower reactivity of ethanol when compared to methanol. The results are shown in Table 6. In the case of transesterification under homogeneous conditions, as the length of carbon chain of the alcohol increases, the nucleophilicity of the alkoxide anions decreases leading to a decrease in the reactivity.[18] The effect is probably similar in the present case.

The only compound that presented relevant catalytic activity when the catalyzed reaction and the thermal conversion were compared was manganese laurate; the reason for this behavior is still under investigation. For the three reactions performed with manganese laurate, the conversions were 63, 70 and 75%, with gains in relation to thermal conversion of 1, 8 and 16 p.p., respectively.

Under similar conditions, when raw halloysite was used as catalyst, the higher gains in relation to the thermal conversion were of 13.95% (M.R. = 6:1 methanol:lauric acid; 160 °C, 2 h and 12% of catalyst) and 19.41% (M.R. = 12:1 methanol:lauric acid; 160 °C, 2 h and 12% of catalyst).[19] When metakaolins were used as catalysts, conversion gains of 54.2% (M.R. = 60:1 methanol:oleic acid, 130 °C, 2 h and 5% of catalyst) and 11.1% (M.R. = 60:1 methanol:oleic acid, 130 °C, 2 h and 5% of catalyst) were recently reported for calcined and sulfuric acid activated standard Kga-1b and Kga-2 kaolinites, respectivelly.[20]

In general, lower conversion gains are reported for the layered laurates (see Tables 4, 6 and Tables S1-S3) but this kind of comparison is difficult to be made due to the completely different behavior of the layered laurates in comparison to traditional heterogeneous catalysts.

Table 6. Results for ethyl esterification

Exp.	Catalyst	Reaction conditions			Results	
		M.R.	Catalyst / %	T / °C	Ester / %	C – T (Ester p.p.)
52	-	6:1	-	140	62	-
53	-	14:1	-	140	59	-
54	MnL_2	6:1	2	140	63	1
55	MnL_2	6:1	10	140	70	8
56	MnL_2	14:1	10	140	75	16
57	NiL_2	6:1	2	140	-	-
58	NiL_2	6:1	10	140	-	-
59	NiL_2	14:1	10	140	-	-
60	CuL_2	6:1	2	140	60	–2
61	CuL_2	6:1	10	140	59	–3
62	CuL_2	14:1	10	140	41	–18
63	LaL_3	6:1	2	140	62	0
64	LaL_3	6:1	10	140	62	0

Exp = experiment; M.R. = molar ratio (alcohol: acid); C – T = Catalysed conversion – thermal conversion; (-) without catalyst.

As expected, conversion values were lower for ethyl esterification than for methyl esterification.

Catalysts reusability tests

Based on the catalysis results for the esterification of lauric acid to methyl laurate obtained for each catalyst, and the observed structure reconstruction or transformation of the catalysts after the reactions, we performed reuse tests to verify the catalytic activity after the first cycle as well as the structure of the re-isolated solid. In these analyses, lanthanum and copper laurates were evaluated, because they were the ones that presented the fastest and best structure reconstruction. Manganese oxide was isolated after rotary evaporation as a dark solid and nickel laurate was reconstructed very slowly. Consequently, both materials were not evaluated in further cycles. The conditions in which the reusability tests were performed were those under which the highest conversion percentages were observed in the first use, following the factorial design.

For copper laurate, the conditions of experiments 31 and 36 presented in Table S2 were used. The values obtained for the second and third cycle in experiment 31 were 80.95 and 82.68%, respectively (Figure 6). These results, when compared with the first use, presented a conversion of 77.94%, representing a small increase in the production of ester. The values obtained for the reuses regarding experiment 36 were respectively 83.40 and 85.42%, demonstrating similar behavior, that is, a slight increase in the ester percentage compared to the first reaction cycle, in which the result was 81.48% conversion (Figure 6).

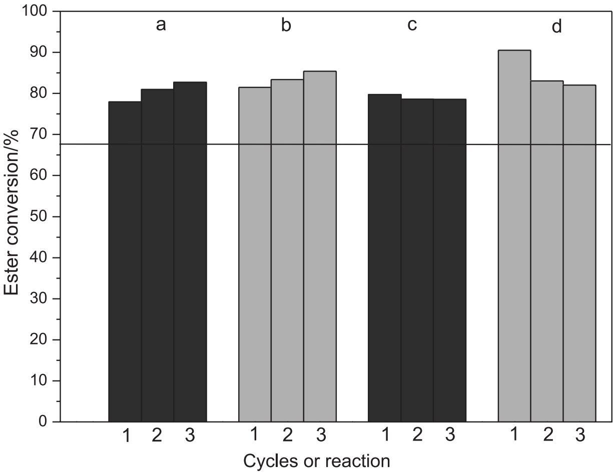

Figure 6. Conversions into ester using layered laurates in three reaction cycles. The black line that crosses the graph represents the thermal conversion. a = CuL_2, MR 6:1, 2% catalyst, 140 °C; standard deviation: ± 1.38% (Exp. 31); b = CuL_2, MR 6:1, 10% catalyst, 140 °C; standard deviation: ± 1.14% (Exp. 36); c = LaL_3, MR 6:1, 2% catalyst, 140 °C; standard deviation: ± 0.38% (Exp. 42); d = LaL_3, MR 6:1, 10% catalyst, 140 °C; standard deviation: ± 2.68% (Exp. 47).

The results obtained with the first and second reuse under the condition reported in experiment 42 were 78.59 and 78.54%, respectively, values that are comparable with the first reaction (79.73%) (Table S3 and Figure 6). However, for the condition of experiment 47, whose first reaction resulted in a conversion into ester of 90.50%, the values were slightly lower (83.03 and 82.01% for the first and second reuse, respectively). This reflects a slight loss of catalytic activity for the lanthanum laurate. Knowing that losses during recovery were significant, the decrease in activity can be attributed to a volume effect, since the proportions of reactants and catalyst were maintained, but the total volume of the mixture was smaller. This implied in larger evaporation to maintain the reactor pressure constant and in artificial reduction of the molar ratio, thus negatively affecting the ester conversion.

Characterization of the compounds after the esterification of lauric acid

The solids were characterized by XRD and FTIR after the methyl esterification reactions of lauric acid (Figure 7). The main peaks of the XRD patterns can be indexed in the original structure, although sometimes small transient peaks could be observed. As the time of crystallization was not controlled, the changes in the intensities of the XRD peaks can be attributed to small variations in the crystallization degree. Also, the bands of the FTIR spectra can be attributed to the original structure, not showing any new functional group from any possible impurity. This information let us conclude that the main structures of both catalysts were maintained after three consecutive uses.

Figure 8 displays a schematic representation of the structure of the zinc octanoate and the proposed mechanism for the esterification of lauric acid using melted layered laurates. It should be noted that the laurates were added to the reactor in the solid state and were submitted to melting in the reaction medium, resulting in the partial fragmentation of the structure. The resulting structure fragments (clusters) were responsible for the catalytic activity, since only part of the bonds of the carboxylate ion-metal, in the form of a bidentade bridge, are broken.[13] The coordination of the carboxylates in the monodentade form leaves the metal ions only partially coordinated, probably being the active center, as proposed in the mechanism based on the model of Langmuir-Hinshelwood of Figure 8.[21,22] After cooling, the catalyst is reconstructed and can be recovered for subsequent reuses. This is similar to the behavior of ionic liquids.[23-26]

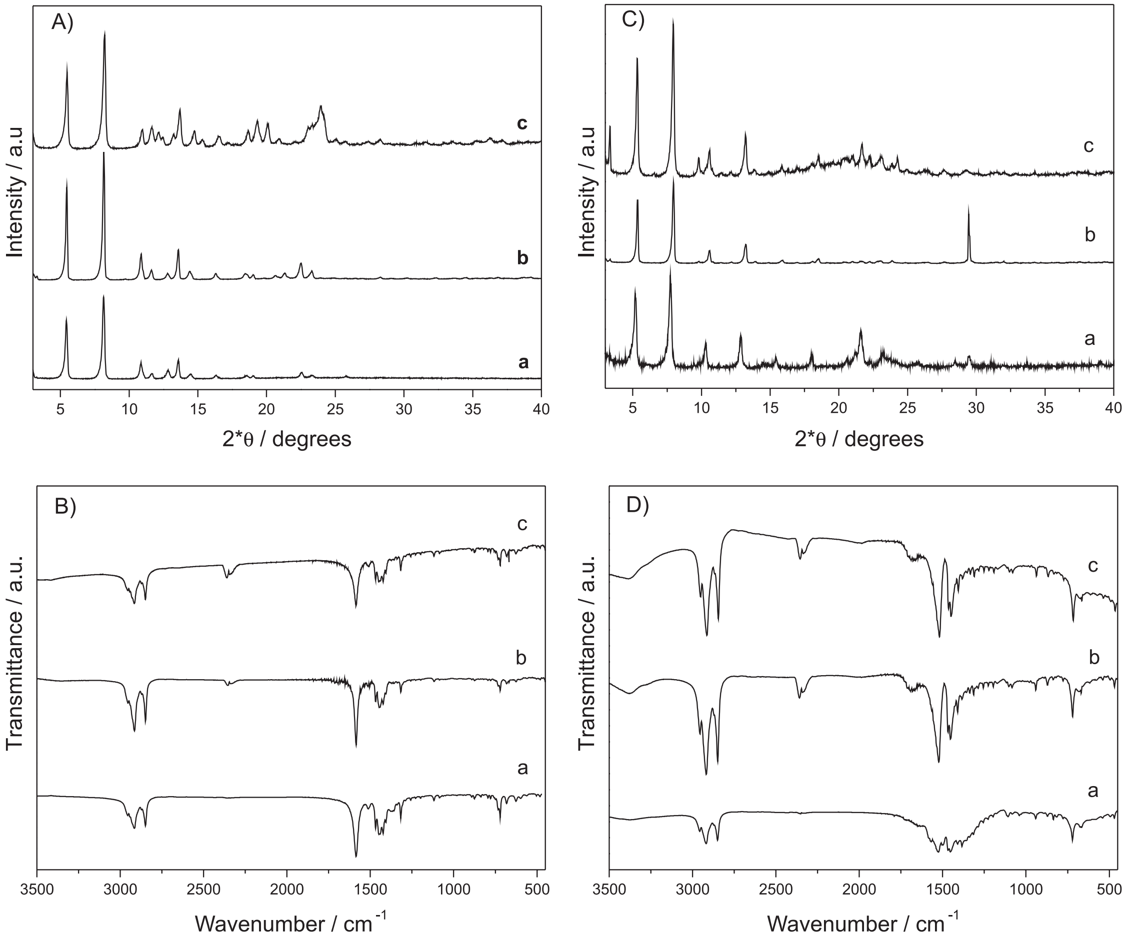

Figure 7. XRD patterns (A, C) and FTIR spectra (B, D) of the laurates before (a) and after two reactions of reuse (b, c). A and B copper laurate; C and D lanthanum laurate.

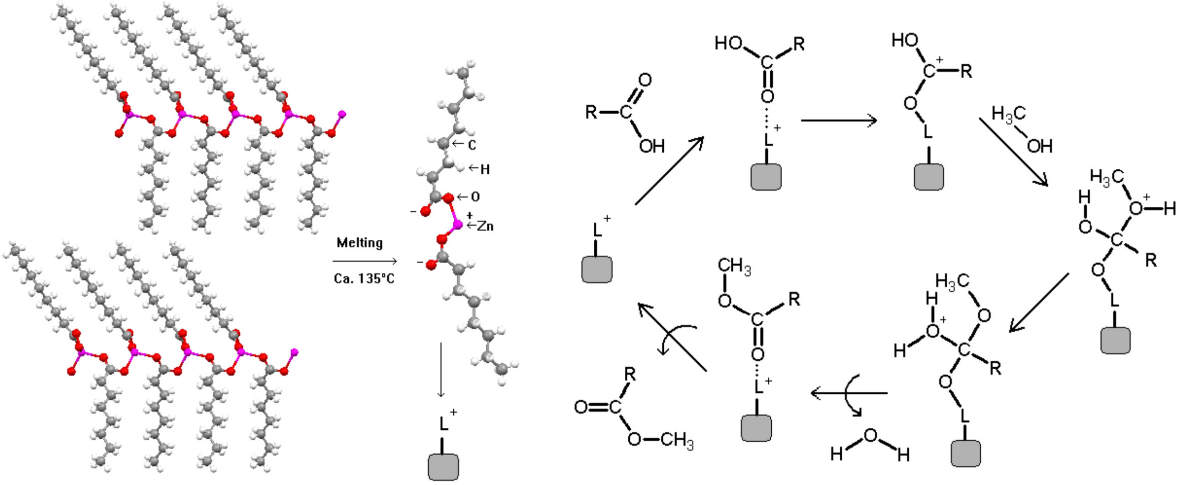

Figure 8. Schematic representation of the zinc octanoate structure and the proposed catalytic mechanism involving layered metal laurates (adapted from references 10-12, 21 and 22).

Conclusions

The synthesized compounds presented layered structures and basal spacings in agreement with the presence of alkyl chains arranged as tilted bilayers between the inorganic layers. The X-ray powder diffraction profiles showed that the compounds are probably isostructural and that the structuring of the layers is obtained by coordination of the carboxylate groups to different metal centers in a bridge bidentade arrangement.

The compounds melted in the reaction medium and, after cooling, the original structures could be re-isolated. After melting the catalysts behaved as homogeneous catalysts or ionic liquid-like catalysts; consequently, the activity is independent of the surface area of the crystal obtained during synthesis.

The possibility of reusing the copper and lanthanum laurates in the methyl esterification reactions was also verified by tests, which roughly presented conversion values very close to the initial ones.

In the comparison of reactivities, based on the conversion results, all the catalysts showed very similar profiles. This also corroborates the evidence that all compounds have similar or identical structures. As observed in the melted state and supposedly in the reaction medium, all the metals are still partially coordinated to the carboxylate ligands and the activity in similar conditions originates from intrinsic properties of each metal cation with the synergistic effect of the carboxylate and the coordination mode.[13]

The tests of catalytic activity in the methyl esterification of lauric acid demonstrated that in all cases the compounds promoted catalysis when compared with the thermal control, reaching conversions between 80% and 90% in some conditions. However, only manganese laurate demonstrated the ability to catalyze the ethyl esterification reactions of lauric acid, presenting conversions close to 75%.

To the best of our knowledge, this is the first systematic study in which a class of layered metal laurates was evaluated in the methyl and ethyl esterification of lauric acid. Further studies are in progress to evaluate layered carboxylates in the esterification of other fatty acids and complex mixtures of fatty acids and the transesterification of vegetable oils and animal fats.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

We gratefully acknowledge CNPq, CAPES and FINEP for the financial support of this work.

References

1. Pereira, R. G.; Oliveira, C. D.; Oliveira, J. L.; Oliveira, P. C. P.; Fellows, C. E.; Piamba, O. E.; *Renew. Energ.* **2007**, *32*, 2453.
2. Gerpen, J. V.; *Fuel Process. Technol.* **2005**, *86*, 1097.
3. Ma, F.; Hanna, M. A.; *Bioresour. Technol.* **1999**, *10*, 1.
4. Cordeiro, C. S.; Arizaga, G. G. C.; Ramos, L. P.; Wypych, F.; *Catal. Commun.* **2008**, *9*, 2140.
5. http://dspace.c3sl.ufpr.br/dspace/bitstream/handle/1884/18854/CLAUDINEY%20SOARES%20CORDEIRO%20-%20TESE%20DE%20DOUTORADO.pdf?sequence=1 accessed in August, 2011.
6. Markley, K. S.; *Fats and Oils: A Series of Monographs on the Chemistry and Technology of Fats, Oils and Related Products*; Interscience Publishers Inc.: New York, 1961.
7. Bruns, R. E.; Scarminio, I. S.; Neto, B. B.; *Planejamento e Otimização de Experimentos*; Unicamp: Campinas , São Paulo, Brasil, 1995.
8. AOCS - Official methods and recommended practices of the American Oil Chemists' Society, AOCS Press; Champaign, 2004.
9. Aranda, D. A. G.; Santos, R. T. P.; Tapanes, N. C. O.; Ramos, A. L. D.; Antunes, O. A. C.; *Catal. Lett.* **2008**, *122*, 20.
10. http://cod.ibt.lt/ Crystallographic Open Database, accessed in October, 2010.
11. http://www.ccdc.cam.ac.uk/products/mercury accessed in October, 2010.
12. Lacouture, F.; Peultier, J.; François, M.; Steinmetz, J.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 556.
13. Barman, S.; Vasudevan, S.; *J. Phys. Chem. B* **2006**, *110*, 22407.
14. Nakamoto, K.; *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.
15. Deacon, G. B.; Phillips, R. J.; *Coord. Chem. Rev*. **1980**, *33*, 227.
16. Alcock, N. W.; Tracy, V. M.; Waddington, T. C.; *J. Chem. Soc., Dalton Trans.* **1976**, 2243.
17. Akanni, M. S.; Okoh, E. K.; Burrows, H. D.; Ellis, H. A.; *Thermochim. Acta* **1992**, *208*, 1.
18. Sridharan, R.; Mathai, I. M.; *J. Sci. Ind. Res.* **1974**, *22*, 178.
19. Zatta, L.; Gardolinski, J. E. F. C.; Wypych, F.; *Appl. Clay Sci.* **2011**, *51*, 165.
20. Nascimento, J. R.; Angelica, R. S.; Costa, C. E. F.; Zamian, J. R.; Rocha Filho, G. N.; *Appl. Clay Sci*. **2011**, *51*, 267.
21. Cordeiro, C. S.; Silva, F. R.; Wypych, F.; Ramos, L. P.; *Quim. Nova* **2011**, *34*, 477.
22. Yan, S.; Salley, S. O.; Simon, K. Y. N.; *Appl. Catal., A* **2009**, *353*, 203.
23. Earle, M. J.; Plechkova, N. V.; Seddon, K. R.; *Pure Appl. Chem.* **2009**, *81*, 2045.
24. Domingos, J. B.; Dupont, J.; *Catal. Commun.* **2007**, *8*, 1383.
25. Himmler, S.; Hormann, S.; Van Hal, R.; Schulz, P. S.; Wasserscheid, P.; *Green Chem.* **2006**, *8*, 887.
26. Lisboa, F. S.; Arizaga, G. G. C.; Wypych, F.; *Top. Catal.* **2011**, *54*, 474.

Submitted: March 15, 2011

J. Braz. Chem. Soc., Vol. 23, No. 1, S1-S2, 2012.
Printed in Brazil - ©2012 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Layered Metal Laurates as Active Catalysts in the Methyl/Ethyl Esterification Reactions of Lauric Acid

Fábio da Silva Lisboa,[a] José Eduardo F. da Costa Gardolinski,[b]
Claudiney S. Cordeiro[a] and Fernando Wypych*,[a]

[a]Centro de Pesquisas em Química Aplicada (CEPESQ), Departamento de Química, CP 19081 and
[b]Laboratório de Análise de Minerais e Rochas (LAMIR), Departamento de Geologia, CP 19062,
Universidade Federal do Paraná, 81531-980 Curitiba-PR, Brazil

Table S1. Methyl esterification using NiL_2 as catalyst

Exp	Variable			Reaction conditions			Results	
	M.R.	CAT	T	M.R.	Catalyst / %	T / ºC	Ester / %	C – T (Ester p.p.)
19	–1	–1	–1	6:1	2	100	31	8
20	–1	–1	+1	6:1	2	140	81	14
21	–1	+1	–1	6:1	10	100	31	8
22	+1	–1	–1	14:1	2	100	26	14
23	+1	–1	+1	14:1	2	140	66	12
24	+1	+1	–1	14:1	10	100	35	23
25	–1	+1	+1	6:1	10	140	77	10
26	+1	+1	+1	14:1	10	140	68	14
27	0	0	0	10:1	6	120	48	8
28	0	0	0	10:1	6	120	47	8
29	0	0	0	10:1	6	120	48	9

Exp = experiment; M.R. = molar ratio (alcohol:acid); CAT = catalyst; T = temperature; C – T = Catalyzed conversion – thermal conversion. Standard deviation of the central point (Exp. 27, 28 and 29): ± 2.02. Reaction time: 2 h.

---

*e-mail: wypych@ufpr.br

Table S2. Methyl esterification using CuL_2 as catalyst

Variable				Reaction conditions			Results	
Exp	M.R.	CAT	T	M.R.	Catalyst / %	T / ºC	Ester / %	C – T (Ester p.p.)
30	−1	−1	−1	6:1	2	100	38	15
31	−1	−1	+1	6:1	2	140	78	11
32	−1	+1	−1	6:1	10	100	46	23
33	+1	−1	−1	14:1	2	100	34	22
34	+1	−1	+1	14:1	2	140	63	9
35	+1	+1	−1	14:1	10	100	27	15
36	−1	+1	+1	6:1	10	140	82	15
37	+1	+1	+1	14:1	10	140	61	7
38	0	0	0	10:1	6	120	50	10
39	0	0	0	10:1	6	120	50	11
40	0	0	0	10:1	6	120	50	11

Exp = experiment; M.R. = molar ratio (alcohol:acid); CAT = catalyst; T = temperature; C – T = Catalyzed conversion – thermal conversion. Standard deviation of the central point (Exp. 38, 39 and 40): ± 1.58. Rection time: 2 h.

Table S3. Methyl esterification using LaL_3 as catalyst

Exp	Variable			Reaction conditions			Results	
	M.R.	CAT	T	M.R.	Catalyst / %	T / ºC	Ester / %	C – T (Ester p.p.)
41	–1	–1	–1	6:1	2	100	29	6
42	–1	–1	+1	6:1	2	140	79	12
43	–1	+1	–1	6:1	10	100	32	9
44	+1	–1	–1	14:1	2	100	20	8
45	+1	–1	+1	14:1	2	140	62	8
46	+1	+1	–1	14:1	10	100	20	8
47	–1	+1	+1	6:1	10	140	90	23
48	+1	+1	+1	14:1	10	140	64	10
49	0	0	0	10:1	6	120	52	12
50	0	0	0	10:1	6	120	53	14
51	0	0	0	10:1	6	120	52	13

Exp = experiment; M.R. = molar ratio (alcohol:acid); CAT = catalyst; T = temperature; C – T = Catalyzed conversion – thermal conversion. Standard deviation of the central point (Exp. 49, 50 and 51): ± 0.79. Reaction time: 2 h.