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Article

Metal Glycerolates as Catalysts in the Transesterification of Refined Soybean Oil with Methanol under Reflux Conditions

Fábio da Silva Lisboa,[a] Fabiano Rosa da Silva,[b] Claudiney Soares Cordeiro,[b]
Luiz Pereira Ramos[b] and Fernando Wypych*,[a]

[a]Laboratório de Química de Materiais Avançados (LAQMA) and [b]Centro de Pesquisa em Química
Aplicada (CEPESQ), Departamento de Química, Universidade Federal do Paraná,
CP 19081, 81531-980 Curitiba-PR, Brazil

Glicerolatos de metais divalentes foram sintetizados e investigados na transesterificação metílica de óleo de soja refinado. Altas conversões foram obtidas para os monoglicerolatos de estrôncio e bário e diglicerolato de cálcio. O diglicerolato de cálcio se mostrou estável até o terceiro ciclo de reuso, se decompondo em uma mistura inativa de $CaCO_3$ e $Ca(OH)_2$.

Divalent metal glycerolates were synthesized and investigated in the methyl transesterification of refined soybean oil. Higher conversions to monoacylesters were obtained for strontium and barium monoglycerolates and calcium diglycerolate. Calcium diglycerolate was shown to be stable up to a third reuse cycle, decomposing to an inactive mixture of $CaCO_3$ and $Ca(OH)_2$.

Keywords: metal glycerolates, heterogeneous catalysts, transesterification, methyl esters, biodiesel

Introduction

Due to a decrease in the world crude oil reserves, allied to the increasing environmental awareness of our modern society, many researchers are taking the steps to develop new technologies for the sustainable use of the natural resources. One of these technologies considers the replacement of petrodiesel by biodiesel, which is a renewable resource that can be obtained through the transesterification of oils and fats or by esterification of free fatty acids (FFA).[1] The transesterification process for biodiesel production consists in the conversion of triesters (triacylglycerols) into a mixture of alkyl monoesters, which in most cases correspond to fatty acid methyl esters. In the reaction mentioned above, a triacylglycerol reacts with a monohydroxylated alcohol (process can be denominated also alcoholysis) in three steps, each step being ruled by a equilibrium constant and, at the end of the reaction, alkyl monoesters are produced along with glycerol as a co-product.

This reaction occurs by mixing the reactants in appropriate proportions at an adequate temperature, but the reaction kinetics is too low. To overcome this problem, supercritical conditions or chemical catalysts are necessary.[2,3] A great variety of catalysts can be commonly used in transesterification reactions, but the most frequently used for the process involving biodiesel synthesis are alkaline-like sodium or potassium alkoxides, their corresponding hydroxides (which are able to generate the corresponding alkoxides *in situ*) or strong acids like sulfuric, sulfonic or hydrochloric acid.[1] All the above mentioned catalysts are applied in a homogeneous medium.

The use of catalysts in homogeneous medium applied to transesterification reactions when compared to catalysts in heterogeneous medium have the advantage of requiring low temperature for a fast conversion, with high yields. However, the removal of the catalyst from reaction is difficult and requires purification steps that increase the final cost of the product. Other problems are related with the formation of emulsions with the acid raw materials, obtained by the saponification of the fatty acids and corrosion of equipments that may occur depending on the type and properties of the selected catalyst.[4]

For these and other reasons, most of the current research involving transesterification and esterification reactions aims the development of new heterogeneous processes. In spite of some disadvantages such as higher cost and lower

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*e-mail: wypych@ufpr.br

activity, many different compounds have been investigated, like transition metal and alkaline earth oxides, zeolites, raw and activated clay minerals and immobilized enzymes.[5,6]

In some of these investigations, after transesterification or esterification reactions, the initial catalysts were transformed *in situ* into other compounds. Cordeiro and co-workers[7] reported that zinc hydroxide nitrate was transformed into zinc laurate after the methyl esterification of lauric acid and this compound maintained the system catalytically active. Freshly synthesized zinc laurate was also very active and this catalyst could be recycled many times, without losing the original catalytic activity.[7]

Recently, Kouzu *et al.* described the *in situ* transformation of calcium oxide into calcium diglycerolate, an alkoxide derived from glycerol, during the catalytic transesterification of soybean oil with methanol.[8] The same authors proposed that calcium diglycerolate was subsequently transformed into another compound called calcium-X, which had a composition based on one calcium atom connected to one glycerolate and one methoxyl group.[9,10] Until now, this compound has not been isolated and the mechanism of this reaction still needs further investigation.

Calcium glycerolates can be found in the form of diglycerolates and monoglycerolates, among other compositions.[11] The glycerolates are formed by deprotonation of glycerol, which can react with metallic centers forming complexes with several metals like calcium, iron, nickel, cobalt, manganese, zinc, cadmium, molybdenum, etc.[12] Some of these glycerolates, such as zinc monoglycerolate, have been used in cosmetics and pharmaceuticals, as well as in the composition of lubricants and polymer stabilizers.[13]

Glycerolates like zinc and cobalt have very similar X-ray diffraction patterns,[14,15] and the zinc compound has a layered structure, obtained by stacking layers in the (h00) direction (basal direction). The layers are built by bridges formed trough the oxygen atoms of the glycerolate anion and the metal centers, as reported for zinc monoglycerolate.[15]

In the present work, the synthesis and characterization of zinc, calcium, strontium and barium glycerolates are demonstrated, along with an investigation of the catalytic activity of these promising compounds in the transesterification of refined soybean oil with methanol.

Experimental

Synthesis of calcium glycerolates

The syntheses of calcium monoglycerolate and diglycerolate were performed in two steps.[11] In the first step, 3.00 g (0.0535 mol) of commercial CaO without any treatment were mixed with 100 g (1.08 mol) of P. A. grade glycerol in an Erlenmeyer flask and mechanically stirred for 15 minutes. After that, the Erlenmeyer was inserted in a water bath with a temperature of 40 °C and the reaction proceeded for 24 hours. In the second step, the supernatant was transferred in two portions of 5 g to 10 mL polyethylene containers which were subsequently inserted into two steel reactors, separately. These reactors were heated in a drying stove for 7 days at 120 °C and 60 °C to produce, respectively, calcium monoglycerolate and diglycerolate.

An alternative synthetic route was carried out to obtain calcium diglycerolate as described by Kouzu *et al.*,[9] where 7.00 g (0.125 mol) of commercial CaO without any treatment were reacted with 11.5 g (0.125 mol) of glycerol P. A. dissolved in 50 mL (1.23 mol) of methanol. The reaction was performed at methanol reflux for 4 hours.

All solids obtained in these three syntheses were washed and centrifuged four times with a 1:1 isopropanol:glycerol mixture, followed by two washing/centrifugation steps with ethyl ether and drying at 60 °C for 1 hour.

Synthesis of zinc, strontium and barium monoglycerolates

Zinc, strontium and barium monoglycerolates were synthesized by mixing the respective high purity oxides with glycerol, in a molar ratio (metal oxide:glycerol) equal to 1:4, using the same 10 mL polyethylene containers and the steel reactor as described above for the second step of the calcium glycerolates syntheses. The reactors were placed in a drying stove at 120 °C for 7 days. The same centrifugation/washing procedures to wash the solids obtained were used as described for the syntheses of calcium glycerolates.

Catalytic activity experiments for methyl transesterification of refined soybean oil

The catalytic activity and the reuse experiments were performed under methanol reflux conditions with magnetic stirring. Based on previous optimization experiments, the reactants, alcohol and refined soybean oil were mixed in a 50:1 molar ratio, with addition of 2 wt.% of the catalysts in relation to the used mass of refined soybean oil and the reaction time was fixed in 2 hours. The reactions were kept under magnetic stirring at around 500 rpm to avoid mass transfer limitations for biphasic systems.[16]

For comparison purposes with possible formed decomposition compounds, not only the glycerolates were investigated, but also other compounds like chlorides, carbonates and hydroxides. In all cases the solids after reaction were washed with hexane for three times and centrifuged at 4000 rpm. All of these reactions were performed in duplicate and average values were reported.

The qualitative and quantitative methyl ester determinations were performed by high performance size exclusion chromatography (HPSEC) using a Waters® 1515 high performance liquid chromatography (HPLC) system provided with two Ultrastyragel 100 and Progel G1000-HXL columns positioned in series, in which the limits of exclusion corresponded to 10^3 a.m.u., respectively. The analyses were performed in duplicate at 40 °C with an injection volume of 10 µL using UV/HPLC tetrahydrofuran (Vetec®) as mobile phase at a flow rate of 0.8 mL min^{-1}. The detection system was based on refraction index (Waters® 2414 RI detector) and the complete elution was completed after 26 minutes. The quantitative analyses were performed by external calibration, where the reference standards were triolein (1,2,3-tri-[(*cis*)-9-octadecenoil]-glycerol), diolein (1,3-di-[(*cis*)-9-octadecenoil]-glycerol), mono-olein (1-mono-[(*cis*)-9-octadecenoil]-*rac*-glycerol) and methyl oleate, all purchased from Sigma-Aldrich®. These standards were used as models for the analyses of triacylglycerol, diacylglycerol, monoacylglycerol and methyl esters, respectively.

Instrumental characterization

X-ray powder diffraction (XRPD) patterns were recorded with a Shimadzu XDR-6000 instrument using CuK$_\alpha$ radiation (λ = 1.5418 Å), dwell time of 2° min^{-1}, current of 30 mA and voltage of 40 kV. The samples were placed and oriented by gently hand pressing on 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 (Vetec). The pellets were pressed at 8 t for 5 minutes prior to analysis, with measurements being made in the transmission mode with accumulation of 32 scans and a nominal resolution of 2 cm^{-1}.

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

Scanning electron microscopy (SEM) images were obtained after depositing the samples on copper stripes. The samples were sputtered with gold using an SCD030 Balzers Union FL 9496 equipment and the images obtained with a JEOL JSM-6360LV microscope, using voltages of 15 or 20 kV.

Results and Discussion

From this point onwards we will describe the synthesized compounds by their acronyms: calcium monoglycerolate (CaMGly), calcium diglycerolate (CaDGly-1 or CaDGly-2), strontium monoglycerolate (SrMGly), barium monoglycerolate (BaMGly) and zinc monoglycerolate (ZnMGly).

The XRPD profiles of all synthesized monoglycerolates presented a typical intense basal diffraction peak indexed as (h00) in the region around 10° in 2θ (see Supplementary Information Figure S1). The basal distances obtained for the first basal peak of each monoglycerolate compound were: calcium, 8.57 Å; strontium, 8.70 Å; barium, 8.07 Å; and zinc, 8.10 Å. These basal distances are characteristic of structures having the glycerolate anion coordinated to metallic center in the structure.[12,14,17,18] In addition, the synthetic monoglycerolates were obtained in high purity, with the exception of the one containing barium, which is slightly contaminated with barium carbonate.

Besides calcium monoglycerolate, calcium diglycerolate was also obtained, but in two different crystal orientations: the first one, called CaDGly-1, shows a very intense peak along (111) direction (Figure 1a), and the second one, called CaDGly-2, has the most intense peak along (200) direction (Figure 1b).

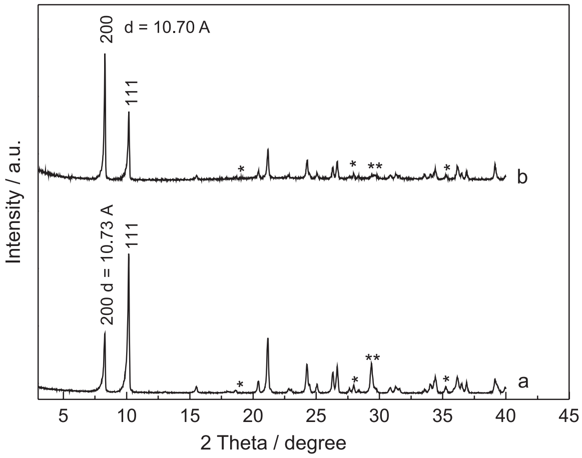

Figure 1. X-ray powder diffraction patterns obtained for both phases of calcium diglycerolate: (a) CaDGly-1 and (b) CaDGly-2.

León-Reina *et al.* predicted the crystal structure for calcium diglycerolate and the XRPD patterns obtained in our work are very similar to that described by these authors,[19] with the difference only in the relative intensity between peaks 200 and 111 for the solid CaDGly-2.

This fact can be explained by the two different routes used for the calcium diglycerolate synthesis. The first one, that originated the phase called CaDGly-2, was conducted in a closed system (autoclave), with greater reaction time than the other one (7 days) and glycerol acting as both the reactant and the solvent, while the second route was made in methanol reflux with vigorous magnetic stirring for only few hours (4 hours), thereby, the temperature, reaction time for crystal growth and solvent effects can possibly have influenced crystal formation with different preferred orientation.[20-22]

The basal distances for the two phases of calcium glycerolate were around 10.7 Å, in accordance with the phase described by Fujii and Kondo.[11] The XRPD patterns also showed a small contamination of calcium hydroxide and calcium carbonate, which are indicated by one and two asterisks, respectively, in Figure 1.

Fourier transform infrared (FTIR) spectroscopy has shown that all synthesized compounds presented vibrational modes that are expected for organic species bonded to metals centers and are very similar together (see Figure S2 and Table 1).

Table 1. Vibrational bands (cm^{-1}) observed by FTIR and their corresponding attributions

	νOH	νCH/CH$_2$	νCO	νCC	νMOC	νMO
CaMGly	3415	2972-2785	1141	1066	875	445
SrMGly	3341	2969-2704	1140	1065	857	422
BaMGly	3358	2937-2877	1109	1051	856	497
ZnMGly	3413	2935-2844	1125	1064	877	418
CaDGly-1	3260	2934-2836	1130	1074	872	420
CaDGly-2	3397	3003-2851	1106	1050	873	406

M: metal.

The stretching of O–H bonds can be seen in the region of 3260-3415 cm^{-1} and the vibrational modes for C–H and H–C–H appear in region of 2700 and 3000 cm^{-1}. Other characteristic bands were observed at 1100-1140 cm^{-1} (C–O), at 1050-1060 cm^{-1} (C–C), 850-875 cm^{-1} (M–O–C) and 400-450 cm^{-1} (M–O, where M = metal). The FTIR spectra of CaDGly-1 and CaDGly-2 also revealed an intense and broad band at approximately 1415 cm^{-1}, which can be attributed to the vibrational mode for CO_3^{2-} from calcium carbonate contamination as already attested by XRPD (Figure S2).

SEM images of calcium diglycerolate obtained under reflux conditions (CaDGly-1) and in the Parr reactor (CaDGly-2) can be seen in Figures 2a and 2b, respectively. It can be clearly seen that the CaDGly-1 phase exposes mainly the 111 planes while the CaDGly-2 phase exposes the basal planes (h00), as already attested by XRPD (Figure 1). This orientation explains why the compound with the same formulation has different catalytic properties.

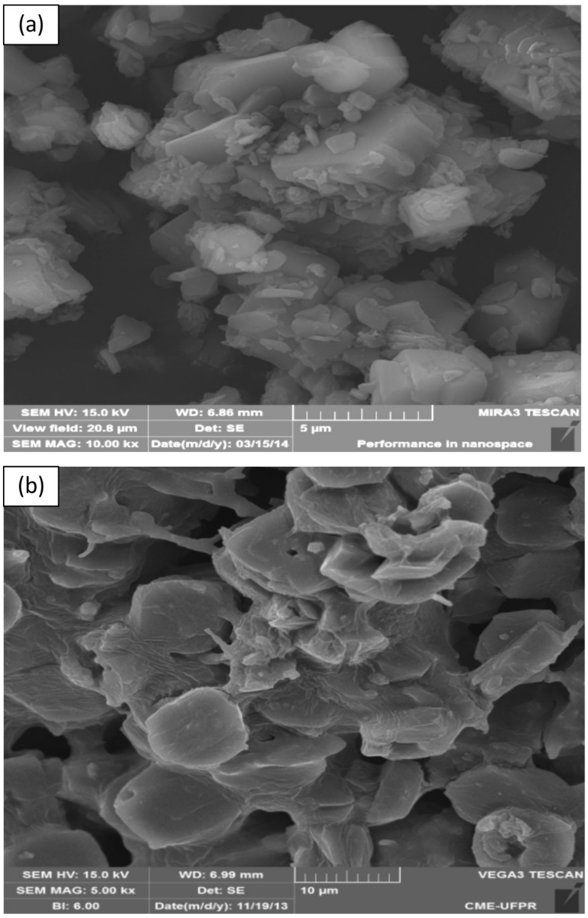

Figure 2. SEM images of calcium diglycerolate in the (a) CaDGly-1 and (b) CaDGly-2 phases.

The thermal analysis curves (simultaneous TGA and DTA) of the synthetic materials can be seen in Figure 3. In general, the TGA curves presented mass loss events until 100 °C attributed to the removal of physisorbed water present in the solids. Such events were observed simultaneously with an endothermic event in the DTA curves of all samples except for calcium monoglycerolate (CaMGly) (Figure 3c), which occurs as an anhydrous phase.

Except for zinc monoglycerolate (ZnMGly), an initial decomposition to carbonate can be seen in the region of 150-200 °C for the CaDGly-1, CaDGly-2, SrMGly, BaMGly patterns and around 300 °C for CaMGly (Figures 3a-e).

This does not occur to ZnMGly because its decomposition forms ZnO in a single step. The final process of mass loss, that forms the respective metal oxides, are around 700 °C for calcium diglycerolates and 750 °C for calcium monoglycerolate, 400 °C for the zinc compound, 950 °C for strontium and could not be seen for the barium compound, because the formation of barium oxide initiates at around 850 °C, but is very slow and completed at temperatures higher than 1000 °C.[23,24]

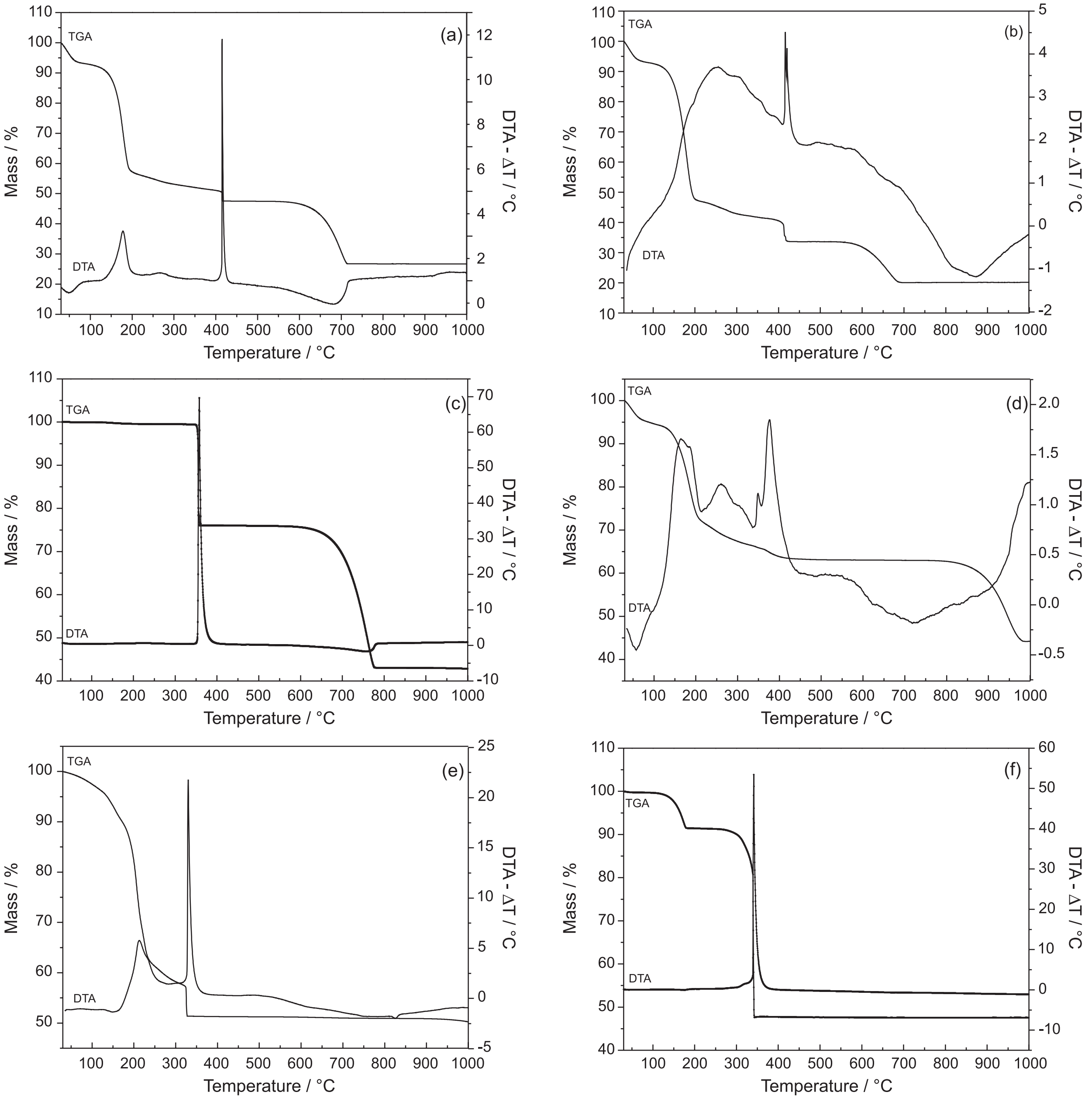

Figure 3. Thermal analysis curves (TGA/DTA) obtained for: (a) CaDGly-1; (b) CaDGly-2; (c) CaMGly; (d) SrMGly; (e) BaMGly and (f) ZnMGly.

The oxidation of organic matter occurred at around 350 °C for all monoglycerolates and for the diglycerolates CaDGly-1 and CaDGly-2, this thermal event was shifted to around 420 °C. All of these mass losses occurred concomitantly with intense exothermic peaks in the DTA curves.

Anhydrous CaMGly (Figure 3c) and dehydrated ZnMGly (Figure 3f) seem to be the more thermally stable compounds, because the TGA curves show well-defined decomposition processes and stability for these solids until around 300 °C. This could make these compounds suitable for tests as catalysts at higher temperatures than under reflux conditions, as recently reported by our research group.[25]

From TGA/DTA measurements of water content, the empirical formula was proposed, and both experimental and theoretical metal oxide contents of the synthetic glycerolates are shown in Table 2.

The proposed formula for the investigated metal glycerolates are consistent with the obtaining of metal:ligand ratio of 1:1 for monoglycerolates and 1:2 for diglycerolates with a slightly higher content of ligand in CaDGly-2.

Methyl transesterification of refined soybean oil

For these experiments a higher molar ration between alcohol and oil, in relation to that commonly seen in many

Table 2. Proposed formula for metal glycerolates based on TGA/DTA analysis

	Moisture / %	Proposed formula	Metal oxides (experimental)	Metal oxides (theoretical[a])
CaDGly-1	6.71	$Ca[C_3H_7O_3]_2(H_2O)_{0.76}$	26.69	25.23
CaDGly-2	6.01	$Ca[C_3H_7O_3]_{2.35}(H_2O)_{0.48}$	20.16	19.55
CaMGly	0	$Ca[C_3H_6O_3]$	42.92	43.08
SrMGly	27.10	$Sr[C_3H_6O_3](H_2O)_{3.15}$	44.18	44.20
BaMGly[b]	25.57	$Ba[C_3H_6O_3](H_2O)_{4.32}$	50.24	50.24
ZnMGly	8.64	$Zn[C_3H_6O_3](H_2O)_{0.48}$	47.66	49.35

[a]Based on the proposed formulas; [b]slightly contaminated with $BaCO_3$ and $Ba(OH)_2$. MGly = monoglycerolate, DGly = diglycerolate.

works with acid or base-catalyzed process, 6:1 to 30:1, was used,[26] because in previous tests the molar ratio of 50:1 (alcohol:oil) presented good ester conversions. The results for the methyl transesterification of soybean oil, obtained by HPSEC analysis, can be seen in Table 3. Pure soybean oil was also analyzed and the analysis showed that the oil contained 98.27% of triacylglycerols (TAG), being free of monoacylglycerols, diacylglycerols or methyl esters (Exp. 1). An analysis of the oil thermal conversion used as a control reaction (carried out in the absence of any catalyst) also showed similar results to Exp. 1, evidencing that under reflux conditions, there is no noticeable conversion of soybean oil into methyl esters (Exp. 2).

Calcium, strontium, barium and zinc monoglycerolates converted 62.79, 99.20, 99.00 and 0.79% of soybean oil tryacylglycerols into methylesters already in the first reaction cycle (Experiments 3, 6, 7 and 8, respectively). The two phases of calcium diglycerolates presented very good conversions: 98.63% for CaDGly-1 (Exp. 4) and 99.90% for CaDGly-2 (Exp. 5).

These behaviors can be partly explained in terms of solid basicity, which was verified by the qualitative tests using 2 drops of phenolphthalein and tropaeolin 0 at 1% in alcoholic solutions in 10 mg of the solids. For all alkaline earth glycerolates, color change to respective basic indicator form and pHs between 8 and 11 were observed, while for zinc monoglycerolate, a pH lower than 8 was obtained and no color alteration was verified. Despite ZnMGly, due to the lower basicity, not presenting any activity under reflux conditions, comparing with the other investigated glycerolates, it could be very active at higher temperatures in a closed system, as recently reported.[25]

Analyzing the solids recovered after each reaction by XRPD it is possible to explain another observed tendency that has influence in the activity of these solids. Figure S3 shows the X-ray powder diffraction patterns of each compound after the methyl transesterification of soybean oil.

It can be clearly seem that only for compounds CaMGly, CaDGly-1 and ZnMGly the structure is preserved after the reactions (Figures S3a, b and e), but for the first and the second ones, calcium carbonate was segregated. The samples CaDGly-2 (phase exposing the 200 plane) and SrMGly were completely decomposed to a mixture of carbonate or hydroxide of the respective metals. The solid BaMGly was dissolved in the reaction medium, and consequently was not recovered after the first reaction.

The stability of these solids in the reaction medium is connected with the high basicity of each one, temperature and moisture present in the solids. The alkoxides can

Table 3. Results for methyl transesterification of soybean oil using metal glycerolates as catalysts

Experiment		Triacylglycerol / %	Diacylglycerol / %	Monoacylglycerol / %	Monoester / %
1	Soybean oil	98.27 ± 1.20	–	–	–
2	Control	97.99 ± 0.62	–	–	0.87 ± 0.03
3	CaMGly	14.45 ± 1.30	10.42 ± 0.12	9.08 ± 0.34	62.79 ± 2.17
4	CaDGly-1	–	–	1.37 ± 0.01	98.63 ± 0.01
5	CaDGly-2	–	–	–	99.90 ± 0.10
6	SrMGly	–	–	0.80 ± 0.20	99.20 ± 0.20
7	BaMGly	–	–	1.00 ± 0.10	99.00 ± 0.10
8	ZnMGly	98.47 ± 0.26	–	–	0.79 ± 0.03

All of these reactions were conducted in methanol reflux and performed in duplicate. The average values were reported.

hydrolyze easily at high temperatures, forming the corresponding metal hydroxides and/or salts.[12]

For both CaDGly-1 and CaDGly-2 the different stability could be explained in terms of preferred orientation for each crystal structure. While CaDGly-1 has the crystals exposing more at (111) plane, CaDGly-2 has the main plane exposed (200) and this surface must be more energetic than the others, as will be discussed later, in the reuse study for CaDGly-1. Léon-Reina *et al.* also proposed that the basal (h00) surface can be responsible for the high activity of calcium diglycerolate,[19] but the crystals obtained exposing these planes are less stable than the crystals exposing the (111) planes, as seen in Figure S4.

Based on the conversion results for methyl transesterification of soybean oil and structure stability, reuse tests were performed to see which ones maintained the activity after the first reaction cycle. Also, other compounds of alkaline earth metals and glycerolates, like salts (soluble in methanol) and hydroxides, were tested to evaluate if the probable products of decomposition had any influence in the observed ester conversions (Table 4).

During the reuse tests for all glycerolates that were recovered after and presented activity at a first reaction, the decay in conversion rate for monoester production was found out and the results were compared with those in Table 3 (Table 4). For calcium and strontium monoglycerolates and calcium diglycerolate (phase CaDGly-2) were observed conversions of 29.57% (Exp. 9), 45.0% (Exp. 12) and 0.0% (Exp. 11), respectively, while the calcium diglycerolate (phase CaDGly-1) maintained a value very close to the first reaction, 98.66% (Exp. 10).

The decreases in monoester conversion observed for the reuse tests (Table 4) could be explained by the total decomposition or segregation of some inactive phase in the initial stages of decomposition, as seen in Figure S4.

For calcium monoglycerolate, a calcium carbonate phase was segregated and for calcium diglycerolate (phase CaDGly-2), it was completely decomposed after the first reaction cycle. These facts probably affected the activity of the solids, because as seen in Table 4, Exp. 15, at reflux condition, calcium carbonate was inactive as well as the other decomposition products of CaDGly-2 (calcium oxide (Exp. 18) and hydroxide (Exp. 16)).

The commercial and untreated CaO was inactive in the transesterification of soybean oil, which becomes active after a thermal treatment to remove surface calcium hydroxides and carbonate.[27] Hence, it seems that the batch used in this study was inactivated by a surface reaction with moisture and carbon dioxide and these could only be eliminated by activation at high temperatures (calcining).

For strontium monoglycerolate (SrMGly), the observed drop in catalytic activity can also be explained by the XRPD pattern of the solids recovered after the first reaction cycle together with results shown in Table 4. Figure S3 shows that the compound structure was not preserved and a mixture of SrO and $Sr(OH)_2$ was segregated. Therefore, in spite of the $Sr(OH)_2$ inactivity (see Table 4, Exp. 22) the presence of SrO retained part of the catalytic activity of the reaction system because this species was shown to be active in the transesterification of soybean oil as well (Exp. 19, on Table 4).[28] An experiment was performed with $SrCO_3$, an expected decomposition product of SrMGly, but no measurable activity was observed (Exp. 20).

Table 4. Results of the reuse tests for methyl transesterification of soybean oil using metal glycerolates and the respective decomposition products

Experiment		Triacylglycerol / %	Diacylglycerol / %	Monoacylglycerol / %	Monoester / %
9	R-CaMGly	47.07 ± 0.10	16.26 ± 0.10	7.08 ± 0.06	29.57 ± 0.07
10	R-CaDGly-1	–	–	1.34 ± 0.15	98.66 ± 0.15
11	R-CaDGly-2	99.80 ± 0.10	–	–	–
12	R-SrMGly	30.80 ± 0.50	17.3 ± 0.10	6.80 ± 0.10	45.00 ± 0.10
13	R-BaMGly	–	–	–	–
14	R-ZnMGly	–	–	–	–
15	$CaCO_3$	98.58 ± 0.01	–	–	0.95 ± 0.00
16	$Ca(OH)_2$	98.60 ± 0.01	–	–	0.91 ± 0.00
17	$CaCl_2$	98.71 ± 0.03	–	–	0.91 ± 0.03
18	CaO[a]	98.58 ± 0.03	–	–	0.80 ± 0.03
19	SrO	–	–	0.90 ± 0.10	99.10 ± 0.10
20	$SrCO_3$	98.40 ± 0.10	–	–	0.80 ± 0.10
21	$SrCl_2$	98.30 ± 0.20	–	–	–
22	$Sr(OH)_2$	97.36 ± 0.12	–	–	0.13 ± 0.08

[a] Non-activated by heat treatment.

Table 5. Results of the reuse tests for CaDGly-1 in the transesterification of soybean oil

Experiment		Triacylglycerol / %	Diacylglycerol / %	Monoacylglycerol / %	Monoester / %
23	CaDGly-1	–	–	0.72 ± 0.40	99.28 ± 0.40
23a	Reuse-1	–	–	1.34 ± 0.15	98.66 ± 0.15
23b	Reuse-2	1.05 ± 0.27	–	2.52 ± 0.22	96.43 ± 0.49
23c	Reuse-3	9.30 ± 0.10	7.18 ± 0.65	–	82.8 ± 0.60
23d	Reuse-4	99.7 ± 0.30	–	–	–

Reuse tests for zinc and barium monoglycerolates were not performed because the first one was not active and the second one was dissolved in the first reaction cycle.

Whereby calcium diglycerolate, CaDGly-1 showed good activity and stability after the first reaction, one replicate of the experiment carried out at room temperature (around 21 °C) was performed in duplicate. These tests led to conversion close to 94% in a single reaction stage. This is a very promising result if compared to the traditional catalysts used in homogeneous medium, suc as sodium methoxide, where similar conversions were achieved at 60 °C for reactions performed for 1 hour.[29] Another advantage of CaDGly-1 is the easy separation of the catalyst from the reaction medium, which is performed by simple filtration or centrifugation.

Reuse tests for CaDGly-1

As the phase CaDGly-1 showed the best performance in the methyl transesterification of soybean oil, in conditions of the experiments 4 and 10 (Tables 3 and 4) and its structure remained practically unchanged (see Figure S3), five consecutive cycles of use were performed under the same conditions used in the first cycle (Table 5). However, after each cycle of reaction, some small adjustments had to be made in order to keep the reaction conditions unchanged, because it was difficult to recover the entire quantity of the catalyst after each reuse, mainly due to physical mass losses. All reused solids were also investigated by XRPD after each reaction cycle (Figure S4).

The results obtained for the first use, first reuse and second reuse cycles (Exp. 23, 23a and 23b, respectively) were higher than 95%. However, in the third cycle of reuse (Exp. 23c) the conversion was reduced to 82.8% and became undetectable afterwards (Exp. 23d). This behavior can be explained by the XRPD patterns of the recovered solids, registered after each cycle of use (Figure S4).

It can be clearly seen that, after the first reaction (Exp. 23, Figure S4a), the diglycerolate CaDGly-1 remains stable without great segregation of calcium carbonate. After the first reuse (Exp. 23a, Figure S4b) the compound presents a decrease in intensity of the (200) diffraction peak, but the diglycerolate is still present, together with the decomposition products, $Ca(OH)_2$ and $CaCO_3$.

After the second reuse (Exp. 23b) the (200) peak from diglycerolate CaDGly-1 vanishes completely (Figure S4c) and an increased amount of nanostructured calcium hydroxide and carbonate was verified. For the third reuse (Exp. 23d) we still have the same solid phase obtained after de second reuse (Figure S4d), but the segregated phases of calcium carbonate and hydroxide become the main components of the mixture, which reduce the ester conversion from 95 to 82.8%.

Finally, the fourth reuse cycle (Exp. 23d, Figure S4e) shows only the decomposition products and the activity drops to almost zero due to the inactivity of these compounds (Table 4, Exp. 15 and 16).

The systematic decrease in intensity of the (200) peak can be attributed to the preferred attack of the crystal of CaDGly-1, which shows that this plane, although more active as discussed by Léon-Reina *et al.*,[19] is also more unstable.

The observed formation of calcium carbonate and calcium hydroxide was expected since all reactions were carried out under air not free from CO_2 and moisture. As CO_2 has an acid behavior and can react with calcium diglycerolate and the moisture present can hydrolyze the alkoxide, both processes lead to the destruction of the catalyst. Kouzu *et al.* showed an unaltered structure for calcium diglycerolate after transesterification of soybean oil under nitrogen for three cycles of use.[8] As our aim is to develop potential catalysts for industrial application and air free of carbon dioxide or moisture is difficult to be imagined in an industrial plant, we did not investigate the stability of our compounds under dry nitrogen flow. In addition, metal methoxides or the compound calcium-X were never observed nor isolated in any of the investigated chemical synthesis/reactions.[9,10]

Conclusions

Strontium, zinc and barium were synthesized as monoglycerolates, while calcium was obtained as monoglycerolate and two different forms of diglycerolate, CaDGly-1 and CaDGly-2, the first one exposing the basal plane (200) and the other one exposing the (111) plane.

Except for zinc monoglycerolate that did not show any activity, and calcium monoglycerolate that presented a partial conversion of 62.79%, all compounds demonstrated to be active for the methyl transesterification of soybean, with almost total conversions. After the first reuse cycle, only calcium diglycerolate in the form CaDGly-1 showed a good catalytic activity and structure maintenance. This compound also presented good value for activity until a third reuse cycle (82.8%) and after that, being completely decomposed into a mixture of inactive calcium carbonate and hydroxide.

The decomposition after a third reuse cycle is not a great problem because the compounds formed could be calcined to reform the calcium oxide (CaO) and the glycerol synthesized as co-product in methyl transesterification of soybean oil can be used to react with calcium oxide to obtain a new batch of calcium diglycerolate.

Another aspect that should aggregate value to the obtained methylesters is the high purity of the obtained glycerol, which in the present work, without any purification step, is in the range of 90-93%.

Works are under way to try to stabilize and immobilize the active phases and optimize the work for a potential industrial application.

Supplementary Information

Supplementary data (Figure S1, XRPD patterns; Figure S2, FTIR spectra; Figure S3, XRPD patterns; Figure S4, XRPD patterns) are available free of charge at http://jbcs.sbq.org.br as PDF file.

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References

1. Ma, F.; Hanna, M. A.; *Bioresour. Technol.* **1999**, *70*, 1.
2. Dasari, M. A.; Goff, M. J.; Suppes, G. J.; *J. Am. Oil Chem. Soc.* **2003**, *80*, 189.
3. Kusdiana, D.; Saka, S.; *Fuel* **2001**, *80*, 693.
4. Zhang, J. H.; Chen, S. X.; Yang, R.; Yan, Y. Y.; *Fuel* **2010**, *89*, 2939.
5. Helwani, Z.; Othman, M. R.; Aziz, N.; Kim, J.; Fernando, W. J. N.; *Appl. Catal., A* **2009**, *363*, 1.
6. Suppes, G. J.; Dasari, M. A.; Doskocil, E. J.; Mankidy, P. J.; Goff, M. J.; *Appl. Catal., A* **2004**, *257*, 213.
7. Cordeiro, C. S.; Arizaga, G. G. C.; Ramos, L. P.; Wypych, F.; *Catal. Commun.* **2008**, *9*, 2140.
8. Kouzu, M.; Kasuno, T.; Tajika, M.; Yamanaka, S.; Hidaka, J.; *Appl. Catal., A* **2008**, *334*, 357.
9. Kouzu, M.; Hidaka, J.; Wakabayashi, K.; Tsunomori, M.; *Appl. Catal., A* **2010**, *390*, 11.
10. Kouzu, M.; Hidaka, J.; *Fuel* **2012**, *93*, 1.
11. Fujii, K.; Kondo, W.; *Z. Anorg. Allg. Chem.* **1968**, *359*, 296.
12. Radoslov, E. W.; Raupach, M.; Slade, P. G.; Taylor, R. M.; *Aust. J. Chem.* **1970**, *23*, 1963.
13. Moleski, R.; Leontidis, E.; Krumeich, F.; *J. Colloid Interface Sci.* **2006**, *302*, 246.
14. Taylor, R. M.; Slade, P. G.; Aldous, G. L.; Wilding, I. R.; Siddiqui, O.; Whitehouse, M. W.; *Aust. J. Chem.* **1992**, *45*, 1179.
15. Hambley, T. W.; Snow, M. R.; *Aust. J. Chem.* **1983**, *36*, 1249.
16. Poljansek, I.; Likozar, B. In *Mass Transfer in Multiphase Systems and its Applications*; El Amin, M., ed.; InTech: Rijeka, Croatia, 2011, ch. 19.
17. Bruylants, P.; Munaut, A.; Poncelet, G.; Ladriere, J.; Meyers, J.; Fripiat, J.; *J. Inorg. Nucl. Chem.* **1980**, *42*, 1603.
18. Fuls, P. F.; Rodrique, L.; Fripiat, J.; *Clays Clay Miner.* **1970**, *18*, 53.
19. León-Reina, L.; Cabeza, A.; Rius, J.; Torres, P. M.; Alba-Rubio, A. C.; Granados, M. L.; *J. Catal.* **2013**, *300*, 30.
20. Wang, M.; Kim, E. J.; Hahn, S. H.; Park, C.; Koo, K. K.; *Cryst. Growth Des.* **2008**, *8*, 501.
21. Li, J. Z.; Li, J. G.; *Mater. Lett.* **2012**, *68*, 40.
22. Kong, L.; Yang, J. X.; Cheng, L. J.; Wang, P.; Zhou, H. P.; Wu, J. Y.; Tian, Y. P.; Jin, B. K.; Tao, X. T.; *J. Mol. Struct.* **2014**, *1059*, 144.
23. Berbinni, V.; Marini, A.; Welham, N. J.; Galinetto, P.; Mozzati, M. C.; *J. Eur. Ceram. Soc.* **2003**, *23*, 179.
24. Lataste, E.; Demourgues, A.; Salmi, J.; Naporea, C.; Gaudon, M.; *Dyes Pigm.* **2011**, *91*, 396.
25. Lisboa, F. S.; Silva, F. R.; Ramos, L. P.; Wypych, F.; *Catal. Lett.* **2013**, *143*, 1235.
26. Demirbas, A.; *Energy Convers. Manage.* **2007**, *48*, 937.
27. Granados, M. L.; Alonso, D. M.; Alba-Rubio, A. C.; Mariscal, R.; Ojeda, M.; Brettes, P.; *Energy Fuels* **2009**, *23*, 2259.
28. Kouzu, M.; Kasuno, T.; Tajika, M.; Sugimoto, Y.; Yamanaka, S.; Hidaka, J.; *Fuel* **2008**, *87*, 2798.
29. Keera, S. T.; El Sabagh, S. M.; Taman, A. R.; *Fuel* **2011**, *90*, 42.

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