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Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol

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ABSTRACT

Recently, we have found that forming a slurry by mixing Ca oxide with biodiesel (approximately 10–15 g of biodiesel per gram of Ca oxide) results both in protection against poisoning by atmospheric CO_2 and H_2O and, when the slurry is used as a catalyst, in a remarkable increase in reaction rate [M. Lopez Granados et al., Energy Fuel 23 (2009) 2259–2263]. By conducting catalytic tests and DRIFT studies with either sunflower oil or model compounds revealed that the presence of minute amounts of monoglycerides (MG) and/or diglycerides (DG) in the biodiesel were the reason for the reaction rate promotion. To observe this effect, the Ca oxide–biodiesel slurry must be pretreated with methanol for a few minutes before proceeding with the transesterification reaction. The DRIFT studies demonstrated that the transesterification of MG and DG during the pretreatment with methanol results in the releasing of glycerol, which then reacts with the catalyst surface, resulting in the formation of very active surface Ca glyceroxide species. In view of this information, it was also demonstrated that the two-step procedure of mixing biodiesel with the catalyst and then carrying out methanol pretreatment could be substituted with pretreatment of the Ca oxide with methanol containing a few milligrams of glycerol per gram of Ca oxide before proceeding with the reaction. In this latter case, the slurry was not required. The DRIFT studies demonstrated that this simpler pretreatment also resulted in the formation of very active surface Ca glyceroxide species.

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1. Introduction

Biodiesel is industrially produced by transesterification between triglycerides and methanol. Homogeneous catalysts dissolved in the methanol, such as acids like H_2SO_4 or bases like KOH or NaOH, are currently used in industrial plants. The utilisation of these catalysts comes with drawbacks associated with their corrosiveness, the rinsing steps required to eliminate them from the biodiesel, the purification steps of the glycerol, and the difficulties in recycling the catalysts. Currently, many research groups are making important strides in the development of solid catalysts that can be used in place of homogeneous catalysts [1–4]. The utilisation of heterogeneous catalysts presents many advantages over homogeneous catalysts. For example, they result in lower investment costs and require less downstream process equipment, reducing the final price of the produced biodiesel [5]. Additionally, a solid catalyst can be easily separated from the reaction mixture by physical methods, such as filtration or centrifugation, and then can be reused, whereas a homogeneous catalyst cannot be reused. Furthermore, the concentration of metals or other elements arising from the catalyst in the reaction products, biodiesel or glycerol can be notably reduced when solid catalysts are used. This simplifies the further purification of the biodiesel and reduces the water consumption required for the purification of the products.

However, the use of solid catalysts also comes with some drawbacks that must be confronted. Besides mass transfer problems associated with the presence of three phases in the reaction mixture and the porous character of the solids, the main barrier for a commercial application is that reaction rates of the surface active sites are significantly slower than those of homogeneous species. In principle, basic solid catalysts are more active than acidic solid catalysts [2,3], so they are the preferred option when the refined oil has a low water and free fatty acid content. Among the variety of basic solid catalysts that have been tested, activated CaO is one of the most useful [4,6–12]. This catalyst, although affected by some leaching from dissolution of its components, can be reused for several runs without significant loss of activity provided that enough catalyst is loaded in the reactor (a wt% larger than 1% in relation to the oil) [13–16]. However, the catalytic rate of this catalyst is not fast enough when compared with homogeneous catalysts, so its activity must be increased.

Recently, we have found that mixing activated CaO with biodiesel in a proportion of a few grams of biodiesel per gram of solid catalyst results in a notable protection of the activated CaO against

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poisoning by atmospheric CO_2 and H_2O that may occur during handling of the solid. We also observed a remarkable increase in the reaction rate when this biodiesel–CaO slurry was used as the catalyst. By using this procedure, the reaction rate became much closer to that of the homogeneous catalysts [17]. This promotion did not occur if the biodiesel was directly incorporated into the reaction mixture or when a slurry was formed between CaO and oil or methanol.

No definitive explanation for the biodiesel promotion effect has yet been given. The possibility of the formation of water-in-oil or oil-in-water microemulsions because of the surfactant properties of biodiesel that can improve the mass transfer between the two immiscible phases was discarded [17]. For that scenario, it was hypothesised that the biodiesel formed a layer covering the surface of the solid that might facilitate the access of either triglycerides or methanol molecules to the surface group because both methanol and oil are soluble in biodiesel. This access, however, would be impeded if methanol or triglycerides were initially covering the surface of the catalyst because they are insoluble in each other.

In this work, we experimentally demonstrated that the latter hypothesis was wrong. We have focused on another hypothesis instead: the effect of monoglycerides (MG), diglycerides (DG) and free glycerol. These molecules can be present in minute amounts in the biodiesel used for the slurry. Their presence is limited by stringent legislation, for instance European EN 14015 norm establishes that the MG, DG and free glycerol present in the biodiesel must be smaller than 0.8, 0.2 and 0.02 wt%, respectively (similar regulations have been set in other countries). However, it will be shown that MG, DG and glycerol present in small concentrations in the biodiesel used for the slurry are responsible for the increase in the reaction rate.

To verify such a hypothesis, we used pure methyl myristate as pure biodiesel for forming the slurry with activated CaO. Different amounts of pure MG, DG or glycerol were incorporated in the methyl myristate or in the methanol. The promotion effect was verified by using this slurry in the transesterification of sunflower oil with methanol. For gaining information of the effect of MG, DG and glycerol on the surface sites of the solid, IR studies of the formed slurry were conducted.

2. Experimental

2.1. Materials

The Ca oxide catalyst (0.1 g) was obtained by heating 0.1785 mg of $CaCO_3$ (Sigma–Aldrich, >99.95%) in a U-shaped quartz reactor at 1073 K (ramp at 10 K min^{-1}) for 1 h under a 40 mL min^{-1} (STP) flow of 20% O_2 in Ar. The activated solid was then cooled to room temperature under the same flow. The biodiesel for the slurry was obtained by methanolysis of sunflower oil, further details of which are given elsewhere [17]. The methanol was supplied by Sharlau (Reag. Ph. Eur., >99.8% GC, H_2O < 0.005%). As pure fatty acid methyl ester (FAME), methyl tetradecanoate (methyl C14 ester), also known as methyl myristate, was used (Fluka, GC $\geqslant$ 99.0 wt%). For the pure monoglyceride (MG) and pure diglyceride (DG), 1-stearoyl-rac-glycerol (99%) and 1,2 palmitoyl-rac-glycerol were selected from Sigma, respectively.

2.2. Catalytic measurements

Once the CaO had been activated in the U-reactor, it was poured into a small flask containing 1.5 g of protective liquid (methyl myristate, methanol, biodiesel, or methyl myristate containing small amounts of MG, DG) and the formed slurry was sonicated for 15 min. The slurry was then added to a three-necked jacketed batch reactor containing the methanol required for the reaction at 323 K and pretreated with this methanol for 15 min with stirring. The flask where the slurry was formed and the batch reactor were previously flushed with N_2 to displace any air contained within. Finally, 50 g of vegetable oil at 323 K was added to the reactor (methanol/oil molar ratio ~14:1).

The subsequent transesterification reaction was carried out at 323 K and atmospheric pressure with vigorous stirring (1000 rpm) for 3–5 h under a N_2 atmosphere. The detailed procedure for the analysis of reactants and products has been published elsewhere [6,13,17]. Briefly, aliquots (~2 mL) were taken at different reaction times for analysis. The reaction was then quenched by adding HCl in excess to neutralise the Ca oxide. Next, dichloromethane was added to form two different phases: an apolar phase (dichloromethane, FAME and glycerides) and a polar phase (glycerol, methanol, water, HCl and $CaCl_2$). Dichloromethane was removed by heating and the content of FAME in the apolar phase was determined in accordance with the European regulated procedure EN 14103 which uses a gas chromatograph (Agilent 6890GC) connected to a flame ionisation detector (FID) equipped with a HP INNOwax capillary column.

2.3. IR characterisation studies

The interaction of some of the molecules of interest with the surface of the activated Ca oxide was studied by recording DRIFT spectra. The general procedure was as follows: in a first series of experiments, the Ca oxide was activated as described above and poured in a flask containing the compound of interest to form a slurry. After 15 min of contact at room temperature with sonication, the slurry was subjected to a given treatment that will be specifically explained when describing the results. Then, the solid was filtered and washed with heptane to remove any compounds that were not chemically absorbed. This solid was then loaded in the sample holder of a high temperature *in situ* chamber (Harrick Scientific Products, NY). A flow of inert gas was circulated through the cell before recording the spectra to remove the low boiling point molecules and physically adsorbed species. Then, 256 DRIFT spectra were recorded at room temperature at a resolution of 4 cm^{-1} with a Nicolet 5700 Fourier transform spectrophotometer equipped with an Hg—Cd—Te cryodetector, working in the range of 4000–650 cm^{-1}. A Praying Mantis (Harrick Co) was used as mirror optical accessory to focus the IR beam on the sample.

3. Results and discussion

3.1. Catalytic activity experiments

Fig. 1 shows the FAME yield obtained by the slurry formed by mixing Ca oxide with 1.5 g of oil, methanol, biodiesel or pure methyl myristate (pure FAME). This amount represented 15 g of slurry agent per gram of solid. After sonication, the slurry was treated with methanol at 323 K for 15 min. The figure clearly shows that the best catalytic performance was obtained when the solid was first protected with biodiesel and that the worst catalytic behaviour was from the oil. Additionally, the slurry with methanol led to an intermediate behaviour. These results were in agreement with those previously reported [17]. Furthermore, when the solid was mixed with pure methyl myristate, the behaviour of the slurry was similar to that obtained with methanol. Methyl myristate is a pure FAME, so this result strongly suggested that it is not the contact with the FAMEs present in the biodiesel that results in the remarkable increase in the reaction rate, but contact with some other component of the reaction mixture.

The data labelled as *"biodiesel with methanol at RT"* corresponded to a Ca oxide–biodiesel slurry directly added to methanol

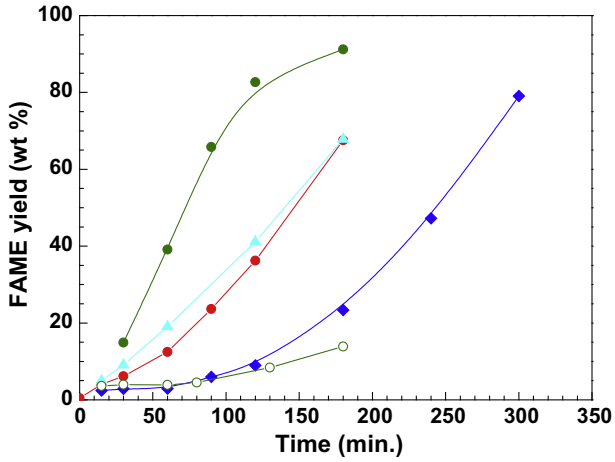


Fig. 1. Yield of FAME (wt%) when the activated Ca oxide catalyst was first mixed with 1.5 g of the following reactants and then pretreated with methanol at 323 K for 15 min before adding the oil and proceeding with the reaction: sunflower oil (◆), methanol (▲), biodiesel (●) and methyl tetradecanoate ester (●). The symbol (○) represents the experiment called "biodiesel with methanol at RT" in which biodiesel was mixed with methanol without pretreatment before proceeding with the reaction. Reaction conditions: 50 g of sunflower oil, 0.2 wt% catalyst with respect to oil, 323 K, and 1000 rpm.

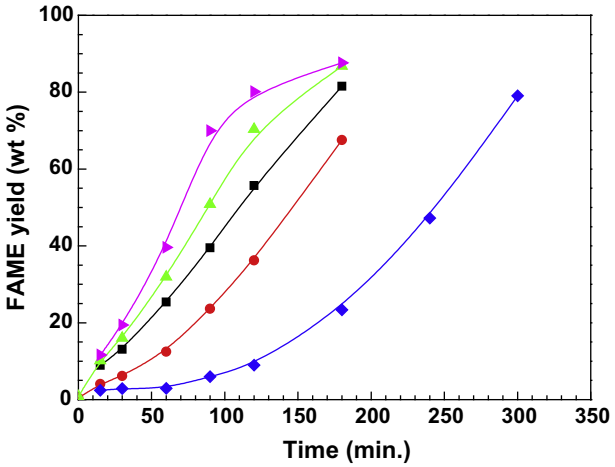


Fig. 2. Yield of FAME (wt%) when the activated Ca oxide catalyst was first mixed with 1.5 g of methyl tetradecanoate containing no 1-stearoyl-rac-glycerol (MG) (●), 10 mg of MG (■), 20 mg of MG (▲) or 30 mg of MG (▶). The symbol (◆) represents mixing with 1.5 g oil. In all the cases, the slurry was pretreated with methanol at 323 K for 15 min before adding the oil to proceed with the reaction. Reaction conditions are the same as in Fig. 1.

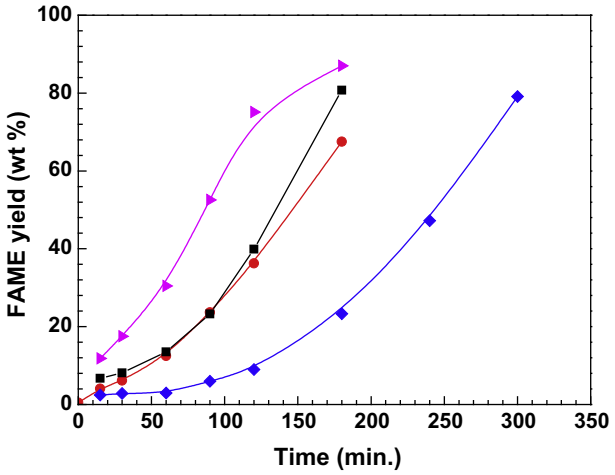


Fig. 3. Yield of FAME (wt%) when the activated Ca oxide catalyst was first mixed with 1.5 g of methyl tetradecanoate containing no 1,2 palmitoyl-rac-glycerol (DG) (●), 10 mg of DG (■) or 20 mg of DG (▶). The symbol (◆) represents mixing with 1.5 g oil. In all cases, the slurry was pretreated with methanol at 323 K for 15 min before adding the oil to proceed with the reaction. Reaction conditions are the same as in Fig. 1.

at RT. Then, oil was incorporated at 323 K and the temperature of the reaction was rapidly increased without agitation up to 323 K. At this point, the reaction was begun by initiating agitation. Interestingly, promotion by biodiesel in this case was not observed. This observation indicated that the step where the reaction was placed in contact with methanol at 323 K for 15 min was required for an effective rate promotion.

We proposed that other components besides the FAMEs present in the biodiesel led to the observed rate increase. The minor components present in the biodiesel were determined to be monoglycerides (MG), diglycerides (DG) and glycerol. As such, their concentrations in biodiesel are limited by regulations (such as EN 14105 and ASTM D6584) to prevent problems during its use as a fuel. Analyses carried out on the biodiesel sample used for the slurry indicated that it contained MG, DG and glycerol (although below the specifications). Therefore, to test whether the presence of minor amounts of MG, DG in the biodiesel explained the observed promotion, a model biodiesel was prepared by adding a very small amount of MG, DG to pure FAME. In our case, methyl myristate was selected as the pure FAME, and pure 1-stearoyl-rac-glycerol and 1,2 palmitoyl-rac-glycerol were selected as sources of MG and DG, respectively.

The positive effect of the presence of small amounts of MG on the reaction rate is clearly shown in Fig. 2. For the sake of comparison, the results for the slurry with oil and methyl C14 ester were also included. In this case, different amounts of pure 1-stearoyl-1-rac-glycerol were added to 1.5 g of pure methyl myristate. The presence of only 10 mg of MG in the initial methyl myristate–Ca oxide slurry resulted in a remarkable increase in the reaction rate. The incorporation of larger amounts of MG (20 and 30 mg) resulted in a larger promotion of the reaction rate. Additionally, the effect of the addition of DG on FAME yield is reported in Fig. 3. The addition of 10 mg of DG to 1.5 g of methyl C14 ester resulted in a small, although clearly visible, increase in the reaction rate. Addition of larger amounts of DG (20 mg) caused a correlated increase in the degree of promotion.

Considering these latter results, we initially proposed the following hypothesis: during the heating step, the slurry in methanol at 323 K yielded FAME and glycerol from the transesterification of MG or DG with methanol, this reaction is catalysed by the own Ca oxide. The glycerol that formed is therefore responsible for the observed promotion in reaction rate. The fact that the slurry must be subjected to the treatment with methanol at 323 K to make the promotion possible (if this step was not done then the promotion did not occur) gave support to this hypothesis.

If this hypothesis was correct, the presence of glycerol in the initial reaction mixture must also promote the activity of CaO. Fig. 4 shows the catalytic activities obtained when Ca oxide was directly added to methanol containing a small amount of glycerol mixtures at 323 K and stirred for 15 min, at which point the oil was added and the reaction initiated. The results demonstrated that glycerol increased the reaction rate.

We have also tested whether this mechanism can be applied to other basic homogeneous or heterogeneous catalysts. No promotion of the catalytic activity was observed when glycerol was mixed with methanolic NaOH for 15 min before proceeding with the reaction. The same lack of promotion was observed when activated Mg oxide was mixed with glycerol (see Supplementary

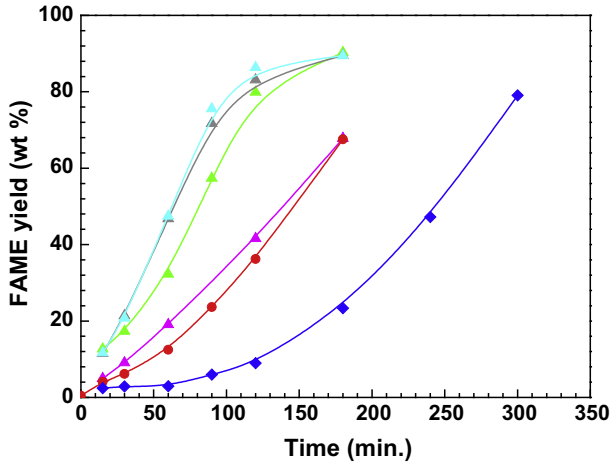


Fig. 4. Yield of FAME (wt%) when the activated Ca oxide catalyst was first mixed with 1.5 g of methanol containing no glycerol (▲), 10 mg of glycerol (▲), 40 mg of glycerol (▲) or 60 mg of glycerol (▲). In all cases, the slurry was pretreated with the methanol–glycerol mixture at 333 K for 15 min before adding the oil to proceed with the reaction. The symbols (●) and (◆) are the experiments represented in Fig. 1 for methyl tetradecanoate and oil. Reaction conditions are the same as in Fig. 1.

Information). As a result, glycerol promotion was only observed for Ca oxide.

3.2. Studies of the interaction of FAME, glycerides and glycerol with the surface of the activated Ca oxide by IR studies

IR spectroscopy is a valuable tool to understand the interaction of organic molecules, such as methanol, and carbonyl containing compounds, such as esters or acids, with the surface sites of catalysts [18,19]. The study of the interaction of FAME, glycerides and glycerol with the surface of the Ca oxide by IR spectroscopy can give clues to the promotion effect of MG, DG and glycerol on the transesterification reaction rate. We have conducted the IR studies subjecting the Ca oxide to the same treatments that resulted in the promotion, since then we can observe the IR features of the active species responsible of the promotion. Before proceeding with these experiments, we also recorded the IR spectra when Ca oxide is contacted with methyl C14 ester and methanol as these spectra are relevant blanks. We recorded as well all the IR spectra of pure compounds adsorbed over KBr; this latter information is reported in Supplementary Information (SI). DRIFT technique was selected for the IR studies (unless otherwise indicated).

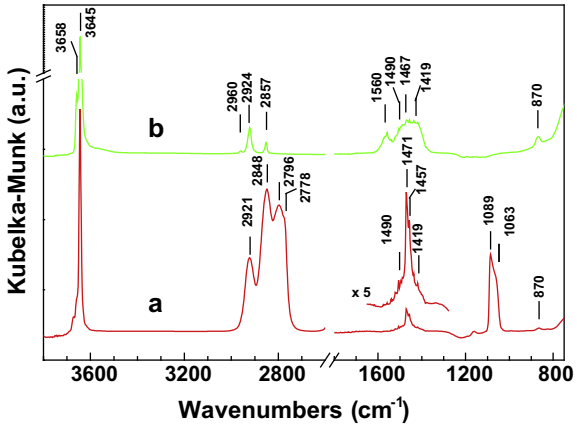


Fig. 5. DRIFT spectra of solid Ca oxide mixed with (a) methanol or (b) methyl tetradecanoate. See text for details of the reaction procedure.

Fig. 5 represents the DRIFT spectra recorded when the activated Ca oxide was in contact with methanol and the methyl C14 ester. Table 1 summarises the assignment of the most relevant bands. The DRIFT spectrum of methanol chemisorbed on Ca oxide was represented in trace a of Fig. 5. The region between 1650 and 1250 cm^{-1} is also represented as fivefold-magnified region for a clearer identification. The spectrum was quite different to that obtained for pure liquid methanol (see Supplementary Information). The O—H stretching band observed in liquid methanol at approximately 3325 cm^{-1} was not observed, indicating that this bond was absent. The bands at 2921, 2848, 2796 and 2778 cm^{-1} were assigned to the stretching vibrations of C—H bonds and the bands at 1471 and 1457 cm^{-1} to C—H bending modes of CH_3 [20]. Two bands appeared at 1089 and 1063 cm^{-1}, which were assigned to the stretching vibration of the C—O bonds. All the former data could be explained by the formation of surface calcium methoxide as a result of the interaction of surface Ca—OH groups with methanol molecules. Actually, the C—O and C—H bands of the spectrum of Na methoxide were at quite similar wavenumbers to those discussed here [21]. Several methoxy C—O bands have also been observed by Lavalley and co-workers [22] when methanol was chemisorbed on MgO surfaces and were ascribed to different methoxide species chemisorbed on different Mg—O sites (on flat terraces or on low coordination sites). Therefore, a similar situation could be expected on Ca oxide. The 3658 and 3645 cm^{-1} bands are assigned to the stretching vibrations of OH groups of $Ca(OH)_2$ present at the surface of the Ca oxide [6,23]. It is well known that the surface of the Ca oxide cannot be fully dehydrated with conventional activation conditions, and a few layers of amorphous calcium hydroxide must be present as a covering on the Ca oxide [6,24] (see Supplementary Information). These bands from OH groups of $Ca(OH)_2$ indicated that although methanol was chemisorbed, there were still domains of calcium hydroxide in the outer regions of the Ca oxide, very likely existing as subsurface domains below the outermost surface layer. Vibrations of unidentate carbonate species from the unavoidable carbonation of the surface were deduced from the shoulders at 1490 and 1419 cm^{-1} and from the band at 870 cm^{-1}. As explained in Supplementary Information, the carbonation occurred despite precautions taken during manipulation [6,25].

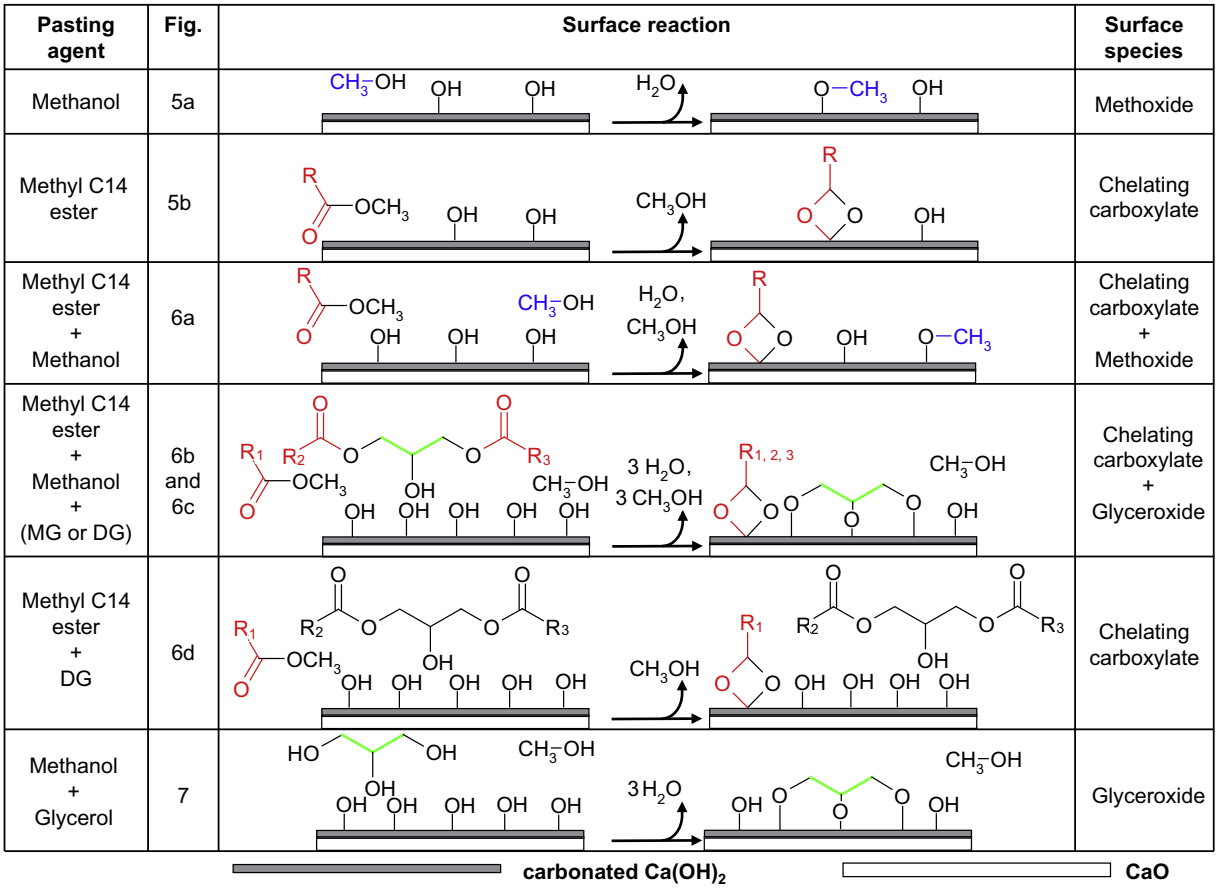
Scheme 1 summarises how methanol is chemisorbed over the Ca oxide surface. In this scheme, the presence of a carbonated Ca hydroxide layer coating an inner Ca oxide core was considered (see Supplementary Information). The thickness of the Ca hydroxide layer was undetermined, but it must be at least several nanometres deep. Water must also be formed during methanol chemisorption, but we could not assess whether water was chemisorbed or released as proposed in Scheme 1. The data could not provide an estimation of the methoxy surface coverage and it might be possible that some free surface OH groups were still present on the surface. This situation also applied to the rest of the surface species depicted in this Scheme, which is why the scheme still shows the presence of free surface OH groups after the chemisorption of the different molecules studied. The IR results could neither confirm nor refute whether the O of the surface methoxide came from methanol or from the Ca—OH group.

In the case of methyl C14 ester (spectrum b of Fig. 5, see Table 1 for the assignments of the most intense bands), the DRIFT spectrum was much simpler than that recorded for pure methyl C14 ester and reported in Supplementary Information, especially in the region below 1800 cm^{-1}. The spectrum showed bands from O—H vibrations of surface Ca—OH groups in the range of 3700–3500 cm^{-1}. The intense bands at 2924 and 2857 cm^{-1} are assigned to C—H asymmetric and symmetric stretching vibrations of methylene groups of the alkyl chain of FAME [26,27], respectively. The weaker bands at 2960 cm^{-1} were assigned to the asymmetric

Table 1
Assignment and wavenumbers (cm^{-1}) of the main DRIFTS bands shown in Figs. 5–7.

Compounds mixed with Ca oxide	ν_{O-H} in Ca—O—H (cm^{-1})	ν_{C-H} in C—H (cm^{-1})	(C—H), (C—O—H) bending and (C—C) st. modes (cm^{-1})[a]	ν_{C-O} in ester C=O, CO_3^{2-} or carboxylate (cm^{-1})	ν_{C-O} in alcohol or ester (cm^{-1})	References
Methanol	3658, 3645	2921, 2848, 2796, 2778	1471, 1457	(1490, 1419), 870	(1089, 1063)	[20,21]
Methyl C14 ester	3658, 3645	2960, 2924, 2857		(1560, 1455), (1490, 1409), 870		[26,27]
Methyl C14 ester–methanol	3658, 3645	2924, 2854, 2804, 2771	1471, 1457	(1569, 1455[b]), (1490, 1420), 870	(1085, 1063)	[20,26]
Methyl C14 ester–MG–methanol	3658, 3645	2960, 2924, 2852, 2820, 2771	997, 804	(1652, 1325), (1568, 1455), (1490, 1416), 870	(1130, 1074)	[20,26,30]
Methyl C14 ester–DG-methanol	3658, 3645	2960, 2924, 2852, 2820, 2771	997, 804	(1652, 1325), (1568, 1455), (1490, 1416), 870	(1130, 1074)	[20,26,30]
Methyl C14 ester–DG	3658, 3645	2960, 2920, 2850		(1568, 1455), (1490, 1416), 870		[26,27]
Glycerol–methanol	3658, 3645	2917, 2827, 2777	1457, 993, 804	(1694, 1651, 1612, 1354), (1490, 1416), 865	(1130, 1074)	[20,26,30]

[a] See text for discussion.
[b] Overshadowed by the most intense band of methoxy at 1457 cm^{-1}.



Scheme 1. Simplified scheme of the surface reactions involving the sites at the surface of activated Ca oxide and the molecules studied in this work.

vibrations of the CH_3 groups of FAME. The shape and the position of this set of bands differed from those of the pure methyl myristate deposited over KBr (see Supplementary Information), which suggested that methyl C14 ester molecules were in a different environment than that observed when condensed on KBr.

The 1800–800 cm^{-1} region was dominated by only four bands at 1560, 1490 (sh), 1467 and 1419 (sh) cm^{-1}. The shoulders at 1490 and 1419 cm^{-1}, along with the band at 870 cm^{-1}, were assigned to monodentate carbonate species on the Ca oxide surface [28]. The bands at 1560 and 1467 cm^{-1} were assigned to the antisymmetric and symmetric stretching vibrations of carboxylate groups [26,29]. The small separation between the signals (ca. 90 cm^{-1}) indicated that they arose from a chelating carboxylate species (no other unidentate or bidentate species were observed). Therefore, the FAME molecules were chemisorbed on the hydrated Ca oxide surface as chelating carboxylate species.

Scheme 1 summarises the adsorption mode of the FAME molecules over the surface of the hydrated Ca oxide deduced from the

latter results. From the data, it was clear that the ester group was broken and the acid moiety remained chemisorbed. The methanol side did not remain chemisorbed because the band corresponding to the C—O stretching vibration of the methoxide moiety of the ester, which should have been located between 1100–1200 cm^{-1} [22], was not observed. The methanol molecules that must be formed during the interaction must have been rinsed out during the heptane wash step or evaporated. This observation indicated that the surface had a larger affinity for the formation of carboxylate species than for the methoxide species derived from FAME molecule. This latter result must be considered when discussing glyceride adsorption.

According to this model, the C—H bending bands of the acid chain between 1500 and 1300 cm^{-1} must also be present in this region of the spectra (see Supplementary Information), but they must have been overshadowed by the more intense carbonate and carboxylate bands. Furthermore, the progression bands of the twisting, wagging and rocking modes that can be observed for the pure methyl C14 ester and glycerides condensed over KBr were no longer observable. The zigzag configuration of the methylene chain that caused these progression bands in the condensed phases over KBr (see Supplementary Information) was no longer valid for the chemisorbed state. The situation was that, when the acid chains were chemisorbed on the surface-specific sites, they were not closely packed but instead had unrestricted movement. Therefore, they did not present the zigzag conformation with lateral interactions that caused the set of progression bands.

Fig. 6 displays the DRIFT spectra obtained by mixing CaO with other molecules of interest and following a similar procedure to those used for the promotion of the catalytic activity. Experimentally, 0.1 g of CaO was mixed with 1.5 g of methyl C14 myristate containing 30 mg of either MG or DG. The blank experiment without MG or DG was also carried out. The slurry was then added to approximately 5 mL of methanol at 323 K and kept at this temperature for 15 min under agitation. This process was similar to the procedure used for the data in Figs. 2 and 3 for testing the rate promotion of MG and DG. After this treatment, the solid was filtered and washed with heptane and loaded in the sample holder of the *in situ* DRIFTS cell. The most intense bands and their assignments are summarised in Table 1.

Spectrum a in Fig. 6 shows the blank experiment where Ca oxide was mixed with pure methyl myristate and this slurry placed in contact with 5 mL of methanol at 323 K for 15 min. The spectrum was compatible with the presence of both methoxide and carboxylate species resulting from the chemisorption of both the alkyl acid chain of the ester and of methanol. Thus, the bands at 2924, 2854, 2804 and 2771 cm^{-1} (C—H stretching modes), at 1471 and 1457 cm^{-1} (C—H bending mode) and at 1085 and 1063 cm^{-1} (C—O stretching modes) could be assigned to methanol chemisorbed on Ca oxide. Additionally, the band at 1569 corresponded to one of the two bands for the chelating myristate species chemisorbed on Ca oxide (carboxylate asymmetric stretching), and the symmetric vibration was overshadowed by the more intense C—H stretching modes of methanol at 1471 and 1457 cm^{-1} (see Fig. 5a and b). The C—H stretching modes of the myristate chain, which should appear between 3000 and 2800 cm^{-1}, were overshadowed by the more intense bands of the methoxide species and the C—H bending bands by the more intense carbonate and carboxylate bands (see below). The methoxide species must have arose from the methanol, as demonstrated in Fig. 5. Furthermore, the bands at 1490 (sh), 1420 and 870 cm^{-1} arose from the inevitable formation of unidentate carbonate species. The bands from the hydroxyl groups of the surface $Ca(OH)_2$ and discussed in previous figures were also observed at 3658 and 3645 cm^{-1}. No significant differences were observed with respect to those discussed in Fig. 5, so they were not included in this Figure for the sake of clarity. Scheme 1 summarises the latter conclusions, namely that myristate and methoxide species coexisted as chemisorbed molecules on the surface of the Ca oxide. The chemisorption of myristate that gave rise to the release of methanol. Methoxide species must have arose from the chemisorption of methanol, releasing H_2O.

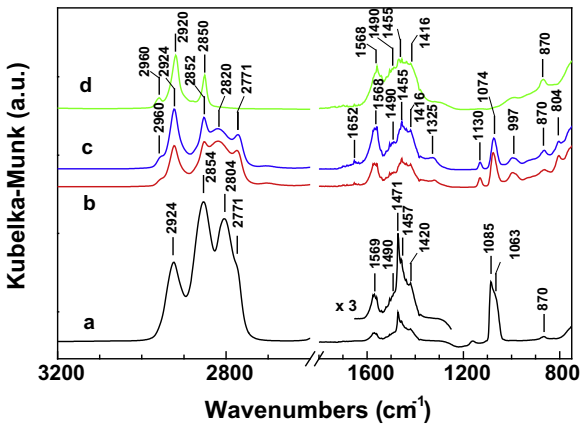


Fig. 6. DRIFT spectra of Ca oxide contacted with (a) methyl tetradecanoate and methanol; (b) methyl tetradecanoate, 1-stearoyl-rac-glycerol (MG) and methanol; (c) methyl myristate, 1,2 palmitoyl-rac-glycerol (DG) and methanol; and (d) methyl tetradecanoate and 1,2 palmitoyl-rac-glycerol (DG). See text for details of the reaction procedure.

Spectrums b and c of Fig. 6 show the result when CaO was mixed with methyl C14 ester containing either 30 mg of MG or DG and then exposed to 5 mL of methanol at 323 K for 15 min. Both of these spectra were similar, so they will be discussed together. The intense and broad band for the O—H stretching vibration in the range 3500–3000 cm^{-1} that were detected when liquid MG or DG were deposited over KBr was not observed (see Supplementary Information), indicating that the glycerol moiety of MG and DG did not have any free OH groups. The C—H vibration bands of the fatty acid chains were visible at 2960, 2924 and 2852 cm^{-1}. The bands at 1568 and 1455 cm^{-1} were the same features observed in Fig. 5a for the chemisorption of FAME molecules. These bands provided evidence for the presence of fatty carboxylate chelating species. In this case, both myristate (from the FAME) and stearate or palmitate (from the MG or DG) were likely species contributing to these bands. Additionally, the bands at 1490, 1416 and 870 cm^{-1} corresponded to the unidentate carbonate species derived from the unavoidable carbonation of the surface. Two more carbonate bands were also observed at 1652 and 1325 cm^{-1} and were assigned to bidentate carbonate species [30]. The spectrum showed other remarkable features at 2820, 2771, 1130, 1074, 997 and 804 cm^{-1} that were not observed in the FAME spectra of Fig. 5a and must be assigned to new surface species arising from MG or DG, but these bands will be assigned later.

The bidentate carbonate bands discussed above have not been previously observed when FAME and/or methanol were contacted with Ca oxide. This was an indication that we are now facing a different surface state derived from the presence of new species created from contact with MG or DG. It is important to notice that the bands at 1085 and 1063 cm^{-1} observed in Fig. 6a corresponding to the C—O band of methoxy species were not observed in spectra 6b and c, indicating that methoxy groups were not present (or minor amounts were present and overshadowed by the band at 1074 cm^{-1}) despite the fact that the sample was mixed with methanol at 323 K for 15 min.

Fig. 6d shows the spectrum when the Ca oxide was mixed with methyl myristate and DG, but not subjected to methanol treatment

at 323 K. The bands at 2960, 2920, 2850, 1568 and 1455 cm^{-1} from fatty carboxylate species chemisorbed on Ca oxide were clearly visible, as were the unidentate carbonate bands (1490, 1418 and 870 cm^{-1}). However, the bands at 2820, 2771, 1130, 1074, 990 and 804 cm^{-1} arising from the unknown species did not appear. This result showed that it was the treatment of the slurry containing DG with methanol that created the unknown species. The comparison of these results with those for catalytic activity indicates that these bands arise from the active surface species involved in the rate promotion.

Fig. 7 shows the spectrum when the CaO was put in contact with a mixture of methanol (1.5 g) and 10 mg glycerol for 15 min at 323 K. This spectrum is very relevant because when a similar treatment was conducted in the catalytic activity section, a promotion of the reaction rate was observed. Therefore, the IR features can be related to the species responsible of the promotion. It will be also shown that this spectrum is very helpful in assigning the bands that remained unassigned in Fig. 6d. The bands at 1694, 1651, 1612 and 1354 cm^{-1} could be assigned to the C=O stretching and O—C—O asymmetric stretching vibrations in the bidentate carbonate species [30]. These species were also detected in Fig. 6b and c, although not as well resolved as in this case; they are not relevant for promotion. A remarkable finding is that chemisorbed methoxy species are not formed as the bands at 1084 and 1063 cm^{-1}, which were detected in Fig. 5a and which were typical of methoxy species, are not present notwithstanding the large amount of methanol present in the treatment mixture. This means that the remaining IR bands are derived from the reaction of glycerol with the surface of Ca oxide forming Ca glyceroxy species. Thus, the bands at 2917, 2827 and 2777 cm^{-1} were from the C—H stretching vibration of the glyceroxy species. Furthermore, the bands at 1130 and 1074 cm^{-1} were attributed to C—O stretching vibrations at the C1 and C2 position of the glyceroxy species, that at 993 cm^{-1} to CH_2 rocking modes and that at 804 cm^{-1} to stretching modes of C—C bonds of the glyceroxy species [31]. The largest intensity of the C1—OH band was very likely due to the presence of two C1OH positions in the glyceroxy species. It is worth stressing that vibrations from free O—H groups of glycerol (see Supplementary Information) were not observed in the 3000–4000 cm^{-1} region (this region was not included in Fig. 7 for a better resolution of the bands). This phenomenon meant that all the alcohol groups of the glycerol were involved in chemisorption. The band at 1457 cm^{-1} was assigned to the C—H bending mode of glyceroxy (we can discard that this band is from the O—C—O symmetric vibration of chelating carboxylate species because the asymmetric counterpart of the chelating carboxylate, at 1568 cm^{-1}, was not observed). The band at 865 cm^{-1} can be assigned to the C—C stretching vibration of glyceroxy [31], although it may also arise from a bending mode of carbonate.

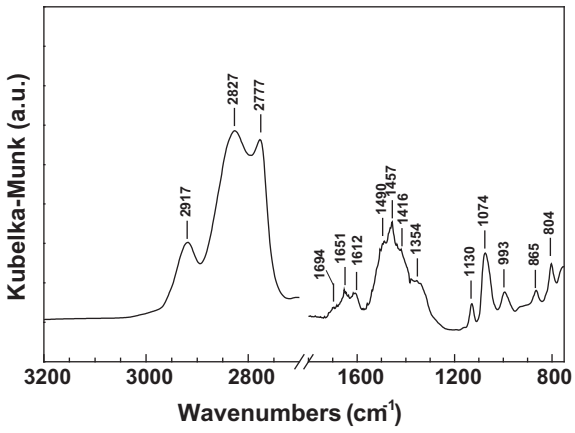


Fig. 7. DRIFT spectra of Ca oxide combined with a mixture of methanol and 10 mg of glycerol. See text for details of the reaction procedure.

Scheme 1 depicts the chemisorption modes of glycerol on the Ca oxide surface. Glycerol reacted with the hydroxyl groups forming C—O—Ca bonds (glyceroxy species) and released water. Methanol remained a spectator, as surface methoxy species were not observed. Summarising, the IR results in Fig. 7 demonstrates that the surface Ca glyceroxy species are responsible for the promotion. In this context, it must be mentioned that a Ca glyceroxide phase has been reported to be more active than Ca oxide [13,15].

The bands in Fig. 6b and c at 2827, 2777, 1130, 1074, 993 and 804 cm^{-1}, which remained unassigned, are now clearly understood. They arose from surface glyceroxy species, the latter resulting from the reaction between the surface of Ca oxide and the glycerol derived from MG and DG (the band at 2917 cm^{-1} is not observed in Fig. 6b and c because it is overshadowed by the band at 2924 cm^{-1} from fatty carboxylate). Scheme 1 depicts what happened when FAME containing a small amount of MG or DG was treated with methanol at 323 K: MG or DG reacted with the methanol forming glycerol *in situ* that was then chemisorbed as surface glyceroxy species, releasing water. The ester molecules (FAME, MG or DG) then formed the chelating carboxylate species, releasing the methanol moiety of the ester. Neither liquid methanol nor that derived from the esters reacted with the surface to form methoxy species. This observation indicated that surface glyceroxy species were preferred over surface methoxy species. This situation was different when the FAME containing MG or DG was mixed with the Ca oxide without previous treatment with methanol. In this case, glycerol was not formed *in situ* and surface chelating carboxylate was only formed from FAME, releasing methanol as a result. The observed carboxylate species could not have come from MG or DG as this would have implied that glycerol was formed *in situ* and so was glyceroxy species.

Summarising, the IR studies in Figs. 5–7 demonstrated that the promotion effect observed when Ca oxide was mixed with biodiesel containing small amounts of MG or DG was due to the formation of glycerol in the previous treatment with methanol at 323 K for 15 min. The glycerol formed *in situ* reacted with the surface of the Ca oxide and formed surface Ca glyceroxide species that are responsible for the reaction rate promotion. It was also evident that MG and DG were not the real promoters; glycerol was the real promoter and MG and DG were just the suppliers of the *in situ* glycerol. Therefore, instead of mixing with biodiesel and making the pretreatment with methanol, Ca oxide can also be promoted by mixing directly with methanol containing a small amount of glycerol (without the requirement of forming a slurry) before proceeding with the biodiesel reaction; then, a very active surface Ca glyceroxide species is also formed.

4. Conclusions

1. A remarkable increase in the reaction rate of Ca oxide was achieved if a biodiesel–Ca oxide slurry was formed (approximately 15 g of biodiesel per gram of CaO) and used as the catalyst. We have demonstrated that the slurry must be pretreated with methanol for a few minutes at the reaction temperature before adding the oil and proceeding with the methanolysis reaction.
2. Minute amounts of MG and DG present in the biodiesel were found to be at the origin of the promotion of the reaction rate. IR studies demonstrated that the mechanism of the promotion was as follows: during the pretreatment of the biodiesel–CaO slurry with methanol, glycerol was formed due to the methanolysis reaction of MG and DG, yielding FAME and glycerol. The glycerol formed *in situ* then reacted with the surface forming very active Ca glyceroxides.

3. Additionally, the two-step procedure of mixing Ca oxide with biodiesel and then methanol pretreatment could be replaced by pretreatment of the Ca oxide with methanol containing a few milligrams of glycerol per gram of Ca oxide prior to the reaction (and without the requirement of forming a slurry). IR studies demonstrated that this simpler pretreatment also resulted in the formation of very active surface Ca glyceroxide species.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.09.016.

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