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Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil

G. Arzamendi, E. Arguiñarena, I. Campo, S. Zabala, L.M. Gandía *

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

Abstract

The catalytic activity and selectivity of several compounds of the alkaline and alkaline-earth metals in the transesterification with methanol at 323 K of refined sunflower oil have been evaluated. Catalytic runs were conducted with a molar methanol/oil ratio of 12:1 in a batch reactor. The considered catalysts were Li, Na, K, Rb, Cs and Ca hydroxides, Na, K, Ca and Mg carbonates, Na and K bicarbonates, sodium phosphates as well as Ca and Mg oxides. Catalysts behaviour mainly depended on their homogeneous or heterogeneous character; that is, on their solubility in methanol. The alkaline metals hydroxides acted as homogeneous catalyst and were the most active ones; little differences were found among them. The K and Na carbonates, Na phosphate and CaO gave good results also. The evolution with reaction time of the selectivity for the different products also depended on the homogeneous or heterogeneous character of the catalyst, as well as on the alkaline or alkaline-earth nature of the metal. The chemical stability under reaction conditions of the most active heterogeneous catalysts has been investigated by checking the presence of the metals in the reaction mixture. This issue has received very little attention in the majority of the previous studies on heterogeneously-catalyzed biodiesel production. It must be stressed that a significant solubility in methanol of the solids has been found in some instances (e.g. K_2CO_3), therefore a contribution of homogeneous reaction routes cannot be discarded.

Keywords: Biodiesel; Transesterification; Methanolysis; Alkaline metals; Alkaline-earth metals

1. Introduction

The dependence of the European Union (EU) on the importations to satisfy the energy requirements is increasing continuously. For example, it has been estimated that if the present trend is maintained, the importations of natural gas will enlarge 80% in the next 25 years. World demand for energy also increases and it is expected that by the year 2030 the overall energy consumption and, as a result, the emissions of CO_2 to the atmosphere extend up to 60%. Moreover, oil and gas prices are rising; they have nearly doubled over the past two years. In view of these perspectives, one of the key areas of the European energy policy is the promotion of the use of renewable primary energy sources. To this end, the EU established years ago the objectives that, by the year 2010, 21% of the consumed electricity should be produced from renewable sources and that at least 5.75% of the gasoline and diesel should be replaced with biofuels [1]. Very recently, a new European strategy for sustainable, competitive and secure energy has been designed [2].

As concerns the transport sector, the dependence on fuels from crude oil is nearly total, amounting up to 96% of the current energy demand for transportation. Therefore, the impact of the penetration of biofuels in this sector can be very important since they are compatible with the existing engine technologies and hence direct substitutes of fossil gasoline and diesel. Furthermore, advantages can be taken of the present storage and distribution infrastructures and sales logistics [3]. The production of conventional biofuels in the EU reached 2.4 millions of metric tons in 2004, 79% of which corresponded to biodiesel and 21% to bioethanol [4]. The EU is the world's leading producer of biodiesel, whereas Brazil has been the world's leader of bioethanol for more than 25 years, producing almost half the world's total.

In the case of biodiesel, production costs are still high due to the high vegetable oil prices and some technological issues. It

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* Corresponding author. Tel.: +34 948 169605; fax: +34 948 169606.
E-mail address: lgandia@unavarra.es (L.M. Gandía).

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has been recognized that new processes based on heterogeneous catalysts, the use of alternative oil-seed crops and the increase of the purity of the co-produced glycerol have to be considered in order to improve the economics and competitiveness of biodiesel production [3].

Biodiesel is obtained by transesterification of the triglycerides found in vegetable oils and animal fats with an excess of a primary alcohol (most commonly methanol) in presence of a homogeneous or heterogeneous catalyst [5–7]. When using methanol the reaction is also known as methanolysis. As a result, biodiesel is a mixture of the methyl esters of the fatty acids contained in the lipid feedstock; glycerol is coproduced in the process. Methanolysis of triglycerides is a multiple reaction including three reversible steps in series as follows:

$$\mathrm{TG} + \mathrm{MeOH} \rightleftarrows \mathrm{DG} + \mathrm{ME} \qquad (1)$$

$$\mathrm{DG} + \mathrm{MeOH} \rightleftarrows \mathrm{MG} + \mathrm{ME} \qquad (2)$$

$$\mathrm{MG} + \mathrm{MeOH} \rightleftarrows \mathrm{GLY} + \mathrm{ME} \qquad (3)$$

where TG, DG, MG, ME, GLY and MeOH stand for triglycerides, diglycerides, monoglycerides, methyl esters or biodiesel, glycerol and methanol, respectively.

As concerns the operating variables, the methanol/oil molar ratio and the nature and concentration of the catalyst are among the most important [7]. Temperature has also a strong effect although at atmospheric pressure its value is limited to the normal boiling point of the alcohol used, around 338 K in the case of methanolysis reactions. Because of the transesterification reactions are reversible, an excess of alcohol has to be used with relation to the stoichiometric alcohol/oil molar ratio (3:1). The most suitable alcohol amount may be different from case to case since whereas the biodiesel yield increases with the excess of methanol, production costs rise, reaction volume increases notably and the separation of glycerol becomes more difficult.

Regarding the transesterification catalyst, they can be catalogued as homogeneous, heterogeneous or enzymes. It is well known that the basic catalysts are more active than the acidic ones; nevertheless, when the free fatty acids and water contents of the feedstock are high the use of mineral acids is recommended. Within this context, a catalyst is considered homogeneous if it is soluble in methanol, although it should be noted that methanol and vegetable oils are immiscible. The homogeneous catalysts most frequently used in the synthesis of biodiesel are the alkaline metal hydroxides NaOH and KOH in concentrations ranging from 0.3 to 2 wt.% referred to the initial oil mass [5–8]. The oil conversions achieved with these catalysts after short reaction times are high (around 95% after 90 min); however, they have several drawbacks: (i) neutralization and washing of the produced biodiesel and glycerol have to be carried out; (ii) the catalyst cannot be reutilized, (iii) the catalysts are sensitive to free fatty acids and water; (iv) large amounts of wastewater are generated; (v) the process becomes highly energy demanding. In order to overcome these problems the use of heterogeneous catalysts may be considered. In this case, the recuperation of the catalysts can be easily carried out by filtration thus simplifying the purification of the transesterification products. As a matter of fact, washing and neutralization steps are not necessary in industrial heterogeneous processes, such as in the one (Esterfip-H$^{\mathrm{TM}}$) recently commercialized by Axens (Institut Français du Pétrole Group Technologies) [9,10].

Several compounds have been checked as solid catalysts for the synthesis of biodiesel. Alkaline-earth metals oxides and hydroxides, mainly of calcium and magnesium and barium to a lesser extent due to the toxicity of its compounds, are the natural extension of the classic sodium and potassium hydroxides [11,12]. Other alkaline metals compounds that have shown promising results as heterogeneous transesterification catalysts are anhydrous and hydrated trisodium phosphate [13] as well as potassium carbonate on alumina [14]. Basic oxides such as ZnO, CeO_2 and La_2O_3 have been considered also, the performance of zinc oxide notably standing out [15]. Recently, Mg-Al hydrotalcites have been proposed as methanolysis catalysts with very promising results [16,17]. As concerns acid solids, numerous compounds have been checked and as a general rule, they are less active than the basic solid catalysts, which is in accordance with the behaviour showed by their homogeneous counterparts. Some examples are a great variety of zeolites, ion exchange resins, sulfonic acid-functionalized silicas, superacid solids as WO_3 on zirconia and sulphated oxides of Zn and Sn [18–21]. Presently, the main disadvantage of the heterogeneous transesterification catalysts both basic and acid is their low activity in comparison with the basic homogeneous catalysts.

In this work, the results obtained in the methanolysis of refined sunflower oil at 323 K with a series of catalysts consisting of several alkaline and alkaline-earth metals compounds are presented. Emphasis has been put in the activity, chemical stability under reaction conditions and selectivity for the different class of reaction products of the various catalysts.

2. Experimental procedures

2.1. Transesterification reactions

Transesterification reactions with methanol (Scharlau, HPLC grade) were carried out at 323 K and atmospheric pressure in batch reactors. Refined edible-grade sunflower oil (Urzante, Navarra, Spain; acid value of 0.07 mg KOH/g [22]) was used and a molecular weight of 879.5 g/mol was assumed [23]. All the experiments were carried out with a methanol/oil molar ratio of 12:1.

Two different experimental setups were used depending on the homogeneous or heterogeneous character of the catalysts. When using the homogeneous alkaline metals hydroxides, a 2 L jacketed glass reactor fitted with a reflux condenser, a nitrogen inlet, a stainless steel agitator comprising a turbine (370 rpm), a thermocouple probe, a heated circulating water bath and a sampling device was employed. The reactor included a recirculation loop comprising a diaphragm-type metering pump and a stainless steel three-way ball valve also for sampling purposes. These experiments were conducted with

300 g of sunflower oil. Samples (about 1 g) were taken out from the reactor at different reaction times. Additional details on this setup and the experimental procedures can be found elsewhere [24]. In the case of the heterogeneous catalysts a setup allowing carrying out 5 parallel reactions in closed glass flasks (60 ml) immersed in thermostatic water baths at 323 K with magnetic stirring was considered. 20 g of sunflower oil, the required amount of supported catalysts and the volume of methanol needed to reach an alcohol/oil molar ratio of 12:1 were added into the flasks. Samples (about 0.5 g) were withdrawn at various intervals by means of a polyamide tube crossing the flask stoppers and connected to a 2 ml polypropylene syringe.

All the samples taken were stored in 30 ml sealed glass flasks. The reaction was short-stopped by addition in each flask of some drops of a glacial acetic acid (Scharlau, HPLC grade) solution (0.6N) in tetrahydrofuran (Scharlau, HPLC grade) to neutralize the catalysts. Samples were further diluted with about 7 or 14 g of additional tetrahydrofuran (THF) depending on the amount of sample, 0.5 or 1 g, respectively. Once filtered with Acrodisc® syringe filters with 0.2 μm nylon membrane, samples were analyzed by size exclusion chromatography (SEC) with differential refractive index detector at room temperature [24,25].

2.2. *Catalysts and characterization techniques*

All catalysts used in this work were commercial products: $LiOH·H_2O$ (Sigma–Aldrich, 99.995%), NaOH (Sigma–Aldrich, pellets 99.998%), Na_2CO_3 (Fluka, >99.5%), $NaHCO_3$ (Scharlau, >99.7%), Na_3PO_4 (Scharlau, >98%, max. 2% of free alkali), Na_2HPO_4 (Scharlau, >98%), NaH_2PO_4 (Scharlau, >98%), KOH (Aldrich, pellets 99.99%), K_2CO_3 (Aldrich, 99.995%), $KHCO_3$ (Scharlau, >99.5%), K_2HPO_4 (Scharlau, >98%), RbOH (Aldrich, 99.9%, 50 wt.% aqueous solution), $CsOH·H_2O$ (Aldrich, 99.95%), CaO (Aldrich, 99.9%), $Ca(OH)_2$ (Sigma–Aldrich, 99.995%), $CaCO_3$ (Sigma–Aldrich, 99.999%), MgO (Sigma–Aldrich, >99%), $Mg(OH)_2·4Mg\text{-}4MgCO_3·5H_2O$ (Aldrich, 99%). The alkaline metals hydroxides delivered in pellet form were ground in an agate mortar to facilitate their dissolution in methanol. Other compounds delivered in powder form were used as received and dispersed in methanol prior to reaction.

In transesterification studies it is customary to express the catalyst concentration as a percentage referred to the amount of oil loaded into the reactor. In this work, a typical catalyst such as NaOH has been adopted as reference at concentrations of 0.1 and 0.2%. The lowest concentration was used in the series of experiments in which the performance of the alkaline metals hydroxides was compared. The required amount of each hydroxide was adjusted taking into account the respective molecular weight in order to work in all cases with a catalyst concentration equivalent to 0.1% NaOH. Preliminary experiments performed with some of the remaining compounds evidenced their lower activity compared with the homogeneous alkaline hydroxides and therefore, catalyst concentrations equivalent to 0.2% or up to 1% NaOH were adopted for these compounds.

Prior to start the transesterification reactions, the required amount of catalyst was dissolved or dispersed in part of the methanol. Sunflower oil and the rest of the alcohol were preheated up to 323 K in the reactor. The reaction started when the methanol containing the catalyst was added into the reactor.

The heterogeneous catalysts were characterized by nitrogen adsorption. The nitrogen adsorption–desorption isotherms at 77 K of the solid catalysts were measured by the static method in an automatic volumetric Micromeritics® ASAP 2010 adsorption analyzer. Prior to the measurements, samples were degassed at 353 K. The BET equation was applied to five adsorption data taken at relative pressures below 0.2 in order to calculate the specific surface areas [26].

2.3. *Catalysts stability*

The chemical stability of the most active heterogeneous catalysts has been investigated by analyzing the presence of free sodium, potassium or calcium in the reaction mixture. This is a very important issue since if the metal is found, neutralization and washing steps of the produced biodiesel and glycerol would be necessary, thus nullifying the possible advantage of using these compounds as heterogeneous catalysts for this process.

Some of the samples taken from the reactor to monitor the evolution of the methanolysis reaction were carefully filtered and then introduced in a rotary evaporator at room temperature. After evaporation, the dry fraction was treated with 50 ml of 0.1N hydrochloric acid. The resulting solution was analyzed by Atomic Absorption Spectrophotometry (AAS, PerkinElmer 373) in order to determine the Na, K or Ca concentration. Dissolved compounds were referred to the total metal in the amount of catalyst in the sample withdrawn from the reactor.

3. Results and discussion

3.1. *Performance of the alkaline metals hydroxides*

All the hydroxides of the alkaline metals checked were completely soluble in methanol and then, behaved as homogeneous catalysts. Whereas NaOH and KOH are typical methanolysis catalysts, to our best knowledge there are no previous reports on LiOH, RbOH and CsOH as catalysts for the synthesis of biodiesel. In this study, the oil conversion (X_{TG}), selectivities (S_i) and yields (Y_i) for diglycerides (DG), monoglycerides (MG) and glycerol (GLY) were calculated as follows:

$$X_{TG} = \frac{N_{TG0} - N_{TG}}{N_{TG0}} \tag{4}$$

$$S_i = \frac{N_i}{N_{TG0} - N_{TG}} \tag{5}$$

$$Y_i = \frac{N_i}{N_{TG0}} \tag{6}$$

where N_{TG0}, N_{TG} and N_i are the moles of oil initially charged into the reactor, moles of oil remaining at time t, and moles of the product i (i = DG, MG, GLY) in the reactor at time t, respectively. It was assumed that sunflower oil consisted exclusively of triglycerides, which is reasonable according to the SEC analyses.

The evolution with reaction time of the sunflower oil (300 g) conversion for a series of methanolysis reactions carried out at 323 K and molar methanol/oil ratio of 12:1 with the alkaline metals hydroxides is depicted in Fig. 1. Catalysts concentration was equivalent to 0.1% NaOH. As it can be seen, exception made of LiOH, the performance of the remainder hydroxides is almost the same. In the case of the lithium hydroxide it seems than a kind of induction period exists; however, in spite of the lower initial transesterification rate, after about 90 min of reaction the oil conversion (about 85%) achieved is not far from the one (around 90%) obtained with the other hydroxides.

The selectivities of the alkaline metal hydroxides for the several reaction products are plotted against the oil conversion in Fig. 2. In this case, the results obtained with all the catalysts are very similar. A higher dispersion of the selectivity results is apparent at low oil conversions. This is due to the higher errors inherently associated to the quantitation of very small amounts of converted oil. The evolution of the selectivities given by the homogeneous catalysts is accordance with the scheme of three reactions in series represented by Eqs. (1)–(3). Diglycerides are the primary products and hence, selectivities for these products decrease continuously from initial values close to 1 as the oil conversion increases since they are successively converted first into monoglycerides and then into glycerol. Selectivities for monoglycerides are very low; they hardly surpass 20% for oil conversions around 10%. This result, and the fact that selectivities for monoglycerides are always lower than for diglycerides suggest that for the homogeneous catalysts the last step (Eq. (3)) is not the limiting one since, once formed, monoglycerides are easily converted into glycerol.

The close catalytic performance of the alkaline metals hydroxides is not surprising since they are very strong bases soluble in methanol. In fact, it should be noted that the methoxide anion is believed to be the active transesterification species [19,27]; therefore, all these catalyst can easily react with the alcohol to yield the corresponding methoxide according to the following reaction where A stands for an alkaline metal:

$$\mathrm{AOH} + \mathrm{MeOH} \leftrightarrow \mathrm{AOMe} + \mathrm{H_2O} \qquad (7)$$

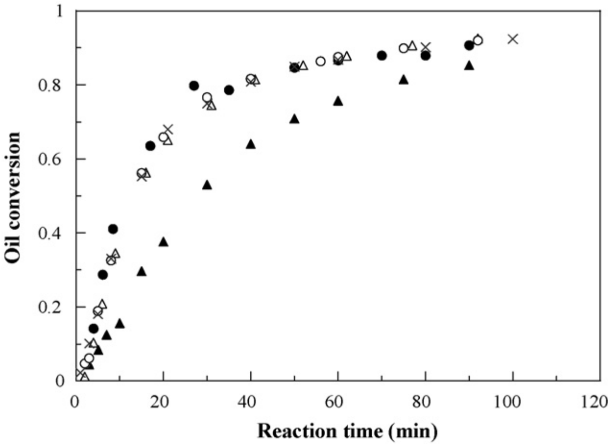

Fig. 1. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 323 K, methanol/oil molar ratio of 12:1 and catalyst concentration equivalent to 0.1% NaOH. Catalysts: LiOH (▲), NaOH (△), KOH (●) RbOH (○), and CsOH (×).

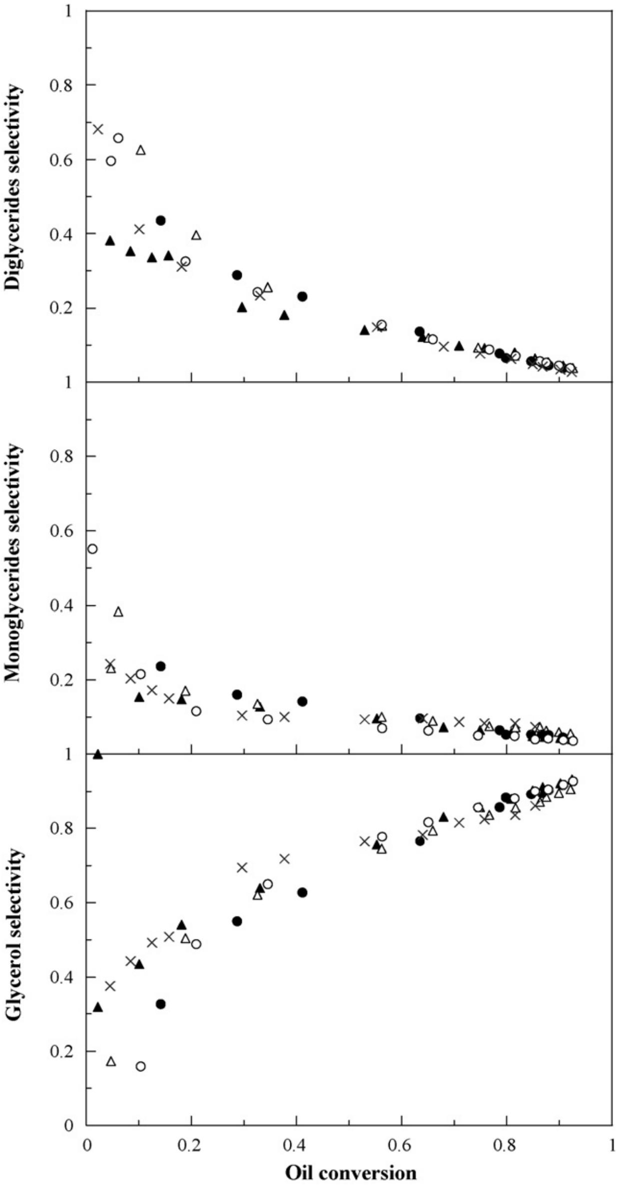

Fig. 2. Selectivities for diglycerides, monoglycerides and glycerol as a function of sunflower oil conversion for a series of transesterification reactions carried out at 323 K, methanol/oil molar ratio of 12:1 and catalyst concentration equivalent to 0.1% NaOH. Catalysts: LiOH (▲), NaOH (△), KOH (●) RbOH (○), CsOH (×).

3.2. *Performance of the heterogeneous catalysts*

This section is devoted to the catalysts evaluated in this work different from the alkaline metals hydroxides, that is, sodium and potassium carbonates, bicarbonates and phosphates and calcium and magnesium oxides, carbonates and hydroxides. Some of these compounds resulted almost insoluble in methanol whereas others showed a significant solubility. Anyway, in the context of the methanolysis reactions all of them are usually considered heterogeneous catalysts and for the sake of clarity it is more convenient to study them together.

When no solid catalyst was present in the reaction mixture samples representative of the reactor content were easily taken by means of a three-way valve installed in a recirculation loop connected to the reactor. The presence of suspended solids complicated the use of this setup with the heterogeneous catalysts and reaction samples were withdrawn by means of a syringe. In this case, one has to be very careful in order to extract a representative sample of the reactor content due to the high initial viscosity of the reaction mixture. This makes sample extraction with a syringe slow, which can result in some phase separation by settling [24].

Several compounds considered in this study as heterogeneous catalysts exhibited negligible activity. They are included in Table 1, where the sunflower oil conversion achieved after a given reaction time is included, as well as the specific surface area of some of the solids. Methanolysis reactions were conducted at 323 K with an alcohol/oil molar ratio of 12:1 and a concentration of solid catalyst equivalent to 0.2% NaOH. Due to the low practical interest of these catalysts, their chemical stability under reaction conditions and other characteristics such as the selectivities for the several reaction products were not studied. The most active heterogeneous catalysts evaluated in this work were potassium carbonate, sodium carbonate and phosphate, calcium oxide and finally calcium hydroxide. The evolution with reaction time of the sunflower oil (20 g) conversion for a series of methanolysis reactions carried out under the above-mentioned conditions with these catalysts is shown in Fig. 3. The activity exhibited by these compounds is well below that of the alkaline metals hydroxides in spite of using a concentration (0.2% NaOH) twice the one considered with the homogeneous catalysts. The exception is K_2CO_3, which is remarkably active. In fact, whereas the alkaline metals hydroxides achieved 90% sunflower oil conversion in about 100 min, potassium carbonate at double concentration required 108 min. Sodium carbonate and phosphate exhibited a very similar behaviour and achieved 90% oil conversion after 8 h. The specific surface are of these samples were low and similar, being in the 0.3–0.7 m^2/g range. However, as indicated in Table 1, potassium and sodium bicarbonates and hydrogen phosphates showed negligible catalytic activity. This can be interpreted in terms of the basic strength of the anions in these compounds. In fact, carbonate is the conjugate base of a very weak acid, the hydrogen carbonate ion (HCO_3^-), which in turn is the conjugate base of carbonic acid, a weak acid. As a result the basic strength of the carbonates is higher than that of the bicarbonates. Similarly, the phosphate anion is a relatively strong base since it is the conjugate base of a very weak acid, the hydrogen phosphate anion (HPO_4^{2-}). Thus it is reasonable to expect a more efficient formation of surface methoxide anions and hence higher methanolysis activity in presence of carbonates or phosphates than bicarbonates, hydrogen phosphates or dihydrogen phosphates, in accordance with our results. Due to the high electropositive character of the alkaline metals, their compounds such as oxides, hydroxides, carbonates or phosphates are more basic than their alkaline-earth metals counterparts. This is in line with the higher methanolysis activity exhibited by the sodium and potassium compounds in comparison with the calcium ones (see Fig. 3).

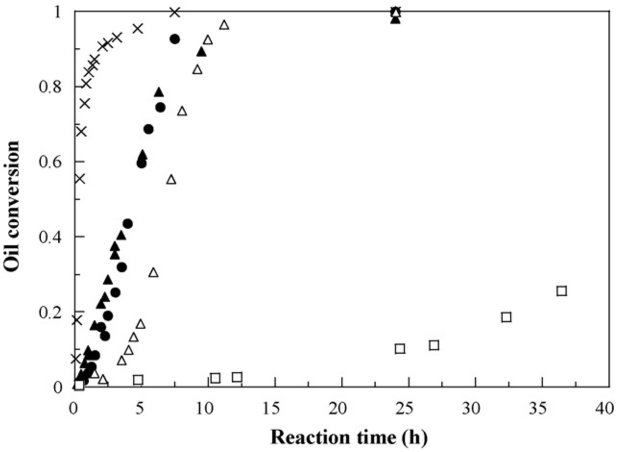

Fig. 3. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 323 K, methanol/oil molar ratio of 12:1 and catalyst concentration equivalent to 0.2% NaOH. Catalysts: K_2CO_3 (×), Na_2CO_3 (●), Na_3PO_4 (▲), CaO (△), and $Ca(OH)_2$ (□).

Table 1
Alkaline and alkaline-earth metals compounds having low methanolysis activity (323 K)

Catalyst	Reaction time (h)	Oil conversion (%)	S_{BET} (m^2/g)
$NaHCO_3$	4	1	–
Na_2HPO_4	4	0.2	–
NaH_2PO_4	4	0	–
$KHCO_3$	4	0.7	–
K_2HPO_4	4	0.6	–
CaO[a]	24	1.5	10 ± 0.6
$CaCO_3$	24	2.5	0.6 ± 0.1
MgO	24	3.5	96 ± 4
MgO[a]	24	2.5	37 ± 1
$Mg(OH)_2 \cdot 4MgCO_3$	24	2.5	20 ± 0.5

[a] Samples calcined in a muffle at 773 K for 12 h.

Uncalcined calcium oxide was the only alkaline-earth metals compound included in this study showing a significant catalytic activity; anyway, it required up to about 10 h of reaction to achieve 90% oil conversion. As indicated in Table 1, when calcined for 12 h at 773 K, calcium oxide becomes an almost inactive solid. This fact cannot be attributed to sintering since the specific surface area of the fresh CaO is 27 m^2/g, and that of the calcined sample 10 m^2/g. Although basicity, that is, the number of exposed basic sites per unit mass will decrease as the specific surface area decreases, the reported loss is not high enough to justify the negligible methanolysis activity of calcined calcium oxide. Also shown in Table 1 is that both fresh and calcined MgO are also poorly active in spite of their relatively high specific surface areas, especially for the uncalcined sample (96 m^2/g). It is well known that basic catalysts have to be activated, usually by means of high-temperature thermal treatments and outgassing, in order to remove water and surface carbonates thus developing catalytic activity. In the case of CaO and MgO, basic sites appear upon treatments above 673 K; however, very strong basic sites such as those required to form the methoxide anion do not appear for samples calcined in air [28]. For example, Dossin et al. subjected a commercial MgO powder to a pretreatment under dry nitrogen at 973 K for 12 h in order to remove any adsorbed CO_2 and water and prevent any contact with the ambient air; the solid was active in the transesterification of ethyl acetate with methanol [29]. The generation of very active coordinatively unsaturated O^{2-} acting as Lewis basic sites requires very high pretreatment temperatures [17,28]. In our case, calcination of MgO at 773 K was not sufficient for developing methanolysis activity.

As indicated in Table 1, the catalytic activity of bulk calcium and magnesium carbonates is very low, in accordance with the results found by Suppes et al. in the methanolysis of soybean oil at 393 K, methanol/oil molar ratio of 6:1 and catalyst concentration of about 10 wt.% [18], although the activity increased remarkably at 533 K [30]. This suggests that, in our case, at 323 K, the activity exhibited by CaO is not due to the possible presence of surface calcium carbonates. Calcium hydroxide, on the other hand, showed some methanolysis activity (see Fig. 3); it should be noted that the specific surface area of this compound was very low ($0.9\ m^2/g$) compared to that of uncalcined CaO ($27\ m^2/g$) thus explaining its poor performance. Therefore, hydroxide sites associated to the hydrated surface of CaO could be responsible for the activity exhibited by this oxide. Upon calcination at 773 K the surface becomes dehydrated, so calcium hydroxide sites are not present thus explaining the severe methanolysis activity loss experienced after this pretreatment.

Calcium compounds are widely available and very cheap; therefore, they would be very interesting for the biodiesel industry. Nevertheless, the performance of both CaO and $Ca(OH)_2$ at a catalyst concentration equivalent to 0.2% NaOH has no practical interest. However, this is a low catalyst concentration since values in the 0.4–2% range are typical in methanolysis reactions [7]. In order to evaluate the possible benefits of increasing the concentration of these catalysts experiments were carried out also at CaO and $Ca(OH)_2$ concentrations equivalent to 1% NaOH; the results are depicted in Fig. 4. As expected, the oil conversion increases significantly, especially when using calcium oxide. For example, with this five-fold increase of the CaO concentration the sunflower oil conversion after 5 h of reaction passes from about 40 to more than 95% which is a very interesting value. There is likely margin for additional gain in oil conversion by increasing the equivalent catalyst concentration up to a still reasonable value of 2%. As regards calcium hydroxide the oil conversions remain very modest in spite of the catalyst concentration increase due to the very low surface area of this solid. Moreover, it can be seen that for the period in which the reactor behaviour is differential (oil conversion below 10%) the conversion increase does not correspond with the five-fold increase in the catalyst concentration. It should be noted that the reaction mixture is a three-phase oil/methanol/catalyst system. The methoxide species are formed upon adsorption of methanol on the catalyst surface and the reaction becomes mass transfer-controlled [17] which can explain the moderate increase of the oil conversion.

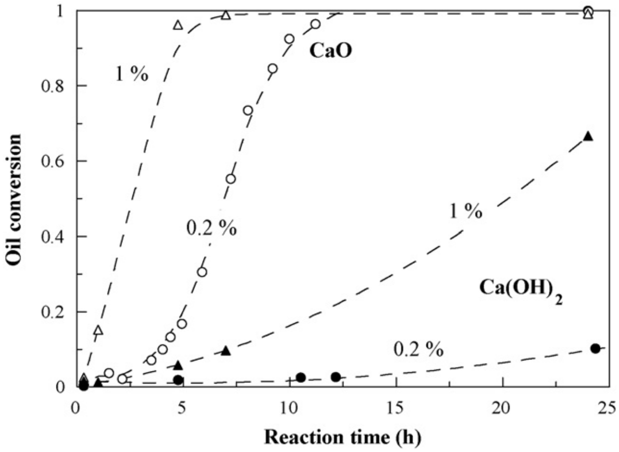

Fig. 4. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out with CaO and $Ca(OH)_2$ at 323 K, methanol/oil molar ratio of 12:1 and catalyst concentration equivalent to 0.2% (triangles) and 1% (circles) NaOH.

3.3. Catalysts solubility

Apart from the issues related to the basicity and texture of the heterogeneous catalysts that have been considered in the preceding section, the solubility of the catalysts is also a very important factor that should be taken into account to correctly interpret their performance and assess their practical interest. This matter frequently receives little attention and often solid catalysts are assumed to be insoluble in methanol. However, if the solid catalyst becomes partly dissolved additional steps would be required during the refining of the produced biodiesel and glycerol thus complicating the fabrication process. From a mechanistic point of view the solubility of the catalyst makes possible that the transesterification reaction can proceed via two distinct routes. On the one hand the nucleophilic attack of methoxide anions present on the methanol phase on a carbon atom of the carbonyl groups of acylglycerols (triglycerides, diglycerides and monoglycerides) [5]. On the other hand through an Eley-Rideal type mechanism including the reaction between methanol adsorbed on a basic active site of the catalyst surface and acylglycerols from the liquid phase [29].

As explained in Section 2.3 the presence of free sodium, potassium or calcium in the reaction mixture has been investigated by performing AAS analyses on samples withdrawn from the reactor. This study has been limited to the most active solid catalysts. The results are presented in Fig. 5 as percentage of the amount of catalyst initially charged into the reactor dissolved at two different oil conversion levels: 50% and near reaction completion. Potassium carbonate was the most soluble compound with about 55% dissolved at the reaction end (5 h) although up to 40% was readily dissolved after only 1.3 h. In contrast, sodium compounds resulted much

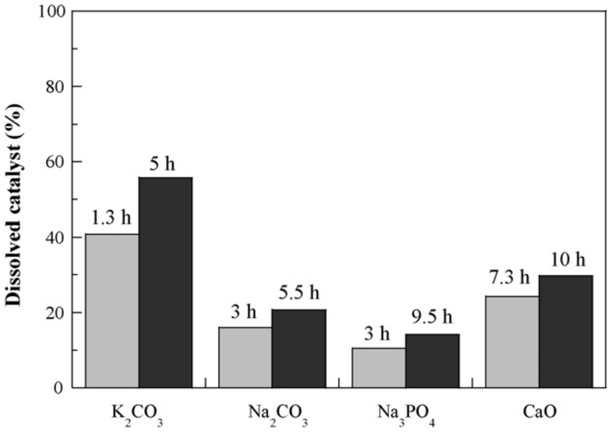

Fig. 5. Percentage dissolved of the indicated catalysts under reaction conditions at two oil conversion levels: 50% (grey bars) and about 100% (black bars). Reaction time at which samples were withdrawn from the reactor is also indicated.

more stable with up to 20% Na_2CO_3 and 15% Na_3PO_4 dissolved after reaction completion. This difference in solubility helps to understand the very different catalytic activity exhibited by these compounds, as shown in Fig. 3. Thus the good catalytic performance of K_2CO_3 can be attributed to its solubility in methanol that facilitates the formation of active methoxide species in the methanol phase. However, catalyst solubility is not the only factor conditioning the activity since an almost inactive compound such as sodium bicarbonate is also partly soluble (up to 15% after 4 h of reaction). As explained before bicarbonate is a weaker base than carbonate, and then less active.

Calcium oxide was also moderately soluble with about 25% dissolved after 7.3 h (50% oil conversion) which can explain its relatively good performance compared to Na_2CO_3 and Na_3PO_4. This finding is in accordance with previous work by Gryglewicz [11] with compounds of Ca, Mg and Ba used for the methanolysis of rapeseed oil.

In view of these results, sodium compounds seem to have a promising potential as heterogeneous methanolysis catalysts due to its lower solubility combined with a reasonable activity. This is especially true for sodium phosphate as confirmed in a recent study by De Filippis et al. [13]. Nevertheless, from a practical point of view, the stability under reaction conditions of these catalysts has to be considerably improved. To this end, a possibility is to disperse the alkaline-metals salts on conventional catalytic supports such as alumina. For example, Xie et al. have studied the solubility of potassium species for a series of KNO_3/Al_2O_3 catalysts which were found chemically stable with the exception of samples loaded with up to 35 wt.% KNO_3 [17].

3.4. Methanolysis selectivity

The selectivities for diglycerides, monoglycerides and glycerol of the heterogeneous catalysts in a series of reactions conducted at 323 K, 12:1 molar methanol/oil ratio and a solid catalyst concentration equivalent to 0.2 wt.% NaOH are included in Fig. 6.

On comparing Figs. 2 and 6 it is clear that the methanolysis selectivity of the alkaline metals carbonates and phosphates is close to that of the corresponding hydroxides. Taking into account that whereas the alkaline metals hydroxides are completely soluble in methanol the carbonates and phosphates, especially those of sodium, are only partly soluble, it seems that the methanolysis selectivity is not greatly affected by the route, homogeneous or heterogeneous, of the reaction as far as alkaline metals compounds are concerned. These are very selective catalysts for biodiesel synthesis; this results obviously in high biodiesel yields, as illustrated in Fig. 7 where it can be seen that with the alkaline metals-based catalysts the biodiesel yield is close to the oil conversion (dotted line).

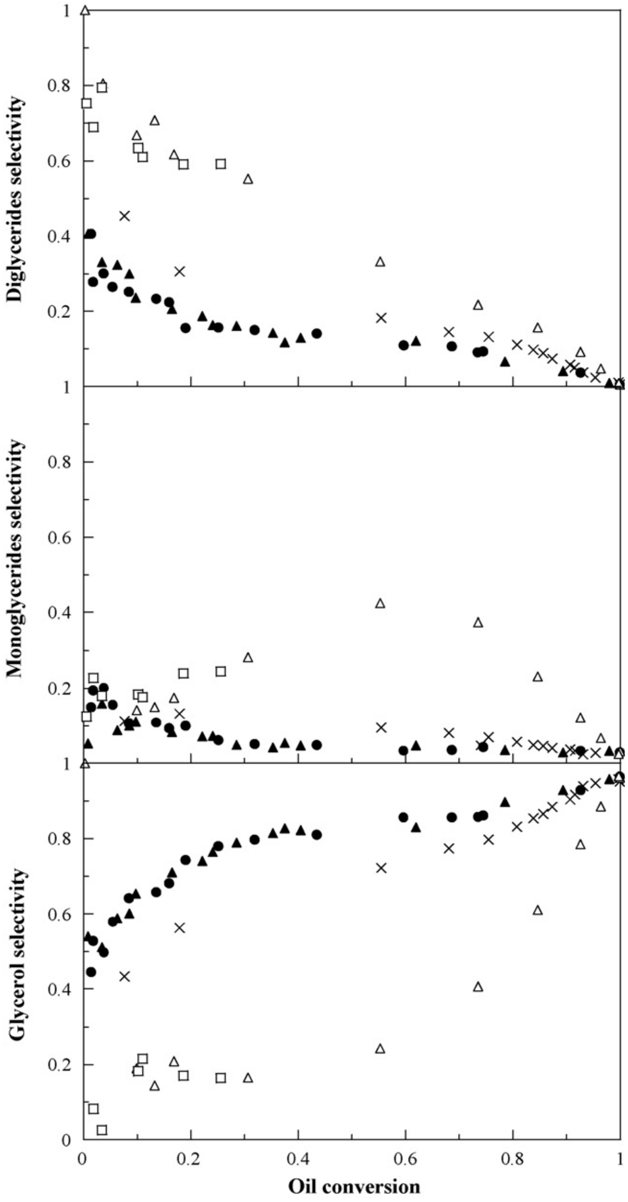

Fig. 6. Selectivities for diglycerides, monoglycerides and glycerol as a function of sunflower oil conversion for a series of transesterification reactions carried out at 323 K, 12:1 methanol/oil molar ratio and catalyst concentration equivalent to 0.2% NaOH. Catalysts: K_2CO_3 (×), Na_2CO_3 (●), Na_3PO_4 (▲) CaO (△), and $Ca(OH)_2$ (□).

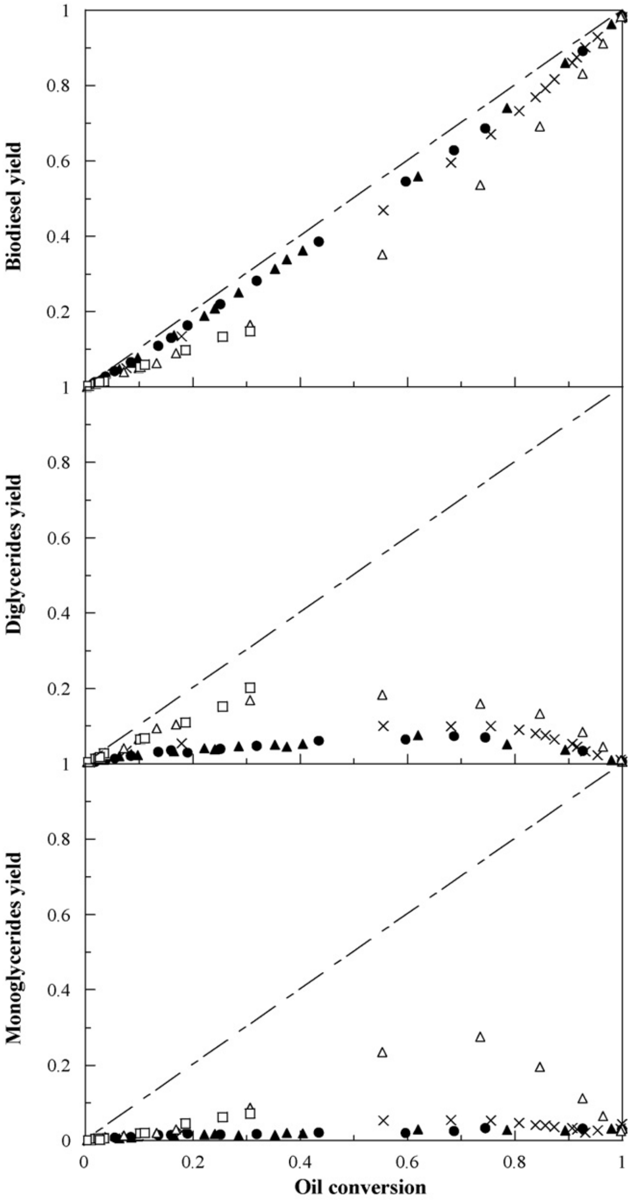

Fig. 7. Yields for biodiesel, diglycerides and monoglycerides as a function of sunflower oil conversion for a series of transesterification reactions carried out at 323 K, 12:1 methanol/oil molar ratio and catalyst concentration equivalent to 0.2% NaOH. Catalysts: K_2CO_3 (×), Na_2CO_3 (●), Na_3PO_4 (▲) CaO (△), and $Ca(OH)_2$ (□).

On the other hand, the alkaline-earth metals compounds, in this case CaO and $Ca(OH)_2$, exhibited a different behaviour. As can be seen in Fig. 6, may be that due to their lower activity, these catalysts are noticeably selective for the intermediate methanolysis products: diglycerides and surprisingly monoglycerides. This is in contrast with previous results (see Fig. 2) on homogeneous (NaOH, KOH) [24] and heterogeneous ($NaOH/SiO_2$, $NaOH/Al_2O_3$) [31] catalysts showing that monoglycerides, once formed, were easily converted to glycerol and methyl esters. Selectivities for these products were only significant at very low oil conversion levels (below 10%). When using CaO, however, a maximum selectivity for monoglycerides of up to 45% is achieved at about 55% oil conversion and, as shown in Fig. 7, a maximum methanolysis yield for monoglycerides close to 30% can be obtained. Selectivities for diglycerides are high also with CaO and $Ca(OH)_2$, but at lower oil conversions. In this case a maximum yield of about 15–20% is achieved. As regards the reaction selectivity, the performance of calcium hydroxide is very similar to that of CaO which also supports the hypothesis that the activity of calcium oxide can be due to the presence of surface calcium hydroxide. These results reduce the potential of CaO and $Ca(OH)_2$ as catalyst for the synthesis of biodiesel. It should be noted, however, that there is an increasing interest in obtaining renewable glycerol monoesters or monoglycerides that have important applications as food emulsifiers as well as in the pharmaceutical, cosmetic and detergent industry [15,32].

4. Summary and conclusions

In this work, the activity and selectivity of a variety of commercial alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil at 323 K have been investigated. The hydroxides of the alkaline metals (Li, Na, K, Rb, and Cs) were completely soluble in methanol and behaved as homogeneous catalysts. These were very active methanolysis catalysts that at the very low concentration equivalent to 0.1% NaOH, taken as reference, achieved sunflower oil conversions above 90% after 100 min of reaction. Selectivities for methyl esters (biodiesel) were also high. Differences in performance among the several alkaline metals hydroxides were not significant so there is no advantage in using lithium, rubidium or cesium compounds in place of the conventional NaOH or KOH.

As concerns the remainder catalysts, some of them showed negligible activity; they were: $NaHCO_3$, Na_2HPO_4, NaH_2PO_4, $KHCO_3$, K_2HPO_4, $CaCO_3$, calcined CaO, fresh and calcined MgO as well as $Mg(OH)_2 \cdot 4MgCO_3$. However, K_2CO_3, Na_2CO_3 and Na_3PO_4 resulted moderately active thus evidencing the effect of the basic strength of the anions in these compounds in the formation of active methoxide species. This explains the higher methanolysis activity of carbonates or phosphates than bicarbonates, hydrogen phosphates or dihydrogen phosphates. Potassium carbonate at a concentration equivalent to 0.2% NaOH required only 108 min to achieve 90% oil conversion. Sodium carbonate and phosphate exhibited a very similar behaviour and achieved 90% oil conversion after 8 h. However, these compounds were moderately soluble in the reaction mixture which can also contribute to their higher activity. The percentage of catalyst dissolved at reaction completion amounted up to 55% for K_2CO_3, 20% for Na_2CO_3 and 15% for Na_3PO_4.

Uncalcined calcium oxide was the only alkaline-earth metals compound included in this study showing a significant catalytic activity; however, when calcined for 12 at 773 K it becomes almost inactive, which was not due to catalyst sintering. The activity of the fresh CaO can be attributed to the presence of active sites associated to surface calcium hydroxide that were absent in the calcined catalyst. Calcium oxide was also moderately soluble in the reaction mixture, up to about

30% at complete conversion after 10 h of reaction. Nevertheless, the most noticeable feature of both CaO and $Ca(OH)_2$ is their noticeable selectivity for the intermediate products of the methanolysis reaction, especially monoglycerides. This is in contrast with previous results found with homogeneous and heterogeneous catalysts in methanolysis reactions carried out at conditions relevant for the synthesis of biodiesel.

The results obtained in this work indicate that the catalytic performance of the alkaline and alkaline-earth metals compounds is controlled by a balance between solubility, basic strength and specific surface area of the solids.

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