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TRANSESTERIFICATION OF SOYBEAN OIL WITH METHANOL ON ALUMINA-SUPPORTED CaO CATALYSTS MODIFIED WITH MgO OR ZnO

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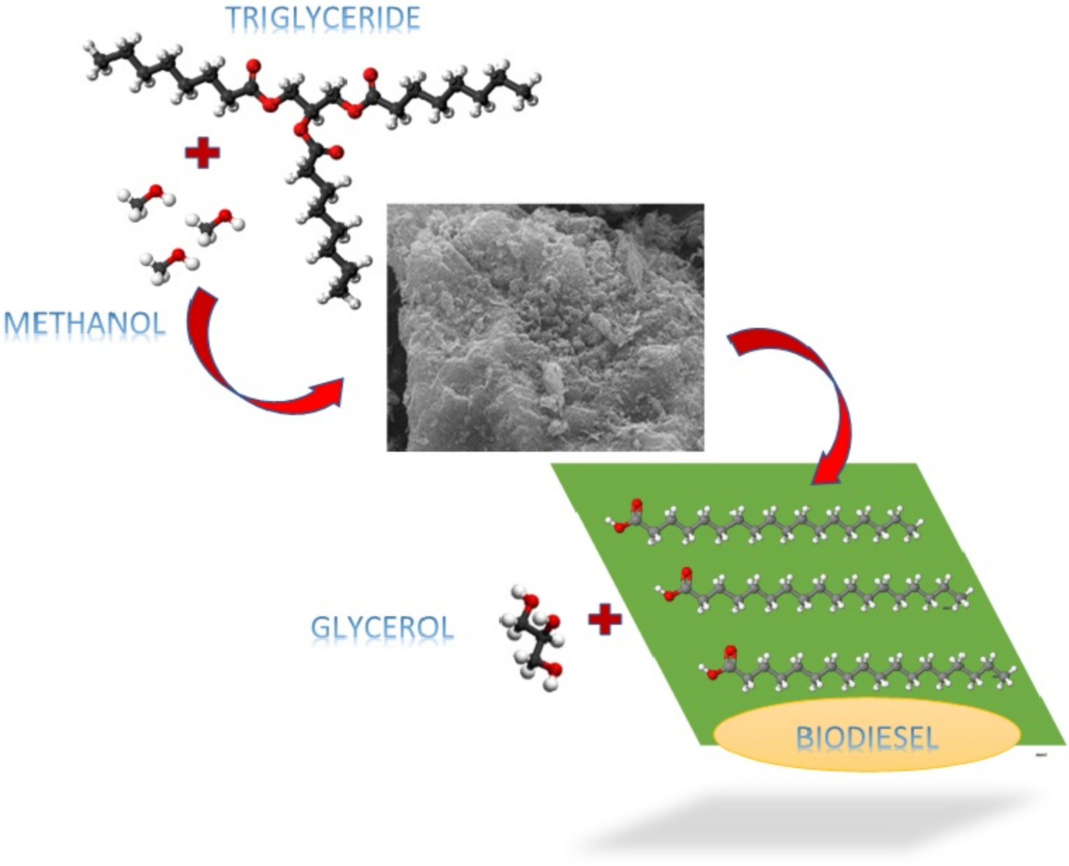
Resumen Gráfico



Resumen

Con el fin de estudiar la reacción de transesterificación de aceite de soja empleando metanol, se prepararon catalizadores de CaO, MgO y ZnO soportados en γ-Al_2O_3, y mezclas en relaciones molares 0.25, 0.5, 1 y 5 entre Mg/Ca y Zn/Ca. Los catalizadores fueron caracterizados empleando difracción de rayos X, fisisorción de N_2 y microscopía de barrido electrónico. Los catalizadores preparados presentaron en todos los casos características de sólidos mesoporosos, de gran área superficial, exhibiendo la fase cristalina óxido. Los catalizadores mezcla de MgO y CaO exhibieron selectividades a ésteres metílicos de ácidos grasos (FAME) muy cercanas al 100%, aunque ninguno superó en rendimiento a FAME al catalizador puro de MgO, que presentó un máximo de 57%. Los catalizadores mezcla de ZnO y CaO de proporciones 0.25, 0.5 y 1 Zn/Ca presentaron selectividades a FAME muy cercanas al 100%, y un rendimiento a FAME máximo de 37% para el catalizador 1 Zn/Ca.

Abstract

In order to study the transesterification reaction of soybean oil with methanol, γ-Al_2O_3-supported CaO, MgO and ZnO catalysts were prepared, as well as mixtures of Mg/Ca and Zn/Ca having molar ratios of 0.25, 0.5, 1 and 5. The catalysts were characterized using X-ray diffraction (XRD), N_2 physisorption and electron scanning microscopy (SEM). The results were consistent in all the cases with mesoporous solids, with large surface areas, exhibiting the oxide crystalline phase. Mg/Ca mixed catalysts presented fatty acids methyl esters (FAME) selectivities of almost 100%. Nevertheless, no mixture exceeded the FAME yield of the pure MgO catalyst, which showed a maximum of 57%. Zn/Ca mixed catalysts of 0.25, 0.5 and 1 atomic ratios, showed FAME selectivities very close to 100%. A maximum FAME yield of 37% was obtained with the Zn/Ca catalyst having an atomic ratio of 1.

Palabras clave: Transesterificación, aceite de soja, CaO, mezclas de óxidos, MgO, ZnO
Keywords: Transesterification, soybean oil, CaO, mixed oxides, MgO, ZnO

1. Introduction

Biofuels have gained importance due to their capacity to be used as substitutes for fossil fuels. These biofuels can be classified into three categories: first generation biofuels, which are those produced from highly available food sources; second generation, those generated using non-edible raw materials or obtained with advanced technologies, and finally, third generation biofuels, which include biofuels from algae [1]. Among them, biodiesel is one of the most promising options, because it can be produced from a wide variety of renewable sources and generates a lower amount of particulate matter and gases harmful to the environment [2].

According to the ASTM, biodiesel is defined as a biofuel composed of a mixture of alkyl esters of long chain fatty acids [3]. To obtain biodiesel, vegetable oils such as sunflower oil, soybean, rapeseed or palm oil are used as raw material. The type of oil used generally depends on the availability and climatic conditions of each region [4, 5]. Vegetable oils have the main advantage of being a renewable source, which allows a large-scale production without being harmful to the environment [6].

Biodiesel is obtained, among other routes, by the transesterification of the triglycerides present in the oil, with a short-chain alcohol, such as methanol, ethanol or butanol. The transesterification reaction involves three consecutive and reversible steps. In each step, a molecule of fatty acid alkyl ester per molecule of alcohol consumed is generated. Thus, triglycerides are successively converted into diglycerides, monoglycerides and, finally, into glycerol, the main secondary product [7, 8]. To perform this reaction, the presence of a catalyst, which may be of the acid or basic type is necessary. Basic solid catalysts are the most promising, due to their characteristics of good recovery and reuse [9].

Within the basic catalysts, one of the most commonly used is CaO. This solid base can be obtained from natural sources, such as minerals [10] (dolomite, hydroxyapatite, etc.), or different types of waste [11]. In addition, it is relatively tolerant to the presence of water and free fatty acids (FFA) in the reaction mixture [12]. On the other hand, a disadvantage of this catalyst is that the CaO-catalyzed transesterification is much slower than the homogeneous catalytic reaction which is currently used to produce biodiesel. Therefore, extensive research is carried out to improve the catalytic activity of CaO based systems [13]. A variety of modification strategies for improving the catalytic performance of CaO have been proposed: doping CaO catalyst with an alkali-metal [14], nano-sizing the CaO particles[15] and combining CaO with another metal oxide [16], among others.

This last strategy is the one proposed in the present work. The metal oxides selected to modify the CaO catalyst are MgO and ZnO. To do so, CaO-ZnO and CaO-MgO catalysts containing varying proportions of both metals were prepared by the coprecipitation method using ammonium carbonate as precipitant. The physicochemical properties of the catalysts were studied by using several characterization techniques and their catalytic activity was tested in the transesterification of soybean oil with methanol.

2. Materials and Methods

Catalyst preparation

γ-Al_2O_3-supported CaO, MgO and ZnO catalysts were prepared, both pure and in mixtures with molar ratios of 0.25, 0.5, 1 and 5 between Mg/Ca and Zn/Ca. In all the cases, the composition corresponds to 0.27 mol% of metal on the γ-Al_2O_3 (60-100 mesh). The synthesis was carried out by precipitation of the respective carbonates in alkaline medium [17], and subsequent calcination to obtain the oxides. Initially, the necessary amount of the corresponding nitrate was dissolved in an aqueous suspension of alumina. Then, a $(NH_4)_2CO_3$ solution was slowly added as a precipitant, under continuous stirring and using NH_4OH to control the pH of the medium. The system was left to decant for a week, filtered at room temperature and dried in an oven at 60°C for one day. Finally, the solids were calcined for 2 h at the temperature necessary to obtain the oxides.

Catalyst characterization

The surface characteristics of the samples were determined by N_2 physisorption at -196°C in a *Micromeritics ASAP 2020* equipment. The morphology was determined by scanning electron microscopy (SEM), using a *Phillips SEM 505* microscope. The crystalline phases present in the catalysts were corroborated by X-ray diffraction (XRD), using Cu Kα radiation ($\lambda = 0.154$ nm) on a *Phillips PW 1390* diffractometer.

The scan was performed from $2\theta = 5°$ to 75°, and then, the obtained diffractograms were compared with the JCPDS (Joint Committee of Powder Diffraction Standards) cards. The crystallite size for each sample was also calculated using the Scherrer equation and the Williamson-Hall method, which allows taking into account not only the contribution of the crystalline domain, but also that of the micro deformations (Equation 1):

$$D_{Sch} = \frac{0.9\,\lambda}{\beta\cos(\theta)} \qquad (1)$$

where β is the width at half height of the most intense peak of the diffractogram, θ is the angle where it is located, κ a constant, λ the wavelength of the CuKα radiation, D_{Sch} the size of crystallite to be calculated and ε an expression dependent of θ that considers the micro deformations ($\beta/4\text{tg}\theta$) [18,19].

Catalytic test

The catalytic activity was evaluated in the transesterification reaction between soybean oil and methanol. A 250 cm^3 reactor equipped with a reflux condenser and mechanical agitation was used. The reflux temperature of methanol was 60°C. In all the tests, an alcohol to oil ratio of 6:1 and a 5 wt.% of catalyst was employed.

The progress of the reaction was followed by gas chromatography, using a *GC-2010 Plus Tracera* high sensitivity gas chromatograph equipped with a BID-2010 Plus detector and a MEGA-Biodiesel 105 (15 mx 0.32 mm x 0.10 μm) capillary column. The analysis of the products was carried out based on the EN 14105 and ASTM D6584 standard methods [20,21]. Three consecutive temperature ramps were used: the first one from 50°C to 180°C (at 15°C/min), the second up to 230°C (at 7°C/min), and finally up to 350°C (at 30°C/min). The injector and detector temperatures were set at 350°C. Samples were taken at 2, 4 and 6 h of reaction. Before being injected into the GC, the samples were submitted to a derivatization procedure. To do this, 100 mg of the reaction mixture were taken in each case, placed in a 10 mL vial, and 80 µL of 1,2,4-butanetriol (internal standard 1), 100 µL of tricaprin (internal standard 2) and 100 µL of N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) as derivatizing agent were added. The mixture was stirred for 20 min at room temperature, to finally add 8 mL of n-heptane to it.

3. Results and Discussion

Morphological and structural characterization

All the prepared catalysts were analyzed by N_2 physisorption in order to characterize their textural properties. The results have been gathered in Table 1, which also lists the γ-Al_2O_3 support for comparative purposes (entry 12).

Table 1. Textural characteristics of the prepared catalysts determined by N_2 physisorption

Entry	Catalyst	S_{BET} (m^2/g)	V_{pore}(cm^3/g)	D_{pore}(Å)
1	CaO/γ-Al_2O_3	143	0.38	106
2	MgO/γ-Al_2O_3	233	0.43	77
3	ZnO/γ-Al_2O_3	178	0.42	98
4	0.25 Mg/Ca	152	0.37	97
5	0.5 Mg/Ca	150	0.39	105
6	1 Mg/Ca	180	0.40	90
7	5 Mg/Ca	174	0.42	95
8	0.25 Zn/Ca	171	0.37	86
9	0.5 Zn/Ca	161	0.38	95
10	1 Zn/Ca	158	0.38	96
11	5 Zn/Ca	140	0.41	117
12	γ-Al_2O_3	252	0.36	58

In the first place, it is observed that all the catalysts have a specific surface area smaller than that of the γ-Al_2O_3 support. As a general trend, the addition of a second metal oxide together with CaO increases the surface area, in comparison with that of the CaO/γ-Al_2O_3 catalyst (entry 1), except in the case of the 5Zn/Ca catalyst (entry 11). However, for each series of catalysts (Mg/Ca and Zn/Ca) different effects are observed.

As it has been reported in bibliography for similar MgCa catalysts [22], it is observed that by increasing the MgO content in the mixed oxides, the S_{BET} value presents variations (entries 4-6). An exception is the 5Mg/Ca catalyst (entry 7) for which a slight decrease in the specific surface area was observed. For the catalysts of the Zn/Ca series, it was found that the surface area decreases as a higher proportion of Zn is added (entries 8-11). This effect is opposite to that expected taking into account the S_{BET} values of the pure oxide catalysts ZnO/γ-Al_2O_3 (entry 3) and CaO/γ-Al_2O_3 (entry 1) and could be assigned to a differential precipitation of the carbonates of both metals in the initial stages of preparation of the catalysts [16].

The analysis of the pore volume of the different studied catalysts does not reveal too much difference with the value of the starting γ-Al_2O_3, while the pore diameter values are in all the cases greater than that of the pure γ-Al_2O_3.

The N_2 adsorption isotherms obtained for the catalysts of the Mg/Ca and Zn/Ca series are presented in Figures 1 and 2, respectively. In each figure, the isotherms obtained for the pure supported oxides have been included for comparative purpose. All the obtained isotherms can be described as type IV according to the IUPAC classification, which correspond to mesoporous materials [23]. Point B is located at very low relative pressures, indicating the presence of micropores.

The isotherms obtained for the Mg/Ca mixtures with different metals ratio (Figure 1) are very similar to each other, looking more like the isotherm of MgO/γ-Al_2O_3 as the proportion of Mg increases.

Figure 2 shows the N_2 adsorption isotherms obtained for the catalysts of the Zn/Ca series. The presence of a hysteresis cycle indicates that percolation occurred in the pores of the material during desorption. The catalysts containing a higher proportion of Zn (Zn/Ca = 0,5, 1 and 5) present desorption branches of irregular shape, indicating percolation in different types of pores.

The X-ray diffraction patterns of both series of catalysts studied are presented in Figures 3 and 4. Both figures include the diffractograms of the corresponding pure supported oxides. Figure 3 corresponds to the Mg/Ca catalysts series. In that figure, the X-ray diffractograms corresponding to CaO/γ-Al_2O_3(curve a) and Mg/Ca mixtures of 0,25, 0,5 and 1 ratios (curves b, c and d, respectively), signals belonging to the CaO phase, located at 2θ° = 29.5°, 37.5 ° and 39.5° were observed (JCPDS card No 43-1001).

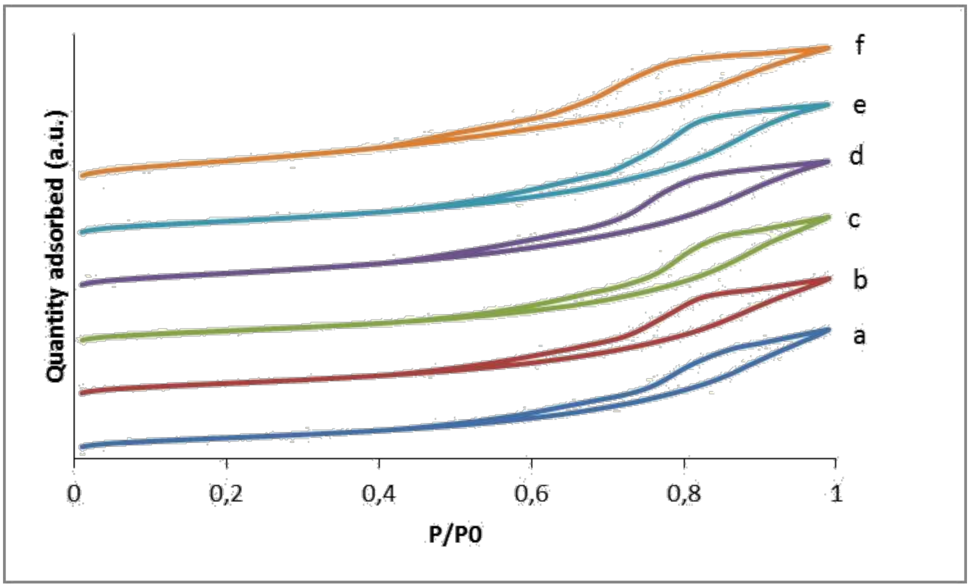


Figure 1. N_2 adsorption isotherms for the catalysts of the Mg/Ca series. The isotherms corresponding to CaO/γ-Al_2O_3 and MgO/γ-Al_2O_3 are also included. a: CaO/γ-Al_2O_3; b: 0.25 Mg/Ca; c: 0.5 Mg/Ca; d: 1 Mg/Ca; e: 5 Mg/Ca; f: MgO/γ-Al_2O_3

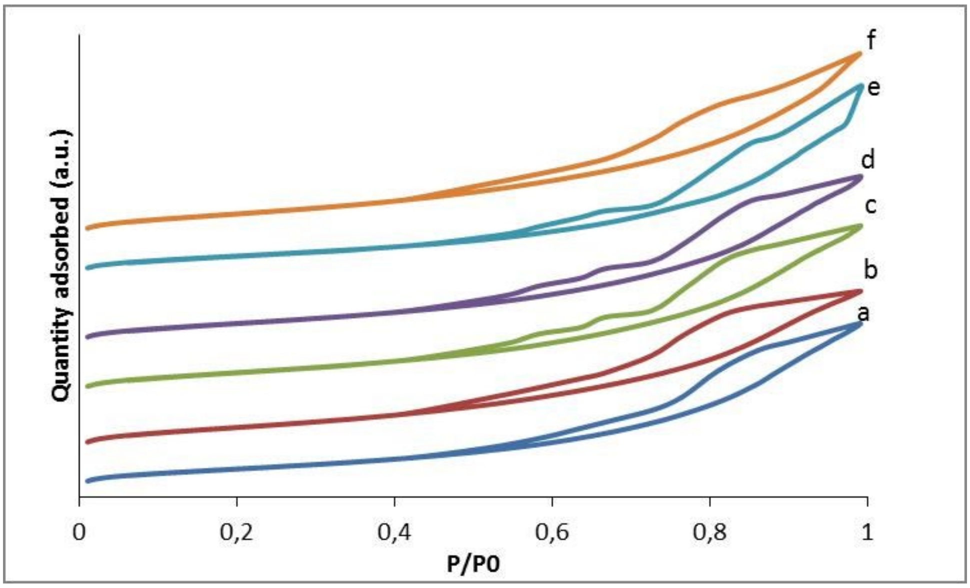


Figure 2. N_2 adsorption isotherms for the catalysts of the Zn/Ca series. The isotherms corresponding to CaO/γ-Al_2O_3 and ZnO/γ-Al_2O_3 are also included. a: CaO/γ-Al_2O_3; b: 0.25 Zn/Ca; c: 0.5 Zn/Ca; d: 1 Zn/Ca; e: 5 Zn/Ca; f: ZnO/γ-Al_2O_3.

In the spectrum of the 0.5 Mg/Ca sample (curve c) a peak at 2θ = 53° appears, which also corresponds to a crystalline phase of CaO (JCPDS card n° 43-1001). In the diffractogram corresponding to the 5 Mg/Ca catalyst (curve f), no peaks assignable to neither the CaO phase nor the MgO phase are observed. In the X-ray diffraction pattern of the MgO/γ-Al_2O_3

catalyst, no peak corresponding to a crystalline phase of magnesium oxide was detected. It is well established in the literature that MgO forms very small particles [24]. Most likely in both cases (5Mg/Ca and MgO/γ-Al_2O_3 catalysts) because of the small size of the particles, the XRD technique does not allow defining a crystalline phase. In this same sense, Taufiq-Yap et al. have reported Mg and Ca mixed oxides catalysts, where the formation of mixed crystalline phases is not observed, and the MgO particles are much smaller than those of CaO [17]. The wide peaks belonging to the γ-Al_2O_3 support, located at 2θ = 37.6°, 45.8° and 66.8° (JCPDS card n° 29-1480), are present in the six diffractograms of Figure 3.

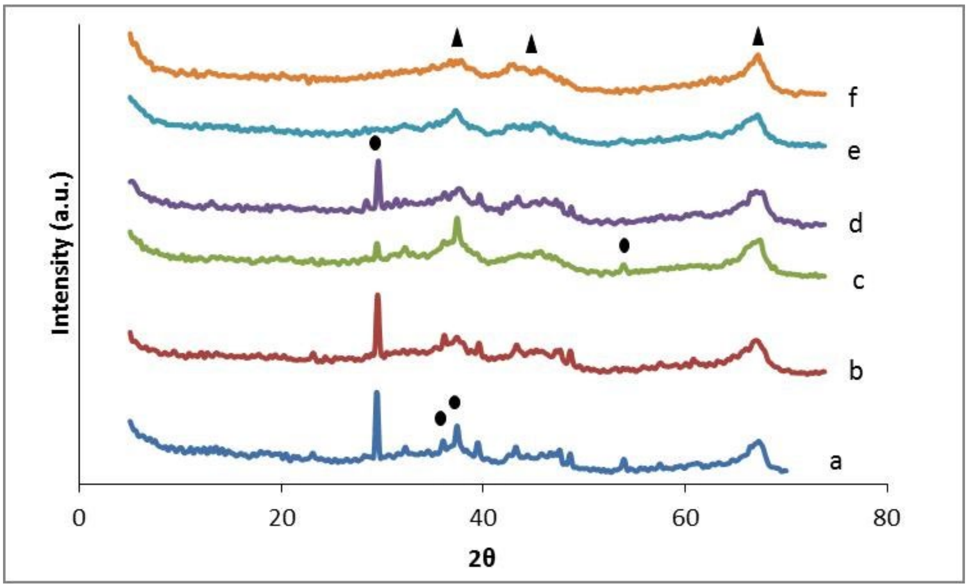


Figure 3. XRD patterns obtained for the catalysts of the Mg/Ca series and the pure supported oxides, MgO/γ-Al_2O_3 and CaO/γ-Al_2O_3. a: CaO/γ-Al_2O_3; b: 0.25 Mg/Ca; c: 0.5 Mg/Ca; d: 1 Mg/Ca; e: 5 Mg/Ca; f: MgO/γAl_2O_3. ▲: γ-Al_2O_3 phase; ●: CaO phase.

From the patterns of Figure 3, and using Equation 1, the crystallite size for CaO phase (the only one that was identified from the diffraction patterns) was calculated. The results are presented in Table 2.

The data show a decrease in the crystallite size of the CaO particles by increasing the proportion of Mg, up to the point where it is not possible to calculate that size due, to the absence of signals in the diffraction pattern.

Figure 4 shows the X-ray diffraction patterns obtained for the Zn/Ca catalyst series. In the diffractograms of the samples with higher calcium proportion (samples 0.25 Zn/Ca, curve (b) and 0,5 Zn/Ca, curve (c)) peaks corresponding to the CaO phase are observed at 2θ = 29° and 37° (JPCDS card N° 43-1001). The diffractogram of the sample 1Zn/Ca (curve (d)) shows the peak at 2θ = 29° of CaO phase significantly smaller than in the above samples, while the peaks of the zincite phase of ZnO located at 2θ = 31.7°, 34.4° and 36.2° (JPCDS card N° 36-1451) start to develop. These peaks are markedly more defined in the 5 Zn/Ca catalyst, due to the high proportion of ZnO present. Again, in all the diffractograms the broad peaks belonging to γ-Al2O3, located at 2θ = 37.6°, 45.8° and 66.8° (JPCDS card N° 29-1480) are present. Crystallite size of the catalysts were calculated using Scherer's equation (Equation 1), based on the most intense peak for both CaO and ZnO (Table 3).

Table 2. Crystallite sizes for the CaO phase in the Mg/Ca catalyst series

Catalyst	Crystallite size of CaO phase (nm)
$CaO/\gamma\text{-}Al_2O_3$	32
0.25 Mg/Ca	67
0.5 Mg/Ca	47
1 Mg/Ca	44
5 Mg/Ca	-
$MgO/\gamma\text{-}Al_2O_3$	-

As in the case of the catalysts of the Mg/Ca series, the crystallite size of CaO decreases markedly as the amount of the second metal increases (in this case, Zn). This fact may be due not only to the lower amount of Ca present, but to an interaction between both metals. Regarding zinc, the crystallite size for the ZnO phase could only be calculated for the 5Zn/Ca and $ZnO/\gamma\text{-}Al_2O_3$ catalysts, due to the low crystallinity detected for the rest of the catalysts in the series.

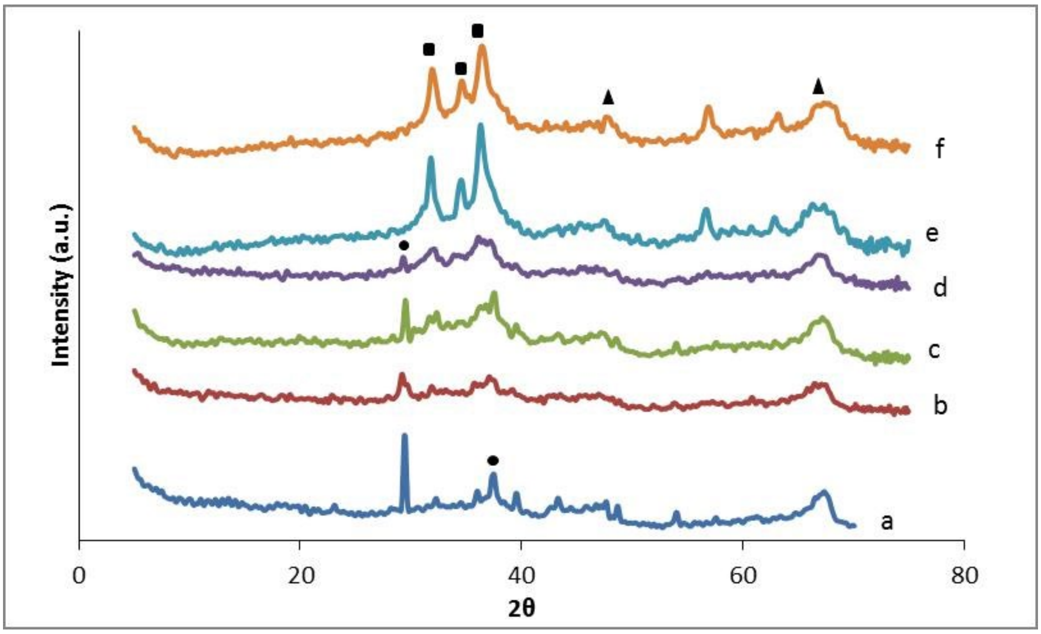


Figure 4. XRD patterns obtained for the catalysts of the Zn/Ca series and the pure supported oxides, ZnO/γ-Al_2O_3 and CaO/γ-Al_2O_3. a: CaO/γ-Al_2O_3; b: 0.25 Zn/Ca; c: 0.5 Zn/Ca; d: 1 Zn/Ca; e: 5 Zn/Ca; f: ZnO/γ-Al_2O_3. ▲: γ-Al_2O_3 phase, ●: CaO phase, ■: ZnO

Table 3. Crystallite sizes for CaO and ZnO phases in the Zn/Ca catalyst series

Catalyst	Crystallite size (nm)	
	CaO	ZnO
CaO/γ-Al_2O_3	32	-
0.25Zn/Ca	31	-
0.5Zn/Ca	24	-
1Zn/Ca	13	-
5Zn/Ca	-	6
ZnO/γ-Al_2O_3	-	18

The images of all the prepared catalysts obtained by scanning electron microscopy (SEM) are shown in Figures 5 and 6. Figure 5 presents the images obtained for the catalysts of the Mg/Ca series, including the micrographs of the pure oxide catalysts, MgO/γ-Al_2O_3 and CaO/γ-Al_2O_3. In all the cases, quite porous surfaces exhibiting small particles on it were observed. The spindle-shaped particles correspond to the CaO phase, and cannot be observed in the catalysts with higher Mg proportion (1Mg/Ca and 5Mg/Ca). SEM micrographs of Mg-containing samples show that the MgO particles are very small, which agrees with the absence of peaks corresponding to that phase in the diffraction patterns.

Figure 6 shows the SEM images obtained for the catalysts of the Zn/Ca series, including CaO/γ-Al_2O_3 and ZnO/γ-Al_2O_3 catalysts. As in the case of the Mg/Ca catalyst series, the surfaces have roughness and a very porous appearance. As the proportion of Zn increases, more *flake-like* particles, belonging to the ZnO phase, are observed. These *flake-like* particles are well defined in the ZnO/γ-Al_2O_3 catalyst.

Catalytic activity

Both series of catalysts, Mg/Ca and Zn/Ca were evaluated in the transesterification of soybean oil with methanol. Figure 7 depicts the conversion results obtained at 2, 4 and 6h of reaction for the Mg/Ca catalysts series, including the pure CaO/γ-Al_2O_3 and MgO/γ-Al_2O_3 catalysts. As can be seen, the final conversion of triglycerides increases as the proportion of MgO in the catalyst increases up to a Mg/Ca ratio of 1, then it keeps almost constant. However, none of the mixtures exceeded the conversion obtained with the pure CaO/γ-Al_2O_3 or MgO/γ-Al_2O_3 catalysts.

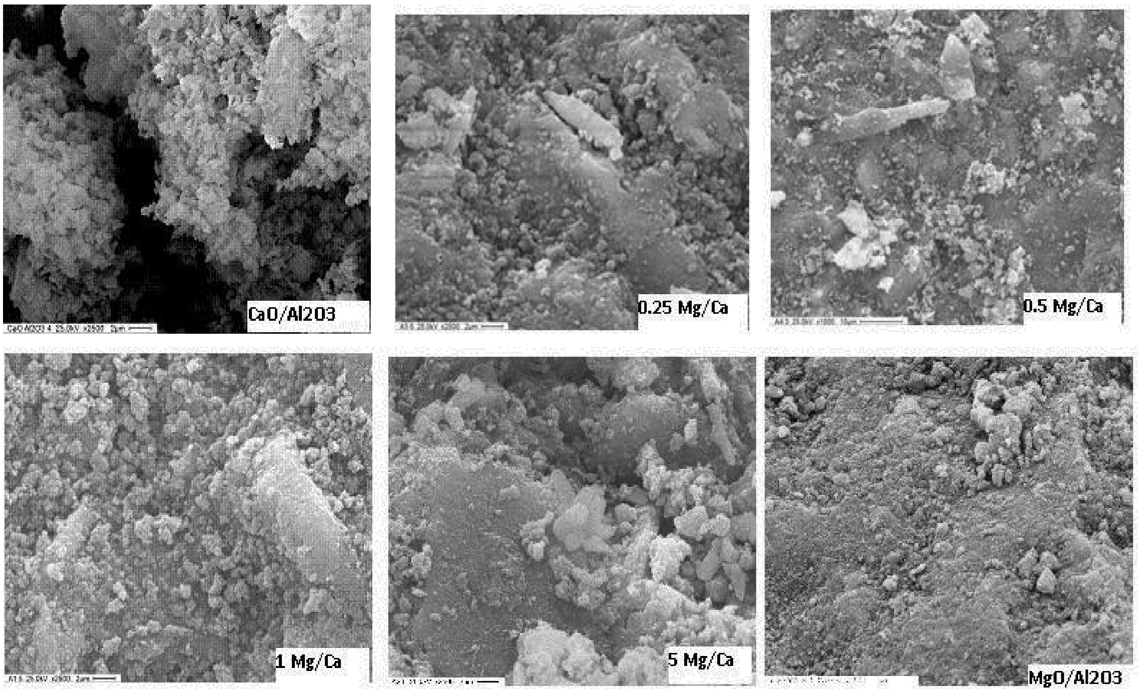


Figure 5. SEM micrographs obtained for the catalysts of the Mg/Ca series (magnification: 2500X) (The identification of the sample is given in the insert in the lower right corner of each image).

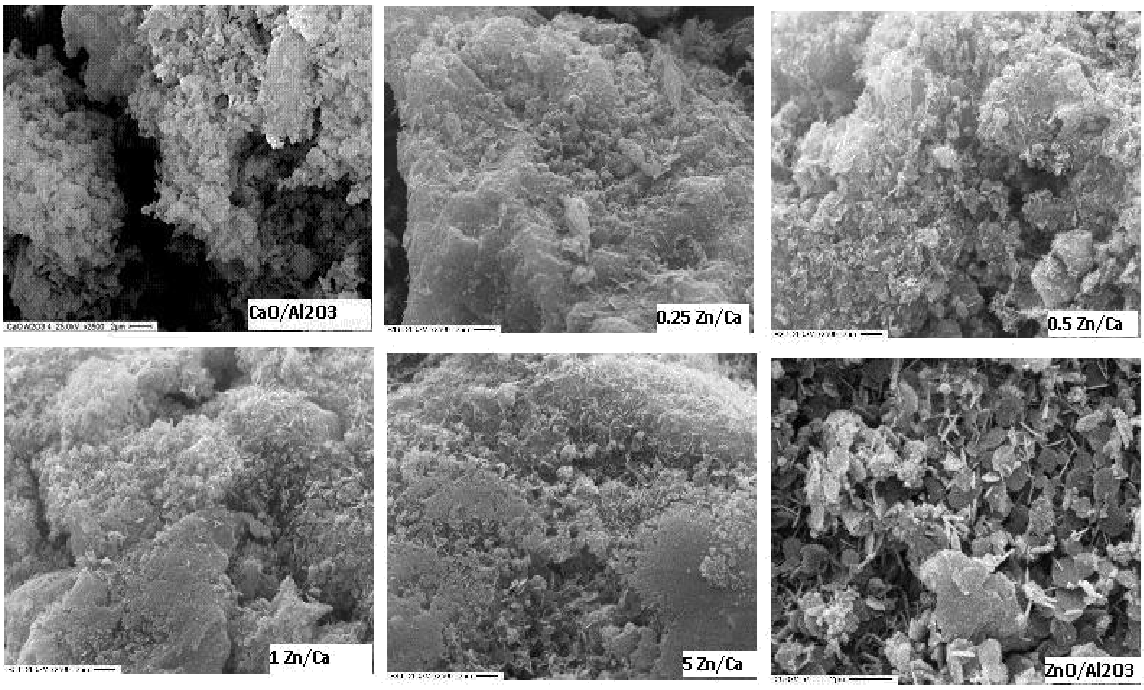


Figure 6. SEM micrographs obtained for the catalysts of the Zn/Ca series (magnification: 2500X) (The identification of the sample is given in the insert in the lower right corner of each image).

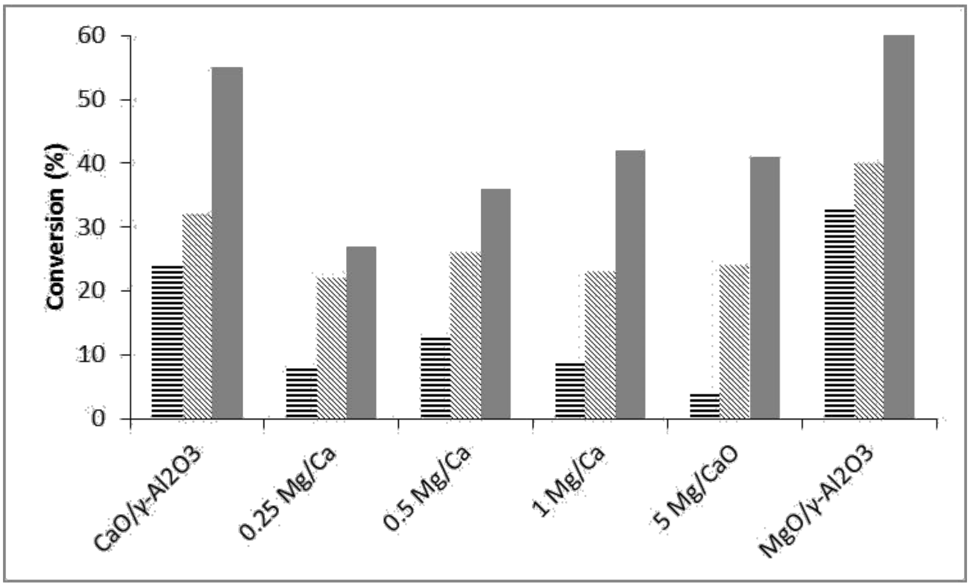


Figure 7. Conversion of triglycerides obtained for the Mg/Ca catalysts series in the transesterification of soybean oil with methanol, at 2, 4 and 6 h of reaction (for experimental conditions, see the Materials and Methods section).▤: 2h; ▧: 4h; ■: 6h

The selectivity to mono- (MG) and diglycerides (DG) and to fatty acids methyl esters (FAME), as well as the FAME yield, are shown in Figure 8.

It is worth noting that, even with the lowest MgO addition (0.25Mg/Ca catalyst), the selectivity towards FAME is highly increased, in relation to that of the CaO/γ-Al_2O_3 catalyst. This catalyst showed a selectivity towards FAME of 32%, whereas the selectivities to FAME of all the catalysts containing Mg, as well as that of the MgO/γ-Al_2O_3 catalyst, were very close to 100%. This fact indicates that the reaction proceeds to the desired stage, which is the conversion of each triglyceride molecule in three methyl esters. It is clear that the most important contribution towards obtaining these good results comes from the MgO, which as a function of its higher basicity and surface area provides the active sites for the transesterification to occur [25].

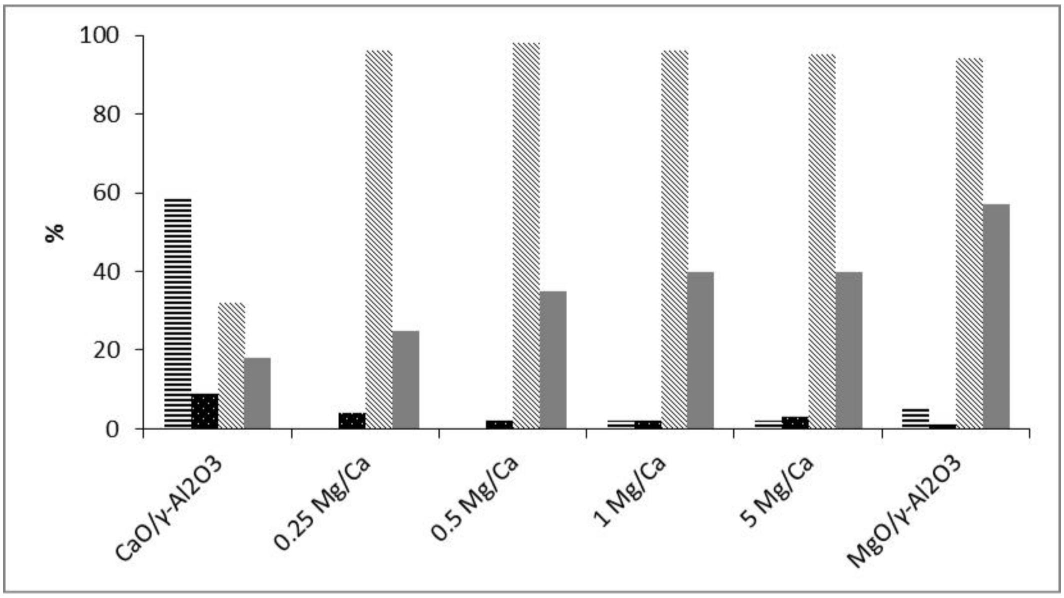


Figure 8. Selectivity (%) to monoglycerides (MG), diglycerides (DG) and FAME and FAME yield for the Mg/Ca series catalysts and the pure oxide MgO/γ-Al_2O_3 and CaO/γ-Al_2O_3catalystsin the transesterification of soybean oil with methanol, after 6 h of reaction. ▤: S_{MG}; ■: S_{DG}; ▧ :S_{FAME}; ■: FAME yield.

With regard to the CaO/γ-Al_2O_3 catalyst, although it presented a conversion value higher than that of any of the Mg/Ca mixtures, its selectivity is mainly directed towards monoglycerides (*ca.* 60%), that is why its FAME yield was so low (18%). The formation of calcium glyceroxide during the transesterification reaction may be responsible for this poor FAME yield of CaO/γ-Al_2O_3 catalyst. The maximum FAME yield among the Mg/Ca catalysts was found for the 1Mg/Ca and 5Mg/Ca samples (40% in both cases). This value, however, does not exceed the FAME yield obtained with the MgO/γ-Al_2O_3 catalyst (57%).

The influence of the surface area on the performance of the Mg/Ca series catalysts can be analyzed in the light of the results reported in Table 1. In that table, it can be observed that the surface area increases as the Mg/Ca ratio increases, with respect to the CaO/γ-Al_2O_3 catalyst. According to the mechanism usually proposed for the transesterification reaction using heterogeneous catalysts, a higher surface area leads to a higher number of pores and, consequently, active sites for the catalysis to take place [8, 25]. In this sense, it is observed that 1 Mg/Ca and 5 Mg/Ca catalysts showed almost equal FAME yields (*ca.* 40% in both cases), possibly because their specific BET surfaces areas are also similar (180 and 174 m^2/g for 1Mg/Ca and 5Mg/Ca, respectively).

As a next step, the effect of mixing ZnO and CaO to obtain a Zn/Ca series of catalysts was studied. Figure 9 presents the conversion results obtained for the catalysts of the Zn/Ca series, in which the catalytic performance of the pure $CaO/\gamma\text{-}Al_2O_3$ and $ZnO/\gamma\text{-}Al_2O_3$ is also included.

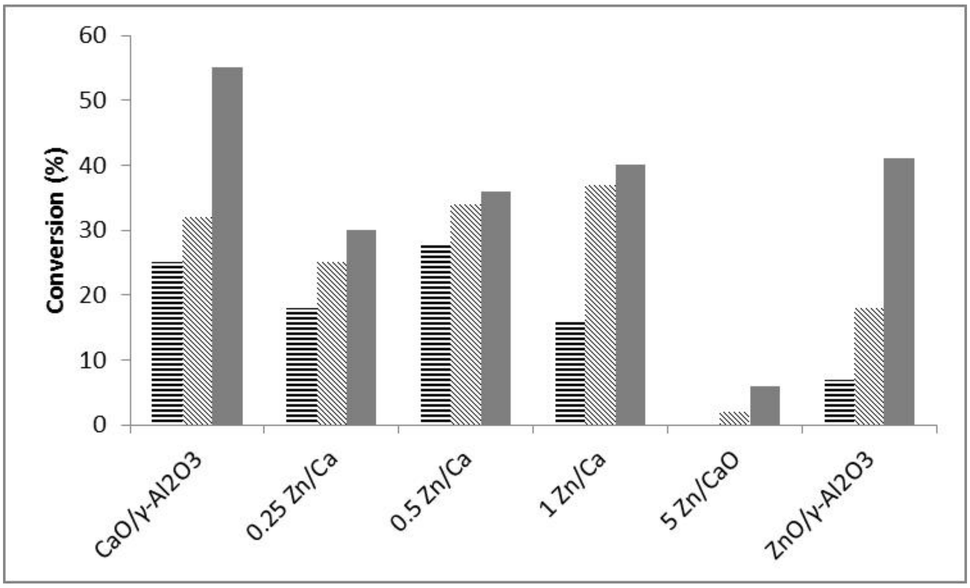


Figure 9. Conversion of triglycerides obtained for the Zn/Ca catalysts series in the transesterification of soybean oil with methanol, at 2, 4 and 6 h of reaction (for experimental conditions see the Materials and Methods section); ▤:2h; ▧: 4h; ■: 6h

As in the case of the addition of MgO, it was found that the addition of ZnO to the CaO catalyst did not improve the conversion of triglycerides, since the values obtained with all the catalysts of the Zn/Ca series were lower than the conversion achieved by the $CaO/\gamma\text{-}Al_2O_3$ catalyst. As a general trend, it is observed that, within the series of catalysts, when increasing the proportion of Zn, better conversion results are obtained. A surprisingly low result was obtained with the 5 Zn/Ca catalyst, which reached a conversion even lower than that of the $ZnO/\gamma\text{-}Al_2O_3$ catalyst (only 6% vs. 41%). These results are in agreement with those presented by Ngamcharussrivichai *et al.* [16], who found that when the amount of Zn was increased over a Ca/Zn ratio of 1, the transesterification activity of the catalyst markedly decreased.

In any case, it can be said that the addition of Zn fails to generate a system with a better catalytic activity than that of the base $CaO/\gamma\text{-}Al_2O_3$ system. This can be attributed to the Lewis acid characteristics of Zn, which decreases the basicity of the catalyst, a fact that is not favorable for the transesterification reaction of oils with low amounts of free fatty acids, such as soybean oil [26].

When analyzing the data of FAME selectivity obtained (Figure 10), it is observed that it improves remarkably, regardless of the proportion of Zn in the catalyst. The catalysts 0.25 Zn/Ca and 0.5 Zn/Ca reached FAME selectivities very close to 100%, thus improving the performance of the pure oxide catalysts CaO/γ-Al_2O_3 (32%) and ZnO/γ-Al_2O_3 (75%).

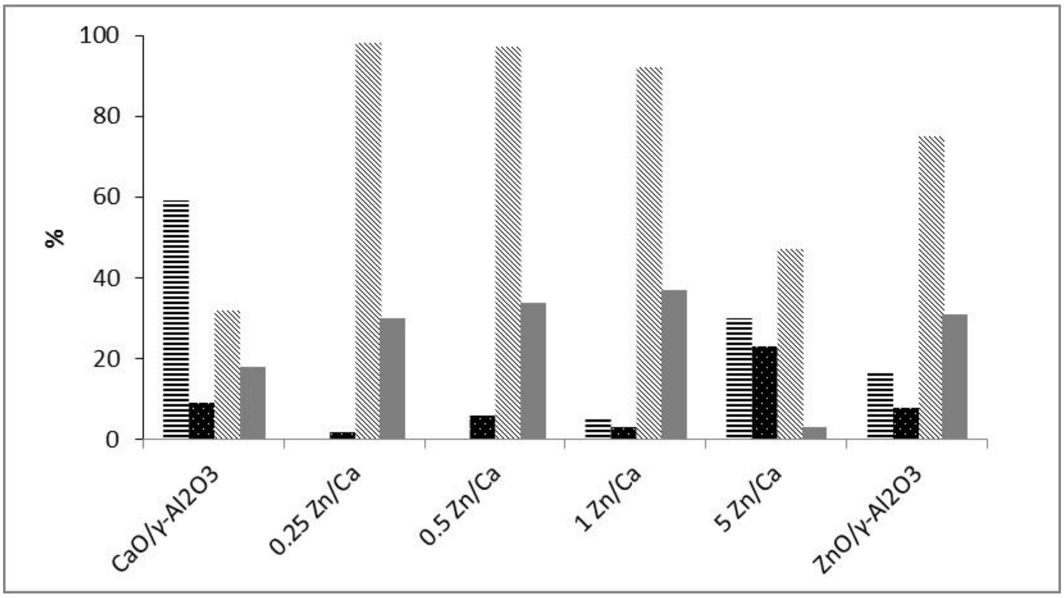


Figure 10. Selectivity (%) to monoglycerides (MG), diglycerides (DG) and FAME and FAME yield for the Zn&Ca series catalysts and the pure oxides ZnO//γ-Al_2O_3 and CaO/γ-Al_2O_3 catalysts in the transesterification of soybean oil with methanol, after 6 h of reaction. ▤: S_{MG}; ▩: S_{DG}; ▧: S_{FAME}; ■: FAME yield.

A subsequent increase in the proportion of ZnO does not improve the results of the transesterification, since the selectivity to FAME decreases as a consequence of the increase in selectivity to monoglycerides (MG).

4. Conclusions

In the present work, CaO-MgO and CaO-ZnO supported catalysts have been synthesized, containing different proportions of each of the metals. All the prepared catalysts were characterized and evaluated in the transesterification of soybean oil with methanol.

The catalysts were prepared by co-impregnating the corresponding nitrates on a dispersion of γ-Al_2O_3, controlling the pH of the precipitation. The use of the support provided a considerable surface area where the catalysis could take place. All the catalysts were classified as mesoporous.

All the catalysts presented acceptable conversion results, however, the behavior of the Mg/Ca and Zn/Ca series was different. The addition of Mg in the catalysts of the Mg/Ca series, although it did not produce an increase in the conversion of triglycerides, markedly improved the FAME selectivity, reaching almost 100% regardless of the Mg/Ca ratio. MgO makes a significant contribution to the basicity of the catalyst, which favors the transesterification reaction, taking place in the basic sites of the catalyst.

In the case of the Zn/Ca series, all the mixtures, except for the 5Zn/Ca catalyst, showed FAME selectivities very close to 100%. Although the mixtures did not exceed the conversion exhibited by the pure CaO/γ-Al_2O_3 and ZnO/γ-Al_2O_3 oxides, they showed higher FAME yields, due to the increase in selectivity.

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