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Transesterification of vegetable oils over CaO catalysts

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ABSTRACT

The transesterification of different vegetable oils to biodiesel under thermal and ultrasound activation was carried out using commercial solid base CaO (CS) and microcrystalline CaO particles (MS) catalysts. The last sample was prepared from the first one using a simple, green and reproducible method and characterized by XRD, LLS, DRIFT and DR-UV–Vis techniques. Each catalyst (i.e., CaO (CS) and CaO (MS)) was used as well, freshly pre-activated at 623, 788 and 873 K or ultrasonicated at room temperature, in methanol. Ultrasounds activation of the reactant molecules led to conversions of the vegetable oil of 97% at 348 K for a molar ratio of methanol to vegetable oil of 4:1. Ultrasonicated catalysts can be reused for several runs without significant deactivation.

1. Introduction

Biodiesel, defined as fatty acids alkyl esters (FAAE) obtained by the transesterification of vegetable oils or animal fats with alcohols (e.g., methanol, ethanol) (Fig. 1), is a renewable and biodegradable fuel used as alternative energy source for diesel engines, with superior properties such as higher cetane number, higher flash point or better lubricity efficiency [1,2]. As transesterification agent methanol is preferred due to its economical advantages

The transesterification reaction is generally catalyzed by acids [3] bases [4] and enzymes [5]. Although using enzymes leads to satisfying selectivities, the applicability of this method is economically limited by the high price of the enzymes, the very large reaction volumes and the reaction rates. On the other hand, in non-catalytic conditions but in supercritical methanol the process involves temperatures up to 675 K, pressures of 65 MPa and 42:1 alcohol:oil molar ratio, limiting its application to industrial level [6,7].

Currently, the production of biodiesel at an industrial level is developed by using homogenous basic catalysts, such as NaOH, KOH or K and Na methoxides [8]. However, the performance of homogenous basic catalysts in the transesterification process depends on the free fatty acid (FFA) or water content [9,10]. Therefore a content higher than 0.5 wt.% FFA or 0.06 wt.% water lead to the soap formation and to the reduction of the homogeneous basic catalyst activity. A solution for overcoming this problem is represented by the use homogeneous acid catalysts (H_2SO_4, H_2SO_3, HNO_3) because their performances are not strongly affected by the presence of free fatty acids or water and they can simultaneously catalyze both esterification and transesterification reactions [11]. However, these catalysts involve longer reaction times (up to 96 h) and higher alcohol:oil molar ratios (up to 150:1 mole) [12]. Furthermore the acid catalysts are more corrosive than the basic ones limiting their applications in industry. One of the greatest disadvantages of using homogeneous catalysts is the necessity of a purification step of the reaction that is a non-friendly environmental process producing high amounts of waste waters. Solving these problems may be achieved by using heterogeneous catalysts, which can be easily recovered at the end of the reaction, and also used for more reaction cycles without any pretreatment. In addition, heterogeneous catalysts are not corrosive [13].

Among heterogeneous catalysts, CaO received a special attention a great advantage of its using being cheap sources like limestone and calcium hydroxide [14]. Suppes et al. [15] reported conversions higher than 95% in the soybean oil transesterification using calcium carbonate but only above 473 K. Liu et al. [16] tested calcium oxide in the transesterification of soybean oil, using a 12:1 molar ratio of methanol to oil to obtain a conversion rate of 95%. Kouzu et al. [17] reported that CaO obtained from calcination of pulverized limestone shows a high activity in transesterification of refined soybean oil. The yield of methyl esters reached 93% after 1 h reaction time at methanol reflux temperature and methanol to oil molar ratio of 12:1. There are also reports showing that CaO is sensible at the reaction medium [18–21], and also on the fact the catalytic activity of CaO can be regenerated if it is subjected to a thermal reactivation in order to remove the main poisoning species (mostly carbonate groups) from the surface [22]. This oxide is active in other catalytic reactions as well [23–26].

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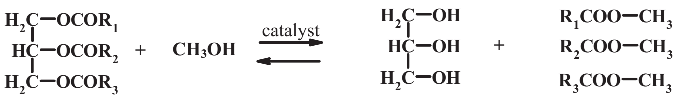

Fig. 1. The transesterification of triglycerides with methanol.

The aim of this study is to compare the behavior of two different calcium oxide catalysts in the transesterification of sunflower, soybean and rapeseed oils working under autoclave and ultrasound conditions.

2. Experimental

2.1. Catalyst preparation

Calcium oxide (MS) was prepared accordingly to the procedure proposed by Klabunde [27]. Accordingly, 5 g of commercially available CaO was boiled in 500 mL of distilled water overnight under reflux and vigorous stirring. After cooling, the slurry was filtered, and the filter cake dried under vacuum at 393 K. The dried powder was heated at 773 K under vacuum for 10 h. For comparison, a commercial CaO (CS) sample, purchased from Aldrich, has also been used. For simplicity, CaO prepared from commercial CaO is denoted as CaO (MS) (MS = Microcrystalline Sample) while the commercial CaO sample is denoted as CaO (CS) (CS = Commercial Sample).

2.2. Catalyst characterization

The textural characteristics of CaO (MS) were determined using N_2 adsorption/desorption isotherms at −196 °C acquired with a Micromeritics ASAP 2020. X-ray diffraction (XRD) patterns were recorded with a Shimadzu XRD 7000 diffractometer using a CuKα radiation. The radiation intensity was measured by scanning in the 2θ range between 10° and 60°. DRIFT investigation of the catalysts was carried out using a Thermo Nicolet 4700 spectrometer, with the following parameters: 300 scans, 600–4000 cm^{-1} scan range at a 4 cm^{-1} resolution. DR-UV-Vis spectra were collected with an Anlytik Jena Specord 250 spectrometer in the 200–800 nm range. Particles size determination of catalyst before and after reaction was carried out with a Mastersizer 2000 device which used laser light scattering (LLS) technique with following parameters: two laser sources with wavelengths at 455 nm and 653 nm respectively. The fresh or tested CaO were dispersed in 2-propanol before being analyzed.

2.3. Catalytic tests

Typical experiments were carried out using 23 mL sunflower, rapeseed or soybean oil, 5 mL methanol (molar ratio oil:methanol of 1:4) and 300 mg CaO catalyst. Each catalyst was tested as well, thermal pre-activated at 623, 788 and 873 K, under argon for 2 h or ultrasonicated in methanol, for 1 h, at room temperature. The fresh activated catalysts were kept in a nitrogen glass box to protect them by the water and carbon dioxide from atmosphere. The catalyst was first dispersed in methanol directly in the glass box then vegetable oil was added. The reaction was carried out either in a stainless steel autoclave of 50 mL (thermal activation) or under ultrasound irradiation. Under autoclave conditions the stirring rate was 1200 rpm, reaction temperatures of 313–348 K and reaction time 10–120 min. The ultrasound experiments were carried out with an Elma Transsonic 460/H bath working at a frequency of 35 kHz using the same reaction conditions as in thermal activation. The temperature inside the reaction vessel was controlled using a thermocouple. The analysis of the reaction products was made using a Varian ProStar 310 HPLC equipped with a C18 column with inner diameter of 4 mm and the length of 30 cm. The mobile phase was a mixture of methanol (pump A) and isopropanol:hexan in a volume ratio 5:4 (pump B), A:B 85:15 with a flow of 0.8 mL min^{-1}. The analysis was made with a UV–Vis detector working at $\lambda = 205$ nm. The identification of reaction products was carried out using a GC–MS Carlo Erba Instruments QMD 1000 equipped with a Factor Four VF-5HT column with the following characteristic: 0.32 mm × 0.1 μm × 15 m. The analysis program was assigned using a temperature program and a pressure of 58 kPa with a He as the carrier gas. The samples were solubilized in CH_2Cl_2.

The experimental procedure to test the recyclability of the catalysts was the following. The first run carried out was described above. Before stopping the reaction stirring an aliquot was sampled and analyzed following the method described. After stopping the stirring the mixture was centrifuged at 6000 rpm for 10 min. The recovered solid was subjected the reaction-sampling-analysis-centrifugation sequence for several successive runs out of the activation-outgassing step.

The leaching of calcium was checked by ICP-AES technique (Analyst 800 Perkin–Elmer apparatus) at $\lambda = 422.8$ nm (typical for Ca). The sample were prepared using a typical procedure for the analysis of oil: in a digestion vessel to 0.5 mL sample, 10 mL of nitric acid (65 wt.%) and 2 mL of hydrogen peroxide (30 wt.%) was added and the obtained mixture was heated under microwaves at 483 K for 15 min.

3. Results and discussions

3.1. Catalysts characterization

The textural characteristics of prepared catalysts are presented in Table 1. CaO (MS) catalyst exhibits both a high surface area and pores enough large to allow the penetration of triglyceride to active basic sites. However from textural point of view there is a major difference between the CaO (MS) and the commercial CaO (CS) catalyst (Table 1).

Powder X-ray diffraction (XRD) has been extremely helpful in showing that the small size of the MS-sample did not cause the change in the position of the X-ray reflections of the commercial CaO sample (Fig. 2). Thus, the prepared CaO (MS) possesses the expected cubic internal crystal structure, characterized by three strong diffraction peaks at 2θ 32°, 37° and 53° associated to the (1 1 0), (2 0 0) and (2 2 0) reflections. The XRD patterns are in agreement with data already reported [28]. The calculus of the particle size using the Scherrer's formula indicated 22 nm for CaO (MS) and 34 nm for CaO (CS), respectively.

The IR spectra of investigated catalysts are presented in Figs. 3 and 4. In the case of fresh CaO (MS) catalyst, an intense band was observed at 3645 cm^{-1}, due to the vibration of the OH groups attached to Ca^{2+}. Thermal activation under argon caused an almost total extinction of this band, while the transesterification reaction led to apparition of a broad band in the 3700–3000 cm^{-1} range (Figs. 3 and 4). This fact is due to the OH group vibrations of the bound H_2O on the surface of the solid sample. Moreover, the band at 1648 cm^{-1} [29] confirmed the adsorption of water on the catalyst surface.

Table 1
Textural characterization of prepared catalysts.

Catalyst	BET surface area ($m^2\ g^{-1}$)	Pore volume (cm^3/g)	Average pore size (nm)
CaO (MS)	74	0.13	20
CaO (MS) ultrasonicated	84	0.13	21
CaO (CS)	2	0.02	-

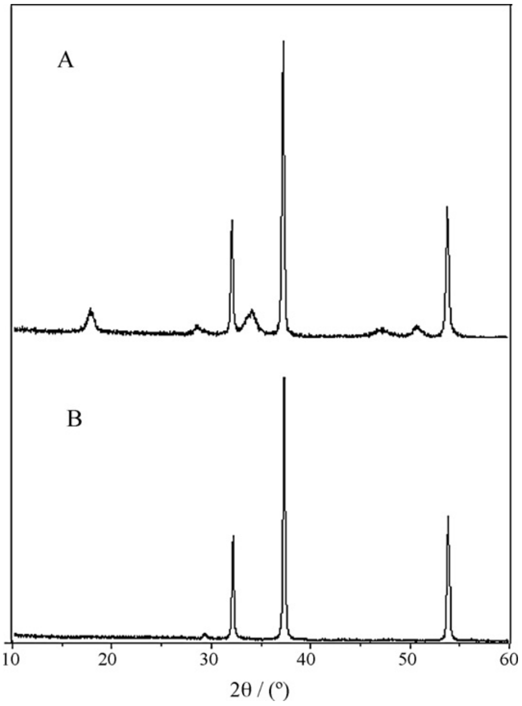

Fig. 2. XRD pattern of the commercial CaO (CS) (A) and microcrystalline CaO (MS) (B) catalysts.

The bands at 1480, 1433, 1070 and 870 cm^{-1} are characteristic for symmetric and asymmetric stretching vibrations of the O–C–O bonds. These bonds are the result of the attachment of the monodentate carbonate on the surface of the CaO due to the short contact of the catalyst with the air from the room [30].

Furthermore, after reaction, in the 3000–2800 and 1300–1000 cm^{-1} range, new bands assigned to C–H, C–O–C, –C–O, and –C═O vibrations were observed. These bands resulted from the adsorption of glycerides, glycerol or methyl ester of fatty acids on the surface of the catalyst.

Fig. 5 shows DR-UV–Vis spectra of fresh and tested CaO catalysts. The UV–Vis spectra of fresh catalyst exhibit two minima of reflectance at 315 nm (I) and 365 nm (II), respectively, which correspond of a charge transfer transition from oxygen surface ($O^{2-}{}_{5C}$ and $O^{2-}{}_{4C}$) to its immediate surroundings [31]. Actually, these sites correspond to the basic centres of the catalysts. After reaction, it was observed a diminution of these bands intensity due to the blockage of these species by the reaction products.

3.2. Catalytic behavior

3.2.1. Transesterification of sunflower oil in autoclave conditions

The catalytic activity of both CaO samples (i.e., CS and MS) depends on the activation temperature. In the case of non-activated catalysts, the active sites are blocked by strongly chemisorbed H_2O and CO_2 molecules, and the conversions are very low (Fig. 6). However, even under these conditions the CaO (MS) catalyst was highly active in comparison with the commercial sample, in agreement with the higher surface area and smaller particle size. The concentration of oxygen ($O^{2-}{}_{5C}$ and $O^{2-}{}_{4C}$) surface species was also higher. Obviously, the incomplete transformation of di- and monoglycerides to methyl esters leads to differences between the conversion and yield in methyl esters (Fig. 6).

Interestingly, like in the case of MgO [32,33], the synthesis of CaO following the (MS) route favored a lower activation temperature than that generally reported in the literature for bulk oxides, typically above 973 K [21]. The behavior of the CaO (CS) catalyst is however similar with that of previously reported bulk oxides.

Recycling tests showed that after the first catalytic cycle both the biodiesel conversion and the yield in methyl esters were not changed, but after the second cycle the conversion decreased with 30% while the yield to methyl esters with 35% (Fig. 7). Such a behavior may be the consequence of the blocking of the active sites with reactants and reaction products or of the Ca^{2+} leaching during transesterification. Although the leaching was clearly evidenced from ICP-AES (e.g., 325 ppm of Ca^{2+} after the second cycle and 825 ppm after the third cycle), such a dramatically decrease of both the conversion and yield is not justified by this effect. Previous data [34] suggested that transesterification takes also place in homogeneous phase on metal alcoxide species. Therefore the only explanation of this behavior could be indeed the blocking of part of catalytic sites with organic molecules. DRIFTs measurements brought arguments in this sense (see Figs. 3 and 4).

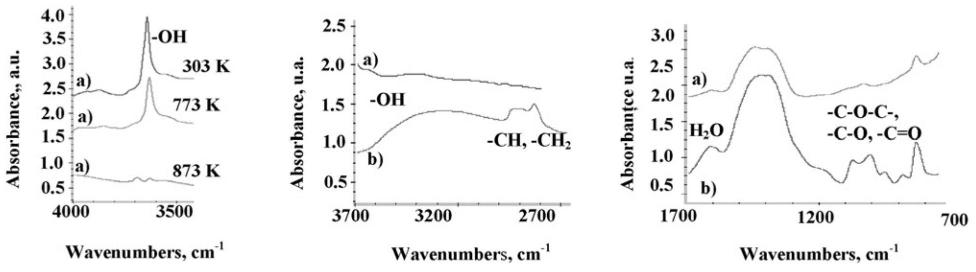

Fig. 3. DRIFT spectra of commercial CaO (CS) fresh (a) and tested under ultrasound conditions (b).

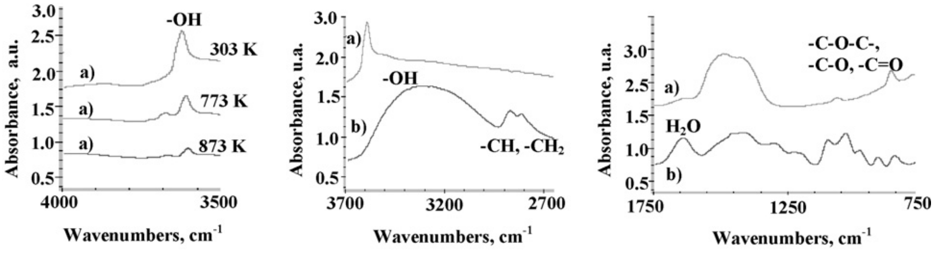

Fig. 4. DRIFT spectra of CaO (MS) fresh (a) and tested under ultrasound conditions (b).

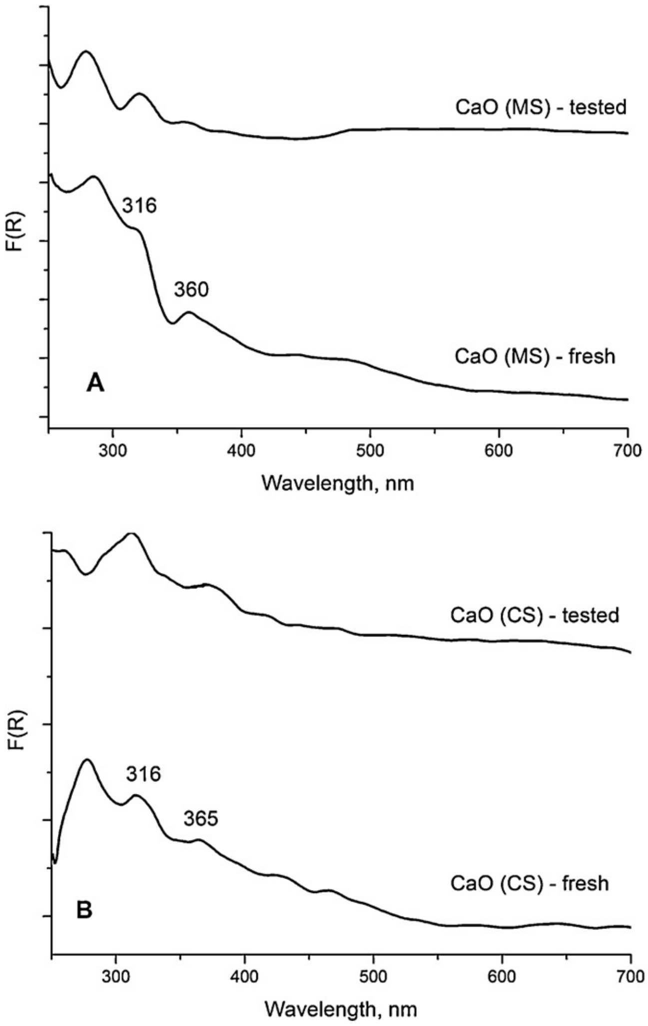

Fig. 5. DR-UV–Vis spectra of fresh and ultrasound tested catalyst: (A) CaO (MS); (B) CaO (CS).

3.2.2. Transesterification of vegetable oils under ultrasound conditions using thermal activated CaO (MS)

The performances of the tested catalysts under ultrasound conditions were superior to those tested under conventional heating conditions. One of the most striking features in sonochemistry is that there is often an optimum value for the reaction temperature. In contrast to classical chemistry, most of the time it is not necessary to go to higher temperatures to accelerate a process. Therefore, although the temperature is a decisive parameter in the transesterification process [35], in this case its increase from 313 K to 348 K was not accompanied by any major change neither of the conversion nor of the yield in methyl esters (Fig. 8). Under these conditions the catalytic performances of the studied materials are comparable with those of the homogeneous base catalysts, under thermal activation. Thus, conversions of sunflower oil reached over 80% in only 45 min. Moreover, the leached Ca^{2+} species (less than 100 ppm) are not active species, probably due to the generation of soaps by interaction with the fatty acids from sunflower oil (Fig. 9). Generally, sonochemistry in heterogeneous systems is the result of a combination of chemical and mechanical effects of cavitation, and it is very difficult to ascribe sonochemistry to any single global origin, other than the overriding source of activity, namely, cavitation [36]. Nevertheless, it was demonstrated that in heterogeneous ionic reactions, as also the transesterification is, only the

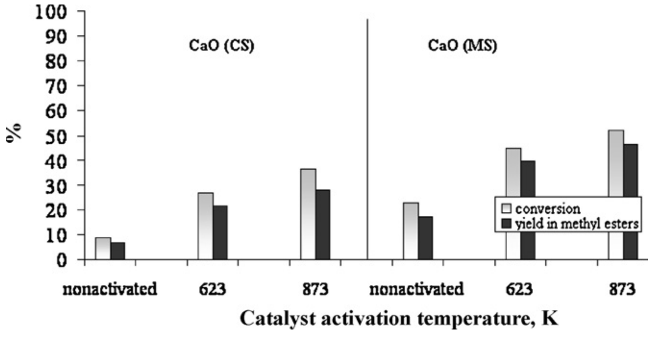

Fig. 6. The variation of the sunflower oil conversion and the yield to methyl esters as a function of the catalyst thermal pre-treatment (reaction conditions: thermal activation, 1200 rpm, 348 K, 45 min).

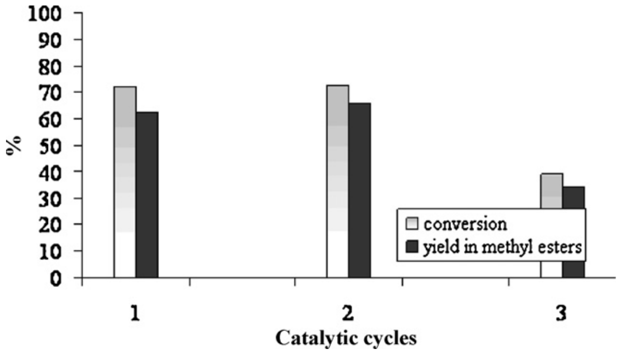

Fig. 7. Catalytic recycling of the microcrystalline CaO (MS) catalyst pre-treated at 788 K (reaction conditions: thermal activation, 1200 rpm, 348 K, 2 h).

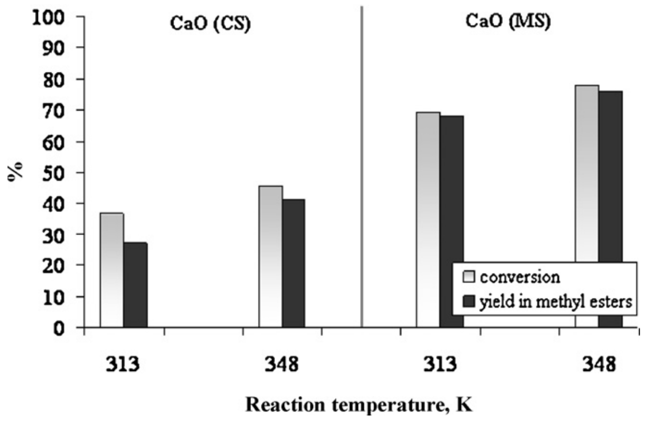

Fig. 8. The variation of the sunflower oil conversion and the yield to methyl esters as a function of the reaction temperature in the presence of CaO samples pre-activated at 788 K (reaction conditions: ultrasound activation, 45 min).

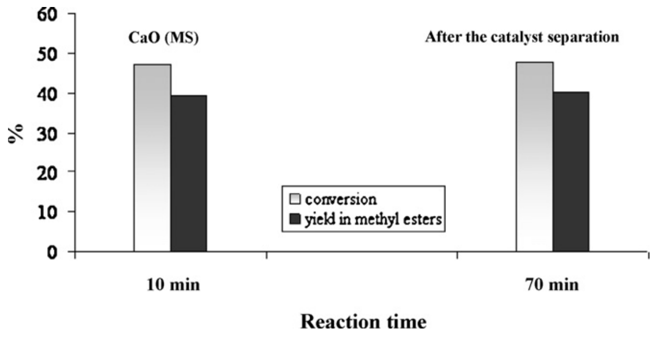

Fig. 9. Leaching test in the presence of CaO samples pre-activated at 788 K (reaction conditions: ultrasound activation, 348 K, 45 min).

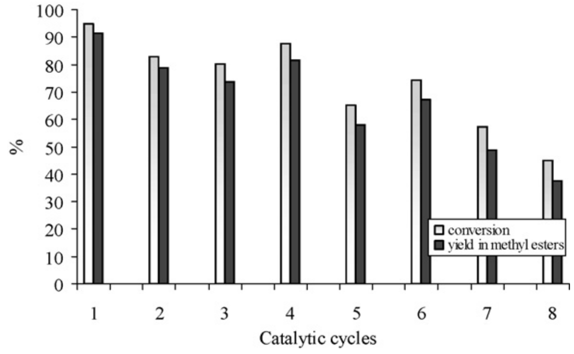

Fig. 10. Catalytic recycling of the microcrystalline CaO (MS) catalyst pre-treated at 788 K (reaction conditions: ultrasound activation, 348 K, 2 h).

mechanical role of ultrasonic waves should be expected, which lead to enhanced reaction rates and yields [37]. Whatever the mechanism is the real benefit of using ultrasound lies in its unique selectivity and reactivity enhancement.

Apart of selectivity and reactivity enhancement, under ultrasound activation the solid surfaces (especially powders) collapse because it produces enough energy to cause fragmentation, even for finely divided materials. Such an effect is leading to an increased active surface area and favors an efficient mixing and enhanced mass transport. For very fine powders the particles are accelerated to high velocity by cavitational collapse and may collide to cause surface abrasion. These phenomena may generate particles with different sizes, and also the sticking of small particles. Such rearrangements of the solid particles (e.g., fragmentations, sticking of small particles) affect the catalytic performances as it has been observed for microcrystalline CaO (MS) sample during the cycles experiments (Fig. 10).

The effect of the ultrasounds on the solid catalysts was also proved from the comparative determination of the particle size distribution for fresh and tested catalysts using light scattering technique (Fig. 11). Thus, in the case of the CaO (CS) catalyst the ultrasounds irradiation provoked a fragmentation of the particles, while for the CaO (MS) catalyst an agglomeration was observed under both thermal and ultrasound activation conditions. However, the agglomeration was more evident under ultrasounds irradiation (Fig. 11, B, b and c). These values differ essentially on those determined from XRD, demonstrating the formation of some agglomerations under the reaction medium.

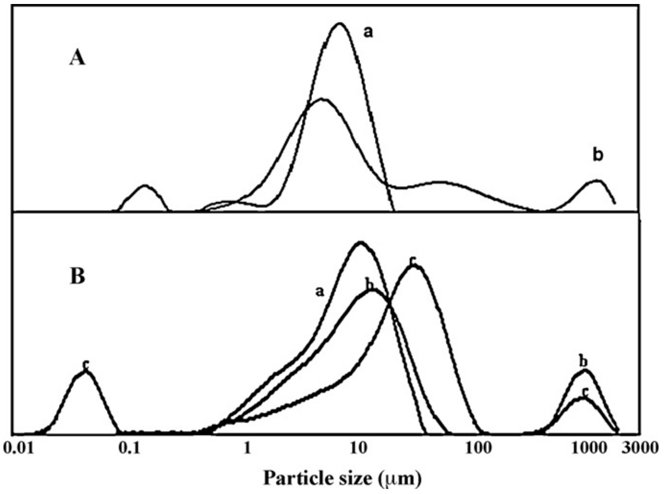

Fig. 11. Particles size distribution of the CaO (CS) catalyst (A) (a – fresh sample, b - tested under ultrasounds conditions) and of the CaO (MS) catalyst (B) (a) CaO (MS) fresh; (b) CaO (MS) tested under autoclave conditions; (c) CaO (MS) tested under ultrasound conditions).

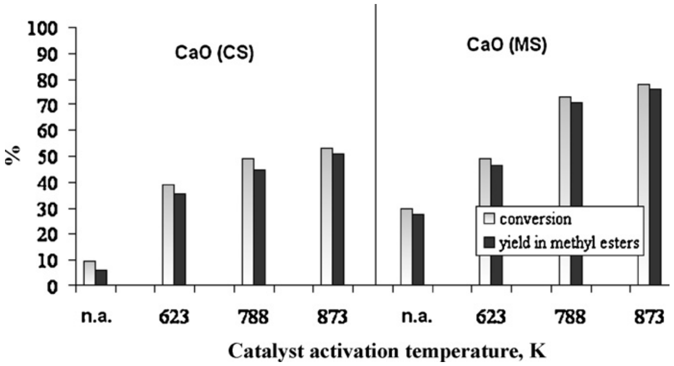

Fig. 12. The variation of the conversion and yield in methyl esters as a function of the preactivation temperatures of the catalysts (n.a. – non-activated; reaction conditions: ultrasound activation, 45 min).

As expected under ultrasound conditions the catalytic performances were also influenced by the catalysts activation temperature (Fig. 12), both the conversion and yield to methyl esters increasing with the increase of the activation temperature.

Obviously, the nature of the vegetable oil influences the catalytic performances. However, under ultrasound irradiation on the investigated catalysts the transesterification took place with similar conversions and yields irrespective of the oil nature (Fig. 13).

3.2.3. Transesterification of vegetable oils under ultrasound conditions using ultrasound activated CaO (MS)

The ultrasonication of the CaO (MS) catalyst at room temperature in methanol led to similar performances with those of the CaO (MS) catalyst preactivated at 873 K (Fig. 14). For the thermal preactivation the enhancement of the catalytic activity was assigned to the removal of the surface hydroxide and carbonates species formed through the interaction of CaO with atmospheric water and carbon dioxide. These species are less basic than calcium oxide, and hence less active for transesterification. However, as DRIFT spectra showed (band at 2858 cm^{-1}) in the case of ultrasonication it seems that responsible for the catalytic performances are the methoxy species formed on the surface of CaO (MS) (Fig. 15).

Using the ultrasonicated catalyst the reaction temperature has a higher influence than using thermal pre-activated catalysts (see Fig. 8). Thus, for the ultrasonicated catalyst the increase of the temperature from 313 K to 348 K led to a conversion of sunflower oil from 75% to 92% (Fig. 16), while for the thermal pre-activated CaO

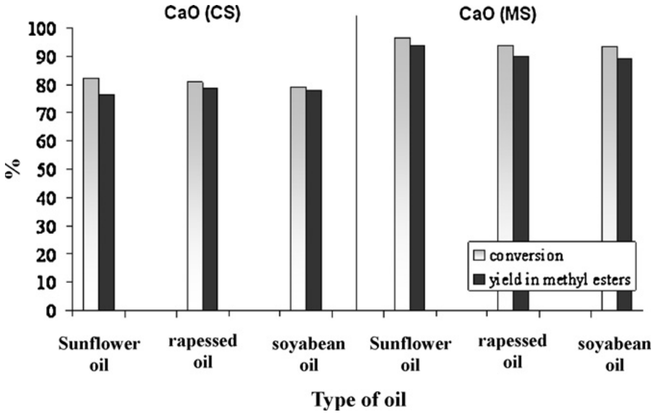

Fig. 13. The variation of the vegetable oil conversion and the yield to methyl esters as a function of the oil nature, in the presence of CaO samples pre-activated at 873 K (reaction conditions: ultrasound activation, 348 K, 2 h).

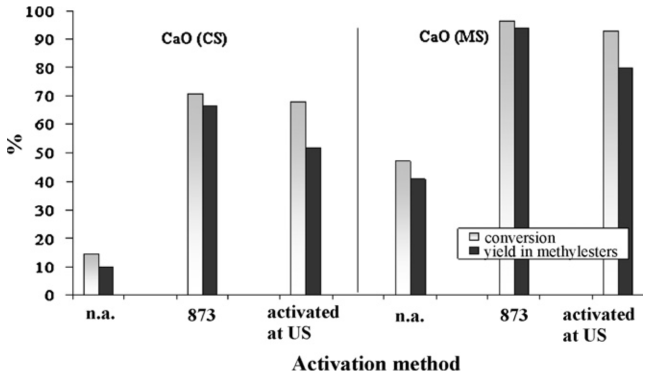

Fig. 14. The variation of the sunflower oil conversion and the yield to methyl esters as a function of the catalysts pre-treatment (reaction conditions: ultrasound activation, 348 K, 2 h).

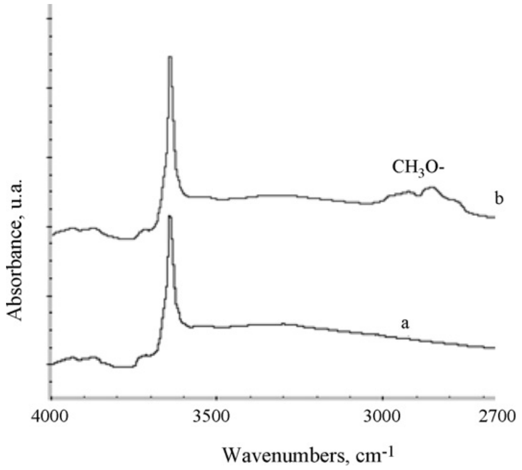

Fig. 15. The DRIFT spectra of fresh CaO (MS) (a) and ultrasound activated CaO (MS) catalyst (b).

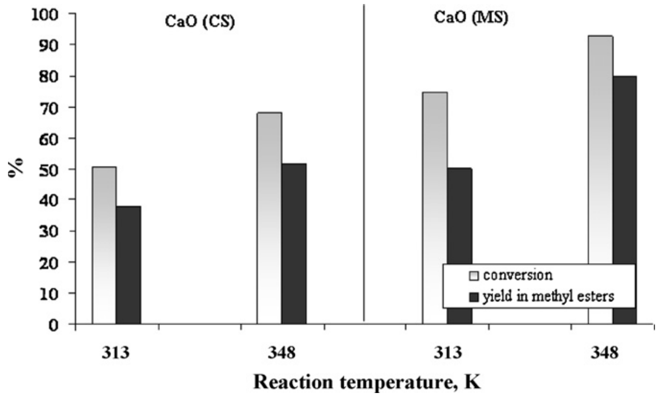

Fig. 16. The influence of the reaction temperature upon the conversion of sunflower oil and the yield to methyl esters in the presence of ultrasonicated CaO samples (reaction conditions: ultrasound activation, 2 h).

(MS) catalyst at 788 K the same difference in reaction temperature led to a smaller increase from 70% to 80% (Fig. 8).

4. Conclusions

In summary it was demonstrated that using appropriate reaction conditions microcrystalline CaO (MS) catalysts, obtained from a cheap and available commercial CaO (CS) material, display highly catalytic performances in the vegetable oil transesterification to biodiesel. The catalytic activity and the yields to methyl esters depend both on the catalysts preactivation method and on the catalytic activation method (e.g., thermal or ultrasound irradiation). Under ultrasound irradiation the catalytic performances of the catalysts thermally preactivated at 788 K are comparable with those of the classical homogeneous base catalysts. Thus, under ultrasound irradiation at 348 K, conversions of sunflower oil over 80% were reached in only 45 min. An even higher conversion (92%) was obtained using a room temperature ultrasonicated microcrystalline CaO (MS) catalyst. The same level of conversion can be also reached in the presence of microcrystalline CaO (MS) catalyst thermally pretreated at a temperature of 873 K.

For the thermally preactivated catalysts the enhancement of the catalytic performances is assigned to the removal of the surface hydroxides and carbonates species. For room temperature ultrasonicated catalysts the catalytic performances were assigned to the methoxy species formed on the surface of the microcrystalline CaO (MS) during activation.

Irrespective of the catalytic activation conditions, CaO leached during the transesterification, but in different proportions. For thermally activated catalysts the leached Ca^{2+} species generates active calcium alcoxide, while for the ultrasound activated catalysts the leached Ca^{2+} species form non-active calcium soaps with the fatty acids contained in the vegetable oil.

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