

# THE SYNTHESIS OF CaO LOADED ONTO $\text{Al}_2\text{O}_3$ FROM CALCIUM ACETATE AND ITS APPLICATION IN TRANSESTERIFICATION OF THE SUNFLOWER OIL

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Transesterification of sunflower oil was carried out over CaO loaded onto  $\gamma\text{-Al}_2\text{O}_3$  as heterogeneous base catalysts. The solid base catalysts were synthesized by the modified wet impregnation of calcium acetate monohydrate onto neutral  $\gamma\text{-Al}_2\text{O}_3$ , calcined at different temperatures in an inert atmosphere and characterized by FESEM, XRPD and FTIR techniques. The catalyst containing 5.5 wt. % CaO supported on  $\gamma\text{-Al}_2\text{O}_3$  calcined at 700 °C exhibited the highest FAME yield at mild reaction conditions (60 °C, atmospheric pressure, methanol-to-oil molar ratio of 9:1 and 0.51% of active species-CaO by weight of oil). The best CaO/ $\gamma\text{-Al}_2\text{O}_3$  catalyst showed a similar or lower catalytic activity than some other CaO-based catalysts at a smaller amount of the catalyst (at least two times less than in other studies).

**Keywords:** biodiesel, calcium oxide, calcification, gamma alumina, impregnation, transesterification.

## Introduction

Biodiesel is a biodegradable, renewable fuel with similar properties to that of fossil diesel fuel and can be used directly in diesel engines without or after small modification [1] or as a mixture with fossil diesel fuel. Biodiesel offers many advantages over fossil diesel fuel such as high flash point, high cetane number, low viscosity, high lubricity, biodegradability, environmental advantages due to less carbon monoxide emissions, as well as fewer emission profiles compared to conventional fossil fuels [2]. The transesterification (alcoholysis) reaction of oils or fats (mainly triacylglycerols) with an alcohol (most frequently, methanol or ethanol) commonly in the presence of a catalyst (a base, an acid or an enzyme) produces biodiesel (a mixture of fatty acid alkyl esters) and glycerol (by-product). Non-catalytic transesterification is also possible under alcohol supercritical conditions (temperature 250-400 °C and pressure 35-60 MPa) [2]. Enzymes as a catalyst tolerate the presence of free fatty acid (FFA) and water in low-quality feedstocks like waste cooking oils [3]. However, nowadays enzymes are too expensive for commercial use in the biodiesel production [4]. Being the most economic, acid or base-catalyzed transesterification is the most commonly used process for the biodiesel production [2, 5]. Acid and base catalysts may be either homogeneous or heterogeneous [6]. Homogeneous catalysts generally provide much faster reactions, but they cannot be reused or regenerated. These catalysts are consumed in the reaction and their separation from products is difficult and requires the application of

the appropriate biodiesel purification method resulting in higher production costs [7]. Base-catalyzed transesterification is a moderately fast reaction under mild operation conditions [7]. However, the appearance of water and FFAs in the oily feedstock may cause problems like soap formation which reduces the ester yield. Being capable of handling esterification and transesterification of triacylglycerols (TAG) simultaneously, acid catalysts are suitable for the oily feedstocks containing a high amount of FFAs and water [8]. However, this process requires a higher molar ratio of alcohol to oil and a much longer reaction time, compared to base-catalyzed processes [9]. Independently of the used catalyst, a transesterification reaction can be speeded up in the presence of a cosolvent (e.g. tetrahydrofuran, n-hexane) [10].

Heterogeneous base catalysts have attracted great attention of many researchers in the last decades. Among them, calcium oxide in various forms (neat, doped, supported or mixed) is often applied as a catalyst for transesterification of different oily feedstocks because of its high basicity, mild reaction conditions, high biodiesel yield, low cost and easy preparation from natural or waste sources. A way to improve its catalytic performance is to load calcium oxide on various supports. The common methods include the deposition of CaO from precursor salts onto the carrier by wet impregnation, sol-gel method, precipitation or co-precipitation followed by thermal activation. CaO is usually loaded on alumina carrier by the wet impregnation method using calcium

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nitrate [11, 12] or calcium acetate [13] as precursor salts. The loaded amount of CaO varies from one group to another: 20 wt. % [11], 35.5 wt. % [13] and  $\geq 50$  wt. % [12], while the optimum temperature for the thermal activation process is in the range from 450 to 718 °C. In these studies, the fatty acid methyl ester (FAME) yield higher than 90% were achieved in less than 5 h of methanolysis reactions over CaO/Al<sub>2</sub>O<sub>3</sub> catalysts. Also, Umdu et al. [14] obtained a high ester yield of 97.5% from microalgal lipids using a CaO/Al<sub>2</sub>O<sub>3</sub> catalyst containing 80 wt. % of CaO. However, Yan et al. [15], who used CaO/Al<sub>2</sub>O<sub>3</sub> prepared from lime acetate by the incipient wetness method and calcination at 700 °C for 8 h in N<sub>2</sub> atmosphere reported the oil conversion of only 36% within the reaction time of 8 h at moderate reaction conditions.

This paper presents the preparation, characterization and application of CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> heterogeneous base catalysts for the biodiesel production from sunflower oil. The catalysts were prepared by the modified impregnation method using calcium acetate as a precursor salt and activated by thermal calcination in inert atmosphere. The aim of the study was to determine the relationship between the catalytic activity of CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in the methanolysis of sunflower oil and the calcination temperature in order to find the optimal regime of thermal activation. Also, the catalytic activity of the obtained CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was compared with the literature results of other CaO-based catalysts used under similar reaction conditions.

## Experimental

### Materials

Commercial sunflower oil (Vital, Serbia) was used; its composition is given elsewhere [16]. The acid, saponification and iodine numbers of the oil were 0.24 mg KOH/g, 190 mg KOH/g and 129 g I<sub>2</sub>/100 g, respectively. Methanol (99.5%) for the oil methanolysis was from Zorka-Pharma (Serbia), while HPLC grade n-hexane, 2-propanol and methanol were purchased from Lab-Scan (Ireland). The standards for FAME contained methyl esters of palmitic, stearic, oleic, linolenic and linoleic acids (20% of each ester), triolein, diolein and monoolein were purchased from Sigma Co (USA). Other material used were: calcium acetate monohydrate p.a. supplied from Centrohém (Serbia), commercial spherical (1-3 mm) gamma-alumina (anhydrous, specific surface area: 122 m<sup>2</sup>/g and cumulative pore volume: 0.631 cm<sup>3</sup>/g, according to Hg porosimetry) purchased from Rhone-Poulenc (France) and deionized water (0.056  $\mu$ S/cm).

### Catalyst preparation

The catalyst was prepared from the aqueous solution of calcium acetate and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using the modified wet impregnation method. Prior to use,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was dried at 120 °C for 24 h and kept in a desiccator. Alumina was added to the 25 wt. % aqueous solution of calcium acetate, and the suspension was periodically stirred for 2 h at

room temperature. The resulting suspension was heated overnight at 120 °C in order to remove the residual water. Then, the dry catalyst precursor loaded onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was calcined by employing a suitable temperature regime with a final temperature in the range of 500 to 750 °C (Table 1) for 4 h in N<sub>2</sub> atmosphere. The calcination of the samples was carried out in a quartz reactor with a tube vertical furnace with a single uniform heating zone and a maximum operating temperature of 1200 °C (Carbolite Furnaces CTF 12/75). The furnace temperature was controlled using a programmed temperature controller adjustable up to 8 ramps and 8 dwells (Eurotherm 818P). After thermal activation, the catalyst was stored in the sealed vials in a desiccator with potassium hydroxide in order to prevent poisoning of the catalyst by atmospheric CO<sub>2</sub> and moisture.

**Table 1.** CaO content and the preparation procedure for CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples.

Designation	Sample		Preparation procedure				
	CaO* /wt. %	WI	tw <sup>b</sup> /h	T <sub>w</sub> <sup>c</sup> /°C	Calcinations		
		C[Ca(CH <sub>3</sub> COO) <sub>2</sub> ] <sup>a</sup> wt. %			T <sub>D</sub> <sup>d</sup> /°C	t <sub>c</sub> <sup>e</sup> /h	T <sub>c</sub> <sup>f</sup> /°C
Ca-500/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.2	25	2	25	120	4	500
Ca-550/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.4	25	2	25	120	4	550
Ca-600/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.1	25	2	25	120	4	600
Ca-650/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.2	25	2	25	120	4	650
Ca-700/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5.5	25	2	25	120	4	700
Ca-750/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5.3	25	2	25	120	4	750

<sup>a</sup>Impregnation salt concentration; <sup>b</sup>Mixing time of alumina and calcium acetate solution; <sup>c</sup>Temperature of mixing; <sup>d</sup>Drying temperature; <sup>e</sup>Calcination time; <sup>f</sup>Calcination temperature; \*ICP-OES determination of calcium in the prepared catalyst.

### Catalyst characterization

The physical and chemical properties of the catalysts were determined by using the X-ray powder diffraction (XRPD) analysis, inductively coupled plasma optical emission spectrometry (ICP-OES), field emission scanning electron microscope (FESEM) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). XRPD patterns were collected at room temperature on a Philips PW-1710 automated diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.54178$  nm), operated at 40 kV and 30mA. Diffraction data were collected in the 20-80° 2 $\theta$  range with a step size of 0.03° and counting time of 1 s per step for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample and in the 3-60° 2 $\theta$  range with a step size of 0.03° and counting time of 1 s per step for other samples. FESEM images were obtained by using a Tescan MIRA3 XMU with the accelerating voltage of 10 kV. The samples were placed over an aluminum drum and covered with an Au and Pt film. A chemical analysis of the activated catalyst before and after the reaction was performed by using ICP-OES using an axial Thermo Scientific iCAP 6500 Duo ICP instrument with a concentric nebulizer. Advanced Microwave Digestion System (ETHOS 1, Milestone) was used to digest the acidified samples. Method parameters of the microwave system were ramped to 220 °C in 10 min, hold for 20 min,

and then cooled down for 1 hour. The measurement of IR spectrum was performed using ATR-FTIR on Thermo Scientific Nicolet 6700 FT-IR Smart iTR to know the surface groups existing on the catalyst surface. The crystal type used was diamond with DTGS KBr detector. All spectra were collected at the range of 525 to 4000  $\text{cm}^{-1}$  with the resolution of 2  $\text{cm}^{-1}$  using an average of 64 scans.

#### Transesterification procedure

Transesterification reactions were carried out in a 250 ml three-neck glass vessel, equipped with a reflux condenser and a magnetic stirrer, immersed in a thermostated water chamber. The temperature was kept constant at 60 °C by circulating water from the thermostated bath (Dema, Slovenia). The desired amounts of methanol (corresponding to the initial methanol-to-oil molar ratio of 9:1) and catalyst (corresponding to 0.51 wt. % of active species-CaO to the oil) were added to the reactor. The methanol-catalyst suspension was thermostated at 60 °C under agitation for 30 min, and then the separately thermostated sunflower oil was added to the reactor. After that, the reaction was timed. The samples were taken from the reaction mixture during the reaction and immediately immersed into icy water for stopping the reaction. After centrifugation (3500 rpm) for 10 min, the upper layer was withdrawn, dissolved in a solution of 2-propanol and n-hexane (5:4, v/v) in a ratio of 1:200, and filtered through a 0.45  $\mu\text{m}$  Millipore filter. The filtrate was used for HPLC analysis, as described elsewhere [17]. The experiments were conducted twice for each catalyst sample.

## Results and discussion

### Catalysts characterization

ICP-OES measurements were performed to determine the elemental composition of the catalysts. Table 2 shows the average chemical composition of the catalyst Ca-700/ $\gamma\text{-Al}_2\text{O}_3$  with the highest catalytic activity. The quantities of the active species in all catalysts are given in Table 1.

**Table 2.** The average chemical composition of the activated Ca-700/ $\gamma\text{-Al}_2\text{O}_3$  catalyst.

Elements, wt. %						Oxides, wt. %				
Ca	Al	Si	Fe	Na	O*	CaO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}$
3.9	49.9	0.46	0.017	0.004	45.7	5.5	93.5	0.98	0.025	0.006

\*O=100- $\sum$ element<sub>x</sub> (x=Ca, Al, Si, Fe and Na).

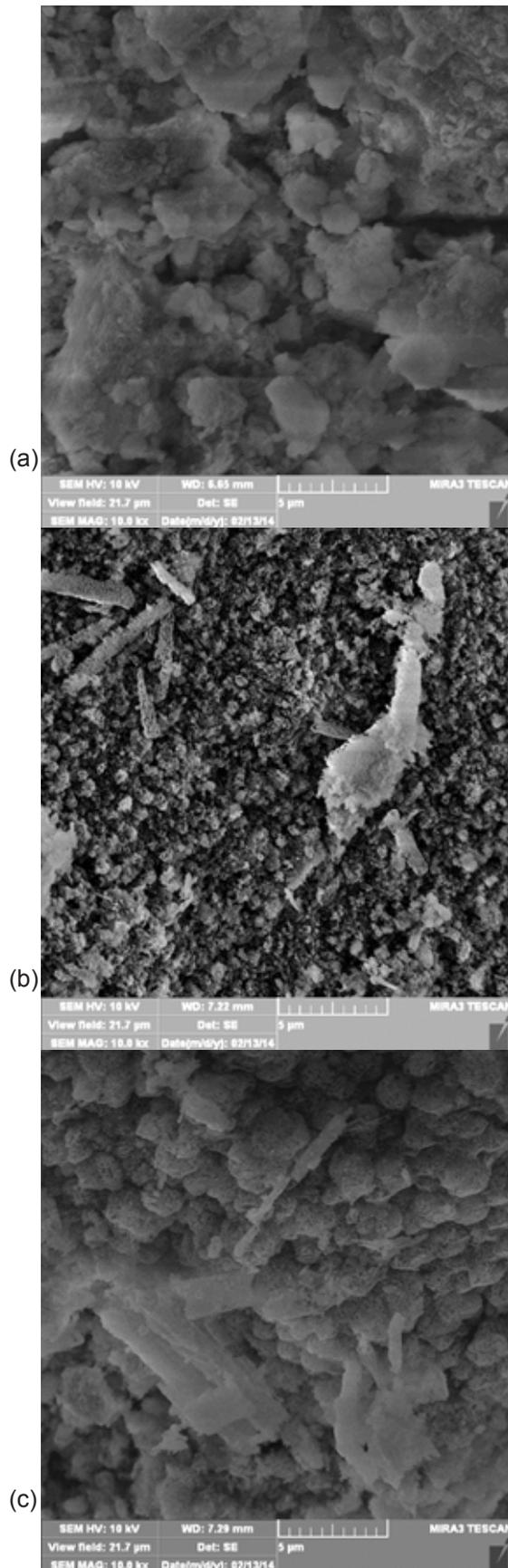
Compared to the characteristics of the carrier, the process of impregnation and calcination lowered both the surface area of the CaO-loaded catalysts by some 14% and the total cumulative pore volume by 7%, while the average pore diameter was increased from 18 nm to 20 nm. Assuming cylindrical pores, these morphological characteristics of the catalyst classified the prepared

catalyst as mesoporous materials which were appropriate for the transesterification reaction.

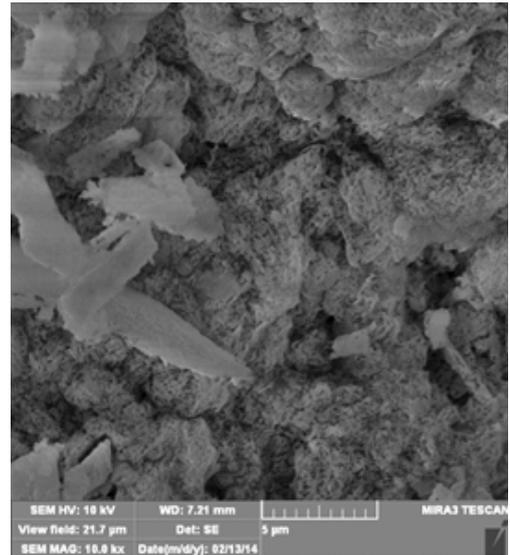
FESEM image of the carrier and some CaO/ $\gamma\text{-Al}_2\text{O}_3$  catalysts are shown in Figure 1. The  $\gamma\text{-Al}_2\text{O}_3$  is characterized by the mainly non-uniform amorphous structure with a different particle size. By calcination at temperatures higher than 500 °C,  $\gamma\text{-Al}_2\text{O}_3$  acquired a more uniform structure. The amorphous structure with the presence of small amounts of the crystallites was dominant in all catalysts presented by micrographs (Figure 1 b, c and d). Such catalyst structure was confirmed by FTIR and XRPD analysis. As it can be seen from Figure 2 and Figure 3, XRPD and FTIR spectral lines are characterized by broad peaks and bends, typical for amorphous morphology. The catalyst calcined at 500 °C consists of spherical particles of the average diameter of around 0.5  $\mu\text{m}$ , with the presence of rod-shaped and small plates crystals most probably formed as a crystalline phase of CaO or  $\text{CaCO}_3$ . The increase in the calcination temperature led to the formation of larger amorphous spherical particles with an average diameter of about 2  $\mu\text{m}$  (650 °C). The crystal phase was also agglomerated at this temperature and the crystals had the form of pseudo rectangular plates. The highest degree of agglomeration of the catalyst particles was evident at the highest temperature of 750 °C. Spherical amorphous particles present at lower temperatures disappeared, while the non-uniform agglomerated structure appeared. At this temperature, crystals were largest and with the pattern of irregular plates. All images show surfaces with high porosity.

XRPD patterns of CaO/ $\gamma\text{-Al}_2\text{O}_3$  samples obtained at different calcination temperatures along with that of the catalyst carrier are presented in Figure 2. XRPD patterns of the catalyst carrier exhibit typical  $2\theta$  reflections of cubic  $\gamma\text{-Al}_2\text{O}_3$  at 33.7°, 45.7°, 60.6° and 66.7° (JCPDS 50-0741). As expected, characteristic reflections originating from  $\gamma\text{-Al}_2\text{O}_3$  are present in all catalyst samples, particularly distinctive being the reflections at  $2\theta$  of 45.7° and 19.4°. A very diffuse reflection at  $2\theta=19.4^\circ$  visible on all catalysts samples is the evidence of amorphous surface morphology, as noted by the FESEM analysis. The presence of calcium acetate, i.e. the precursor salt was not registered on diffractograms, even at the lowest calcination temperature. As it can be seen in Figure 2, the characteristic peaks of calcium acetate in the region from 5-25°  $2\theta$  [18], and particularly intense in the region from 5-10°  $2\theta$  [18], are not present. Diffractograms reflections that confirm the existence of CaO ( $2\theta=32.3^\circ$  and  $37.4^\circ$ , JCPDS 82-1690) are detected in all catalysts. For both reflections, especially for  $2\theta=37.4^\circ$ , broadening of peaks with increasing the calcination temperature is evident, which is in favor of the already observed intensified agglomeration of particles with the increase of the calcination temperature. Calcium carbonate present in the catalyst samples is identified via characteristic reflections at  $2\theta=39.5^\circ$  and  $36.1^\circ$ , and the especially intense and sharp pick at  $29.5^\circ$   $2\theta$  (JCPDS 50-0741). Sharp picks of  $\text{CaCO}_3$  probably mean that they represent the

majority of noticeable crystalline phases in micrographs (Figure 1).

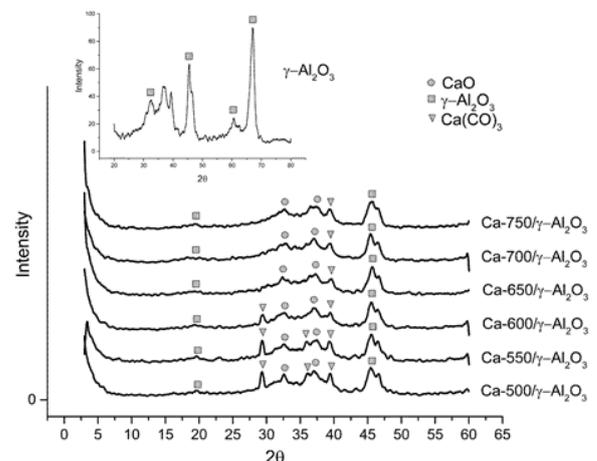


(d)



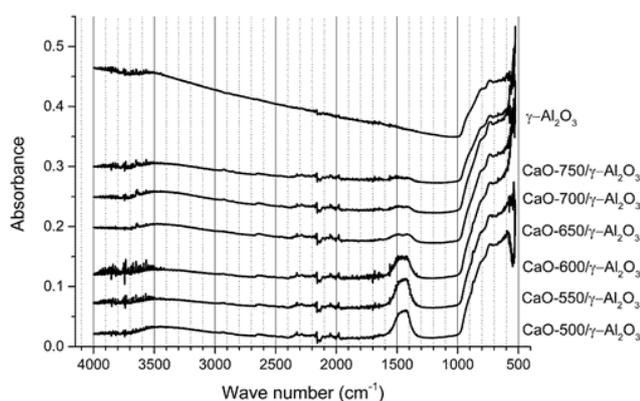
**Figure 1.** FESEM exterior surface image of CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support: a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, b) CaO-500/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, c) CaO-650/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and d) CaO-750/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

With increasing the calcination temperature, the intensity of CaCO<sub>3</sub> characteristic peaks decreases and some of them disappear. Thus, at 500 °C and 550 °C all three above-mentioned peaks are visible. At 600 °C, the peak at  $2\theta=36.1^\circ$  was already lost. At 650 °C, only the peak at  $2\theta=39.5^\circ$  remained, but its intensity decreased with the further temperature increase. This could be attributed to the thermal decomposition of calcium acetate in the N<sub>2</sub> atmosphere which occurs in several steps [18]. The first step is the loss of bounded water, the second is the decomposition of calcium acetate to the CaCO<sub>3</sub> and CO<sub>2</sub> and the last is the decomposition of generated CaCO<sub>3</sub> to CaO and CO<sub>2</sub>. It is obvious that the decomposition of CaCO<sub>3</sub> bound to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a carrier occurred at temperatures higher than 600 °C. It should be noted that the occurrence of small amounts of CaCO<sub>3</sub> on the surface of the catalyst might be caused by the contact of the catalyst with CO<sub>2</sub> from the air during the measurement procedure.



**Figure 2.** XRPD patterns of CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

A series of broad intense peaks belonging to the amorphous  $\gamma$ - $\text{Al}_2\text{O}_3$  dominate over the low wavenumber region of the IR spectrum from  $1000$ - $500\text{ cm}^{-1}$  [19], which can be observed in Figure 3. Two bends characteristic for the Al-O bonds at  $\sim 750\text{ cm}^{-1}$  and  $\sim 550\text{ cm}^{-1}$  are particularly distinctive in this spectral range [20]. Spectral lines of a very low intensity broad band from  $3600\text{ cm}^{-1}$  to  $3100\text{ cm}^{-1}$  are present in spectra of all catalysts due to the presence of a small amount of moisture physisorbed from the air during the measurement [20]. Strong IR spectral lines characteristic for CaO are placed in the far-infrared range ( $\sim 400\text{ cm}^{-1}$  and  $290\text{ cm}^{-1}$ ) [21] and one weak band is in the range from  $500\text{ cm}^{-1}$  to  $560\text{ cm}^{-1}$  [22]. The measurement range of the employed ATF-FTIR instrument does not cover the far-infrared region, while the spectral lines higher than  $500\text{ cm}^{-1}$  may be overwhelmed by the dominant absorption related to  $\gamma$ - $\text{Al}_2\text{O}_3$ . Nevertheless, at the beginning of the measured absorption range, about  $525\text{ cm}^{-1}$ , an intense band with increased intensity at a decreased wavelength was observed on the spectrograms of all catalyst samples. This band could be attributed to CaO present in all catalyst samples, which was already detected by XRPD analysis. The presence of CaO in all catalyst samples is also confirmed by partly obscured (from  $\text{CaCO}_3$ ) spectral bands at  $1420\text{ cm}^{-1}$  and  $875\text{ cm}^{-1}$ . A strong doublet band centered around  $1450\text{ cm}^{-1}$  characterized by the presence of  $\text{CaCO}_3$ , which was due to the main asymmetric  $\nu_{\text{as}}\text{CO}_3$  band (at  $1460\text{ cm}^{-1}$ ) [23]. The intensity of this band decreases with increasing the calcination temperature and above  $600\text{ }^\circ\text{C}$  it cannot be detected, confirming the degradation of  $\text{CaCO}_3$  into CaO, which agrees with the XRPD analysis.

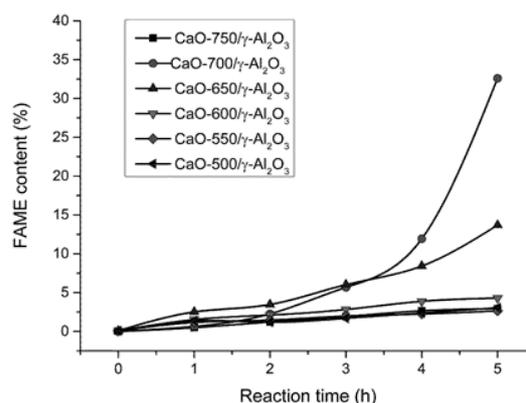


**Figure 3.** Vibrational spectra (ATR-FTIR) of fresh  $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$  catalysts and  $\gamma\text{-Al}_2\text{O}_3$  support.

#### Transesterification study

The activity of  $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$  was tested in the transesterification reaction of sunflower oil. The reaction was performed under atmospheric pressure at following reaction conditions: temperature of  $60\text{ }^\circ\text{C}$ , methanol-to-oil molar ratio of 9:1 and 0.51% of active species-CaO in the catalyst sample (by weight of the oil).

Since the calcination temperature affected structural and catalytic properties of the catalyst [24], the impregnated catalysts were calcined at different temperatures to find the optimal calcination temperature for achieving the maximum catalytic activity. As it can be seen in Figure 4,  $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$  catalysts calcined at temperatures lower than  $600\text{ }^\circ\text{C}$  showed the negligible activity since the FAME content did not exceed 5%. A negligible increase in the catalyst activity was observed with the increase of the calcination temperature from  $500\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$ . This result could be explained by the presence of an inactive  $\text{CaCO}_3$  phase on the catalyst surface as indicated in XRPD and FTIR analysis. At calcination temperatures lower than  $600\text{ }^\circ\text{C}$ , the decomposition of  $\text{CaCO}_3$  bounded to the carrier was incomplete (II stage thermal decomposition of precursor salt-calcium acetate in inert atmosphere). With increasing the calcination temperature from  $600\text{ }^\circ\text{C}$  to  $700\text{ }^\circ\text{C}$ , the catalyst activity raised significantly, and at  $700\text{ }^\circ\text{C}$  it reached the maximum with the FAME content of nearly 35% in 5 h. On the other hand, the FAME formation rate in the presence of  $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$  calcined at temperatures higher than  $700\text{ }^\circ\text{C}$  was remarkably reduced and the FAME content obtained in the reaction catalyzed by  $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$  calcined at  $750\text{ }^\circ\text{C}$  was only 3%. The reduction of the FAME content with increasing the catalyst calcination temperature above  $700\text{ }^\circ\text{C}$  can be explained by the progressive agglomeration of particles occurring at high temperatures. Significant agglomeration, confirmed by FESEM analysis (Figure 1-d), resulted in lower availability of the active species on the catalyst surface, which significantly decreased its catalytic activity. It is noteworthy that pure  $\gamma\text{-Al}_2\text{O}_3$  showed no catalytic activity.



**Figure 4.** The effect of the calcination temperature on the FAME content during sunflower oil methanolysis (reaction conditions: methanol-to-oil molar ratio 9:1, 0.51 wt. % of active species-CaO based on oil,  $60\text{ }^\circ\text{C}$ ).

According to the authors' best knowledge, the transesterification reaction has not yet been studied in the presence of the catalyst such as used in the present study. However, the obtained results can be compared

with previous studies of the sunflower oil methanolysis catalyzed by CaO-based catalysts under similar reaction conditions (Table 3). It can be concluded that similar or higher FAME yield was obtained using other CaO-based catalysts, compared to that obtained using CaO-700/ $\gamma$ - $\text{Al}_2\text{O}_3$ . Miladinović et al. [25] obtained the FAME yield over 98% in 5 h of the methanolysis reaction over calcined quicklime, but at higher methanol-to-oil molar ratio and catalyst amount. On the other hand, Vujičić et al. [26] achieved the yield of only 20% using neat calcined CaO at smaller methanol-to-oil molar ratio and a higher catalyst amount. It is well known that the FAME yield depends not only on the composition and the morphology of the used catalyst but also on the applied reaction conditions. It should be emphasized that the amount of the active catalyst used in these investigations was at least two times lower than those applied in the previous studies of transesterification in the presence of CaO-based catalysts. Accordingly, Correia et al. [27] reported that the increase of the catalyst amount from 1wt. % to 3 wt. % at unchanged other reaction conditions led to a significant increase in the FAME yield from 24.4% to 97.8%, respectively.

**Table 3.** The comparison of the catalytic activity of the CaO-based heterogeneous catalyst in the methanolysis reaction of edible sunflower oil under similar reaction conditions.

Catalyst	Reaction condition			Yield, %/ (Reaction time, h)	Reference
	methanol-to-oil molar ratio	Amount of catalyst (to oil), wt. %	Reaction temperature °C		
CaO (neat)	6:1	1	60	<20/(5)	[26]
Quicklime	12:1	1	60	98/(5)	[25]
CaO (from egg shell, 14.7% atomic concentration of Ca)	9:1	1	60	24.4/(3)	[27]
		2		85.5/(3)	
		3		97.8/(3)	
CaO/ZnO (4 wt. % of CaO)	12:1	1.3	60	<40/(3)	[28]
				<80/(5)	
CaO-700/ $\gamma$ - $\text{Al}_2\text{O}_3$ (5.5 wt. % of CaO)	9:1	0.51 (active species-CaO)	60	35/(5)	This study

## Conclusion

This study showed that CaO/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst is catalytically active in the transesterification reaction for the biodiesel production. This CaO-loaded catalyst can be easily synthesized by the incipient wetness impregnation method. The catalyst structure and activity can be optimized by selecting the calcination temperature. For a neutral carrier  $\gamma$ - $\text{Al}_2\text{O}_3$  and CaO loading of about 5.5 wt. % the optimal calcination temperature for the activation of the catalyst is 700 °C. The fastest reaction and the best FAME content are observed with the catalyst prepared by calcination at 700 °C. Compared to other CaO-based catalysts, the the best CaO/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst shows a

similar or less activity which is attributed to a much lower amount of CaO present in the catalyst system. Its catalytic performance can be improved by increasing the catalyst loading. These results showed that the CaO/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst have promising potential for the use in the biodiesel production processes.

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## Izvod

# SINTEZA CaO NANEŠENOG NA Al<sub>2</sub>O<sub>3</sub> OD PREKURSORA KALCUJUM ACETATA I NJEGOVA PRIMENA U TRANSESTERIFIKACIJI SUNCOKRETOVOG ULJA

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Transesterifikacija jestivog suncokretovog ulja izvršena je korišćenjem CaO nanešenog na  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> kao heterogenog baznog katalizatora. Katalizator je sintetisan korišćenjem modifikovane metode mokre impregnacije gde je kalcijum acetat monohidrat kao precursor nanešen na neutralnu  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Karakterizacija katalizatora je urađena korišćenjem sledećih metoda: FESEM, XRPD i FTIR. Na katalitičku aktivnost, a samim tim i prinos metil estara masnih kiselina, utiču morfologija i sastav katalizatora pripremljenog kalcinacijom na različitim temperaturama. U reakciji transesterifikacije suncokretovog ulja pri umerenim reakcionim uslovima (60 °C, molski odnos metanola:ulja 9:1 i količina CaO 0,51% u odnosu na masu ulja) katalitički najaktivniji je katalizator sa 5,5 mas. % CaO nanešenih na nosač i kalcinisan na 700 °C. U poređenju sa literaturnim rezultatima drugih katalizatora baziranih na CaO, primenjenim u sličnim reakcionim uslovima CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> je pokazao sličnu ili nižu katalitičku aktivnost. Razlog tome je zato što je u ovom radu korišćena najmanje dva puta manja količina katalizatora po eksperimentu u odnosu na istraživanja sa kojima je vršeno poredjenje.

**Ključne riječi:** biodizel, gama alumina, impregnacija, kalcijum oksid, kalcifinacija, transesterifikacija.