

20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

Mechanochemically synthesized CaO·ZnO catalyst for biodiesel production

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Abstract

The transesterification of triglycerides (vegetable oil) with methanol using CaO·ZnO mixed oxides catalyst were conducted to produce FAME (Fatty Acid Methyl Esters, i.e. biodiesel). Catalyst was synthesized by ball milling of CaO and ZnO powder mixture (using molar ratio of Ca and Zn of 1:2 and 1:4) with the addition of water, as well as solely by ball milling (molar ratio of 1:2) of mentioned powders and subsequent. After ball milling prepared mixtures were calcinated at 700 °C in air atmosphere. The samples of formed catalysts were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The particle size distribution as well as the base strength using Hammett indicator was determined, too. CaO·ZnO catalysts were used in the methanolysis of sunflower oil, at 60 °C and 1 bar, using molar ratio of sunflower oil to methanol of 1:10 and with 2 wt% of catalyst based on oil weight. All catalysts exhibited good activity in the methanolysis of sunflower oil, with the yield of FAME above 90 % after 4 hours of reaction.

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Keywords: Biodiesel; heterogeneous catalyst; CaO·ZnO catalyst; ball milling

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1. Introduction

Fatty acid methyl esters (biodiesel) are produced by the transesterification of triglycerides, which is one of the main constituents of vegetable oils, and methanol. The homogeneous base catalysts (NaOH and KOH) are generally used for the industrial production of biodiesel. However, their utilization in vegetable oils, and moreover in the case of waste vegetable oil transesterification, very often forms soaps as undesirable byproducts, which in turn generates large amounts of wastewater during the separation of the catalyst and formed products [1].

A successful heterogeneous process of biodiesel synthesis will solve most of the economical and environmental drawbacks of a classical and to-day mainly applied in industry homogeneous process. Very important characteristic of the heterogeneous catalyst for potential application in the process of biodiesel synthesis is its leaching in contact with methanol. One of the most widely used catalysts in many recently performed researches is CaO due to its availability, low cost and high catalytic activity for synthesis of biodiesel [2]. However, it was proved that leaching of this catalyst was also observed [3]. Thus it is important to improve CaO properties which can be done by using some support material or other metal oxides [4-9].

Several researchers have shown that the combination of CaO with other metal oxides such as ZnO [4-8] and MgO [9] can provide higher yield of FAME (Table 1). Ngamcharussrivichai et al [5] synthesized Ca/Zn mixed oxide catalyst with different Ca/Zn ratio and reported that amount of active compound (CaO) plays an important role in catalyst activity. Catalyst obtained by coprecipitation of the corresponding mixed metal nitrate solution in the presence of a soluble carbonate salt and calcined at 800 °C showed excellent catalytic activity (the FAME yield > 94%, the methanol/oil ratio 30:1, the amount of CaO·ZnO catalyst 10 wt % with the Ca/Zn ratio of 0.25, and the reaction time 1 h), but it requires higher amount of catalyst (10%).

Table 1. Literature review of the activity of mixed oxides of Ca and Zn or Mg as heterogeneous catalysts for biodiesel production

Catalyst	Oil	wt%	Reaction conditions			Yield, %	Ref.
			T, °C	Molar ratio	Time, h		
CaO·ZnO	sunflower	1.3	60, air atmosphere	12:1	2	> 90	[4]
CaO·ZnO	palm kernel	10	60, air	30:1	1	>94	[5]
Ca/Zn ratio of 0.25 CaZn ₂ (OH) ₆ ·2H ₂ O	sunflower	4	60, N ₂	12:1	0.75	> 90	[6]
CaO·ZnO	<i>Jatropha curcas</i>	4	65, air	15:1	6	> 80	[7]
CaO·ZnO	sunflower	2	60, air	10:1	4	97.5	[8]
CaO·MgO	<i>Jatropha curcas</i> oil	3	120, air	25:1	3	90	[9]

In order to study potential catalyst for biodiesel production the mixture of CaO·ZnO was prepared and characterized. It was synthesized by ball milling of CaO and ZnO powder mixture with or without addition of water followed by subsequent calcination at 700 °C in air atmosphere. Such procedure of mechanochemical treatment of different powders is widely used for the activation and synthesis of a broad class of materials due to its relative simplicity-solid phase reactions without usage of solvents. Mechanochemical process is also characterized with reduced energy requirements and much easier work-up procedure [10].

Different molar ratio of CaO and ZnO (1:2 and 1:4) with addition of water, as well as CaO and ZnO (molar ratio of 1:2) without addition of water, were used as starting materials for mechanochemical treatment. Mechanochemical treatment of CaO and ZnO with addition of water led to formation of calcium zinc hydroxide dihydrate [11], while it is not the case when procedure without water was used. After calcination at 700 °C, mixture of CaO·ZnO was obtained.

2. Materials and methods

Commercial edible sunflower oil (Dijamant, Zrenjanin, Serbia; molecular weight 876.6 g mol⁻¹, acid value of 0.202 mg NaOH g⁻¹) and methanol (99.5% purity, Fluka, Switzerland) were used for experimental studies. Catalysts were synthesized by mechanochemical treatment. CaO (obtained after calcination of Ca(OH)₂) and ZnO (Kemika, Zagreb, Croatia) were used for catalyst synthesis. Mechanochemical treatment was carried out in the planetary ball mill Fritsch Pulverisette 5, in air atmosphere. Two zirconia vials of 500 cm³ volume each charged with 500 g zirconia 10 mm diameter balls were used as milling mediums. The balls to powder mass ratio was approx. 30. A powder mixture of CaO and ZnO, with the molar ratio of 1:2 and 1:4 with stoichiometrically required addition of water necessary for formation calcium zinc hydroxide dihydrate (CaZn₂(OH)₆·2H₂O) were used as starting materials for mechanochemical treatment.

A mixture of CaO and ZnO powder, with the molar ratio of 1:2 was also used as starting materials for mechanochemical treatment and preparation of mixed oxide of CaO·ZnO. Angular velocity of supported (basic) disc, measured by tachometer, was 250 rpm (26.2 rad s⁻¹).

Prepared catalysts are listed in Table 2 and denoted as follows: CZH for ball-milled with addition of H₂O and CZ for ball-milled without addition of H₂O (subscript number represents the molar ratio of CaO:ZnO (2 for 1:2 and 4 for 1:4) while after dash line in subscript temperature of calcination, i.e. 700 °C, is also signed).

3. Catalyst characterization

XRD patterns were recorded with Ital Structure APD2000 X-ray diffractometer in Bragg–Brentano geometry using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) and step-scan mode (range: 10–70° 2 θ , step-time: 0.50 s, step-width: 0.1°).

Thermogravimetric analysis (TGA) were carried out on SDT Q600 instrument in air atmosphere, with the flow rate of 100 mL min⁻¹ at the 20 °C min⁻¹ heating rate ranging from 25 to 800 °C.

Fourier-transform infrared (FTIR) spectra were recorded using BOMEM (Hartmann & Braun) spectrometer. Measurements were conducted in wave number range of 4000–400 cm⁻¹, with 4 cm⁻¹ resolution.

The particle size distribution was measured by laser particle size analyzer (PSA) on Mastersizer 2000 (Malvern Instruments Ltd, UK), which covers the particle size range of 0.02–2000 μm .

Hammett indicator experiments were conducted to determine the basic strength of catalysts. The following Hammett indicators were used: phenolphthalein ($H^- = 9.3$), thymolphthalein ($H^- = 10.0$), thymolviolet ($H^- = 11.0$) and 4-nitroaniline ($H^- = 18.4$). Typically, 500 mg of the catalyst was mixed with 1 mL of Hammett indicators solution that was diluted in 20 mL methanol. After 2 hours of equilibration the color of the catalyst was noted. The basic strength of the catalyst was observed to be higher than the weakest indicator that underwent the color change, and lower than the strongest indicator that underwent no color change. To measure the basicity of solid bases, the method of Hammett indicator-benzene carboxylic acid (0.02 mol L⁻¹ anhydrous ethanol solution) titration was used.

Synthesized catalysts were tested in the methanolysis of sunflower oil. Experiments were performed in the 300 cm³ batch autoclave (Autoclave Engineers) equipped with a heater and a mixer. Defined

amounts of sunflower oil, methanol and catalyst were used for synthesis performed in a batch autoclave. All catalyst samples were tested at 60 °C and 1 bar, with molar ratio of sunflower oil to methanol of 1:10 and with 2 wt % of catalyst (based on oil). The reaction samples were withdrawn periodically. The reaction samples were taken out from the reactor at different reaction times, and after filtration and separation of the residual methanol using rotational evaporator, analyzed by gas chromatography (Varian 3400) with a FID detector and MET-Biodiesel capillary GC column (14 m x 0.53).

4. Results

4.1. XRD analysis

The X-ray diffraction analysis was conducted to investigate the structure and crystallinity of the catalysts. The XRD pattern of CZ₂ showed characteristic peaks of ZnO (JCPDS 36-1451), and none of characteristic peaks of calcium species (CaO) was observed (Fig. 1).

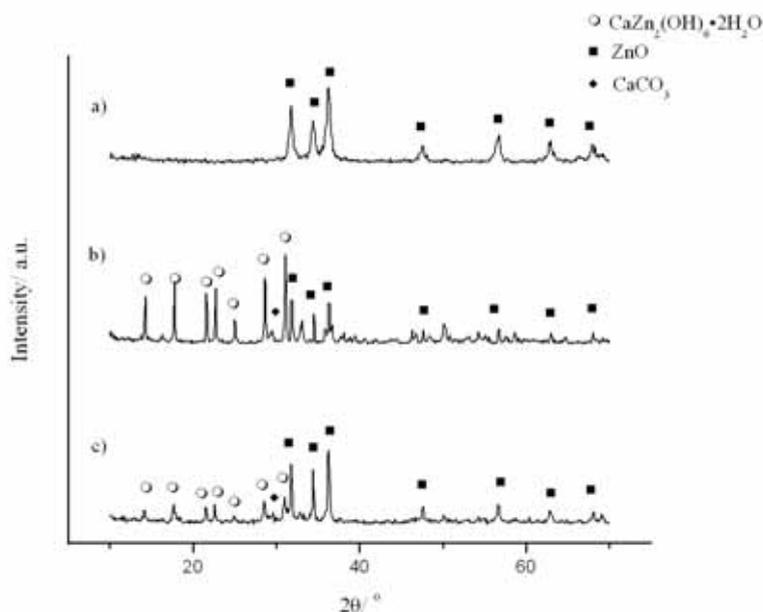


Fig. 1. XRD patterns of synthesized catalysts : (a) CZ₂ , (b) CZH₂ and (c) CZH₄

XRD pattern of the CZH₂ resulted in peaks that corresponded mainly to calcium zinc hydroxide hydrate CaZn₂(OH)₆·2H₂O (JCPDS 25-1449). The presence of ZnO peaks in CZH₂ indicates that the formation of calcium zinc hydroxide hydrate was not completed. Small peak at 29.4 2θ is assigned to CaCO₃ (JCPDS 5-586), which is obtained by the reaction of CaO with CO₂ from air at the beginning of the milling process. It can be concluded that mechanochemical reaction of CaO and ZnO powders with added stoichiometrical amount of water yielded a mixture of CaZn₂(OH)₆·2H₂O, ZnO and CaCO₃ phases. Ball milling of CaO and ZnO powders with molar ratio of 1:4 with water addition (CZH₄) resulted in weakening of the XRD peaks of calcium zinc hydroxide hydrate and the appearance of more intense peaks of ZnO.

4.2. TGA analysis

The TGA diagram (Fig. 2) of calcium zinc hydroxide hydrate is characterized by two-step decomposition [12]. The first dominant step of weight loss could be observed from 120 to 180 °C, which may be attributed to the elimination of hydrated water and dehydration of $\text{Zn}(\text{OH})_2$ to form ZnO . In respect to the initial composition of used powders, it should be approximately 23.3%. A second region, from 350 to 400 °C corresponds to the dehydration of $\text{Ca}(\text{OH})_2$ (5.8%) [12]. Finally, above 650 °C and up to 700 °C there is a weight loss which indicates the presence of calcium carbonate.

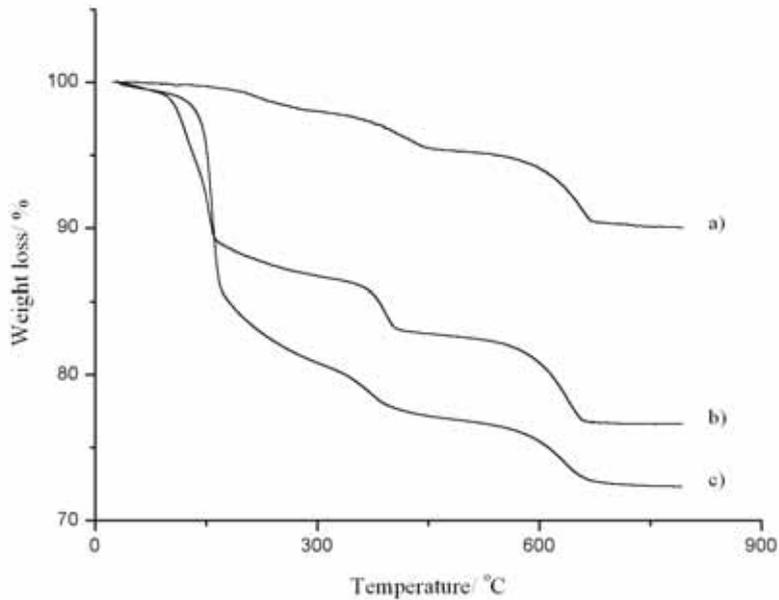


Fig. 2. TGA curves of (a) CZ_2 , (b) CZH_4 and (c) CZH_2

For CZH_2 the first weight loss up to 200 °C was 18.9%, which is less than theoretical one and in agreement with XRD results that mechanochemical synthesis of calcium zinc hydroxide dihydrate was not completed, while for CZH_4 it was 13.8 wt%. Also, the weight loss of 4.7 % and 6.2% for CZH_2 and CZH_4 , respectively, at 650 °C indicates that during mechanochemical treatment the reaction of CO_2 and CaO and formation of CaCO_3 occurred

For CZ_2 up to 400 °C, there was weight loss corresponding to H_2O release (4.5%). A weightloss of 5 wt% at about 660 °C is attributed to a decomposition of CaCO_3 to form CaO .

From TGA diagrams (Fig.2), it was concluded that for mechanochemical treatment with water addition formation of calcium zinc hydroxide hydrate took place, in comparison to sample prepared without addition of water.

4.3. FTIR analysis

FTIR spectra were recorded for CZH₂, CZ₂ and CZH₄ samples and are presented in Figure 3. Characteristic bands for calcium zinc hydroxide hydrate CaZn₂(OH)₆·2H₂O are: two sharp bands at 3615 and 3505 cm⁻¹, assigned to ν(OH) stretching vibrations, band which is characteristic of the O–H stretching vibration of Ca(OH)₂ at 3643 cm⁻¹, bridging OH bending mode is visible at 940 cm⁻¹, the HOH bending mode of lattice water appears at 1600 cm⁻¹, the stretching bands at 3150, 3034 and 2880 cm⁻¹ are attributed to the O–H groups from H₂O molecules and the bending vibration of Zn–O–H is noticed at 1070 cm⁻¹ [13]. The presence of carbonates was determined for all the samples, which is confirmed by the broad band centered at 1465 cm⁻¹. The fundamental bands of CaCO₃ can be seen at 1465, 874, 712 cm⁻¹ and the band at 2350 cm⁻¹ from the vibrations in CO₂ molecule [14].

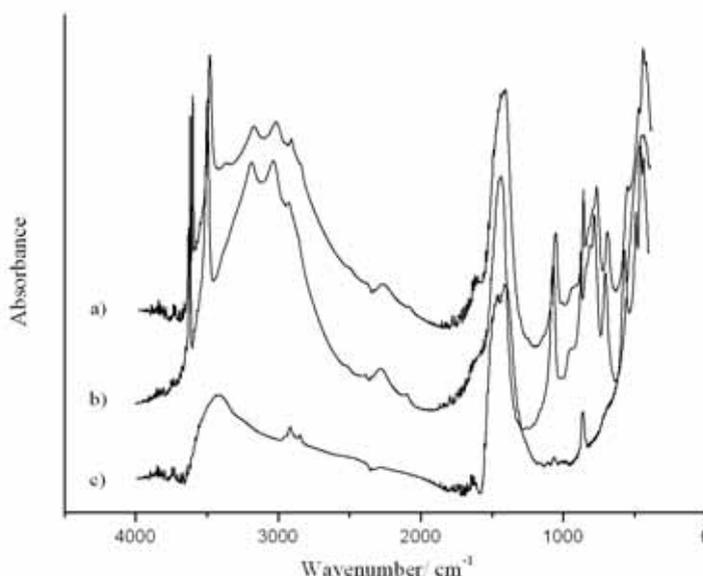


Fig. 3. FTIR spectrum of (a) CZH₄, (b) CZH₂ and (c) CZ₂

4.4. The particle size distribution

The particle size distribution of the prepared catalysts CZH₂, CZ₂ and CZH₄ is shown in Fig. 4a. Difference is notable between the catalyst obtained by ball milling with and without addition of water with the molar ratio of CaO:ZnO of 1:2. The particle size distribution of the CZ₂ catalyst is uniform with the size range of 0.2–40 μm, for the CZH₂ bimodal distribution is obtained: a larger fraction of the powder particles is within the size range of 0.2–40 μm and the rest is within the range of 40–300 μm, while for CZH₄ particle size distribution is between CZ₂ and CZH₂. After calcination at 700 °C, particle size distribution shifts to smaller values for CZH₂₋₇₀₀ and CZH₄₋₇₀₀, while for CZ₂₋₇₀₀ remained almost the same (Fig. 4b). Such an effect could be expected because calcination process of CZH₂ and CZH₄ causes

removal of H₂O and CO₂ from the CaZn₂(OH)₆·2H₂O and CaCO₃, inducing particle crushing and diminution.

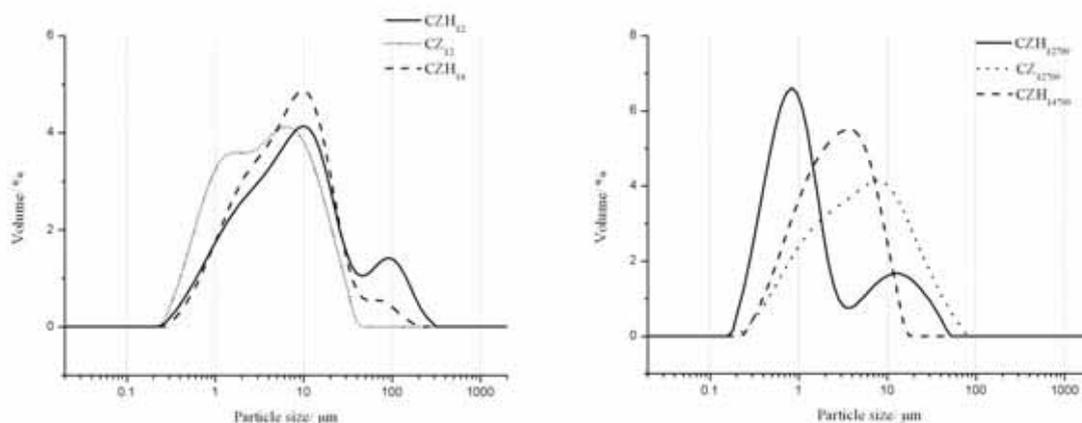


Fig. 4. Particle size distribution of the prepared samples (a) before calcination and (b) after calcination at 700 °C

4.5. The basic strength of prepared catalysts

The basic strength of calcinated catalysts, which were prepared by ball milling is given in Table 2. A higher basicity was found for catalyst prepared with water addition. Better dispersion of CaO on the surface of ZnO could remarkably increase the basicity of the catalyst. Obviously, the basicity of CZH₂₋₇₀₀ is the highest, and it could influence the catalytic activity for the biodiesel synthesis. Namely, the reaction activity mainly depends on the number of basic sites present at the catalyst surface as well as on their strength [15]. The difference in the distribution of basic sites for each catalyst indicates that the basicity and base strength distributions are influenced by the presence of CaO in the CaO·ZnO mixed oxides.

Table 2. Synthesized catalysts used working condition, molar ratio of CaO:ZnO, calcinations procedure and basic strength

Catalyst denotation	Molar ratio of Ca(OH) ₂ and ZnO, medium	Preparation method	Calcination temperature, °C	Basic strength (H ⁻)	Basicity (mmol g ⁻¹)
CZH ₂	CaO:ZnO 1:2 +H ₂ O	ball-milling 7 h	/	/	/
CZH ₂₋₇₀₀	CaO:ZnO 1:2 +H ₂ O	ball-milling 7 h	700	11.0-18.4	0.072
CZ ₂	CaO:ZnO 1:2	ball-milling 7 h	/	/	/
CZ ₂₋₇₀₀	CaO:ZnO 1:2	ball-milling 7 h	700	10.0-11.0	0.09
CZH ₄	CaO:ZnO 1:4 +H ₂ O	ball-milling 7 h	/	/	/
CZH ₄₋₇₀₀	CaO:ZnO 1:4 +H ₂ O	ball-milling 7 h	700	9.3-10.0	0.38

Catalysts prepared with water addition showed high activity after 4 h of reaction. Taking both the base strength and the catalytic activity into account, it might be concluded that the observed activities of catalysts seem to be related to their base strengths, i.e. the higher base strengths of the catalysts result in

the higher conversions of triglycerides. The CZ₂₋₇₀₀ sample possessed the weakest base strength, consequently exhibiting weaker catalytic activity.

4.6 Activity of prepared catalyst

Among the catalysts prepared by ball milling, sample CZH₂₋₇₀₀ possessed the highest catalytic activity due to the small particle size and base strength. The catalysts prepared by ball milling with water addition have higher activities and faster reaction rates than that obtained by ball milling without water addition. The particle size effect is attributed to the formation of small CaO particles at the surface of the large ZnO particles, since small particles had the properties of well accessible basic sites. Finally, one can conclude that more accessible basic sites facilitated the transesterification reaction.

The obtained experimental results indicate that the activity of synthesized catalysts increases with addition of water to initial powder mixture, while the reaction rate increases with increasing the CaO to ZnO molar ratio from 1:4 to 1:2.

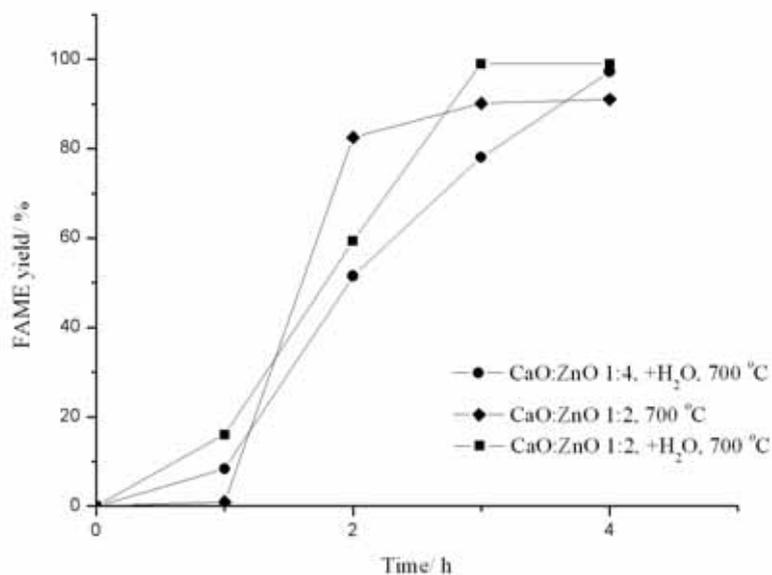


Fig. 5. FAME yields for catalysts synthesized by ball milling and calcined at 700 °C, experimental conditions 60 °C and 1 bar, molar ratio of methanol to sunflower oil of 10:1 and with 2 wt% of catalyst

Fig. 6 shows the comparison of the experimental data obtained in this study for catalyst CZH₂₋₇₀₀ with the results published by other authors who have also used CaO·ZnO as a catalyst in the transesterification reaction. Reaction conditions for the transesterification are shown in Table 1.

Although carbonates formation is reduced when CaO is used as strating material instead of Ca(OH)₂ [8], this change of initial compounds used for catalyst preparation didn't have influence to increase the rate of transesterification reaction.

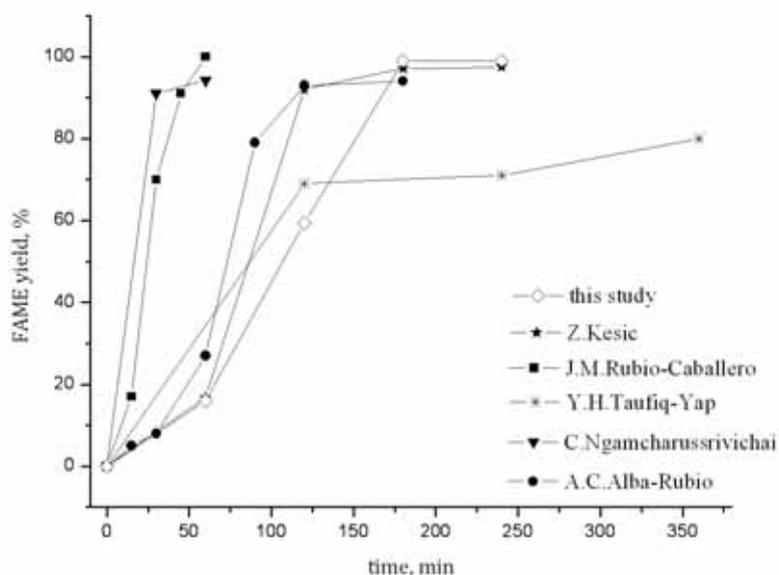


Fig. 6. Comparison of the experimental data obtained in this study with the results of the studies in which CaO·ZnO has been used as catalyst

Conclusion

Experiments performed in this study showed that CaO·ZnO mixture as a heterogeneous catalyst exhibited good activity in the methanolysis of sunflower oil. Different samples of CaO·ZnO precursor were obtained by ball milling of CaO and ZnO powders with or without the addition of water.

After the calcination at 700 °C, catalyst obtained by ball milling with water addition was more active compared to the catalyst prepared without water addition. The reasons for the different activity of synthesized catalysts could be explained by the difference of their basicity. The highest catalytic activity exhibits the catalyst obtained by mechanochemical treatment of CaO and ZnO powders (molar ratio of CaO:ZnO of 1:2) with added water, and subsequent calcination at 700 °C. Such prepared catalyst gave FAME formation of almost 99 wt% after 3 h reaction of sunflower oil and methanol (1:10 molar ratio) in a batch reactor at 60 °C.

Acknowledgements

Financial support of the Ministry of Education and Science of the Republic of Serbia (Grant No. 45001) is gratefully acknowledged.

References

- [1] Sharma YC, Singh B, Upadhyay SN. Advancements in development and characterization of biodiesel: A review. *Fuel* 2008; **87**:2355–2373.
- [2] Lopez Granados M, Zafra Poves MD, Martín Alonso D, Mariscal R, Cabello Galisteo F, Moreno-Tost R, Santamaría J, Fierro JLG. Biodiesel from sunflower oil by using activated calcium oxide. *Appl Catal B* 2007; **73**:327–336.
- [3] López Granados M, Martín-Alonso D, Sadaba I, Mariscal R, Ocon P. Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: The case of triglycerides methanolysis using CaO. *Appl Catal B* 2009; **89**:265–272.
- [4] Alba-Rubio AC, Santamaría-González J, Mérida-Robles JM, Moreno-Tost R, Martín-Alonso D, Jiménez-López A, Maireles-Torres P. Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts *Catal Today* 2010; **149**:281–287.
- [5] Ngamcharussrivichai C, Totarat P, Bunyakiat K. Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. *Appl Catal A* 2008; **341**:77–85.
- [6] Rubio-Caballero JM, Santamaría-González J, Mérida-Robles JM, Moreno-Tost R, Jiménez-López A, Maireles-Torres P. Calcium zincate as precursor of active catalysts for biodiesel production under mild conditions. *Appl Catal B* 2009; **91**:339–346.
- [7] Taufiq-Yap YH, Lee HV, Hussein MZ, Yunus R. Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel. *Biomass Bioenergy* 2011; **35**:827–834
- [8] Kesić Z, Lukić I, Brkić D, Rogan J, Zdujić M, Liu H, Skala D. Mechanochemical preparation and characterization of CaO-ZnO used as catalyst for biodiesel synthesis. *Appl Catal A* 2012; **427-428**:58–65.
- [9] Taufiq-Yap YH, Lee HV, Yunus R, Juan JC. Transesterification of non-edible *Jatropha curcas* oil to biodiesel using binary Ca–Mg mixed oxide catalyst: Effect of stoichiometric composition. *Chem Eng J* 2011; **178**:32–347
- [10] Avvakumov E, Senna M, Kosova N, *Soft Mechanochemical Synthesis*. Kluwer Academic Publishers, 2001.
- [11] Zhu XM, Yang HX, Ai XP, Yu JX, Cao YL. Structural and electrochemical characterization of mechanochemically synthesized calcium zincate as rechargeable anodic materials. *J Appl Electrochem* 2003; **33**:607–612.
- [12] Wang S, Yang Z, Zeng L. Study of calcium zincate synthesized by solid-phase synthesis method without strong alkali. *Mater Chem Phys* 2008; **112**:603–606.
- [13] Lin T, Mollah MA, Vempati R, Cocke D. Synthesis and Characterization of Calcium Hydroxyzincate Using X-ray Diffraction, FT-IR spectroscopy, and Scanning Force Microscopy. *Chem Mater* 1995; **7**:1974–1978.
- [14] Nakamoto K, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed, John Wiley & Sons: New York, 1997.
- [15] Bancquart S, Vanhove C, Pouilloux Y, Barrault J. Glycerol transesterification with methyl stearate over solid basic catalysts I. Relationship between activity and basicity. *Appl Catal A* 2001; **218**:1–11.