CI&CEQ
Chemical Industry & Chemical Engineering Quarterly

Available on line at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

Chem. Ind. Chem. Eng. Q. 21 (1) 1–12 (2015) CI&CEQ

ŽELJKA KESIĆ[1]
IVANA LUKIĆ[1]
MIODRAG ZDUJIĆ[2]
ČEDOMIR JOVALEKIĆ[3]
HUI LIU[4]
DEJAN SKALA[5]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
[2]Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Serbia
[3]University of Belgrade, Institute for Multidisciplinary Research, Belgrade, Serbia
[4]University of Geosciences, School of Environmental Studies, Wuhan, China
[5]University of Belgrade, ICTM Department of Catalysis and Chemical Engineering, Belgrade, Serbia

SCIENTIFIC PAPER

UDC 544.47:54-185:662.756.3

DOI 10.2298/CICEQ131026041K

MECHANOCHEMICAL SYNTHESIS OF $CaO{\cdot}ZnO{\cdot}K_2CO_3$ CATALYST: CHARACTERIZATION AND ACTIVITY FOR METHANOLYSIS OF SUNFLOWER OIL

Article Highlights

- Ball milling of CaO, ZnO and water with/without addition of K_2CO_3
- Sample characterization using different analytical methods
- Activity of CaO·ZnO catalyst with different amounts of K_2CO_3 for biodiesel synthesis
- Comparison of catalyst activity at moderate temperature

Abstract

The goal of this study was to prepare a CaO·ZnO catalyst containing a small amount of K_2CO_3 and analyze its activity for biodiesel synthesis. The catalyst was prepared using the following procedure: CaO and ZnO (mole ratio of 1:2), water and K_2CO_3 (in various amounts) were mechanochemically treated and after milling heated at 700 °C in air atmosphere for obtaining mixed $CaO{\cdot}ZnO/_xK_2CO_3$ oxides (x = 0, 1, 2 and 4 mol of K_2CO_3 per 10 mol of CaO). All the samples were characterized by X-ray diffraction (XRD), inductively coupled plasma (ICP), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR), scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS), particle size laser diffraction (PSLD) distribution, solubility measurement of Ca, Zn and K ions in methanol as well as by determination of their alkalinity (Hammett indicator method). Prepared $CaO{\cdot}ZnO/_xK_2CO_3$ composite powders were tested as catalysts for methanolysis of sunflower oil at 70 °C using mole ratio of sunflower oil to methanol of 1:10 and with 2 mass% of catalyst based on oil weight. The presence of K_2CO_3 in prepared samples was found to increase the activity of catalyst, and that such effect is caused by homogeneous-heterogeneous catalysis of biodiesel synthesis.

Keywords: mechanochemical synthesis; CaO; ZnO; K_2CO_3; mixed oxides; biodiesel synthesis.

Biodiesel or mixture of fatty acid methyl or ethyl esters is an ideal environmentally friendly substitute for conventional diesel oil usually obtained from crude oil or fossil fuels. It is safe, non-toxic, biodegradable, and contains usually less than 10 ppm of sulfur-based organic compounds [1].

Transesterification reaction of triglycerides or vegetable oil with methanol or ethanol occurs in the presence of acid or basic catalysts. Among the available biodiesel production methods, homogeneous base-catalyzed transesterification is the most commonly applied processing technique [2]. However, depending on the characteristics of raw material it suffers from several drawbacks, such as formation of soaps as undesirable byproducts and generation of large amount of wastewater during separation of the catalyst from the derived products [3].

The main advantages of heterogeneous catalysts application compared to homogeneous are easy separation and further reuse of solid catalyst. Various heterogeneous catalysts, such as alkali earth oxides, hydrotalcites, alkali-doped oxides and mixed metal oxides have been investigated for biodiesel synthesis

Correspondence: D. Skala, University of Belgrade, ICTM Department of Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia.
E-mail: skala@tmf.bg.ac.rs
Paper received: 26 October, 2013
Paper revised: 12 December, 2013
Paper accepted: 18 December, 2013

[4]. One of the most widely used catalyst is CaO, owing to its availability, low cost, and high catalytic activity [5,6]. Also, mixed oxide catalysts with CaO as active component are frequently used for transesterification reaction [7-9]. The CaO·ZnO mixed oxides with CaO:ZnO mole ratio of 1:2 has been found to be also active catalysts for methanolysis of sunflower oil [8,9].

In order to increase catalytic activity of CaO, the effect of addition of low amounts of promoter (alkali metal salts like $LiNO_3$) during preparation of CaO catalyst was studied as well [10,11]. MacLeod *et al.* [11] have prepared a series of alkali-doped metal oxide catalyst and showed that increased base strength of CaO is responsible for better catalytic activity. However, undesired metal leaching from prepared catalysts, mainly leaching of promoters, was also detected.

Calcium and magnesium oxides can be used not only as precursors but also as catalyst support in transesterification reactions; *e.g.*, KF/MgO–CaO was an effective catalyst for transesterification of soybean oil with methanol [12].

Many research studies have focused on analyzing K_2CO_3 catalyst activity for methanolysis of vegetable oil [13-18]. The obtained data showed that 90% of oil conversion could be achieved for less than 2 h at moderate temperature. As mentioned above, the main problem is relatively high solubility of potassium carbonate in methanol; it was determined that about 55% of K_2CO_3 could be dissolved after 5 h of methanolysis [13].

For this reason, potassium carbonate is usually used as promoter to modify the base properties of alumina, alumina/silica, cinder or hydrotalcite as support [14-17]. However, activity of catalyst containing potassium carbonate is mainly the result of potassium leaching into methanol [16]. It has been shown that hydrotalcite loaded with K_2CO_3 could be reused five times, yielding more than 92% of biodiesel from vegetable oil [17]. On the other hand, rather large amount of catalyst must be used to reach desired conversion of vegetable oil [16]. Salts of other alkali metals (Li and Na) were also investigated as promoters of CaO, BaO, and MgO used as catalysts for transesterification of canola oil. All of these modifications had a goal of suppressing undesirable leaching of potassium [18]. According to recently reported data, Na_2CO_3 added to CaO–methanol–sunflower oil mixture could suppress the leaching of Ca^{2+} and Na^+ below 5 ppm [19,20].

Preparation of different composites by mixing solids without the addition of large amounts of liquid solvents is the basis of mechanochemical synthesis [21]. Due to its relative simplicity, it is one of the prospective methods that could be used for the activation and synthesis of a broad class of catalyst [22]. The mixed calcium-zinc hydroxide hydrate ($CaZn_2(OH)_6{\cdot}2H_2O$) was prepared by mechanochemical synthesis starting from $Ca(OH)_2$, ZnO, and H_2O and compared to classical procedure of its preparation based on coprecipitation procedure [8]. Activity of CaO·ZnO catalyst obtained by subsequent calcinations at 700 °C for 3 h was tested for methanolysis of sunflower oil [8].

Recently, instead of $Ca(OH)_2$ as a component of mechanochemical synthesis of $CaZn_2(OH)_6{\cdot}2H_2O$, CaO was used together with ZnO and H_2O with a goal to decrease the amount of calcium carbonate formed during ball milling [23]. In an attempt to further improve catalytic performance and to increase basicity of composite containing calcium and zinc oxide, the addition of potassium carbonate (K_2CO_3) during ball milling of CaO, ZnO and the required amount of water was examined in this work. The goal of K_2CO_3 use together with CaO and ZnO was to promote the mechanochemical synthesis of $CaZn_2(OH)_6{\cdot}2H_2O$ and to include potassium into the matrix or to impregnate the formed mixed hydroxide of calcium and zinc. The various initial mole ratio of K_2CO_3 to CaO (1:10, 2:10 and 4:10) was used for the preparation of $CaZn_2(OH)_6{\cdot}2H_2O/_xK_2CO_3$ (signed as CZK_x; x = 1, 2 and 4) followed by calcinations at 700 °C (signed as $CZK_{x,700}$). The catalytic activity of $CZK_{x,700}$ was tested for sunflower oil methanolysis and biodiesel production.

EXPERIMENTAL

Catalyst preparation

Powder mixtures of CaO (obtained by calcination of lime originated from southern part of Serbia), and ZnO (Kemika, Croatia), in the molar ratio of 1:2 with 6 g of water, (in excess of stoichiometrically required amount of water), as well as addition of K_2CO_3 (Fluka, Switzerland) were used as starting materials for mechanochemical treatment. Mole ratios of K_2CO_3 to CaO were 1:10, 2:10 and 4:10 ($CaO{\cdot}ZnO/_xK_2CO_3$ where x = 1, 2 and 4). Mechanochemical treatment was carried out in the planetary ball mill Fritsch Pulverisette 5 in air atmosphere. Two zirconia vials with volumes of 500 cm^3 each charged with 500 g zirconia *ca.* 10 mm diameter balls were used as milling medium. The balls to powder mass ratio was very close to 30. Mechanochemical treatment was done in two steps: the first hour with lower

milling intensity (angular velocity of about 150 rpm) and the next two hours with higher milling intensity (angular velocity of about 250 rpm). Angular velocity of supported (basic) disc was measured by tachometer. It should be pointed out that the process of mechanochemical treatment of CaO, ZnO and K_2CO_3 with water proceeded throughout several distinct steps. In the very beginning, the powder mixture uniformly covered the zirconium balls and vial wall. With the progress of milling, a "sticky" paste (composed, most likely, of CaO, ZnO, formed $Ca(OH)_2$, $CaCO_3$ and a minor amount of formed $CaZn_2(OH)_6{\cdot}2H_2O$) was spread on the vial wall, whereas later on, the powder mixture with higher amount of K_2CO_3, *i.e.*, $CaO{\cdot}ZnO/xK_2CO_3$ (x = 4) often transformed to spherical globules. In order to induce a mechanochemical effect, globules were manually crushed, so that prolonged milling up to 3 h produced very fine powders.

Catalyst characterization

XRD was performed on a D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. CuKα radiation (λ = 0.15418 nm), with a step size of 0.02° in the range of 10–70° 2θ was used for all samples. The peaks were identified using the Powder Diffraction File (PDF) database created by International Centre for Diffraction Data (ICDD).

Elemental analysis of the powders was performed by inductively coupled plasma mass spectrometry using Thermo Scientific ICAP 6000 series instrument.

Thermogravimetric analysis (TGA/DTG) were carried out on a SDT Q600 instrument in air atmosphere with flow rate of 100 ml min^{-1} at a 10 °C min^{-1} heating rate up from 25 to 800 °C.

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

The valence state and atomic concentration of elements in the surface layers were determined using XPS. Measurements were performed in a VC Escalab II spectrometer using non-monochromatic MgKα radiation ($h\nu$ = 1253.6 eV). The base pressure of instrument was 1×10^{-10} Torr. Electrostatic surface charging was observed in all investigated samples owing to their poor electric conductivity. Therefore, C 1s with the binding energy (BE) of 285.0 eV from carbon contaminations was used as the reference level. The binding energies reported here were measured within ±0.2 eV. XPS surface compositions were calculated from photoelectron peak areas of each element after correcting for instrument parameters.

The morphology and elemental chemical analysis of powders obtained by ball milling followed by calcination was studied by a scanning electron microscope (JEOL JSM-6610LV) and an energy dispersive X-ray spectrometer (EDS INCAEnergy 350 microanalyzer).

The particle size distribution was measured by particle size laser diffraction (PSLD) on a Mastersizer 2000 (Malvern Instruments, 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 h 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.

The solubility of the catalyst in methanol at 60 °C was determined by measuring the Ca(II), K(I) and Zn(II) concentration using a HITACHI Z-2000 polarized Zeeman atomic absorption spectrophotometer.

Methanolysis reaction

Refined edible sunflower oil (Dijamant, Serbia; acid value of 0.202 mg NaOH g^{-1}) and methanol (99.5% purity, Fluka, Switzerland) were used. Transesterification was carried out in a 300 cm^3 batch autoclave (Autoclave Engineers, USA) equipped with a heater, temperature controller, and a mixer. The mole ratio of sunflower oil to methanol was 1:10 with 2 mass% of catalyst based on oil weight, with the reaction conditions being 70 °C and 1 bar. The agitation speed was 300 rpm. The reaction samples were taken out from the reactor for given times, and after filtration and separation of the residual methanol, analyzed by gas chromatography (Varian 3400) with a FID detector and MET-Biodiesel capillary GC column (14 m×0.53 m, film thickness 0.16 μm). It should be pointed out that for all methanolysis reactions "fresh" catalyst was used, *i.e.*, calcination of mechanochemically synthesized samples was done immediately before experimental run in order to minimize reaction of CaO with ambient CO_2.

Leaching in methanol

When a heterogeneous catalyst is used there is always a possibility of metals leaching, which might contaminate the biodiesel and reduce the lifetime of the catalyst. Therefore, to evaluate lixiviation, the following experimental procedure was employed. The activated catalyst was placed in contact with methanol and kept under stirring conditions (300 rpm) at 70 °C for 4 h. After the reaction, the catalyst was removed by filtration, and methanol was mixed with the necessary volume of sunflower oil, while being kept at 70 °C for 4 h. If catalysts were lixiviated, a different conversion would be observed due to a homogeneous contribution of K(I) and Ca(II). Also, the catalyst treated with methanol, without further washing, was used in transesterification reaction between sunflower oil and methanol under the same reaction conditions.

RESULTS AND DISCUSSION

Characteristic of synthesized CaO·ZnO/$_x$$K_2CO_3$ samples

The XRD patterns of the ball-milled samples with various initial molar K_2CO_3:CaO ratios (x = 0, 1, 2 and 4 mol of K_2CO_3 per 10 mol of CaO) are shown in Figure 1.

Samples synthesized without or with addition of K_2CO_3 reveals phases of calcium zinc hydroxide hydrate ($CaZn_2(OH)_6·2H_2O$) (JCPDS 25-1449) and zinc oxide (JCPDS 36-1451) (Figure 1, CZ – calcium zinc hydroxide hydrate or $CaZn_2(OH)_6·2H_2O$ while CZK_x is abbreviation for sample $CaZn_2(OH)_6·2H_2O/_xK_2CO_3$). Ball milling of CaO and ZnO powders with addition of 2 mol of K_2CO_3 per 10 mol of CaO (Figure 1, CZK_2 for x = 2) resulted in the appearance of somewhat more intense peaks of $CaZn_2(OH)_6·2H_2O$ and in weakening of ZnO compared to the sample prepared with initial molar ratio K_2CO_3/CaO = 1:10 (x = 1). It seems likely that the presence of smaller amount of K_2CO_3 (x = 2), favors the formation of calcium zinc hydroxide hydrate. As the K_2CO_3 content was increased (x = 4), peaks assigned to $CaZn_2(OH)_6·2H_2O$ remarkably decreased (Figure 1, CZK_4), showing that the presence of larger amount of potassium carbonate negatively affected formation of $CaZn_2(OH)_6·2H_2O$. It should be also noted, observing the data shown in Figure 1, that potassium carbonate (JCPDS 49-1093) could not be identified in all analyzed samples.

Results of XRD analysis of the samples after calcination at 700 °C in air is presented in Figure 2.

Calcination leads to the formation of CaO (JCPDS 82-1690) and ZnO phases with only small amounts of $Ca(OH)_2$ (JCPDS 04-0733), while K_2CO_3 or KOH (is possibly formed in reaction between $Ca(OH)_2$ and K_2CO_3) are undetectable. Obviously, the XRD patterns of the mixed oxides prepared with addition of K_2CO_3 ($CZK_{x,700}$) are quite similar to CaO/ZnO mixed oxides ($CZK_{0,700}$) suggesting that K_2CO_3 did not have a significant effect on the phase formation during heat treatment.

The thermogravimetric (TGA) profile of calcium zinc hydroxide hydrate is usually characterized by two-step decomposition (Figure 3).

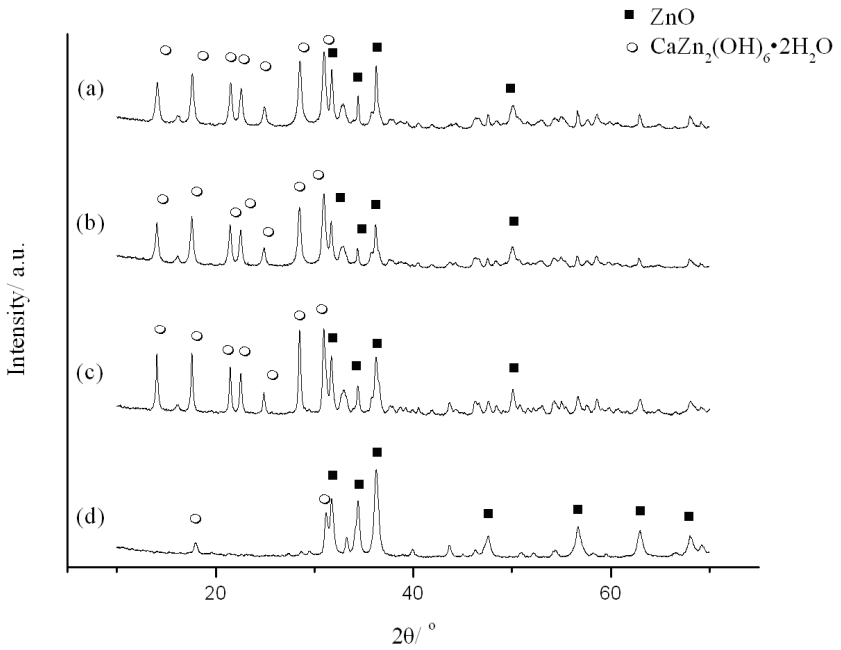

Figure 1. XRD Patterns of the mechanochemically synthesized samples: a) CZK_0; b) CZK_1; c) CZK_2 and d) CZK_4.

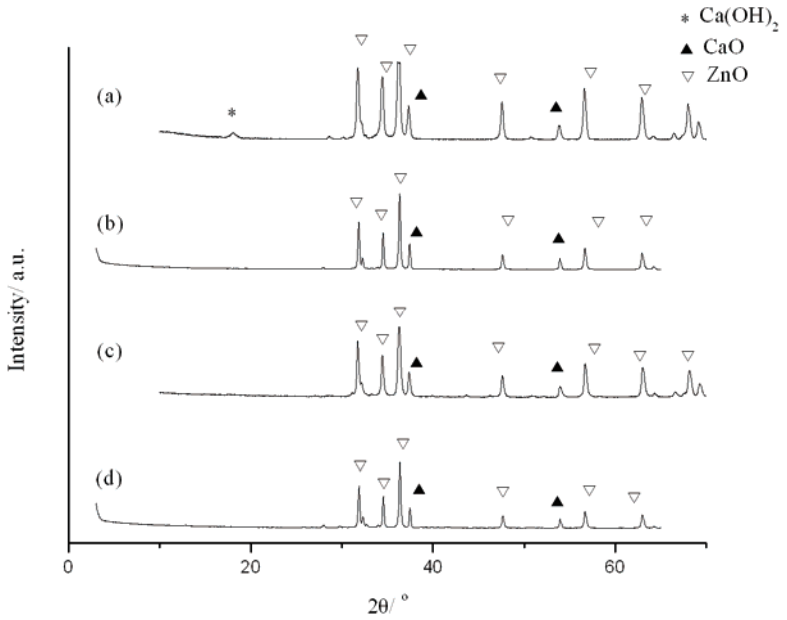

Figure 2. XRD Patterns of the samples obtained by mechanochemical treatment and subsequent calcination at 700 °C: a) $CZK_{0,700}$; b) $CZK_{1,700}$; c) $CZK_{2,700}$ and d) $CZK_{4,700}$.

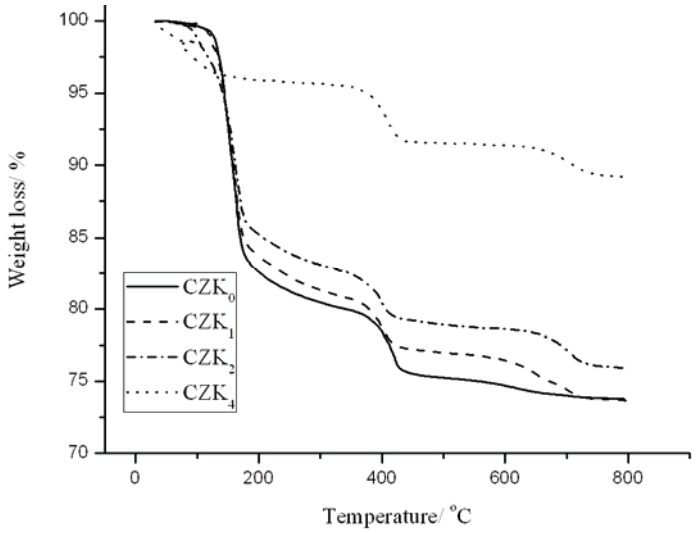

Figure 3. TGA curves of CZK_0, CZK_1, CZK_2 and CZK_4.

The first dominant step of weight loss could be observed from 120 to 180 °C, which may be attributed to the elimination of hydrate water and dehydration of $Zn(OH)_2$ to form ZnO, while second step occurred between 350 and close to 400 °C, arising from dehydration of $Ca(OH)_2$. In respect to the initial composition, the first mass change of calcium zinc hydroxide hydrate should be approximately 23.3%, and the second 5.8% [9,24,25]. Three stages of CZK_x decomposition are observable in temperature ranges of 120–180 °C, 350–400 °C and 600–700 °C. Heating from 400 to 700 °C resulted in the decomposition of $CaCO_3$, which could be formed by the reaction of CaO with CO_2 from air. Pure K_2CO_3 decomposes at about 890 °C [15]. It seems likely that formation of $CaCO_3$ during mechanochemical synthesis hindered the complete formation of $CaZn_2(OH)_6{\cdot}2H_2O$, hence some amount of ZnO was unconsumed. A total mass loss (Figure 3) was slightly higher for the sample synthesized without the addition of K_2CO_3 (CZK_0) than those synthesized with the addition of K_2CO_3 (x = 1, 2). The TGA profiles of CZK_0, CZK_1, and CZK_2 samples clearly show three steps of thermal decomposition during heating from 25 to 800 °C. However, decomposition of $Zn(OH)_2$ and crystal water was not observed for sample CZK_4 (Figure 3) thus confirming results of XRD analysis

(Figure 1, curve d) that $CaZn_2(OH)_6{\cdot}2H_2O$ was not formed in a significant amount. The change in thermal decomposition profile of synthesized samples of CZK_4 may be attributed to the strong interaction of K_2CO_3 and H_2O (dissolving) during ball milling, which suppresses the formation of corresponding mixed calcium zinc hydroxide. The main conclusion could be derived that formation of potassium carbonate and water paste did not enable conversion of CaO and ZnO into corresponding $CaZn_2(OH)_6{\cdot}2H_2O$ only in the case of CZK_4 synthesis. The indication that potassium carbonate makes with water some kind of paste was checked by changing the procedure of mechanochemical synthesis. Experiment was realized with K_2CO_3 (mole ratio of K_2CO_3 to CaO equal to 4:10) added after 2 h of ball milling of CaO and ZnO powders and water. Using such procedure of postponed addition of K_2CO_3 into powder mixture did not change the mechanisms of mixed hydroxide formation.

The Ca, Zn, and K contents were determined by ICP, and the obtained values match well with the amounts of CaO, ZnO and K_2CO_3 used for mechanochemical synthesis. The results of ICP and TG analysis of bulk composition of the prepared samples are summarized in Table 1.

Nominal mass ratio of Ca to Zn used for catalyst preparation is 0.3 (mole ratio Ca/Zn = 1:2) while ICP determined values of Ca/Zn mass ratios are 0.295, 0.331 for CZK_x and 0.316 and 0.281 for $CZK_{x,700}$. Very good agreement between nominal and determined weight ratio of K to Ca were obtained as well. They were 0.163, 0.401 and 0.792 for either CZK_x or $CZK_{x,700}$ samples, which is close to nominal values 0.2, 0.4 and 0.8 for the samples prepared using K_2CO_3/CaO mole ratio equal to 1:10, 2:10 and 4:10, respectively.

The surface characterization of powders before and after calcination was examined by XPS. Instead of the atomic percent that is usually used for representing XPS data, the weight percent of elements at the catalyst surface of the synthesized samples was calculated in order to compare surface (XPS) and bulk (ICP) composition (Table 1).

As it may be seen from Table 1, the surface composition of catalysts significantly differs from their bulk composition. For CZK_0 sample Ca/Zn ratio increased after calcination, showing that CaO is more presented at the surface than expected (Ca/Zn ratio is 0.47). Contrary to CZK_0 calcination of CZK_1 and CZK_2 leads to a decrease of Ca/Zn ratio from initial vales 0.253 and 0.249 to 0.15 and 0.14, respectively.

The K/Ca ratio at surface of catalyst appears to be much higher after mechanochemical treatment compared with the ratio of used starting powders. This can be perhaps explained as a consequence of increased K_2CO_3 dispersion on the surface of catalysts compared to its bulk composition. After calcination at 700 °C, the K/Ca ratio is even higher for CZK_1 and CZK_2, whereas it decreased for CZK_4 catalyst. Evidently, calcination of CZK_1 and CZK_2 causes a higher amount of K_2CO_3 on the surface of the catalyst than in the bulk. That means that $CZK_{1,700}$ and $CZK_{2,700}$ samples are mainly covered by K_2CO_3.

XPS analysis of carbon on the surface of the catalysts indicates that beside K_2CO_3, some amount of $CaCO_3$ is also presented as a result of the reaction of CaO with CO_2 from air. Lopez Granados *et al.* [6] have showed that the carbonation of CaO is very rapid and that only couple of minutes is required to extensively carbonate the sample. The XPS results show that Ca appears on the surface as $CaCO_3$ and $Ca(OH)_2$. Also, it seems likely that in the surface layers of the samples of CZK_1 and CZK_2 the concentration of Ca was reduced during calcination. The lower surface atomic concentration of Ca for $CZK_{1,700}$ and $CZK_{2,700}$ is consistent with Zn migration to the surface as well as K_2CO_3 distribution on the surface layer of catalysts. Since for the CZK_4 sample formation of $CaZn_2(OH)_6{\cdot}2H_2O$ did not occur during milling, the Ca/Zn ratio on the surface (0.33) is very

Table 1. The surface (XPS analysis) and the bulk (ICP and TGA analysis) composition of the synthesized samples

Sample	Surface composition, mass%					Bulk composition, mass%				
	Ca	Zn	K	O	C	Ca	Zn	K	O	C
CZK_0	17.14	52.08	0.00	27.82	2.96	12.22	41.38	-	46.02	0.38
$CZK_{0\text{-}700}$	22.03	46.87	0.00	28.16	2.94	16.56	56.08	-	27.36	-
CZK_1	12.43	49.03	9.00	26.51	3.03	11.20	33.82	1.83	52.03	1.12
$CZK_{1\text{-}700}$	7.92	52.67	12.59	23.65	3.18	15.20	45.89	2.48	36.05	0.38
CZK_2	9.83	39.36	20.37	26.61	3.83	11.70	37.02	4.70	45.14	1.43
$CZK_{2\text{-}700}$	7.04	49.92	15.69	23.53	3.82	15.41	48.77	6.19	28.68	0.95
CZK_4	13.14	22.56	28.73	28.93	6.64	11.19	39.80	8.86	38.07	2.07
$CZK_{4\text{-}700}$	12.19	36.85	19.00	27.04	4.93	12.64	44.97	10.01	30.85	1.53

close to ICP or nominal values (0.28 and 0.3, respectively) after the calcination.

FTIR spectroscopy was employed to investigate the functional groups of prepared samples obtained after ball milling of CaO, ZnO, K_2CO_3 and H_2O (Figure 4).Bands at 1541 and 1385 cm^{-1} were observed for all catalyst samples prepared with addition of K_2CO_3 and as such are attributed to carbonate species, whereas the band at 1385 cm^{-1} indicates the presence of bulk K_2CO_3 [26]. The fundamental bands of $CaCO_3$ can be detected by the peaks at 1465, 874 and 712 cm^{-1} and the band at 2350 cm^{-1} from the vibrations of CO_2. A sharp absorption band at 1650 cm^{-1} is attributed to H-OH bending while a broad band between 3000 and 3500 cm^{-1} is assigned to O-H stretching vibrations [27]. Also, characteristic bands for $CaZn_2(OH)_6{\cdot}2H_2O$ were observed: two sharp bands at 3615 and 3505 cm^{-1} assigned to ν(OH) stretching vibrations, a band which is characteristic of the O-H stretching vibration of $Ca(OH)_2$ at 3643 cm^{-1}, and a bridging OH bending mode visible at 940 cm^{-1}. The bending vibration of Zn-O-H can be noticed at 1070 cm^{-1} while the stretching bands at 3150, 3034 and 2880 cm^{-1} are attributed to the O-H groups from H_2O molecules [28].

The morphology and surface structure of the catalysts were analyzed by SEM and elemental composition by EDS. The SEM images of the samples calcined at 700 °C shown in Figure 5 at two different magnifications.

The $CZK_{0,700}$ powder sample was in the homogeneous form of small spherical particles having similar structure, but some large aggregates are also present (Figure 5b). The effect of K_2CO_3 addition on the morphology of CaO·ZnO mixed oxides is most obvious by comparing SEM images of the $CZK_{0,700}$ (Figure 5b) to $CZK_{1,700}$ powder (Figure 5d). It may be seen that particles of $CZK_{1,700}$ somewhat increase in size, whereby their shape also slightly change. Also, it can be seen that many particles stick together, perhaps as a result of initial sintering during heat treatment at 700 °C. The calcined CZK_1, CZK_2 and CZK_4 show similar particle morphology, which is presented by crystallites with irregular sizes and shapes (Figure 5c-h). Since all samples are considered as catalysts with small surface area and low porosity [8], the size of the particle should correspond to the surface area.

In addition to the XPS and ICP analysis, EDS (several typical points as well as EDS element mapping) was applied to determine the average value of atomic distribution of Ca, Zn, O and K for each catalyst. Detected Ca/Zn mass ratios for the samples $CZK_{0,700}$, $CZK_{1,700,}$ $CZK_{2,700}$, and $CZK_{4,700}$ are 0.236, 0.164, 0.162 and 0.313, respectively. The fairly homogeneous distribution of CaO and ZnO for $CZK_{0,700}$ agrees to previous results obtained with $Ca(OH)_2$ as one of the starting reagent [8]. EDS analysis reveals K/Ca mass ratio of 0.374, 0.665 and 0.563 for samples $CZK_{1,700}$, $CZK_{2,700}$, and $CZK_{4,700}$, respectively. As may be expected, these values are closer to the result of ICP analysis (0.19, 0.39 and 0.73) than XPS analysis (1.59, 2.23 and 1.56).

According to these results it might be concluded that the difference between nominal and measured

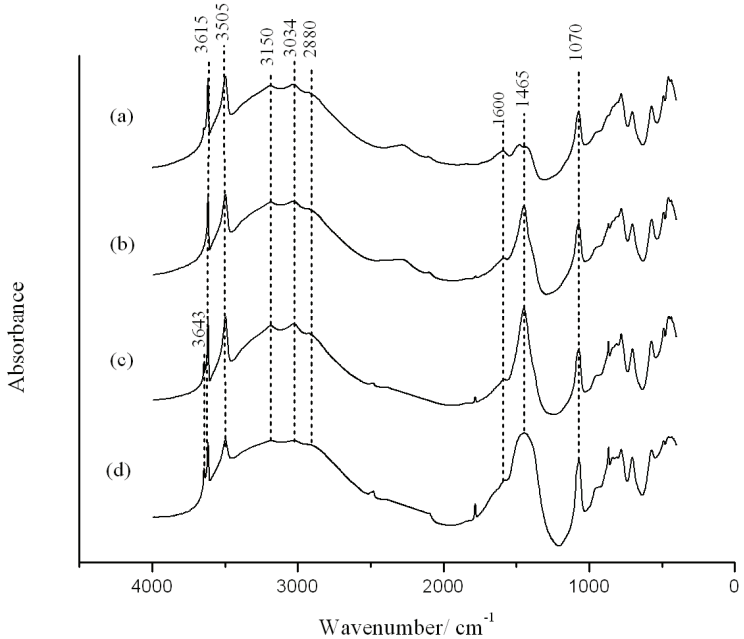

Figure 4. FTIR spectra of: a) CZK_0; b) CZK_1; c) CZK_2; d) CZK_4.

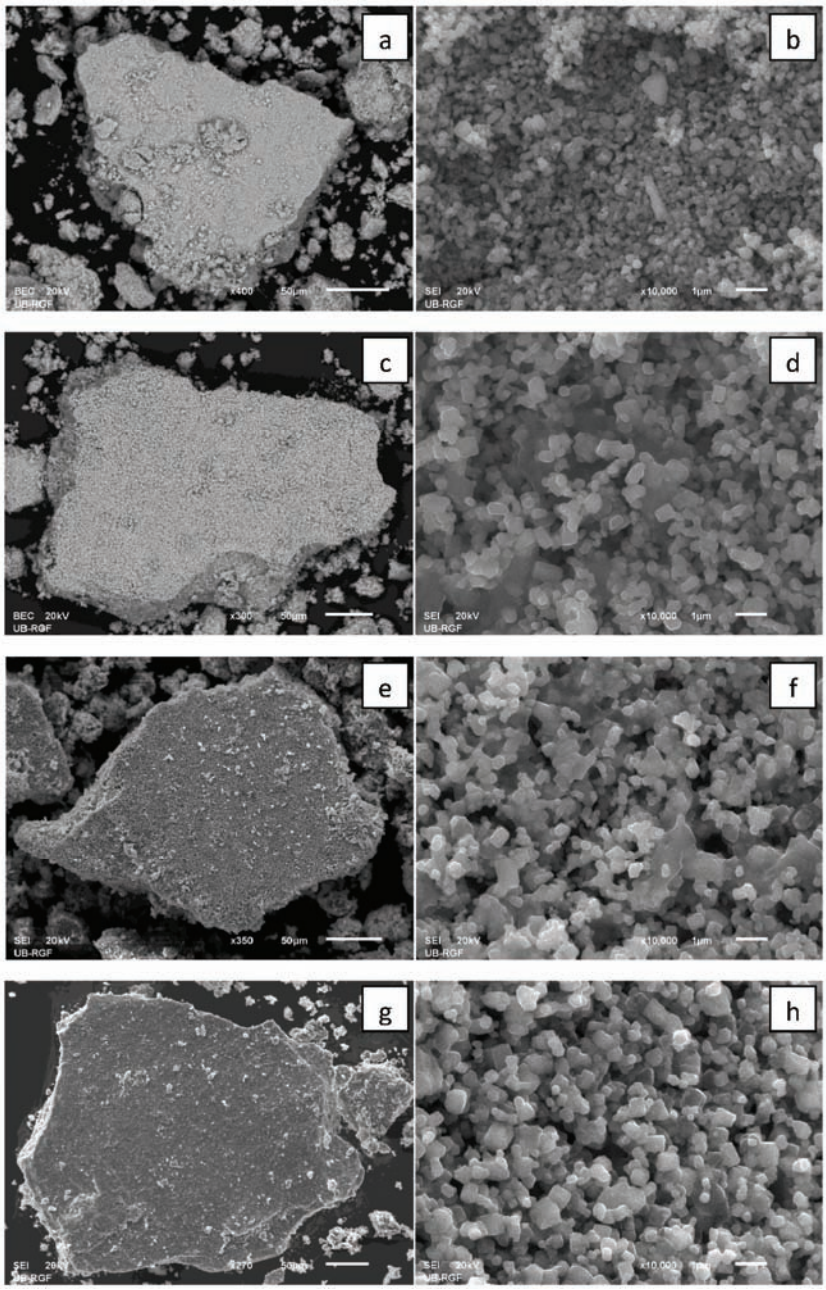

Figure 5. SEM Images of the samples after calcination at 700 °C: a,b) $CZK_{0,700}$; c,d) $CZK_{1,700}$; e,f) $CZK_{2,700}$; g,h) $CZK_{4,700}$.

(SEM/EDS) Ca/Zn mass ratio is higher in the case of $CZK_{1,700}$ and $CZK_{2,700}$ samples than for $CZK_{0,700}$ and $CZK_{4,700}$. The sample $CZK_{4,700}$ has almost identical Ca/Zn mass ratio determined by SEM/EDS (0.313) as nominal or ICP determined value (0.3 and 0.281). The EDS element mapping shows uniform distribution of CaO and ZnO as well as K_2CO_3 for all $CZK_{x,700}$ samples. Therefore, very fine and homogeneous microstructure of composite powders was obtained. EDS element mapping of $CZK_{4,700}$ sample indicated that several clusters of CaO and K_2CO_3 are mainly separated from ZnO.

The results of particle size distributions of ball milled sample as well as the samples after calcination at 700 °C in air (CZK_0 and $CZK_{0,700}$) are relatively uniform with a size range of 0.4–30 μm, while for the samples CZK_x (x = 1, 2 and 4) prepared with addition of K_2CO_3 is bimodal. For samples containing K_2CO_3 the larger fraction of the powder particles is within the size range of 8–100 μm with the rest being within the range of 0.4–8 μm.

Bimodal distribution was detected for all catalyst after calcination at 700 °C ($CZK_{x,700}$; x = 0, 1, 2 and 4). The first is within the size range of 1–3 μm and the

second is in the range of 10-20 μm. It must be pointed out that there is no difference between particles size distribution for the samples synthesized without addition of K_2CO_3 whether CaO or $Ca(OH)_2$ is used as a starting powder [8], so after calcination at 700 °C all the samples have a similar bimodal distribution.

Calcination of the CZK_1 and CZK_2 at 700 °C affects particle size distribution and specific surface area. The specific surface areas of these samples increased from 2.31 (CZK_1) and 1.87 m^2/g (CZK_2) to 3.01 m^2/g (for both $CZK_{1,700}$ and $CZK_{2,700}$), plausibly as a consequence of $CaZn_2(OH)_6{\cdot}2H_2O$ decomposition and formation of CaO·ZnO matrix "impregnated" with an amount of K_2CO_3. At the same time, the specific surface area of CZK_4 after calcination decreased from 3.35 to 2.87 m^2/g ($CZK_{4,700}$) due to removal of H_2O and CO_2 after decomposition of $Ca(OH)_2$ and $CaCO_3$, respectively.

Table 2 summarizes the basic strength of the samples prepared by ball milling and calcination.

All the synthesized $CZK_{x,700}$ catalysts were able to change the color of phenolphthalein (H_- = 9.3) from colorless to purple, but failed to change the color of 4-nitroaniline (H_- = 18.4). The order of basicity is as follows: $CZK_{1,700}$ <$CZK_{0,700}$ < $CZK_{2,700}$ < $CZK_{4,700}$. Increased basicity of $CZK_{2,700}$ and $CZK_{4,700}$ compared to $CZK_{0,700}$ might be explained by the presence of a larger amount of K_2CO_3, which possess, similar to CaO, a strong basic character (Table 2). Moreover, some authors have reported that the surface basicity of the alkaline earth hydroxides could be increased by milling [29], which means that detected basicity of $CZK_{x,700}$ samples could be even higher than expected according to the composition and basicity of individual constituents CaO, ZnO and K_2CO_3. Such phenomena was not observed in this study taking into account sample composition and basicity of individual components that are the main constituents of prepared sample (Table 2, CaO, K_2CO_3 and $CZK_{0,700}$).

Activity of prepared CaO·ZnO with K_2CO_3 for biodiesel synthesis

The results of activity test applying prepared $CZK_{x,700}$ samples with different K_2CO_3 to CaO molar ratio, *x,* as catalyst are presented in Figure 6.

Triglycerides (TG) of sunflower oil and methanol (MeOH) react giving FAME (fatty acid methyl esters) and glycerol (Gly) according to the simple summary equation:

$$TG + 3MeOH \rightarrow Gly + 3FAME$$

Table 2. Basic strength of the catalysts (mmol g^{-1}) prepared by ball milling and calcination at 700 °C

Catalyst	Phenolphthalein (H_- = 9.3)	Thymolphthalein (H_- = 10.0)	Thymolviolet (H_- = 11.0)	4-nitroaniline (H_- = 18.4)
$CZK_{0,700}$	0.116	0.180	0.276	-
$CZK_{1,700}$	0.168	0.098	-	-
$CZK_{2,700}$	0.532	0.612	0.308	-
$CZK_{4,700}$	0.872	0.800	0.728	-
K_2CO_3	4.324	4.188	4.120	-
CaO before calcination	0.490	0.124	-	-

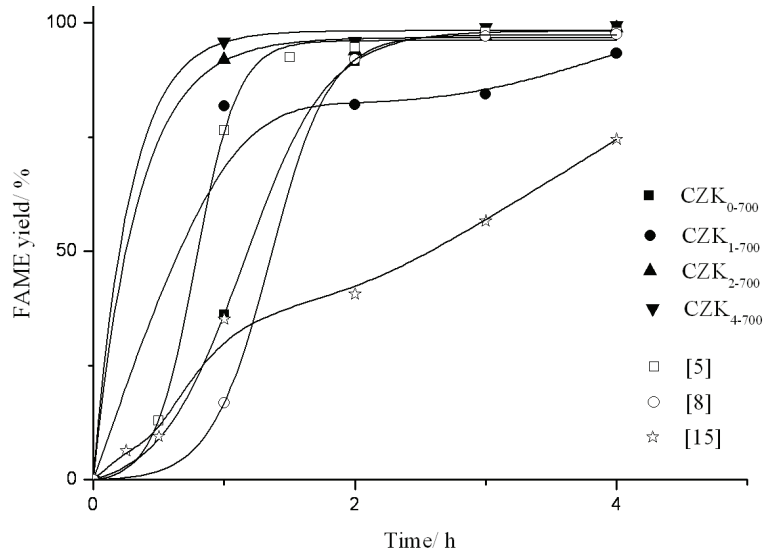

Figure 6. FAME yield versus time obtained with $CZK_{x,700}$ (x=0, 1, 2 and 4), CaO·ZnO [8], CaO [5] and supported K_2CO_3 [15] as catalyst.

FAME yield was derived from the TG conversion (X_{TG}) because only minor amount of diglycerides and monoglycerides (intermediates formed from TG and MeOH) are presented in reaction mixture, as verified by GC analysis:

$$\text{FAME yield} = 100\frac{TG_0 - TG}{TG_0}$$

where TG_0 is the initial mass of triglycerides (sunflower oil) and TG is the triglyceride content in reaction mixture for given reaction time.

It must be pointed out that $CZK_{x,700}$ catalysts (x = = 1, 2 and 4) have a higher initial activity for biodiesel synthesis compared to catalyst $CZK_{x,700}$ (x = 0; this study), and other recently tested catalysts: CaO·ZnO [8], CaO [5], and supported K_2CO_3 on Al-O-Si [15], as shown in Figure 6. All the samples containing K_2CO_3 are very active enabling TG conversion above 80% after the first hour of methanolysis at 70 °C (mole ratio of methanol to oil 10:1 and 2 mass% of catalyst) implying that the addition of K_2CO_3 in the process of CaO·ZnO mixed oxide preparation substantially improved the initial rate of methanolysis compared to pure CaO·ZnO catalyst.

The experimental results of many researches performed with heterogeneous catalyst suggested that a higher basicity could be related to increased activity of the catalysts and resulted to the higher rate of biodiesel synthesis. This is proved for the samples $CZK_{2,700}$ and $CZK_{4,700}$ but not for the $CZK_{1,700}$. In fact, as it was already pointed out the $CZK_{1,700}$ is the only sample which failed to change the color of thymolviolet ($H-$ = 11.0). Although $CZK_{1,700}$ poses weaker basicity, it is more active catalyst for transesterification reaction compared to $CZK_{0,700}$ at the beginning of methanolysis syntehsis. Such observation may be mainly attributed to the leaching of potassium which is very active species. Furthermore, a lower basicity of $CZK_{1,700}$ most likely arises from the higher surface concentration of Zn, since pure Zn is reported as acidic [30].

The large amount of potassium presented at catalyst surface (Table 1) might be easily dissolved in methanol causing also homogeneous catalytic effect of prepared $CZK_{x,700}$ samples (x = 1, 2 and 4). The leaching of alkali metals into methanol from prepared samples $CZK_{x,700}$ is an important parameter responsible for faster methanolysis of triglycerides at the beginning of methanolysis of sunflower oil (Figure 6). The results of determined solubility of Ca(II), K(I) and Zn(II) in methanol at 60 °C are shown in Table 3.

Low solubility of Ca and Zn was detected for all $CZK_{x,700}$ (x = 1, 2, 4) samples and was smaller than that determined for the sample prepared without addition of K_2CO_3 ($CZK_{0,700}$). These results are in accordance with those reported by Alba-Rubio *et al.* [19] who showed that the solubility of Ca was reduced by adding Na_2CO_3 to the reaction mixture at the beginning of the transesterification reaction. At the same time, solubility of potassium from the samples $CZK_{1,700}$ and $CZK_{2,700}$ was almost the same, while for the $CZK_{4,700}$ it was more than four times higher after treatment at 60 °C for 2 h. These data are in direct correlation with catalytic activity of prepared samples containing K_2CO_3 and prove that both potassium presented in solid phase as well as that dissolved in methanol are the main factor influencing the initial rate of triglycerides methanolysis, as shown in Figure 6.

Table 3. Ca, Zn and K solubility in methanol (ppm)

Catalyst	Ca^{2+}	Zn^{2+}	K^+
$CZK_{0,700}$	62.4	7.1	-
$CZK_{1,700}$	39.7	1.9	406.9
$CZK_{2,700}$	8.4	3.6	405.5
$CZK_{4,700}$	23.3	4.5	1807.3

The leaching experiments described in Experimental section were carried out to clarify at the same time “homogeneous” and “heterogeneous” catalytic effect during the sunflower oil methanolysis with $CZK_{x,700}$ (x = 2 and 4) catalyst. Namely, experiments of sunflower methanolysis performed using only methanol prepared by leaching of $CZK_{x,700}$ showed that so-called “methanol activity” could be correlated with the amount of dissolved potassium ion. Thus, a higher yield of FAME was obtained using methanol by leaching of $CZK_{4,700}$ than by $CZK_{2,700}$. These results also agree with the analysis of activity using solid phase after the leaching process. The opposite effect was observed; the solid particles remained after leaching test of $CZK_{4,700}$ had smaller activity comparing to catalyst after the leaching test with $CZK_{2,700}$. The results of these tests evidently indicate that “homogeneous catalytic effect” in FAME synthesis was caused by the presence of smaller ($CZK_{2,700}$) or larger amounts of K_2CO_3 ($CZK_{4,700}$) that was dissolved in methanol.

Calculation of the amount of K_2CO_3 dissolved in methanol on the basis of solubility data (Table 3) shows that 29% of K_2CO_3 could be dissolved from $CZK_{4,700}$ at 60 °C (0.150 g of 0.520 g K_2CO_3 presented in 2.605 g of used catalysis for methanolysis) in comparison to 11% from $CZK_{2,700}$ (0.034 g) and 22% of $CZK_{1,700}$ (0.034 g), respectively. Knowing that reaction mixture used for methanolysis was prepared with 130 g of sunflower oil, 47 g of methanol, and

2.605 g of catalyst, dissolved concentration of K_2CO_3 per mass of sunflower oil is in the range 0.03–0.12% ($CZK_{2,700}$, $CZK_{1,700}$ and $CZK_{4,700}$). It must be also pointed out that the amount of potassium and calcium in prepared $CZK_{x,700}$ samples and the one dissolved in methanol would be much smaller compared to usually used amount of heterogeneous catalysts (CaO, KF/CaO/cinder, K_2CO_3 or K/CaO) for vegetable oil methanolysis [5,16,31-33]. A plausible reason is that as a result of mechanochemical treatment K_2CO_3 is embedded in very fine nanocomposite matrix, thus impeding and delaying K and Ca dissolution.

The Ca, Zn and K contents of $CZK_{2,700}$ have been determined by ICP after the transesterification reaction. Weight ratio of Ca/Zn as well as K/Ca decreased due to dissolution of K and Ca in reaction mixture, whereby Ca and K occur mainly in glycerol with less than 50 ppm of both elements in FAME (biodiesel). This is in an agreement with recently reported results that the most of the leached metal was settled in glycerol layer formed during the reaction [33,34].

Although activity is almost the same for catalyst $CZK_{2,700}$ and $CZK_{4,700}$, the sample prepared with smaller amount of K_2CO_3 (x = 2) has an advantage taking into the account much smaller solubility of K as well as Ca in methanol and thus more important heterogeneous catalytic effect.

CONCLUSION

The formation of mixture of calcium zinc hydroxide hydrate with potassium carbonate ($Ca{\cdot}Zn_2(OH)_6{\cdot}2H_2O/_xK_2CO_3$) was obtained during ball milling of CaO, ZnO, K_2CO_3 and water but only if the initial mole ratio of K_2CO_3 to CaO was $x \leq 2$. For CaO/K_2CO_3 ratios larger than 2:10, the formation of mixed calcium zinc hydroxide is suppressed, and only a mixture of CaO or ZnO phases with K_2CO_3 as well as certain amounts of $Ca(OH)_2$ and $CaCO_3$ could be detected.

Calcination of prepared samples were done at 700 °C in air and their catalytic activity for methanolysis of sunflower oil (70 °C; methanol to oil molar ratio of 10:1; 2 mass% of catalyst) were analyzed. It was found that all samples possessed the desired activity and that the presence of potassium carbonate undoubtedly accelerated the methanolysis reaction. However, increased leaching in methanol as well suppressed formation of calcium zinc mixed hydroxide for $x > 2$ leads to more expressed homogeneous-heterogeneous catalytic effect of prepared $CZK_{4,700}$ sample. The smallest solubility of potassium and calcium into methanol for sample $CaO{\cdot}(2ZnO)_{(2)}K_2CO_3$ ($CZK_{2,700}$) was detected and this sample is pointed out as more acceptable for biodiesel synthesis.

Acknowledgments

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 45001). The authors thank Dr. Smilja Marković from ITS SASA for performing particle size measurements and Dr. Georgi Tyuliev from Bulgarian Academy of Sciences, Institute of Catalysis for performing the XPS analysis.

REFERENCES

[1] M. Zabeti, W.M.A. Wan Daud, M. Kheireddine Aroua, Fuel Process. Technol. **90** (2009) 770–777

[2] G. Vicente, M. Martinez, J. Aracil, Bioresour. Technol. **92** (2004) 297–305

[3] A.P. Singh Chouhan, A.K. Sarma, Renew. Sust. Energy Rev. **15** (2011) 4378–4399

[4] Z. Helwani, M.R. Othman, N. Aziz, J. Kimc, W.J.N. Fernando, Appl. Catal., A **363** (2009) 1–10

[5] V.B. Veljković, O.S. Stamenković, Z.B. Todorović, M.L. Lazić, D.U. Skala, Fuel **88** (2009) 1554–1562

[6] M. Lopez Granados, M.D. Zafra Poves, D. Martin Alonso, R. Mariscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaría, J.L.G. Fierro, Appl. Catal., B **73** (2007) 317–326

[7] Y.H. Taufiq-Yap, H.V. Lee, M.Z. Hussein, R. Yunus, Biomass Bioenerg. **35** (2011) 827–834

[8] Ž. Kesić, I. Lukić, D. Brkić, J. Rogan, M. Zdujić, H. Liu, D.Skala, Appl. Catal., A **427–428** (2012) 58–65

[9] J.M. Rubio-Caballero, J. Santamaría-Gonzáles, J.M. Mérida-Robles, R. Moreno-Tost, A. Jiménez-López, P. Maireles-Torres, Appl. Catal., B **91** (2009) 339–346

[10] D. Martín Alonso, R. Mariscal, M. López Granados, P. Maireles-Torres, Catal. Today **143** (2009) 167–171

[11] C.S. MacLeod, A.P. Harvey, A.F. Lee, K. Wilson, Chem. Eng. J. **135** (2008) 63–70

[12] M. Fan, P. Zhang, Q. Ma, Bioresour. Technol. **104** (2012) 447–450

[13] G. Arzamendi, E. Arguiñarena, I. Campo, S. Zabala, L.M. Gandía, Catal. Today **133–135** (2008) 305–313.

[14] Y.Wang, J. Hua Zhu, W. Yu Huang, Phys. Chem. Chem. Phys. **3** (2001) 2537–2543

[15] I. Lukić, J. Krstić, D. Jovanović, D. Skala, Bioresour. Technol. **100** (2009) 4690–4696

[16] H. Liu, L. Su, F. Liu, C. Li, U. Solomon, Appl. Catal., B **106** (2011) 550–558

[17] G. Teng, L. Gao, G. Xiao, H. Liu, J. Lv, Appl. Biochem. Biotechnol. **162** (2010) 1725–1736

[18] A. D'Cruz, M.G. Kulkarni, L. Charan Meher, A.K. Dalai, J. Am. Oil. Chem. Soc. **84** (2007) 937–943

[19] A.C. Alba-Rubio, M.L. Alonso Castillo, M.C.G. Albuquerque, R. Mariscal, C.L. Cavalcante Jr., M. López Granados, Fuel **95** (2012) 464–470

[20] J.M. Rubio-Caballero, J. Santamaría-Gonzáles, J.M. Mérida-Robles, R. Moreno-Tost, M.L. Alonso-Castillo, E. Vereda-Alonso, A. Jiménez-López, P. Maireles-Torres, Fuel **105** (2013) 518-522

[21] E. Avvakumov, M. Senna, N. Kosova, Soft Mechanochemical Synthesis: A Basis for New Chemical Technologies, Kluwer Academic Publishers, Dordrecht, 2001

[22] K. Ralphs, C. Hardacreand, S.L. James, Chem. Soc. Rev. **42** (2013) 7701-7718

[23] I. Lukić, Ž. Kesić, S. Maksimović, M. Zdujić, H. Liu, J. Krstić, D. Skala, Fuel **113** (2013) 367-378

[24] S. Wang, Z. Yang, L. Zeng, Mater. Chem. Phys. **112** (2008) 603-606

[25] H. Yang, H. Zhang, X. Wang, J. Wang, X. Meng, Z. Zhou, J. Electrochem. Soc. **151** (2004) A2126-A2131

[26] I. Lukić, J. Krstić, S. Glišić, D. Jovanović, D. Skala, J. Serb. Chem. Soc. **75** (2010) 789-801

[27] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., John Wiley & Sons, New York, 1997

[28] T.-C. Lin, M.A. Mollah, R.K. Vempati, D.L. Cocke, Chem. Mater. **7** (1995) 1974-1978

[29] T. Watanabe, J. Liao, M. Senna, J. Solid State Chem. **115** (1995) 390-394

[30] W. Xie, H. Huang, Catal. Lett. **107** (2006) 53-59

[31] C. Baroi, E.K. Yanful, M.A. Bergougnou, Int. J. Chem. React. Eng. **7** (2009) Article A72

[32] L. Wen, Y. Wang, D. Lu, S. Hu, H. Han, Fuel **89** (2010) 2267-2271

[33] D. Kumar, A. Ali, Biomass Bioenergy **46** (2012) 459-468.

[34] L. Čapek, M. Hájek, P. Kutálek, L. Smoláková, Fuel **115** (2014) 443-451.

ŽELJKA KESIĆ[1]
IVANA LUKIĆ[1]
MIODRAG ZDUJIĆ[2]
ČEDOMIR JOVALEKIĆ[3]
HUI LIU[4]
DEJAN SKALA[5]

[1]Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd, Srbija
[2]Institut tehničkih nauka Srpske akademije nauka i umetnosti, Beograd, Srbija
[3]Univerzitet u Beogradu, Institut za multidisciplinarna istraživanja, Beograd, Srbija
[4]University of Geosciences, School of Environmental Studies, Wuhan, China
[5]Univerzitet u Beogradu, IHTM Centar za katalizu i hemisjko inženjerstvo, Beograd, Srbija

NAUČNI RAD

MEHANOHEMIJSKA SINTEZA $CaO{\cdot}ZnO{\cdot}K_2CO_3$ KATALIZATORA: KARAKTERIZACIJA I AKTIVNOST U METANOLIZI SUNCOKRETOVOG ULJA

Cilj ovih istraživanja bio je da se pripremi $CaO{\cdot}ZnO$ katalizator koji sadrži malu količinu K_2CO_3 i analizira njegova aktivnost u sintezi biodizela. Katalizator je pripremljen prema sledećoj proceduri: CaO i ZnO (molski odnos 1:2), voda i K_2CO_3 (u različitoj količini) su tretirani mehanohemijski i nakon mlevenja zagrevani na 700 °C u atmosferi vazduha da bi se dobila smeša oksida $CaO{\cdot}ZnO/xK_2CO_3$ (x = 0, 1, 2 i 4 mol K_2CO_3 na 10 mol CaO). Karakterizacija pripremljenih katalizatora izvršena je metodama rendgenske difrakcije (XRD), indukovane kuplovane plazme (ICP), spektroskopije fotoelektrona dobijenih X-zracima (XPS), termogravimetrijske analize (TGA), infracrvene spektroskopije (FTIR), skenirajuće elektronske mikroskopije i energetske disperzione spektroskopije (SEM/EDS), raspodele veličine čestica (PSLD), merenjem rastvorljivosti katalizatora odnosno Ca, Zn i K jona u metanolu, kao i određivanjem njihove baznosti (metodom Hametovih indikatora). Pripremljeni $CaO{\cdot}ZnO/xK_2CO_3$ kompozitni prahovi testirani su kao katalizatori u reakciji metanolize suncokretovog ulja na 70 °C, pri molarnom odnosu suncokretovog ulja i metanola od 1:10 i sa 2 mas.% katalizatora u odnosu na masu ulja. Pokazano je da prisustvo K_2CO_3 u pripremljenim uzorcima povećava aktivnost katalizatora i da je takav efekat posledica homogeno-heterogene katalize u sintezi biodizela.

Ključne reči: mehanohemijska sinteza, CaO, ZnO, K_2CO_3, mešani oksidi, sinteza biodizela.