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Zdujić, Miodrag, Ivana Lukić, Željka Kesić, Ivona Janković-Častvan, Smilja Marković, Čedomir Jovalekić, and Dejan Skala. “Synthesis of CaOSiO₂ Compounds and Their Testing as Heterogeneous Catalysts for Transesterification of Sunflower Oil.” *Advanced Powder Technology*, March 15, 2019. <https://doi.org/10.1016/j.appt.2019.03.009>.



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Synthesis of CaO–SiO₂ compounds and their testing as heterogeneous catalysts for transesterification of sunflower oil

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Abstract

The powder mixtures of calcium oxide (CaO) and silica gel (SiO₂) in molar ratios of 1:1, 1.5:1, 2:1 and 3:1 were mechanochemically treated with the addition of water, and were subsequently calcined with a goal of synthesizing CaSiO₃, Ca₃Si₂O₇, Ca₂SiO₄ compounds and CaO/Ca₂SiO₄ two-phase mixture. The prepared materials were characterized by XRD, FTIR, SEM/EDS, particle size laser diffraction (PSLD), UV-vis diffuse reflectance spectroscopy (DRS), N₂ adsorption/desorption isotherms, Hammett indicator for basic strength and volumetric analysis for free CaO content. The catalytic activity of calcium silicates with different Ca/Si ratios was tested in the transesterification of triacylglycerols (sunflower oil) with methanol. Samples obtained with initial composition 2CaO·SiO₂ and 3CaO·SiO₂ calcined at 700 °C, and 3CaO·SiO₂ calcined at 900 °C had high catalytic activity, resulting with triacylglycerols conversion and fatty acids methyl ester formation (FAME or biodiesel) above 96%. The activity of these samples can be attributed to the existence of free CaO defined by CaO/Ca₂SiO₄ complex mixture. The effect of different amount of catalyst used for transesterification (0.2–2 wt%) was analyzed using the most active catalyst i.e. 3CaO·SiO₂ calcined at 700 °C as well as possibility of its reuse for biodiesel synthesis. It was also found that CaSiO₃, Ca₃Si₂O₇ and Ca₂SiO₄, phases did not possess catalytic activity.

Keywords: Calcium silicates; Biodiesel, CaO; Catalytic activity.

1. Introduction

The CaO–SiO₂ system has been quite well investigated, primary because of the importance of calcium silicate phases in the cement industry [1].

In the CaO–SiO₂ quasi-binary phase diagram [2] four compounds exist, namely calcium silicate (CaSiO₃), dicalcium silicate (Ca₂SiO₄), tricalcium disilicate (Ca₃Si₂O₇) and tricalcium silicate (Ca₃SiO₅), commonly known by mineralogical names wollastonite, larnite (or belite as is the name used in cement industry), rankinite and alite, respectively. Alite (Ca₃SiO₅) and belite (Ca₂SiO₄) are two major constituents of Portland cement [1]. Wollastonite (CaSiO₃) due to its favorable properties, such as resistance to chemical attack, inertness, stability at high temperatures, and improved flexural and tensile strength, is used in ceramics, metallurgy, plastics and rubber, as well as an additive in paints, as substituent of asbestos, as an insulator and for other applications [3]. Moreover, calcium silicate (CaSiO₃), dicalcium silicate (Ca₂SiO₄) and tricalcium silicate (Ca₃SiO₅) have been found to have good bioactivity and as such they are promising candidates for biomaterials [4][5].

The CaO–SiO₂ system was also investigated as solid base catalysts for biodiesel production. The main goal for its application was to reduce leaching and to improve stability and activity of pure CaO, which possesses a high activity in transesterification of different triacylglycerols (vegetable oils) with alcohol (mainly methanol) into a mixture of fatty acid methyl esters (FAME or biodiesel) and glycerol. Albuquerque et al. [6] first reported the use of CaO-loaded mesoporous silica (MCM-41 and SBA-15) as catalysts for biodiesel synthesis from sunflower oil and methanol, demonstrating their acceptable catalytic activity under mild reaction condition (60 °C) with the triacylglycerols conversion over 95%. Thus, calcium oxide supported on porous silica

prepared by incipient wetness impregnation method [7], CaO–SiO₂ composites prepared through a biomimetic silicification [8] or sol-gel method [9][10], calcium containing silicate mixed oxide as a non-porous and an anionic-surfactant-templated materials prepared by wet chemistry [11] have been used as catalyst for biodiesel synthesis. Sun et al. reported the rod-like Ca_xSiO_{x+2} composites with Ca/Si molar ratio of 1, 2, 3 and 4 formed by hydrothermal method as catalysts for biodiesel synthesis. The most active catalyst in their study was labeled as Ca₄SiO₆ where the authors found out that the main phase formed was Ca₃SiO₅ with a trace amount of CaO [12].

In the majority of articles dealing with the CaO–SiO₂ system, the active sites of the catalyst are presented by CaO, while the carrier stabilizes these active species on its surface. Using pure CaO as a catalyst, the biodiesel yield was found to drop from 90% to 43% after 12 consecutive cycles of the transesterification of palm oil, but the reusability of the catalyst was improved with the addition of SiO₂ [8]. Both, catalytic activity and stability in CaO–SiO₂ catalysts are also in correlation with Ca/Si ratio [8][11]. It was found that with the increase of the amount of Si compounds, the catalytic activity was gradually decreased, while the reusability was significantly improved [8]. Mesoporous CaO/SBA-15 catalysts synthesized via a hydrothermal method, which are the result of better calcium oxide distribution and the formation of Ca–O–Si bonds, showed enhanced stability compared to those prepared by conventional impregnation method, thus also indicating the importance of the catalyst preparation procedure [13].

Recent studies demonstrate that natural material such as dolomite (SiO₂·nH₂O) [14] and peat biochar [15] may be successfully applied for a preparation of a supported CaO catalyst for biodiesel production. The high stability of catalyst was attributed to the Ca–O–Si bond on the catalyst surface. However, it should be noted that these natural materials contain, beside

dominantly Ca and Si, other elements such as K and Mg, which also exhibit catalytic activity in transesterification reaction.

Using commercial CaSiO_3 calcined at $550\text{ }^\circ\text{C}$, biodiesel yield above $> 96\%$ was obtained at room temperature ($28\text{ }^\circ\text{C}$) but at rather extreme conditions : reaction time of 24 h, molar ratio of methanol to soybean oil of 27: 1 and the catalyst dosage of 23 wt% [16].

So far, several methods have been applied for the synthesis of calcium silicates (CaO-SiO_2 mixed oxide materials), namely solid state reactions at high temperatures (typically above $1000\text{ }^\circ\text{C}$), wet chemical methods such as co-precipitation and sol-gel, as well as hydrothermal synthesis. Additionally, the mechanochemical treatment, in particular wet grinding has also been used for the synthesis of calcium silicate hydrates [17][18].

From the foregoing it appears that there is a considerable interest to study these compounds and their potential application in various fields of materials science and technology, such as cement and concrete, biomaterials as well as its application as heterogeneous catalyst for some special chemical reactions, e.g. transesterification of triacylglycerols (vegetable oil) with methanol and formation of corresponding FAMEs or biodiesel.

The goal of this work is to obtain various phases which exist in quasi-binary CaO-SiO_2 phase diagram, and to examine their catalytic activity in transesterification of sunflower oil with methanol. Mechanochemical treatment followed by calcination, as a simple and solvent-free procedure was chosen for the synthesis of calcium silicate with different Ca/Si ratios, **using high purity CaO and SiO_2 as reactants**. Catalytic activity of prepared samples, after their calcinations at various temperatures (700 and $900\text{ }^\circ\text{C}$) was analyzed at $60\text{ }^\circ\text{C}$, using 2 wt% of a catalyst based

on oil with the same molar ratio of methanol and oil (10:1). Duration of transesterification process in batch reactor was 5 h.

2. Experimental

2.1. Catalyst preparation

CaO (Sigma Aldrich, purity 99.99%) and SiO₂ (Sigma Aldrich, high-purity grade silica gel) were used as starting materials. For the preparation of Ca(OH)₂/SiO₂ precursors, mixtures of CaO and SiO₂ (total mass of 30 g) in a molar ratio of 1:1, 1.5:1, 2:1 and 3:1 with the addition of distilled water in the amounts corresponding to molar ratio CaO:H₂O = 1:2 were mechanochemically treated in a planetary ball mill Fritch Pulverisette 5. Milling was carried out for 2 h at an angular velocity of 160 rpm using 300 g hardened steel 13.4 mm diameter balls (balls-to-powder mass ratio of 10) and 500 ml volume vials. For the given milling condition a significant heating of vials did not occurred considering that after 2 h of milling temperature of vial outer surface was around 33 °C.

Ca(OH)₂/SiO₂ precursors of various Ca/Si ratio were heated at 900 °C for 48 h in order to synthesize corresponding (according to quasi-binary phase diagram thermodynamically stable) calcium silicate compounds CaSiO₃ (CaO·SiO₂), Ca₃SiO₇ (3CaO·2SiO₂), Ca₂SiO₄ (2CaO·SiO₂) as well as two-phase CaO/Ca₂SiO₄ mixture. Additionally, precursors were also heated at 400 and 700 °C for 2 h, with a goal of examining the effect of different heat treatment conditions on phase compositions and, consequently to analyze catalytic activity of prepared materials.

2.2. Characterization

Structure evolution was followed by the X-ray diffraction analysis (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$, in the range of $10\text{--}80^\circ 2\theta$, step-length: $0.01^\circ 2\theta$, scan time: 5 s).

The free CaO content in the calcined samples was determined by the volumetric analysis (glycol–ethanol method) [19].

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

UV-vis diffuse reflectance spectra (DRS) were measured by Shimadzu UV-2600 spectrophotometer with an SR2600 Plus Integrating sphere attachment. Spectra were recorded in the 200–1000 nm wavelength range.

The sample morphology was characterized at room temperature by the field emission scanning electron microscopy (FE-SEM, Mira3 XMU TESCAN, Brno, Czech Republic) operated at 15 kV. Elemental chemical analysis was performed by SEM (JEOL JSM-6610LV) equipped with energy dispersive X-ray spectrometer (EDS INCAEnergy 350 microanalyzer).

Fourier-transform infrared (FTIR) spectra were recorded using BOMEM (Hartmann & Braun) spectrometer. The measurements were conducted on a solid sample prepared using KBr pressed disk technique over the wave number range of $4000\text{--}400 \text{ cm}^{-1}$.

Base strength (H^-) was determined by the Hammett indicator method. The following Hammett indicators were used: phenolphthalein ($H^- = 9.3$), thymolphthalein ($H^- = 10.0$),

thymol violet ($H^- = 11.0$) and 2,4-dinitroaniline ($H^- = 15.0$). The experimental details of the procedure have been given elsewhere [20];[21].

Nitrogen adsorption–desorption isotherms were determined using a Micromeritics ASAP 2020 instrument. Before the measurement all the samples were degassed at 150 °C for 10 h under reduced pressure. The specific surface area of samples, S_{BET} , was calculated according to the Brunauer, Emmett, Teller (BET) method from the linear part of the nitrogen adsorption isotherms. The total pore volume, V_{tot} , was given at $p/p_0 = 0.998$. The volume of the mesopores was calculated according to the Barrett, Joyner and Halenda method from the desorption branch of isotherm. The volume of micropores was calculated from alpha-S plot.

2.3. Methanolysis

The catalytic activity was tested in the transesterification of commercial edible sunflower oil and methanol. The methanolysis was performed at temperature of 60 °C in a 250 mL three-necked thermostated glass flask with a condenser and a magnetic stirrer rotating at 500 rpm using the 10:1 molar ratio of methanol to sunflower oil and 2 wt% of the catalyst based on oil weight. In addition, transesterification using lower mass of catalyst (1, 0.5 and 0.2 wt%) with the powder that showed the best catalytic activity, i.e. $3\text{CaO}\cdot\text{SiO}_2$ calcined at 700 °C was also carried out. The samples were taken out from the reactor after 5 h reaction time, and after filtration, analyzed by gas chromatography (Varian 3400) with FID detector, on-column injector and MET-Biodiesel capillary GC column (14 m \times 0.53 film thickness 0.16 μm).

3. Results and discussion

3.1. Catalyst characterization

The structure evolution during milling and calcination of the CaO–SiO₂ powder mixtures of various starting compositions is presented in Figures 1–4. As can be seen, very similar XRD patterns were obtained for all samples that were milled for 2 h. In particular, all peaks can be assigned to the Ca(OH)₂ (portlandite) (PDF#44-1481) as the result of the reaction of CaO with water. It should be noted that silica gel (SiO₂) is amorphous, while for fresh calcium oxide calcined immediately before milling, only CaO (lime) could be identified (PDF#37-1497), see inset of the Fig. 1. Subsequent calcination at 400 °C for 2 h of the mechanochemically treated equimolar CaO·SiO₂ powder mixture led to the decomposition of Ca(OH)₂ to CaO and to the formation of calcium silicate (CaSiO₃) compound (wollastonite) (PDF#42-547) in certain amounts (Fig. 1B). Calcination at higher temperatures, namely 700 °C for 2 h, produced almost single CaSiO₃ phase (Fig. 1C); CaO peaks can hardly be identified on the XRD pattern while all other peaks could be assigned to the CaSiO₃. Long-term calcination at 900 °C for 48 h led to ordering and grain growth of already formed CaSiO₃ phase, as it can be deduced by comparing XRD patterns given at Fig. 1C and Fig. 1D. Similar observation could be stated for 3CaO·2SiO₂ composition (Fig. 2). Mechanochemical Ca(OH)₂/SiO₂ powder mixture was readily transformed to Ca₃Si₂O₇ phase (rankinite) (PDF#22-0539) by calcination at 700 °C for 2 h (Fig. 2B), while, as in the previous case, ordering and grain growth of already formed Ca₃Si₂O₇ phase occurred by long-term calcination at 900 °C for 48 h (Fig. 2C). Apparently, composite materials produced by mechanochemical treatment are macroscopically homogeneous powder with extremely fine microstructure that easily reacts toward corresponding single-phase compound during calcination.

The $2\text{CaO}\cdot\text{SiO}_2$ powder mixture shows somewhat different behavior in the course of calcination (Fig. 3). Calcination at $700\text{ }^\circ\text{C}$ for 2 h was insufficient to induce solid state reaction leading to the formation of Ca_2SiO_4 phase, which is to be expected according to the quasi-binary $\text{CaO}\text{--}\text{SiO}_2$ phase diagram [2]. As can be seen in Fig. 3B, the dominant phase is unreacted CaO , while other peaks could be assigned to the Ca_2SiO_4 phase. **In fact, this sample should also contain unreacted SiO_2 , which due to its amorphous nature could not be revealed on XRD pattern.** After calcination at $900\text{ }^\circ\text{C}$ for 48 h, the XRD analysis reveals that solid state reaction between CaO and SiO_2 was completed (Fig. 3C), thus all the peaks could be assigned to the Ca_2SiO_4 (larnite) compound (PDF#70-0388).

It should be noted that according to the phase diagram [2] the congruent melting points of CaO , SiO_2 , Ca_2SiO_4 and CaSiO_3 are 2627 , 1723 , 2145 , and $1544\text{ }^\circ\text{C}$, respectively; $\text{Ca}_3\text{Si}_2\text{O}_7$ melts peritectically at $1471\text{ }^\circ\text{C}$, while Ca_3SiO_5 melts incongruently at $2068\text{ }^\circ\text{C}$ and decomposes below $1258\text{ }^\circ\text{C}$ to CaO and Ca_2SiO_4 . Bearing this in mind, calcination at $900\text{ }^\circ\text{C}$ for 48 h of the powder mixture $3\text{CaO}\cdot\text{SiO}_2$ led to the formation of CaO and Ca_2SiO_4 phases (Fig. 4D).

The results of free CaO content determination in $\text{CaO}\text{--}\text{SiO}_2$ powder mixtures calcinated at various temperatures (Table 1) are in satisfactory agreement with the phase compositions derived by the XRD analysis. In the $\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot 2\text{SiO}_2$ samples the formation of CaSiO_3 and $\text{Ca}_3\text{Si}_2\text{O}_7$ phases was almost completed by solid-state reactions at $700\text{ }^\circ\text{C}$, with free CaO amounts of 6.47% and 3.56% respectively. For the $2\text{CaO}\cdot\text{SiO}_2$ composition, free CaO content is 23.29% , hence 35.76% CaO remains unreacted, implying that temperature of $700\text{ }^\circ\text{C}$ was obviously insufficient (too low) for the formation of Ca_2SiO_4 phase. For $3\text{CaO}\cdot\text{SiO}_2$ composition, the determined value of free CaO content after calcination at $700\text{ }^\circ\text{C}$ is 28.68% ,

while the value of 24.33% after calcination at 900 °C for 48 h is in very good agreement with the theoretical value of 24.56% for bulk composition of two phase CaO/Ca₂SiO₄ equilibria [2].

FTIR spectra of CaO–SiO₂ powder mixtures of various starting compositions, before and after calcination, are shown in Fig. 5. The broad band at approximately 3430 cm⁻¹, presented at the FTIR spectra of all samples, is associated with the stretching vibrations of OH groups of physically adsorbed water on the surface of the catalyst, while another band associated with the presence of water, commonly assigned to O–H bending vibration, is located at around 1630 cm⁻¹ [13]. The appearance of a sharp band at 3643 cm⁻¹ is normally ascribed to OH groups in Ca(OH)₂ [20]. The presence of carbonates is confirmed by the broad band at 1410–1490 cm⁻¹ assigned to stretching vibrations of O–C–O as well as the band at 874 cm⁻¹ that arises from carbonates group as well [20].

The broad band at about 900–1300 cm⁻¹ observed for all mechanochemically treated CaO–SiO₂ powder mixtures could be attributed to the asymmetric Si–O–Si stretching vibration modes [6]. This broad band split to two or more bands after calcination, as well as the band separation is more expressed for the samples calcined at 900 °C than for those calcined at 700 °C. For CaO·SiO₂ powder mixture after calcination at 900 °C bands at 1010 and 870 cm⁻¹ could be assigned to Si–O–Si and Si–O–Ca bonds, respectively, confirming the occurrence of wollastonite [22]. The bands at 600–800 cm⁻¹ could be attributed to Si–O–Si bending mode [6] while the band obtained at 400–600 cm⁻¹ originated from Si–O bending and Ca–O stretching modes [23]. The absorption bands of silicate group were also evident for other CaO–SiO₂ powder mixtures calcined at 700 and 900 °C with the most intense bands at 1000 and 900 cm⁻¹ assigned to the Si–O–Si asymmetric and symmetric stretch, respectively, and Si–O–Si bending mode (around 500 cm⁻¹) [24].

Basic strength of the samples prepared by ball milling, as well as these samples subsequently calcined at 700 and 900 °C, is given in Table 2. High basic strength, that could be denoted as $11.0 < H^- < 15$, was observed only for the $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$ samples after calcination at 700 °C and $3\text{CaO}\cdot\text{SiO}_2$ calcined at 900 °C. The basicity increased with the increase of Ca/Si molar ratio, indicating that basic sites are generated mainly on the CaO species with the presence of unreacted CaO phase being confirmed by the XRD analysis and the determination of free CaO content for all three samples with high basic strength (Table 1). For comparison, the basic strength of the calcium-based perovskites CaMO_3 ($M = \text{Ti}, \text{Mn}, \text{Zr}$) is between 6.8 and 9.3 [25], which is in accordance with the basic strength of pure CaSiO_3 phase (Table 2), while basic strength of $\text{CaO}\text{--}\text{SiO}_2$ composites highly depend on the Ca/Si molar ratio [8].

Particle size distributions of the milled and calcined powders of various starting compositions are presented in Fig. 6, while the median particle sizes $d(V,0.5)$ are given in Table 1. As can be seen, particles are within the range of 1–50 μm , with the mean particle sizes between 5 and 10 μm . Calcination at 700 °C slightly changes the particle size distribution, which becomes broader with somewhat higher fraction of finer particles. Most likely, solid state reactions leading to the formation of various calcium silicate phases accompanied with dehydroxylation induced particle fracturing. On the other hand, at higher temperature of 900 °C and long holding time of 48 h, aggregation and to some extent sintering of the smallest particles presumably occurred, hence the volume frequency curves are shifted to larger sizes.

The specific surface area, S_{BET} , the total pore volume, V_{total} , mesopores and micropores volume, V_{meso} , the average pore diameter, D_{mean} , and the size of pore that occupied the major part of total pore volume, D_{max} , are given in Table 3. The results of BET analysis indicated that all

synthesized materials are mesoporous. Pore size distribution for catalysts calcined at 700 °C is presented in Fig. 7, showing that the major part of CaO·SiO₂ and 3CaO·2SiO₂ samples volume is occupied by pores with average diameter of around 20 nm, while negligible shift to lower (17.5 nm) and higher (24.6 nm) values for 2CaO·SiO₂ and 3CaO·SiO₂ catalysts, respectively, is observed. The influence of the calcination temperature on textural properties of prepared CaO–SiO₂ powder mixtures was also observed, and it can be noticed that when the calcination temperature increased from 700 °C to 900 °C, the specific surface area, the pore volume and the average pore diameter decreased. It appears that the higher temperature treatment leads to the damage of pore structure, which may be attributed to sintering of catalyst particles but also to a different phase composition (one or two phases) and ordering of already formed phase. Lower specific surface area of samples calcined at 900 °C is in correlation with the results of particle size distribution, where shift to larger particle sizes was observed, while slightly finer particles obtained after calcination at 700 °C led to higher specific surface areas of those samples.

The morphology and surface structure of the catalysts were analyzed by SEM and elemental composition by EDS. The SEM images of all samples are shown in Fig. 8 at two different magnifications. The existence of small particles along with larger agglomerates, formed as a result of merging smaller particles together, can be seen for all catalysts samples. Also, the SEM images confirmed the previous results that sintering during heat treatment at 900 °C occurred, since some large aggregates could be observed for samples calcined at higher temperatures (Fig. 8 E-H). EDS analysis at several points was applied to determine the average value of atomic distribution of Ca, Si and O for each catalyst (Table 4). For one-phase samples, the obtained values of Ca to Si ratio (as an average of 3 points) are in agreement with the expected ones, while for two-phase systems it was observed that this ratio was not equal at all points analyzed,

as can be seen from Table 4. SEM/EDS of $3\text{CaO}\cdot\text{SiO}_2$ calcined at $900\text{ }^\circ\text{C}$ is given separately (Fig. 9) as a representative of two-phase systems. As can be seen, round-shaped particles have much higher content of Ca compared to content of Si, indicating the presence of CaO. On the other hand, crystallites with irregular sizes and shapes have the atomic percent of Ca and Si which is close to theoretical of Ca_2SiO_4 phase.

In order to get more insight into the catalytic properties of synthesized material UV-visible diffuse reflectance spectroscopy (DRS) was employed. The diffuse reflectance was converted into absorption using the Kubelka-Munk approximation (see Supporting Information for further details). The DRS spectra of the products are presented in Fig. 1S. The direct band gap energies were calculated from the Tauc plot (Figures 2S–8S)

From Figures 2S-8S two band gap energies, a primary one and secondary one may be deduced, except for $\text{CaO}\cdot\text{SiO}_2$ sample calcined at $900\text{ }^\circ\text{C}$, i.e. single-phase CaSiO_3 , with one band gap. This sample is the only one for whom the results of free CaO content determination revealed the complete absence of free CaO, while all others had at least traces of it. Composite powder of calcium silicate mixed oxides exhibit remarkably different band energies in comparison to the starting CaO and SiO_2 powders with band gap energy of 6.0 and 6.1 eV, respectively. The values of primary and secondary band gap energies varied from 4.2 to 4.5 eV and from 4.6 to 5.8 eV, respectively. We assume that the two band gap energies arises from two phase system compose of $\text{CaO}\cdot\text{SiO}_2$ mixed oxides and CaO phases [26]. Amorphous SiO_2 should also be presented in some of the samples in which solid state reaction was not completed, particularly in the $2\text{CaO}\cdot\text{SiO}_2$ sample calcined at $700\text{ }^\circ\text{C}$. The primary band gap energy roughly decreases with particle size increase (except for the single-phase CaSiO_3 powder). The small changes of primary

band gap energies can be plausibly attributed to the variation of Ca/Si ratio of corresponding calcium silicate phases and to the residual CaO phase.

3.2. Methanolysis of sunflower oil

Mechanochemically prepared and calcined CaO–SiO₂ powder mixtures with different Ca/Si ratios were applied in the transesterification of sunflower oil at 60 °C. From Table 1 it can be seen that only three samples, namely 2CaO·SiO₂ and 3CaO·SiO₂ calcined at 700 °C, as well as 3CaO·SiO₂ calcined at 900 °C possess high catalytic activity, determined by triacylglycerols conversion above 96%. These three catalysts are composed of two phases CaO and Ca₂SiO₄. All other samples, the pure calcium silicate phases CaSiO₃, Ca₃Si₂O₇ and Ca₂SiO₄ (with some traces of unreacted CaO) obtained after calcination of mechanochemically treated CaO–SiO₂ mixture, exhibited no catalytic activity. It was previously reported that materials with perovskite structure (CaSiO₃ belonging to this class of catalysts) are not active in transesterification of sunflower oil at lower temperature [25].

Furthermore, since the other two binary mixed oxides, i.e. Ca₃Si₂O₇ and Ca₂SiO₄ also did not exhibit catalytic activity, it seems plausible that monoclinic crystal system in which these two compounds crystallize is responsible for such behavior.

Although the surface areas of samples 2CaO·SiO₂ and 3CaO·SiO₂ calcined at 700 °C, and 3CaO·SiO₂ calcined at 900 °C, were 19.3, 13.3 and 4.3 m²/g, respectively (Table 3), the triacylglycerols conversion was above 96% (Table 1). The mean pore diameters of all prepared materials, regardless of their activity, were higher than 8 nm, which is sufficient for the effective diffusion of large triacylglycerols molecules to the active sites within the pores of the catalyst [27]. Obviously, textural characteristics of catalysts indicated that neither surface area, pores volume and pore size distribution **nor particle size distribution** affected the activity of prepared

catalysts in reaction between methanol and triacylglycerols from sunflower oil. Also, band gap energies cannot be correlated with triacylglycerols conversion, implying dominant influence of the amount of free CaO on the catalytic activity. Thus, it can be concluded that catalytic activity of prepared materials arises from the existence of CaO phase, which crystallizes in the rock salt structure. This conclusion is supported by the fact that presence of CaO phase affects the basic strength of catalysts (Table 2), which is considered as one of the most significant factors that affect the activity of different catalysts [28].

To evaluate leaching of the active component of the catalyst in the reaction mixture, the following experimental procedure was performed using one of the most active catalysts, i.e. $3\text{CaO}\cdot\text{SiO}_2$ calcined at $700\text{ }^\circ\text{C}$. The catalyst sample was placed in contact with methanol and kept under reaction conditions for 5 h. After the reaction, the catalyst was removed by filtration, and methanol was mixed with the fresh sunflower oil which was then kept at $60\text{ }^\circ\text{C}$ for 5 h. The result of the experiment after 5 h of reaction revealed that FAME was not detected, thus leaching of active component was not observed. This result confirmed the stabilization of CaO by the presence of another phase, in this case Ca_2SiO_4 . Similar finding was observed for CaO/SBA catalyst where the interaction between CaO and silica was strong enough to prevent the lixiviation [6]. Otherwise, when used as pure compound, CaO is partially dissolved in methanol [6]. On the other hand, Sun et al. reported that leaching of calcium species in methanol led to the loss of calcium sites and concluded that $\text{Ca}_x\text{SiO}_{x+2}$ catalysts played mainly homogeneous catalytic role in this system [12], while extraction of CaO by methanol from CaO/SiO₂ synthesized by the sol–gel method during the transesterification reaction led to reduction of catalyst activity [10].

The possibility to reuse the catalyst was examined using $3\text{CaO}\cdot\text{SiO}_2$ sample calcined at $700\text{ }^\circ\text{C}$. After each reaction cycle, the liquid product was separated from the solid catalyst that remained at the bottom of the flask, and was reused without any pretreatment in future reaction cycles. A new batch of sunflower oil and methanol were then added to the flask and the subsequent cycle was carried out under the same reaction conditions. Very good activity and high triacylglycerols conversion, above 97%, remained for 4 cycles. FTIR analysis was performed to find out if adsorption of compounds present in the reaction mixture on the catalysts surface occurred. The FTIR spectra of fresh and 4-times used catalysts are very similar, indicating the stability of the catalyst during its use in transesterification of sunflower oil (Fig. 10). The only difference is a weak band at 1745 cm^{-1} that originates from the stretching vibration of the ester carbonyl group ($\text{C}=\text{O}$), and slightly more intense bands at 2922 and 2852 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of methylene groups of the alkyl chain of FAME [29], suggesting only negligible adsorption of organic compounds on the catalyst surface.

The additional experiments were performed with $3\text{CaO}\cdot\text{SiO}_2$ sample calcined at $700\text{ }^\circ\text{C}$ to find the effect of the amount of catalyst on triacylglycerols conversion. When the catalyst amount was decreased from 2 to 1 and 0.5 wt%, the corresponding triacylglycerols conversion decreased from 97.2 to 95.5 and 92.7%, respectively. Further decrease of catalyst amount to 0.2 wt% affected the triacylglycerols conversion more significantly, achieving only 0.7% conversion. It is important to emphasize that given values refer to total catalyst amounts in which only free CaO represents the active phase. Recalculating the mass of CaO, on the basis of the results obtained by free CaO determination, it might be concluded that as low as 0.14 wt% of CaO (when 0.5% of catalyst is used) was enough to achieve satisfactory conversion of

triacylglycerols into FAME. According to literature reviews, much higher amounts of pure CaO based on oil (1 wt% or more but preferably 5 wt%) were used for transesterification reaction [30][31]. The findings of this study show that improved and effective dispersion of CaO on Ca_2SiO_4 phase was achieved by mechanochemical treatment and further calcination at 700 °C of the $3\text{CaO}\cdot\text{SiO}_2$ sample, allowing high activity of CaO. Consequently, much higher triacylglycerols conversion with lower amount of catalyst used for biodiesel synthesis was enabled.

This study resolutely demonstrated that pure binary $\text{CaO}\cdot\text{SiO}_2$ mixed oxides are not active in the transesterification process (at least for applied process parameters), while the presence of CaO phase leads to the activity of prepared materials. This fact has not been clearly and prominently identified despite a significantly large number of results regarding catalysts based on calcium oxide [30][31]. To the best of our knowledge, this is the first report in which free calcium oxide content, which has decisive effect on catalytic activity of calcium-based catalysts for transesterification of different oils with methanol, was determined quantitatively.

4. Conclusion

Mechanochemical treatment followed by calcination is a simple and convenient procedure for the preparation of $\text{CaO}\text{--}\text{SiO}_2$ compounds. Mechanochemically prepared precursors, being a very fine homogenized composite powders of $\text{Ca}(\text{OH})_2$ and SiO_2 could easily be transformed by subsequent solid-state reaction to almost single calcium silicate compounds CaSiO_3 , Ca_2SiO_4 , and $\text{Ca}_3\text{Si}_2\text{O}_7$ as well as $\text{CaO}/\text{Ca}_2\text{SiO}_4$ two-phase mixture. The pure calcium silicate phases (CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$ and Ca_2SiO_4) exhibited no catalytic activity, while the catalysts composed of two phases, i.e. Ca_2SiO_4 and CaO, showed high activity in transesterification of sunflower oil

with triacylglycerols conversion above 96%. The $3\text{CaO}\cdot\text{SiO}_2$ calcined at $700\text{ }^\circ\text{C}$ sustained its activity after being used for 4 cycles indicating that the catalyst has good stability. Moreover, this solid base catalyst is insoluble in methanol confirming the stabilization of CaO by the presence of Ca_2SiO_4 phase.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 45001). The determination of free CaO content was realized in the Institute for Testing of Materials, Belgrade, Serbia. **Authors are thankful to Dr. Maria Vesna Nikolić, Institute for Multidisciplinary Research, for DRS measurement.**

References

- [1] H.F.W. Taylor, Cement chemistry, 2nd ed., Thomas Telford, 1997.
doi:10.1146/annurev.pc.10.100159.002325.
- [2] A.I. Zaitsev, M.A. Zemchenko, A.D. Litvina, B.M. Mogutnov, Thermodynamic calculation of phase equilibria in the $\text{CaF}_2\text{--SiO--CaO}$ system, J. Mater. Chem. 3 (1993) 541–546. doi:10.1039/JM9930300541.
- [3] R.L. Virta, 2009 Minerals Yearbook, USGS Miner. Yearb. (2010) 4.
- [4] A.B.Y. Hazar, Preparation and in vitro bioactivity of CaSiO_3 powders, Ceram. Int. 33 (2007) 687–692. doi:10.1016/j.ceramint.2006.12.013.
- [5] E. Hughes, T. Yanni, P. Jamshidi, L.M. Grover, Inorganic cements for biomedical

- application: calcium phosphate, calcium sulphate and calcium silicate, *Adv. Appl. Ceram.* 114 (2015) 65–76. doi:10.1179/1743676114Y.0000000219.
- [6] M.C.G. Albuquerque, I. Jiménez-Urbistondo, J. Santamaría-González, J.M. Mérida-Robles, R. Moreno-Tost, E. Rodríguez-Castellón, et al., CaO supported on mesoporous silicas as basic catalysts for transesterification reactions, *Appl. Catal. A Gen.* 334 (2008) 35–43. doi:10.1016/j.apcata.2007.09.028.
- [7] A. Arumugam, V. Ponnusami, Optimization of recovery of silica from sugarcane leaf ash and Ca/SBA-15 solid base for transesterification of *Calophyllum inophyllum* oil, *J. Sol-Gel Sci. Technol.* 74 (2015) 132–142. doi:10.1007/s10971-014-3586-z.
- [8] G. Chen, R. Shan, S. Li, J. Shi, A biomimetic silicification approach to synthesize CaO–SiO₂ catalyst for the transesterification of palm oil into biodiesel, *Fuel.* 153 (2015) 48–55. doi:10.1016/j.fuel.2015.02.109.
- [9] M. Mohadesi, Z. Hojabri, G. Moradi, Biodiesel production using alkali earth metal oxides catalysts synthesized by sol-gel method, *Biofuel Res. J.* 01 (2014) 30–33. doi:10.18331/BRJ2015.1.1.7.
- [10] G. Moradi, M. Mohadesi, Z. Hojabri, Biodiesel production by CaO/SiO₂ catalyst synthesized by the sol-gel process, *React. Kinet. Mech. Catal.* 113 (2014) 169–186. doi:10.1007/s11144-014-0728-9.
- [11] T.-M. Hsin, S. Chen, E. Guo, C.-H. Tsai, M. Pruski, V.S.Y. Lin, Calcium containing silicate mixed oxide-based heterogeneous catalysts for biodiesel production, *Top. Catal.* 53 (2010) 746–754. doi:10.1007/s11244-010-9462-3.

- [12] H. Sun, J. Duan, P. Chen, H. Lou, X. Zheng, Room temperature transesterification of soybean oil to biodiesel catalyzed by rod-like $\text{Ca}_x\text{SiO}_{x+2}$ solid base, *Catal. Commun.* 12 (2011) 1005–1008. doi:10.1016/j.catcom.2011.03.009.
- [13] H. Sun, J. Han, Y. Ding, W. Li, J. Duan, P. Chen, et al., One-pot synthesized mesoporous Ca/SBA-15 solid base for transesterification of sunflower oil with methanol, *Appl. Catal. A Gen.* 390 (2010) 26–34. doi:10.1016/j.apcata.2010.09.030.
- [14] R. Shan, C. Zhao, H. Yuan, S. Wang, Y. Wang, Transesterification of vegetable oil using stable natural diatomite-supported catalyst, *Energy Convers. Manag.* 138 (2017) 547–555. doi:10.1016/j.enconman.2017.02.028.
- [15] S. Wang, R. Shan, Y. Wang, L. Lu, H. Yuan, Synthesis of calcium materials in biochar matrix as a highly stable catalyst for biodiesel production, *Renew. Energy.* 130 (2019) 41–49. doi:10.1016/j.renene.2018.06.047.
- [16] X.-X. Yang, Y.-T. Wang, Y.-T. Yang, E.-Z. Feng, J. Luo, F. Zhang, et al., Catalytic transesterification to biodiesel at room temperature over several solid bases, *Energy Convers. Manag.* 164 (2018) 112–121. doi:10.1016/j.enconman.2018.02.085.
- [17] E.G. Avvakumov, E.T. Devyatkina, N.V. Kosova, Mechanochemical reactions of hydrated oxides, *J. Solid State Chem.* 113 (1994) 379–383. doi:10.1006/jssc.1994.1384.
- [18] L. Black, K. Garbev, G. Beuchle, P. Stemmermann, D. Schild, X-ray photoelectron spectroscopic investigation of nanocrystalline calcium silicate hydrates synthesised by reactive milling, *Cem. Concr. Res.* 36 (2006) 1023–1031. doi:10.1016/j.cemconres.2006.03.018.

- [19] P. Hewlett, *Lea's Chemistry of Cement and Concrete*, Fourth ed., Elsevier Science & Technology Books, 2004. doi:10.1016/B978-0-7506-6256-7.50031-X.
- [20] Ž. Kesić, I. Lukić, D. Brkić, J. Rogan, M. Zdujić, H. Liu, et al., Mechanochemical preparation and characterization of CaO·ZnO used as catalyst for biodiesel synthesis, *Appl. Catal. A Gen.* 427-428 (2012) 58–65. doi:10.1016/j.apcata.2012.03.032.
- [21] I. Lukić, Ž. Kesić, S. Maksimović, M. Zdujić, H. Liu, J. Krstić, et al., Kinetics of sunflower and used vegetable oil methanolysis catalyzed by CaO·ZnO, *Fuel*. 113 (2013) 367–378. doi:10.1016/j.fuel.2013.05.093.
- [22] R. Puntharod, C. Sankram, N. Chantaramee, P. Pookmanee, K.J. Haller, Synthesis and characterization of wollastonite from egg shell and diatomite by the hydrothermal method, *J. Ceram. Process. Res.* 14 (2013) 198–201.
- [23] A. Chatterjee, P.S. Khobragade, S. Mishra, Physicomechanical properties of wollastonite (CaSiO₃)/styrene butadiene rubber (SBR) nanocomposites, *J. Appl. Polym. Sci.* 132 (2015) n/a–n/a. doi:10.1002/app.42811.
- [24] J.S. Romano, P.D. Marcato, F.A. Rodrigues, Synthesis and characterization of manganese oxide-doped dicalcium silicates obtained from rice hull ash, *Powder Technol.* 178 (2007) 5–9. doi:10.1016/j.powtec.2007.03.042.
- [25] Ž. Kesić, I. Lukić, M. Zdujić, Č. Jovalekić, V. Veljković, D. Skala, Assessment of CaTiO₃, CaMnO₃, CaZrO₃ and Ca₂Fe₂O₅ perovskites as heterogeneous base catalysts for biodiesel synthesis, *Fuel Process. Technol.* 143 (2016) 162–168. doi:10.1016/j.fuproc.2015.11.018.

- [26] A. Mohamed, S. Barghi, S. Rohani, N- and C-modified TiO₂ nanotube arrays: Enhanced photoelectrochemical properties and effect of nanotubes length on photoconversion efficiency, *Nanomaterials*. 8 (2018) 198. doi:10.3390/nano8040198.
- [27] I. Lukić, J. Krstić, D. Jovanović, D. Skala, Alumina/silica supported K₂CO₃ as a catalyst for biodiesel synthesis from sunflower oil, *Bioresour. Technol.* 100 (2009) 4690–4696. doi:10.1016/j.biortech.2009.04.057.
- [28] T. Watanabe, J. Liao, M. Senna, Changes in the basicity and species on the surface of Me(OH)₂-SiO₂ (Me = Ca, Mg, Sr) mixtures due to mechanical activation, *J. Solid State Chem.* 115 (1995) 390–394. doi:10.1006/jssc.1995.1149.
- [29] M. López Granados, A.C. Alba-Rubio, F. Vila, D. Martín Alonso, R. Mariscal, Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol, *J. Catal.* 276 (2010) 229–236. doi:10.1016/j.jcat.2010.09.016.
- [30] D.M. Marinković, M. V. Stanković, A. V. Veličković, J.M. Avramović, M.R. Miladinović, O.O. Stamenković, et al., Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives, *Renew. Sustain. Energy Rev.* 56 (2016) 1387–1408. doi:10.1016/j.rser.2015.12.007.
- [31] Z. Kesić, I. Lukić, M. Zdujić, L. Mojović, D. Skala, Calcium oxide based catalysts for biodiesel production: A review, *Chem. Ind. Chem. Eng. Q.* 22 (2016) 391–408. doi:10.2298/CICEQ160203010K.

Figure captions

Fig. 1. XRD patterns of $\text{CaO}\cdot\text{SiO}_2$ powder mixture (A) milled with water for 2 h and calcined at (B) $400^\circ\text{C}/2$ h (C) $700^\circ\text{C}/2$ h and (D) $900^\circ\text{C}/48$ h. XRD patterns of starting CaO and silica gel is presented in the inset.

Fig. 2. XRD patterns of $3\text{CaO}\cdot 2\text{SiO}_2$ powder mixture (A) milled with water for 2 h and (B) calcined at $700^\circ\text{C}/2$ h and (C) $900^\circ\text{C}/48$ h.

Fig. 3. XRD patterns of $2\text{CaO}\cdot\text{SiO}_2$ powder mixture (A) milled with water for 2 h and (B) calcined at $700^\circ\text{C}/2$ h and (C) $900^\circ\text{C}/48$ h.

Fig. 4. XRD patterns of $3\text{CaO}\cdot\text{SiO}_2$ powder mixture (A) milled with water for 2 h and calcined at (B) $400^\circ\text{C}/2$ h (C) $700^\circ\text{C}/2$ h and (D) $900^\circ\text{C}/48$ h.

Fig. 5. FTIR spectra of (A) $\text{CaO}\cdot\text{SiO}_2$; (B) $3\text{CaO}\cdot 2\text{SiO}_2$; (C) $2\text{CaO}\cdot\text{SiO}_2$; (D) $3\text{CaO}\cdot\text{SiO}_2$ powder mixture.

Fig. 6. Particle size distribution of $\text{CaO}\cdot\text{SiO}_2$; $3\text{CaO}\cdot 2\text{SiO}_2$; $2\text{CaO}\cdot\text{SiO}_2$; $3\text{CaO}\cdot\text{SiO}_2$ powder mixtures milled with water for 2 h and calcined at $700^\circ\text{C}/2$ h and $900^\circ\text{C}/48$ h.

Fig. 7. Pore size distribution of catalysts calcined at $700^\circ\text{C}/2$ h: (A) $\text{CaO}\cdot\text{SiO}_2$; (B) $3\text{CaO}\cdot 2\text{SiO}_2$; (C) $2\text{CaO}\cdot\text{SiO}_2$; (D) $3\text{CaO}\cdot\text{SiO}_2$ powder mixture.

Fig. 8. SEM images of $\text{CaO}\cdot\text{SiO}_2$ calcined at: (A) 700°C , (E) 900°C ; $3\text{CaO}\cdot 2\text{SiO}_2$ calcined at: (B) 700°C , (F) 900°C ; $2\text{CaO}\cdot\text{SiO}_2$ calcined at: (C) 700°C , (G) 900°C ; $3\text{CaO}\cdot\text{SiO}_2$ calcined at: (D) 700°C , (H) 900°C .

Fig. 9. SEM/EDS analysis of $3\text{CaO}\cdot\text{SiO}_2$ calcined at 900

Fig. 10. FTIR spectra of $3\text{CaO}\cdot\text{SiO}_2$: (A) fresh catalyst, i.e. calcined at $700^\circ\text{C}/2\text{ h}$, and (B) used for four times.

Table 1.

Phase composition, free CaO content, median particle size, $d(V,0.5)$, band gap energy, E_g , and triacylglycerols conversion for CaO–SiO₂ samples calcined at 700 °C and 900 °C.

Sample	Calcination temperature (°C)	Phase composition	Free CaO (%)	$d(V,0.5)$ (µm)	E_g (eV)		Triacylglycerols conversion (%)*
					E_{g1}	E_{g2}	
CaO·SiO ₂	700	CaSiO ₃	6.47	5.56	4.4	5.4	0.10
	900	CaSiO ₃	0.00	11.95	–	4.3	0.31
3CaO·2SiO ₂	700	Ca ₃ Si ₂ O ₇	3.56	4.82	4.5	5.4	1.40
	900	Ca ₃ Si ₂ O ₇	0.65	7.29	4.0	4.6	0.52
2CaO·SiO ₂	700	CaO/Ca ₂ SiO ₄	23.29	5.30	4.1	5.1	97.69
	900	Ca ₂ SiO ₄	4.79	6.85	4.4	5.8	0.81
3CaO·SiO ₂	700	CaO/Ca ₂ SiO ₄	28.68	5.81	4.4	5.5	97.21
	900	CaO/Ca ₂ SiO ₄	24.33	6.50	4.2	5.5	96.03

*Reaction conditions: temperature 60 °C, time 5 h, methanol to sunflower oil molar ratio 10:1, catalyst amount 2 wt%.

Table 2.

Basic strength of the prepared catalysts.

Sample	$T_{\text{calc.}}$ (°C)	Phenolphthalein ($H^- = 9.3$)	Thymolphthalein ($H^- = 10.0$)	Thymolviolet ($H^- = 11.0$)	2,4-dinitroaniline ($H^- = 15$)
CaO·SiO ₂	–	–	–	–	–
	700	–	–	–	–
	900	–	–	–	–
3CaO·2SiO ₂	–	0.008 mmol g ⁻¹	–	–	–
	700	0.036 mmol g ⁻¹	–	–	–
	900	–	–	–	–
2CaO·SiO ₂	–	0.124 mmol g ⁻¹	0.044 mmol g ⁻¹	0.072 mmol g ⁻¹	–
	700	0.284 mmol g ⁻¹	0.28 mmol g ⁻¹	0.188 mmol g ⁻¹	–
	900	–	–	–	–
3CaO·SiO ₂	–	0.02 mmol g ⁻¹	0.024 mmol g ⁻¹	–	–
	700	0.364 mmol g ⁻¹	0.304 mmol g ⁻¹	0.312 mmol g ⁻¹	–
	900	0.184 mmol g ⁻¹	0.208 mmol g ⁻¹	0.22 mmol g ⁻¹	–

Table 3.

Textural characteristics of the catalysts.

Sample	$T_{\text{calc.}}$ (°C)	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{micro} (cm ³ /g)	D_{mean} (nm)	D_{max} (nm)
CaO·SiO ₂	700	19.0	0.1003	0.0981	0.0060	19.5	20.5
	900	0.63	0.0010	0.0007	0.0004	9.9	9.8
3CaO·2SiO ₂	700	11.7	0.0502	0.0493	0.0038	16.2	20.7
	900	2.05	0.0034	0.0028	0.0007	8.6	2.8
2CaO·SiO ₂	700	19.3	0.1239	0.1225	0.0061	22.5	17.5
	900	2.10	0.0045	0.0037	0.0008	15.0	2.3
3CaO·SiO ₂	700	13.3	0.0845	0.0844	0.0043	21.3	24.6
	900	4.30	0.0143	0.0136	0.0013	14.9	–

S_{BET} – specific surface area, V_{total} – total pore volume, V_{meso} – mesopore volume, V_{micro} – micropore volume, D_{mean} – mean mesopore diameter and D_{max} – maximum mesopore diameter.

Table 4.

EDS analysis of the surface points of prepared catalysts.

Sample	$T_{\text{calc.}}$ (°C)	O (at%)	Ca (at%)	Si (at%)
CaO·SiO ₂	700	71.66	15.26	13.08
	900	69.56	16.69	14.42
3CaO·2SiO ₂	700	75.02	15.66	9.32
	900	69.67	19.25	11.07
2CaO·SiO ₂	700	70.00	20.92	9.07
		67.73	24.21	8.07
	900	71.48	20.09	8.43
3CaO·SiO ₂	700	68.46	25.61	5.94
		73.68	24.22	2.10
	900	67.87	22.72	9.41
		68.13	29.86	2.01

Fig. 1

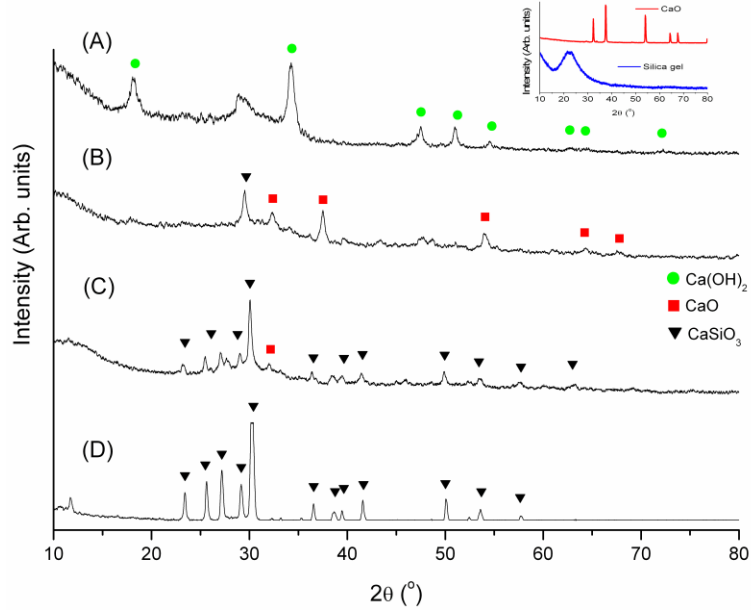


Fig. 2

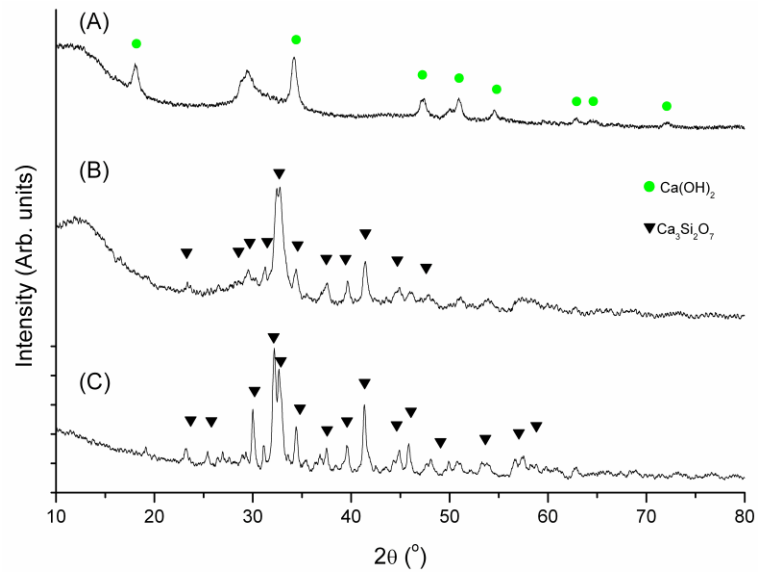


Fig. 3

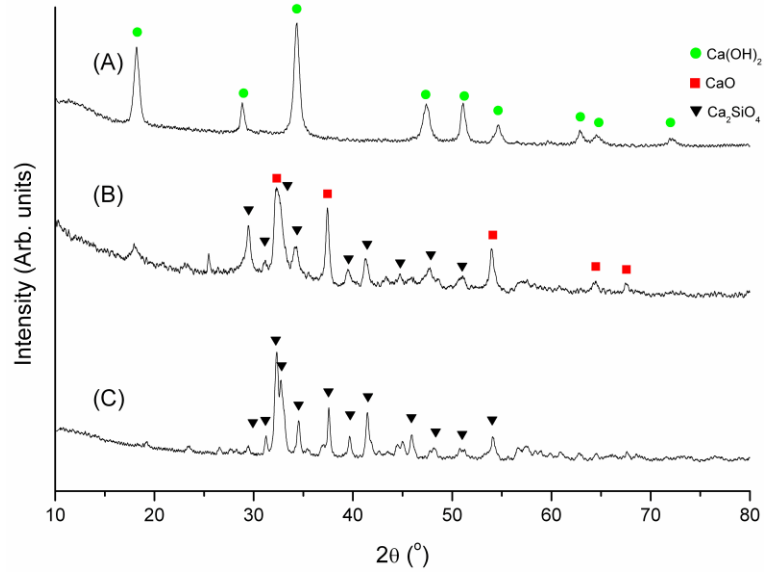


Fig. 4

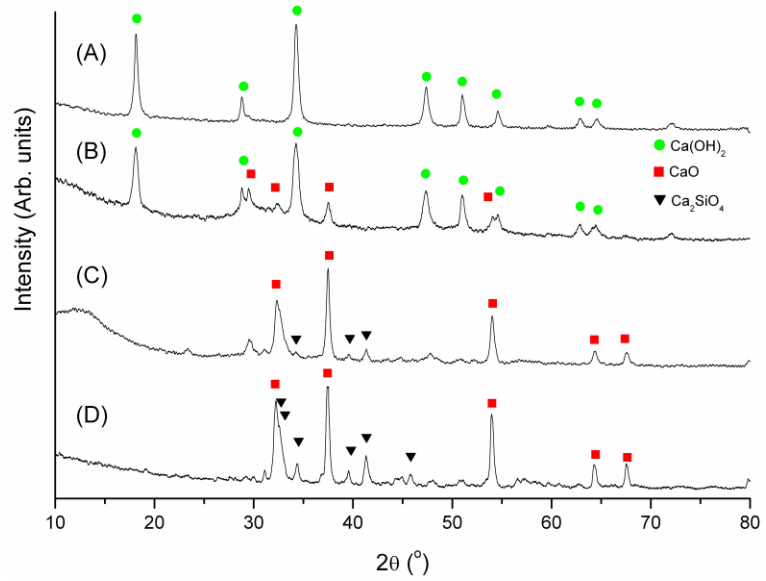


Fig. 5

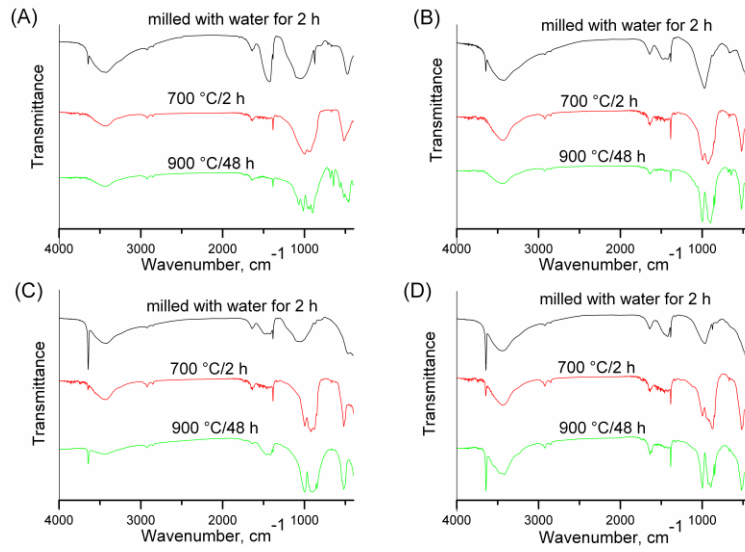


Fig. 6

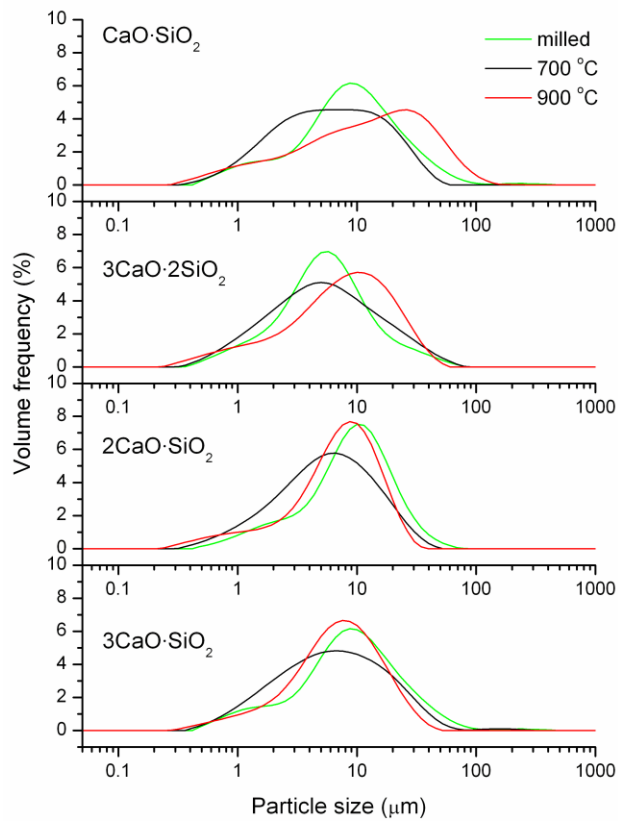


Fig. 7

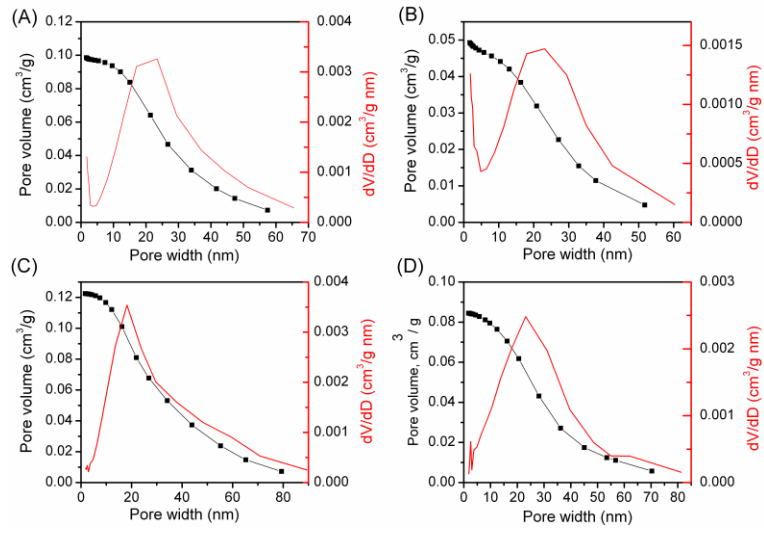


Fig. 8

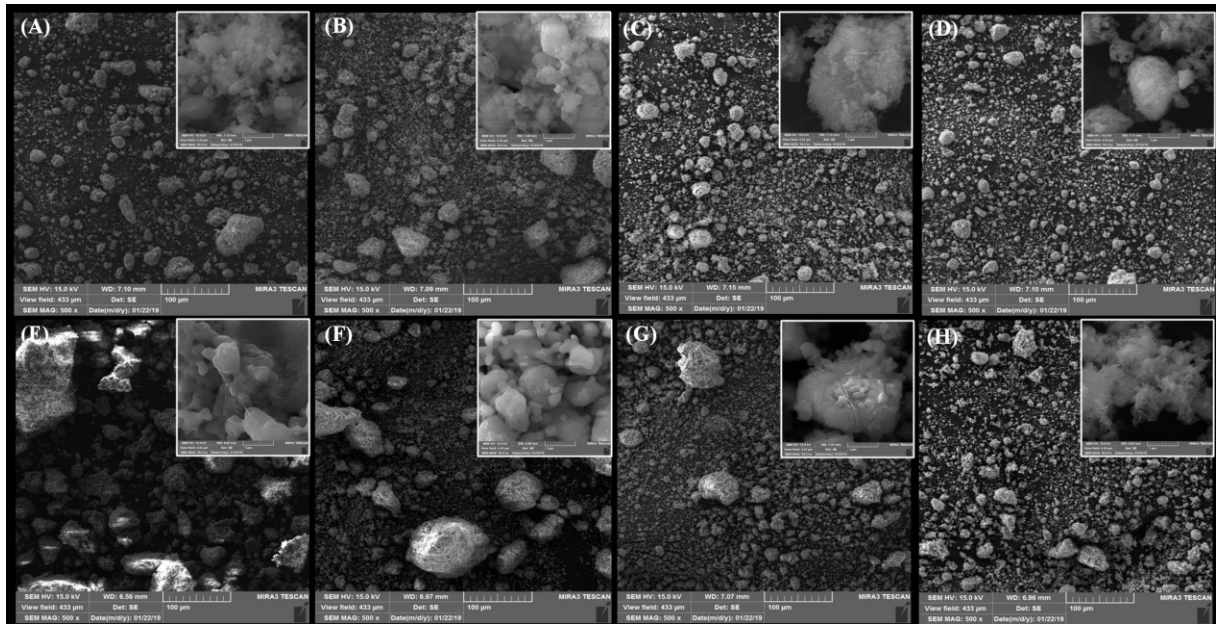


Fig.9

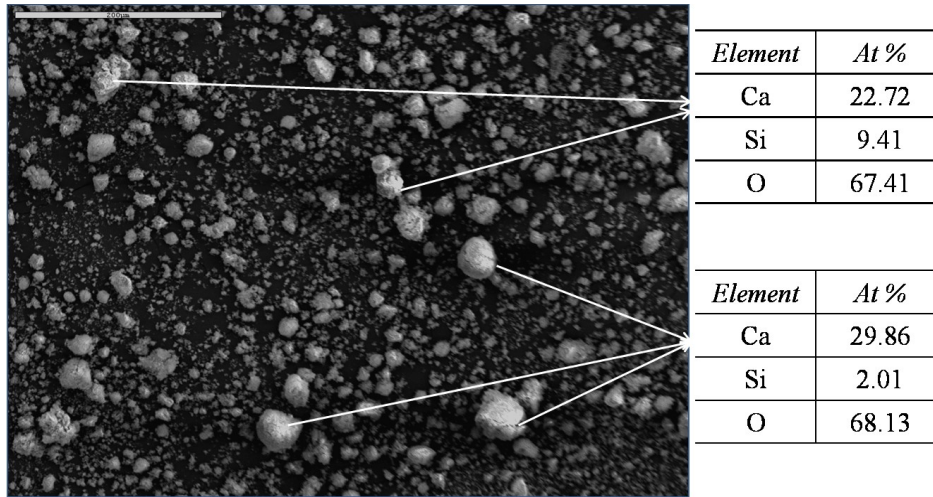


Fig. 10

