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Bulletin of Chemical Reaction Engineering & Catalysis, 15 (2) 2020, 561-567

Research Article

Preliminary Synthesis of Calcium Silicates using Oil Palm Leaves and Eggshells

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Received: 20th April 2020; Revised: 3rd July 2020; Accepted: 8th July 2020; Available online: 30th July 2020; Published regularly: August 2020

Abstract

A new synthetic procedure is described for the synthesis of calcium silicate derivatives, using natural resources such as eggshell (ES) for calcium and oil palm leaves (OPL) for silica, which do not require prepurification. The reaction is performed by directly converting two weight ratio of the precursors, ES:3OPL and ES:6OPL, to dried-powder form by heat treatment at 900 °C for two hours. The results demonstrate that the concentration of the precursors has an effect on the morphology and crystallinity of the calcium silicate derivatives, mainly Ca_2SiO_4 and $CaSiO_3$. X-ray diffraction results reveal that the reaction product obtained using a 1:3 ratio is quite pure, and mainly consisted of calcium silicate in the form of Ca_2SiO_4. The $CaSiO_3$ was also identified in ES:6OPL, together with a small amount of excess non-reacted crystalline silica. Furthermore, a scanning electron microscopy analysis shows that both reaction products have a coarse surface.

Keywords: Eggshell; Oil Palm Leaves; Silica; Calcium-silicate

How to Cite: Yudha S, S., Falahudin, A., Kaus, N.H.M., Thongmee, S., Ikram, S., Asdim, A. (2020). Preliminary Synthesis of Calcium Silicates using Oil Palm Leaves and Eggshells. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15(2), 561-567 (doi:10.9767/bcrec.15.2.7591.561-567)

Permalink/DOI: https://doi.org/10.9767/bcrec.15.2.7591.561-567

1. Introduction

Numerous literatures have paid specific attention to the green synthesis of calcium silicates. For example, wollastonite ($CaSiO_3$) was successfully prepared using a hydrothermal method from CaO obtained from eggshell and SiO_2 extracted from diatomite. This method generates a wollastonite mixture of β-$CaSiO_3$ and α-$CaSiO_3$ [1]. Another approach was developed from natural $CaCO_3$ (eggshell) and commercial SiO_2, using ball mill and sonochemical techniques, leading to the exclusive production of β-$CaSiO_3$ [2]. Other studies reported β-wollastonite as the major phase obtained by reacting CaO from $CaCO_3$ and SiO_2 from rice husk ash [3]. This was also achieved using the ashes of rice husk and straw, in combination with CaO, under sintering at 950 °C [4–5]. Meanwhile, solid-state reactions have also proved effective for the preparation of porous wollastonite with high density and mechanical strength, using $CaCO_3$ and SiO_2 in the presence of active

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carbon at 1320 °C [6]. Another important derivative is Ca_2SiO_4, known as calsil or larnite depending on its crystallite structure, where the basic arrangement of larnite or others (α, β, and γ) has a heteropolyhedral glaserite framework [7]. Extensive research has been conducted on the synthesis of Ca_2SiO_4, including common synthetic and green methods. For instance, Ca_2SiO_4 was prepared from the combination of eggshell and tetraethyl orthosilicate (TEOS) as precursors, using a sol–gel combustion treatment [8]. In addition, other reports established the use of natural silica, rice husk, CaO, and eggshell to form calcium silicate derivatives or silica-impregnated CaO. This technique is dependent on the reaction conditions, and the product derived from the use of silica-impregnated CaO obtained from rice husk and eggshell is effective as a catalyst in biodiesel preparation [9].

Calcium silicate in the form of $CaSiO_3$ has some industrial applications due to its inherent properties including thermal stability, chemical inertness, and low thermal conductivity and expansion [10]. These materials also serve as important fertilizers that ensure the productivity of some plants, and the silicon component plays a major role in increasing resistance against diseases, abiotic stresses, insect attack, and the effect of climate change [11]. Thus, as a silicate fertilizer, the $CaSiO_3$ can be added to urea as a nitrogen source for paddy growth and to enhance tropical soil productivity, a process that is claimed to reduce N_2O emission [12]. Furthermore, a commercially available $CaCO_3$ has been used as a precursor of porous β-Ca_2SiO_4 by its reaction with SiO_2 in the presence of tripholyphospate and polyurethane foam, which serve as stabilizer and template, respectively [13].

From an environmental perspective, the use of sustainable natural resources as precursors in the preparation of advanced materials is preferred over materials of synthetic origin. Some recent researches have reported oil palm leaves (OPL) as a potential source for natural SiO_2, which is used in several purposes [14–15]. In addition, oil palm ash (OPA), which is obtained from an incinerator at the palm oil mill, form nanostructural materials by high-energy ball milling. The resulting product consists of silica or silicon dioxide (SiO_2), which is perhaps the most essential substance in OPA [16]. To the best of our knowledge, no studies describing the use of OPL as a source of silica for the synthesis of materials such as wollastonite, larnite, or calsil have been reported. In contrast with reported procedures, the reactions conducted in this investigation do not require stabilizers, such as: tricalcium phosphate and the surfactant sodium dodecyl sulfate [13,17]. In the context of sustainable technology, this report describes research results pertaining to the synthesis of silica-based materials using local bioresources and the characterization of the obtained products.

2. Materials and Methods

Oil palm leaves (OPL) and eggshell (ES) were washed with aquadest, wiped with tissue, and dried on air. Each material was grounded to powder using a juice mixer and passed through 325 mesh sieves, before repeating the drying process. The synthesis was carried out using two weight ratios of ES and OPL powders, and the corresponding samples were called ES:3OPL and ES:6OPL. For ES:3OPL, 1 g of ES powder was weighed into a furnace crucible, followed by addition of 3 g OPL powder. The mixture was homogenized using a glass spatula, and a small amount of demineralized water was added to form a sticky reaction mixture. The crucible was then placed in a furnace and subjected to a heating process. A similar procedure was applied for the sample ES:6OPL, in which 1 g ES and 6 g OPL powders were subjected to the heating treatment. The furnace temperature was increased from room temperature to 900 °C within 4 h, and was kept at that temperature for 2 h. After cooling down the furnace for 12 h, the sample was ready for further analysis.

X-ray diffraction (XRD) analysis was performed to determine the crystallinity phase and the diffraction pattern of the materials, using an X'PERT Powder-PANalytical PW 30/60 instrument. Surface morphology analysis was acquired on a JEOL JSM 6510 LA instrument equipped with an energy dispersive X-ray (EDX) analyzer. The current measurement conditions are: (a) energy range: 0 − 20 keV, (b) Acc. voltage 20.0 kV, (c) probe current: 1.00000 nA, (d) real time: 51.28 sec, (e) live time: 50.00 sec, (f) dead time: 2 %, (g) counting rate: 2850 cps.

3. Results and Discussion

A solid-state reaction between OPL and ES powders was performed as shown in Figure 1. The amount of the products obtained using the samples ES:3OPL and ES:6OPL was 0.6301 g and 1.561 g, respectively. By mixing the powders of yellow-white ES (Figure 1(a)) and green-brown OPL (Figure 1(b)), the mixture shown in Figure 1(c) was obtained. Subsequent

addition of a small amount of water to ensure homogeneity afforded the material depicted in Figure 1(d). This mixture was heated at 900 °C for 2 h, leading to the formation of a gray-white solid material (Figure 1(e)), which was characterized as shown in Figure 2.

Since the XRD analysis of ES has been largely investigated [18–20], it was not addressed in the present study. Figure 2(a) shows the amorphous characteristic of the OPL powder. The wide peaks at 21.6° and 29.9° and other small peaks can be attributed to the corresponding crystal plane of disordered carbon [21], and are possibly overlapped with those of the silica precursors. After heat treatment at 900 °C for 2 h, the resulting white-gray solid material was subjected to XRD analysis (Figure 2(b)). A mixture of compounds was identified in the material, being crystalline silica the major component. This result is congruent with previous reports revealing the presence of silica in OPL [14–15]. Figure 3 shows the results of further XRD characterization of the reaction products.

Figure 3(a) shows major diffraction peaks at 2θ of 32.1°, 32.4°, and 41.1°, which can be attributed to Ca_2SiO_4 (dicalcium silicate) (JCPDS 00-031-0299), and the XRD pattern was compared with that of other reported approaches [19,22–25]. It should be noted that the present XRD profile reveals that the reaction products mainly consist of the Ca_2SiO_4 phase. This XRD profile was in line with that obtained from the reaction of commercial TEOS as a source of sil-

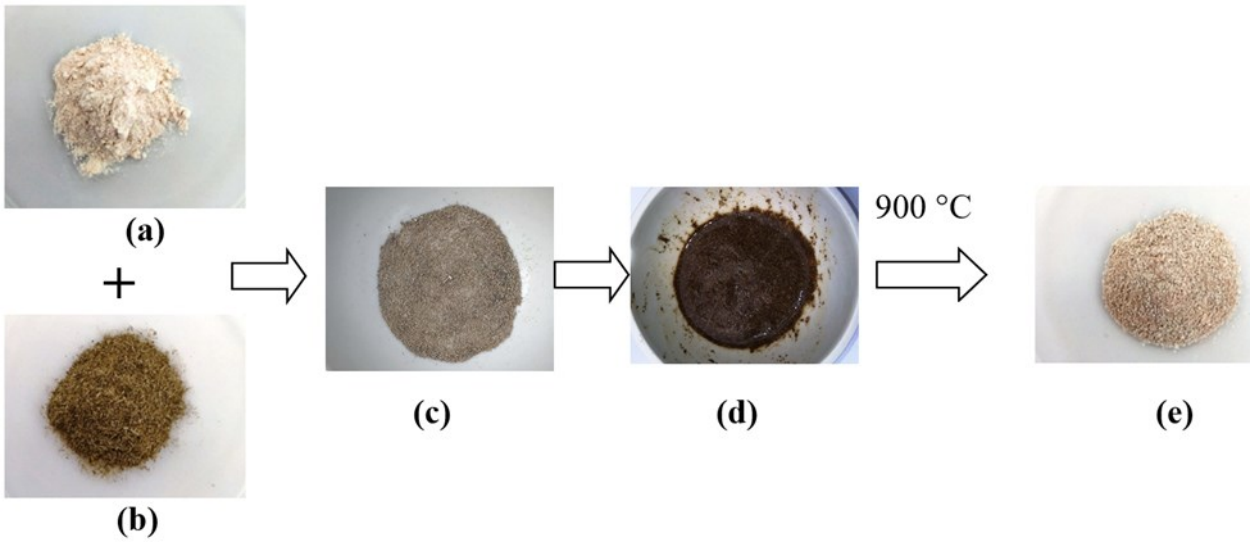

Figure 1. Representative preparation chart for the reaction between ES and OPL. (a) ES powder, (b) OPL powder, (c) dry mixture of ES and OPL, (d) preheated sticky material, (e) final product.

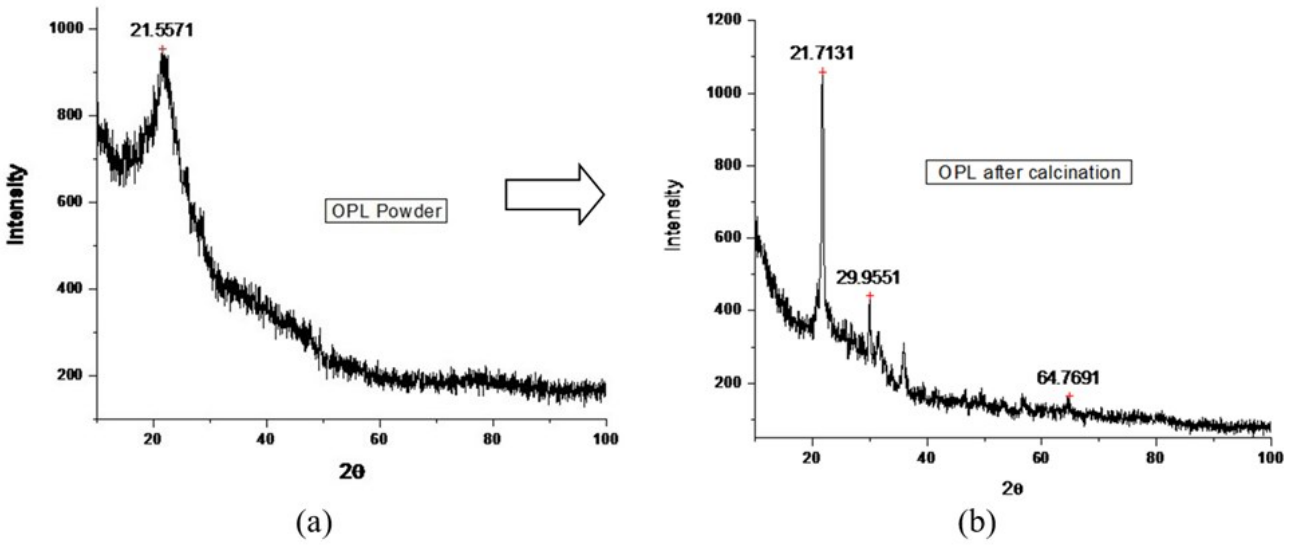

Figure 2. XRD pattern of (a) OPL powder prior calcination, (b) OPL after calcination at 900 °C

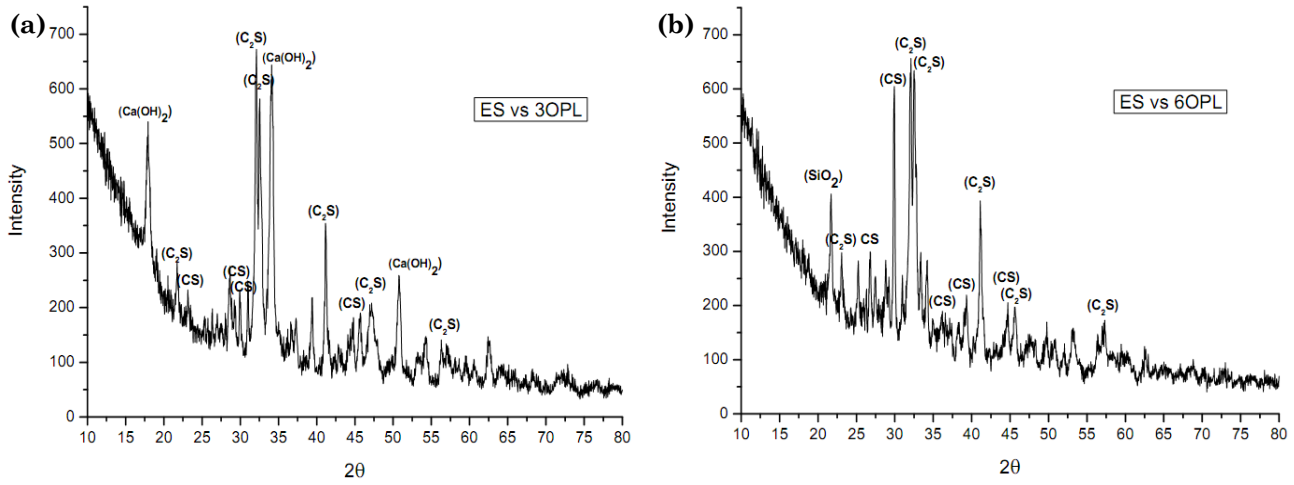

Figure 3. XRD patern of the products of (a) ES:3OPL reaction; (b) ES:6OPL reaction (CS: $CaSiO_3$ and C_2S: Ca_2SiO_4).

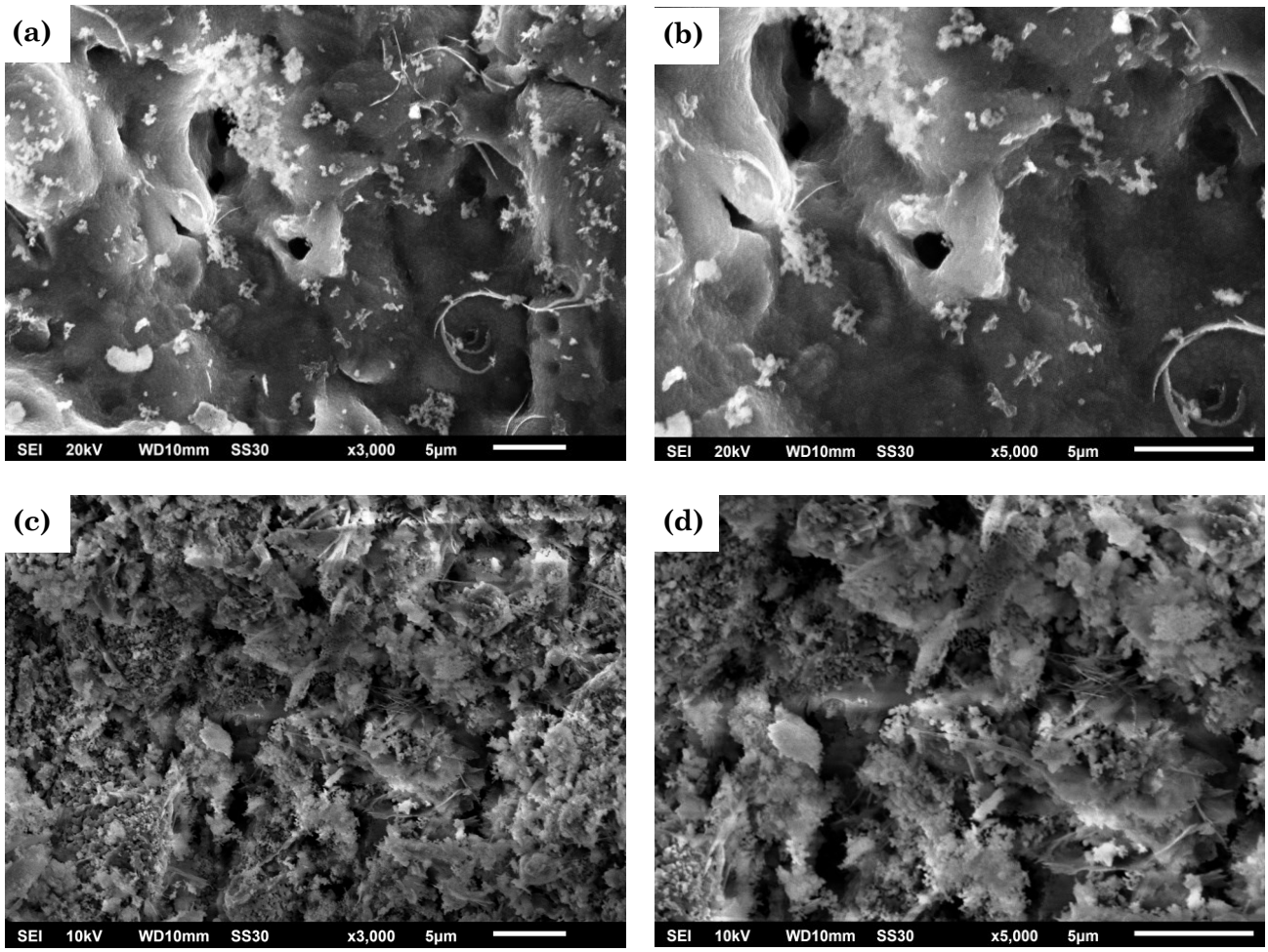

Figure 4. SEM image of (a-b) ES:3OPL and (c-d) ES:6OPL.

ica and calcium nitrate as CaO source and other reports [7,26]. This suggests that the reactions using the ES-to-OPL ratio of 1:3 tend to produce calcium silicates with Ca_2SiO_4 as the major product and $CaSiO_3$ as the minor product. In addition, some impurities were detected, including excess of mineral CaO, which was identified by the presence of peaks at 17.9°, 34.1°, and other overlapped peaks, and was converted to $Ca(OH)_2$ by hydration under air condition. This XRD data was compared with reported results [27–28] and supported by JSPDS 01-073-5492 and ICDD 00-044-1481. Other peaks at 26.8°, 29.92°, 39.3°, 44.7°, and various small peaks were also observed, more clearly in Figure 3(b), indicating the presence of reasonable amounts of $CaSiO_3$. This was compared to previous XRD results on calcium silicates synthesized using pure silica and pure CaO precursors [29], and referred to JCPDS #00–043-1460 [30,23]. It was found that higher amounts of $CaSiO_3$ were obtained in the present study, most likely due to the fact that our method preserves the high content of silica precursor in OPL. Despite the higher content of silica and other products such as $CaSiO_3$ in the reaction mixture having a weight ratio of 1:6, similar products were obtained. The XRD patterns displayed in Figure 3a show that the silica was consumed completely, as indicated by the absence of a silica peak as discussed for Figure 1b, whereas an excess of calcium hydroxide was observed. On the other hand, upon increasing the amount of OPL, a silica peak was observed at $2\theta = 21°$, and no $CaO/Ca(OH)_2$ was found. These evidences indicate that both precursors were converted to the corresponding calcium silicates such as $CaSiO_3$ and Ca_2SiO_4.

Despite the lack of experimental evidence, the reaction mechanism for the formation of the calcium silicates derivatives $CaSiO_3$ and Ca_2SiO_4 can be predicted from other studies [24,31]. The interaction between $CaCO_3$ in ES and silicon-based complex compounds in OPL at 900 °C may proceed as follows:

$$CaCO_3 \text{ (egg shell)} \xrightarrow{[O]} CaO + CO_2 \quad (1)$$

$$\text{Si-complex (oil palm leaves)} \rightarrow SiO_2 \quad (2)$$

$$CaO + SiO_2 \rightarrow CaSiO_3 \quad (3)$$

$$CaSiO_3 + CaO \rightarrow Ca_2SiO_4 \quad (4)$$

The calcium silicate product was subjected to scanning electron microscopy (SEM) analysis, and the corresponding results are depicted in Figure 4. Micrometer-sized particles with various shapes are present in both powders, and an irregular surface morphology can be observed. As can be seen in Figure 4(a)–(b), the product of ES:3OPL exhibits an irregular multi-layered surface, whereas more uniform calcium silicate particles are found in Figure 4(c)–(d) for the product of ES:6OPL. These morphologies are similar to those obtained using other methods [32–33]. From these SEM results, the surface porosity of the materials cannot be predicted.

Furthermore, an EDX analysis was performed to investigate the major elements present in the products, and the results are shown in Figure 5. Figure 5(a) and 5(b) show the sample composition, which mainly consisted of oxygen, silicon, and calcium, with a minor quantity of copper, magnesium, and zirconium. The EDX data shows that the silicon element comes from OPL, which is in agreement with previous reports [14–15]. The Ca/Si ratio could not be determined because the products were not purified. The present method provides new information on the green synthesis of calcium silicates, mainly Ca_2SiO_4 and $CaSiO_3$, which has been reported using other silica sources [3,5,7,34].

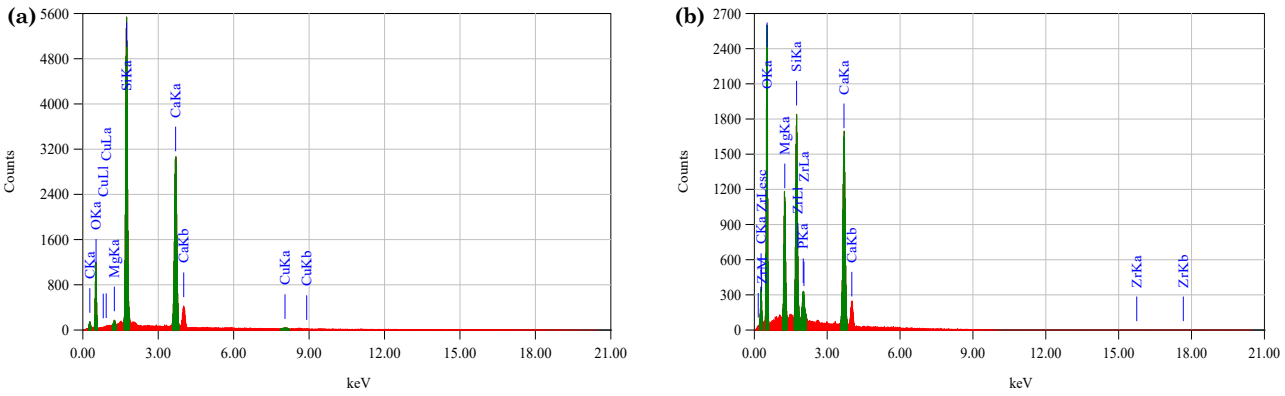

Figure 5. EDX pattern of (a) ES:3OPL and (b) ES:6OPL.

4. Conclusions

Powder materials containing calcium silicate derivatives, mainly Ca_2SiO_4 and a small amount of $CaSiO_3$, were successfully synthesized via the solid-state reaction of ES and OPL powders. This approach was executed by simply mixing both materials in the presence of a small amount of water, followed by heating at 900 °C for 2 h. Further investigation for the application of the reaction products and the use of OPL as a source of silica for preparing other products are on-going in our laboratory.

Acknowledgment

We are thankful for Lembaga Penelitian dan Pengabdian kepada Masyarakat (LPPM) Universitas Bengkulu for financial support under a scheme "Riset Kolaborasi Internasional" – Fiscal Year 2019 (contract number 2182/UN30.15/LT/2019).

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