Synthesis and Characterization of CaO Prepared from Limestone Using Sol-Gel Method

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Abstract

The sol-gel method has been successfully applied to the synthesis and characterization of calcium oxide (CaO) derived from calcite-based natural limestone from Pamekasan, Madura, East Java Indonesia. Controlled dissolution, titration, gel formation, and subsequent calcination at temperatures 650°C and 900°C were the steps involved in the synthesis. X-ray diffraction was used for characterization to identify the phase that had formed. Supporting software, MATCH! used to analyze the phases and structures and Rietica for refinement using the Rietveld method. The $Ca(OH)_2$ phase formed was 59.65 ± 2.45 %wt before the calcination process, according to the XRD results. 23.71 ± 0.61 %wt CaO was produced by the calcination process at 650°C, and 64.52 ± 1.85 %wt was produced at 900°C. Meanwhile, after calcination at 900°C, crystal size analysis using MAUD software produced CaO with a size of 534 ± 74 nm. K CaO powder synthesized using the sol-gel method is calcined at 900°C to get a higher percentage than at 600°C. The CaO powder can be used for CO_2 capture applications because it comes from natural resources and is environmentally friendly.

Introduction

Calcium oxide (CaO), most commonly known as quicklime, is an important substance in the field of materials science with a wide range of applications [1], [2]. It is particularly promising for CO_2 capture, becoming a strong contender because of its high capacity for CO_2 absorption, quick kinetics of absorption and desorption (0.1–0.4 g CO_2/g.minute), affordability resulting from its abundance in nature, safety for the environment, and lack of toxicity [3]–[7]. Its capacity for efficient and sustainable carbon capture is further highlighted by its reusability and effectiveness at high temperatures [8]. CaO's many qualities place it in a unique position

to address environmental issues related to CO_2 emissions, significantly advancing the development of eco-friendly technologies.

It has been attempted to use CaO derived from natural limestone without any processing; however, because of surface area decay and particle size increase through sintering, the adsorption capacity and regeneration stability of pure CaO have significantly decreased during multi-cycle operation [9]. Therefore, steps must be taken to ensure CaO retains its good adsorption capacity and stability. One such step is to create synthetic CaO using the calcination process [1], [10], [11], hydrothermal, precipitation [2], [12], combustion [13], biogenic, and microwave synthesis, can be used to produce CaO with improved qualities [2], and the last is the sol-gel method, which has a large surface area [14]–[19]. The sol-gel method is a low-cost, low-complexity technique that doesn't require high temperatures or pressure control. The sol-gel method is also an effective approach for the synthesis of nanomaterials [20]. In earlier studies, the sol-gel technique as outlined by Habte et al.[21] was successful in synthesizing CaO from eggshells.

Limestone which is abundant on Pamekasan, Madura Island, east Java has low economic value only as a building material [22]. So that it has a high value and can be applied for CO_2 capture, its properties can be improved, which are processed using the sol-gel method to obtain nano-sized CaO. In this study, the sol-gel method was used to synthesize CaO from natural limestone for CO_2 capture applications.

Experimental Method

Material

The limestone was taken from Pamekasan, Madura, East Java, Indonesia from previous research [22], with Ca content of 99.25 %wt and 100 %wt $CaCO_3$ phase. The chemicals utilized in this synthesis include hydrochloric acid (HCl) 37% (SAP), sodium hydroxide (NaOH) 98% (SAP), and distilled water.

CaO Synthesis

The sol-gel method used refers to the research of Habte et.al [21]. The first step in the synthesis of sol-gel was to dissolve 12.5 grams of limestone (which has been ground and sifted with a 400 mesh sieve) in 250 ml of 1 M hydrochloric acid (HCl), while stirring with a magnetic stirrer at a speed of 300 rpm at room temperature until dissolved, following the reaction [21]:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g) \qquad (1)$$
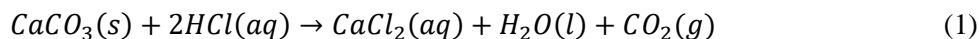
After that, 250 ml of sodium hydroxide (NaOH) 1 M is gradually added as part of a controlled titration procedure [22]. In the titration process, $Ca(OH)_2$ gel is formed by condensation, with the following reaction [21]:

$$CaCl_2(aq) + 2NaOH(aq) \rightarrow Ca(OH)_2(s) + 2NaCl(aq) \qquad (2)$$
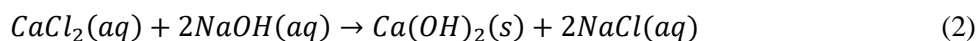
The solution containing $Ca(OH)_2$ gel was left overnight at ambient temperature. After leaving the gel overnight, the sodium chloride (NaCl) byproduct was successfully removed by giving it a thorough washing with distilled water. The gel was filtered and dried for 12 hours at 100°C. The final step in the synthesis is calcination. Two different calcination temperatures

were used in this study, 650°C referring to Khine, et.al [2] and 900°C according to Habte, et. al [21].

$$Ca(OH)_2(s) + Heat \rightarrow CaO(s) + H_2O(l) \tag{3}$$
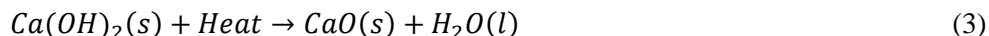
Characterization

The crystal phase of the synthesized CaO powder was analyzed by X-pert MPD X-ray diffraction test with Cu-Kα radiation (λ = 1.5406 Å) at 30 mA and 40 kV and scanning from 10° to 70° with a step of 0.02° at 10.15 s. XRD patterns were compared to powder diffraction files (PDF) from the International Center for Diffraction Data (ICDD) database using Match!3. Moreover, the structural analysis using the Rietica software makes use of the complex Rietveld refining procedure, which makes it possible to precisely extract structural information from the XRD patterns. And the CaO crystal size was analyzed using Material Anlaysis Using Diffraction (MAUD) software [23].

Result and Discussion

The X-ray diffraction patterns of CaO samples synthesized using the sol-gel method are presented in Figure 1. XRD testing was carried out on the $Ca(OH)_2$ precursor before calcination (CHa), then $Ca(OH)_2$ was calcined at 650°C (CHa6501h) and 900°C (CHa9001h). Phase identification was done using Match!. Identify the phases of XRD patterns presented in Table 1. Based on the X-ray diffraction (XRD) patterns of CHa, CHa6501h, and CHa9001h using Match!3 Software in Figure 1, the semiquantitative analysis shown in Table 2 provides a detailed explanation of the crystalline structure of these samples. Regarding CHa, the identified phases correspond to the ICDD reference numbers 000720156 and 000850849, which correspond to $Ca(OH)2$ and $CaCO3$, respectively. This confirms that $Ca(OH)_2$ and $CaCO_3$ are present in the untreated CHa sample, as shown by the XRD patterns shown in Figure 1. Specifically, for CHa6501h, the semiquantitative analysis reveals the presence of CaO (ICDD: 000772010) in conjunction with the ongoing presence of $Ca(OH)_2$ (ICDD: 000841264) and $CaCO_3$ (ICDD: 000851108). This is in complete agreement with the change in the XRD pattern that is seen following one hour of calcination of CHa at 650°C, representing the thermal breakdown of $CaCO_3$ into CaO. Comparably, for CHa9001h, the semiquantitative analysis confirms the presence of CaO (ICDD: 000772376) in addition to $Ca(OH)_2$ (ICDD: 000812040), indicating that the thermal transformation was enhanced during the more rigorous calcination process, which lasted for one hour at 900°C. Notably, the disappearance of the $CaCO_3$ phase in CHa9001h indicates that it was completely converted or depleted during the more intense calcination steps.

In the CHa sample, the identified phases are $Ca(OH)_2$ and $CaCO_3$, the presence of the $CaCO_3$ phase is probably caused by the presence of $CaCO_3$ which has not completely dissolved in HCl. This finding supports earlier studies [22], [23] that found $Ca(OH)_2$ and $CaCO_3$ in the gel before calcination. The main peak of $Ca(OH)_2$ occurs at 2θ = 34.21 and the other peak is 2θ = 18.16; 28.81; 36.81; 47.63; 51.05; and 64.65. The XRD pattern of CHa6501h, which is CHa calcined at 650°C for 1 hour, 3 phases of $CaCO_3$, CaO, and $Ca(OH)_2$ were observed. The CaO phase was observed but the intensity of the CaO peak at 37° is not very high, indicating that

the $Ca(OH)_2$ phase has not been completely decomposed. This observation was also consistent with research conducted by Mirghiasi et al.[1], who used the direct thermal decomposition of $Ca(OH)_2$ to synthesize nano CaO. Meanwhile, in other studies [2] that have synthesized CaO using the precipitation method, the $CaCO_3$ peak disappeared at a temperature of 600°C, and all CaO peaks were observed, in this study, in-situ XRD was used to perform structure and phase transformation observations, with the sample being heated during the scanning process. Likewise, the presence of the $CaCO_3$ phase indicates that at a temperature of 650°C, the $CaCO_3$ phase has not decomposed into CaO, based on the reference $CaCO_3$ will decompose at a temperature of 700 – 900°C.

In the CHa9001h (CHa calcined at 900°C for 1 hour) XRD pattern, the identified phases are CaO and $Ca(OH)_2$, indicating that the $CaCO_3$ phase has been completely decomposed into CaO. The main peak at $2\theta = 37.22$ and the other peaks at $2\theta = 32.07, 53.75, 64.04$, and 67.28 are consistent with previous research [2], [21], which also supports the observation of the CaO peak. However, the presence of $Ca(OH)_2$ peaks due to poor storage, the reaction between CaO and H_2O in air, and delays in XRD analysis after calcination all contribute to this phenomenon [2], [24].
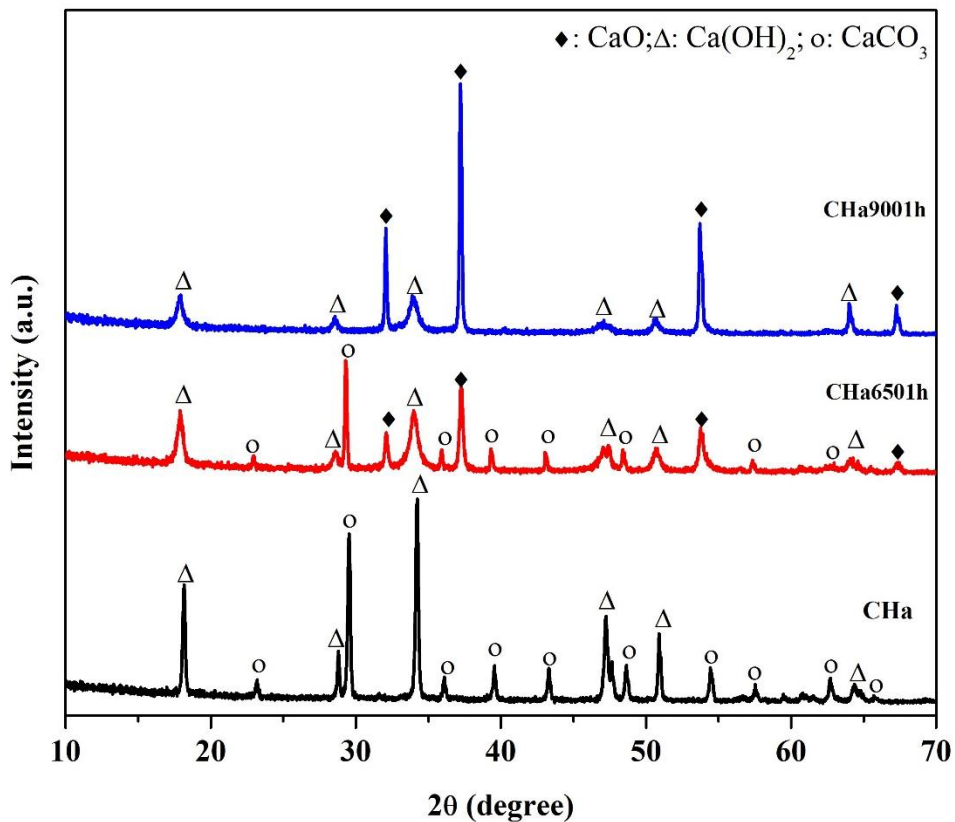

Figure 1. XRD pattern of CHa, CHa6501h, and CHa9001h

Table 1. Semiquantitative analysis of X-ray diffraction patterns of CHa, CHa6501h, and CHa9001h

Sample	Identified phase/ICDD		
	CaO	Ca(OH)$_2$	CaCO$_3$
CHa		000720156	000850849
CHa6501h	000772010	000841264	000851108
CHa9001h	000772376	000812040	

The detailed structural and lattice parameters of CHa, CHa6501h, and CHa9001h are explained in detail in Table 2, which also includes specific crystalline phases for each sample. This is a comprehensive Rietveld refinement analysis (Figure 2). Within the cubic CaO framework, the optimized lattice parameters for CHa6501h and CHa9001h were described, representing a symmetry intrinsic to the F m -3 m space group. The cubic nature of the CaO phase, indicating a face-centered cubic crystal structure, is highlighted by the lattice parameters of a = 4.8131(7) Å for CHa6501h and a = 4.8166(6) Å for CHa9001h. Contrarily, the Ca(OH)$_2$ phase in CHa and CHa6501h conforms to a trigonal crystal system, as indicated by the refined lattice parameters for CHa (a = 3.5974(6) Å, c = 4.9194(16) Å) and CHa6503h (a = 3.5921(7) Å, c = 4.9158(19) ù). A rhombohedral lattice structure is suggested by these parameters, which are consistent with the P -3 m 1 space group. Moreover, the refined lattice parameters a = 4.9959(14) Å, c = 17.0786(68) Å for CHa and a = 4.9900(7) Å, c = 17.0736(33) Å for CHa6503h, showing the trigonal nature of CaCO$_3$ in both compounds, are by the R -3 c H space group. Table 2 explains the lattice parameters and unique symmetries that indicate the structural variability of the phases in each sample and highlights the effect of heat treatments on crystalline transformations.

Table 2. Rietveld refinements, structural, and lattice parameters values of CHa, CHa6501h, and CHa9001h

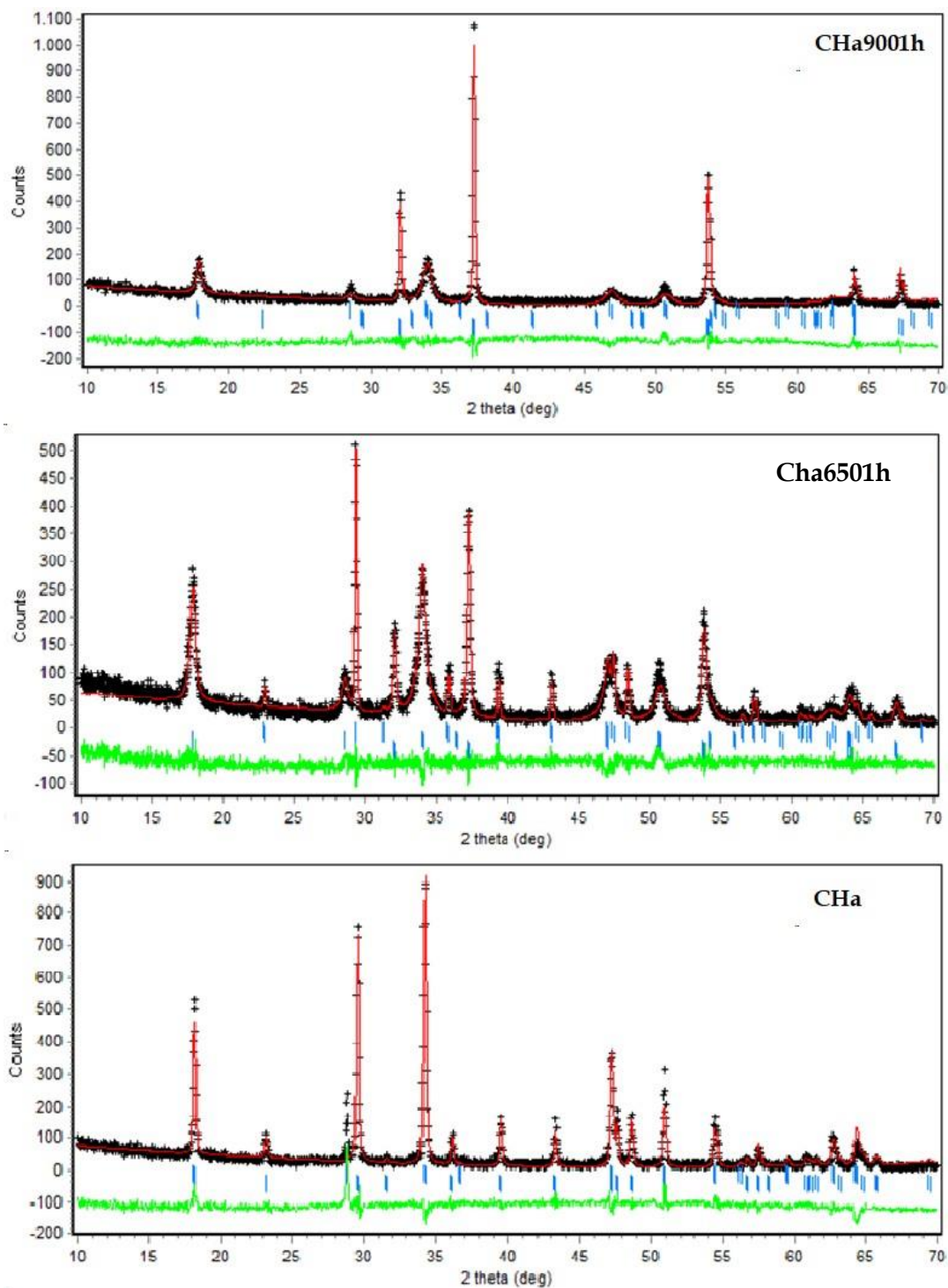| Sample	Crystal System	Space Group	CHa	CHa6501h	CHa9001h
			CaO		
a (Å)	Cubic	F m -3 m	-	4,8131(7)	4.8166(6)
V (Å^3)			-	111.5007	111.7467
			Ca(OH)$_2$		
a (Å)			3.5974(6)	3.5921(7)	3.5945(16)
c (Å)	Trigonal	P -3 m 1	4.9194(16)	4.9158(19)	4.9424(39)
V (Å^3)			55.1350	54.9322	55.3040
			CaCO$_3$		
a (Å)			4.9959(14)	4.9900(7)	-
c (Å)	Trigonal	R -3 c :H	17.0786(68)	17.0736(33)	-
V (Å^3)			369.1512	368.1712	-
GoF (%)			0.497	1.818	0.129
R_{wp} (%)			21.31	19.63	12.65
R_{exp} (%)			30.23	14.56	35.79
R_p (%)			22.10	14.64	20.00

Figure 2. Plot Rietveld refinement of Cha, CHa6501h, and Cha9001h using Rietica software

Table 3. Percentage of phase composition, and refinement using Rietica software with the Rietveld method

Sample	Wt (%)		
	CaO	$Ca(OH)_2$	$CaCO_3$
Cha		59.65 ± 2.45	40.35 ± 2.76
Cha6501h	23.42 ± 0.86	51.87 ± 1.26	24.42 ± 0.86
Cha9001h	64.52 ± 1.85	35.48 ± 1.25	

Table 3 provides a detailed and refined analysis of the phase composition percentage for CHa, CHa6501h, and CHa9001h using the Rietveld method. Similarly to previous analyses, the weight percentages for CHa show a nearly equal distribution between $Ca(OH)_2$ (59.65 ± 2.45 %wt) and $CaCO_3$ (40.35 ± 2.76 %wt), confirming the coexistence of these phases. Of particular note is the phase composition shift observed upon calcining CHa for 1 hour at 650°C (CHa6501h). The decrease in CaO to 23.42 ± 0.86 %wt and the concurrent increase in $Ca(OH)_2$ to 51.87 ± 1.26 %wt indicate a transformation from $CaCO_3$ to CaO during the calcination process. Additionally, there is a trace amount of $CaCO_3$ (24.42 ± 0.86 %wt) that remains, which offers subtle information about the partial conversion of this phase. In contrast, lower $Ca(OH)_2$ to 35.48 ± 1.25 %wt and a significant increase in CaO to 64.52 ± 2.19 %wt are the results of the more stringent calcination conditions at 900°C for 1 hour (CHa9001h). Interestingly, $CaCO_3$ is completely absent, suggesting that at this high temperature, it has either been completely converted or depleted. The results of Habte et al. [16], [22], who reported that $Ca(OH)_2$ was calcined at 900°C to produce CaO powder, are supported by these findings. But in this work, limestone was utilized instead of waste eggshell as it was in Habte, et al.'s work. The same study was carried out by Mirghiasi et al., who calcined $Ca(OH)_2$ for an hour at 650°C. They also noticed that there was still a $CaCO_3$ (calcite) phase, which suggests that $CaCO_3$ had not completely broken down at 650°C. The $Ca(OH)_2$ phase can be found in the 900°C calcination results because CaO and airborne H_2O react so readily to form $Ca(OH)_2$. On the other hand, El Knine et al.'s research [2], which synthesized CaO by the precipitation method, found that CaO formed steadily at 650°C using in-situ XRD, where temperature was applied to perform XRD measurements.
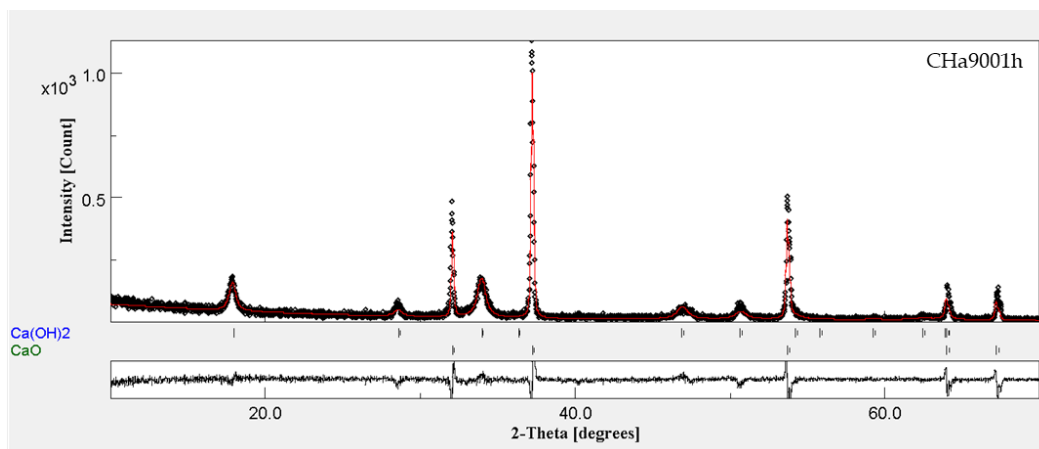

Figure 3. Plot with Rietveld refinement of Cha9001h using MAUD

The Rietveld method—which is illustrated in Figure 3—was utilized to determine the calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$) crystal sizes of Cha9001h. The MAUD software made this process easier [23]. Specifically, it was discovered that the crystal size of CaO was 534 ± 74 nm, while the crystal size of $Ca(OH)_2$ was 44 ± 3 nm. These findings offer useful quantitative information about the structural characteristics of the synthesized materials as well as insight into the various grain sizes and morphologies of the materials. Furthermore, a quantitative indicator of the agreement between the calculated and observed diffraction patterns, the 1.55 goodness-of-fit (GoF) value was calculated, demonstrating the precision and consistency of the Rietveld refinement technique. Previous research results reported by Habte, et. al. [21] reported that the CaO particles obtained were 50 - 198 nm in size as observed with SEM. This proves that the sol-gel method is effective for nanomaterial synthesis.

Conclusion

In summary, calcium oxide (CaO) was successfully produced from limestone using the sol-gel process. After calcination at 650°C, only 23.71 ± 0.61 %wt CaO was produced because the $CaCO_3$ had not decomposed. At 900°C, on the other hand, more calcium oxide (CaO) is formed, 64.52 ± 1.85 %wt, as calcium carbonate ($CaCO_3$) was completely decomposed into CaO in addition to $Ca(OH)_2$ being broken down into CaO. With a crystal size of 534 ± 74 nm, the CaO powder obtained from calcination at 900°C is suitable for CO_2 capture applications. Nanomaterials can be synthesized effectively using the sol-gel method.

Acknowledgment

References

[1]   Z. Mirghiasi, F. Bakhtiari, E. Darezereshki, and E. Esmaeilzadeh, "Preparation and characterization of CaO nanoparticles from Ca(OH)2 by direct thermal decomposition method," *J. Ind. Eng. Chem.*, vol. 20, no. 1, pp. 113–117, 2014, doi: 10.1016/j.jiec.2013.04.018.

[2]   E. E. Khine *et al.*, "Synthesis and characterization of calcium oxide nanoparticles for CO2 capture," *J. Nanoparticle Res.*, vol. 24, no. 7, 2022, doi: 10.1007/s11051-022-05518-z.

[3]   Y. Q. Geng, Y. X. Guo, B. Fan, F. Q. Cheng, and H. G. Cheng, "Research progress of calcium-based adsorbents for CO2 capture and anti-sintering modification," *Ranliao Huaxue Xuebao/Journal Fuel Chem. Technol.*, vol. 49, no. 7, pp. 998–1013, 2021, doi: 10.1016/S1872-5813(21)60040-3.

[4]   H. Guo, S. Wang, C. Li, Y. Zhao, Q. Sun, and X. Ma, "Incorporation of Zr into Calcium Oxide for CO2 Capture by a Simple and Facile Sol-gel Method Incorporation of Zr into Calcium Oxide for CO 2 Capture by a Simple and Facile Sol-gel Method," 2016, doi: 10.1021/acs.iecr.5b04112.

[5]   M. Broda and C. R. Müller, "Sol-gel-derived, CaO-based, ZrO2-stabilized CO2 sorbents,"

Fuel, vol. 127, pp. 94–100, 2014, doi: 10.1016/j.fuel.2013.08.004.

[6]   A. Scaltsoyiannes, A. Antzaras, G. Koilaridis, and A. Lemonidou, "Towards a generalized carbonation kinetic model for CaO-based materials using a modified random pore model," *Chem. Eng. J.*, vol. 407, p. 127207, 2021, doi: 10.1016/j.cej.2020.127207.

[7]   A. M. Kierzkowska, R. Pacciani, and C. R. Müller, "CaO-based CO2 sorbents: From fundamentals to the development of new, highly effective materials," *ChemSusChem*, vol. 6, no. 7, pp. 1130–1148, 2013, doi: 10.1002/cssc.201300178.

[8]   S. A. Salaudeen, B. Acharya, and A. Dutta, "CaO-based CO2 sorbents: A review on screening, enhancement, cyclic stability, regeneration and kinetics modelling," *J. CO2 Util.*, vol. 23, no. July 2017, pp. 179–199, 2018, doi: 10.1016/j.jcou.2017.11.012.

[9]   G. S. Grasa and J. C. Abanades, "CO2 capture capacity of CaO in long series of carbonation/calcination cycles," *Ind. Eng. Chem. Res.*, vol. 45, no. 26, pp. 8846–8851, 2006, doi: 10.1021/ie0606946.

[10]   F. Munawaroh, L. Khamsatul Muharrami, T. Triwikantoro, and Z. Arifin, "Calcium Oxide Characteristics Prepared From Ambunten's Calcined Limestone," *J. Pena Sains*, vol. 5, no. 1, 2018.

[11]   A. Lesbani, S. O. Ceria Sitompul, R. Mohadi, and N. Hidayati, "Characterization and Utilization of Calcium Oxide (CaO) Thermally Decomposed from Fish Bones as a Catalyst in the Production of Biodiesel from Waste Cooking Oil," *Makara J. Technol.*, vol. 20, no. 3, p. 121, 2016, doi: 10.7454/mst.v20i3.3066.

[12]   C.- Pujiastuti, S. Muljani, and K. Sumada, "Precipitated calcium oxide nanosize from limestone and blood clam shells," *J. Nat. Sci. Math. Res.*, vol. 9, no. 1, pp. 12–18, 2023, doi: 10.21580/jnsmr.2023.9.1.13209.

[13]   F. Granados-Correa and M. Jiménez-Reyes, "Evaluation of CO2adsorption capacity with a nano-CaO synthesized by chemical combustion/ball milling," *Mater. Sci. Pol.*, vol. 40, no. 2, pp. 257–269, 2022, doi: 10.2478/msp-2022-0024.

[14]   H. Sun, C. Wu, B. Shen, X. Zhang, Y. Zhang, and J. Huang, "Progress in the development and application of CaO-based adsorbents for CO2 capture—a review," *Mater. Today Sustain.*, vol. 1–2, pp. 1–27, 2018, doi: 10.1016/j.mtsust.2018.08.001.

[15]   M. Broda, A. M. Kierzkowska, and C. R. Müller, "Application of the Sol – Gel Technique to Develop Synthetic Calcium-Based Sorbents with Excellent Carbon Dioxide Capture Characteristics," pp. 411–418, 2012, doi: 10.1002/cssc.201100468.

[16]   R. G. Jalu, T. A. Chamada, and R. Kasirajan, "Calcium oxide nanoparticles synthesis from hen eggshells for removal of lead (Pb (II)) from aqueous solution," *Environ. Challenges*, vol. 4, no. February, p. 100193, 2021, doi: 10.1016/j.envc.2021.100193.

[17]   H. R. Radfarnia and A. Sayari, "A highly efficient CaO-based CO2 sorbent prepared by a citrate-assisted sol-gel technique," *Chem. Eng. J.*, vol. 262, pp. 913–920, 2015, doi: 10.1016/j.cej.2014.09.074.

[18]   G. K. Reddy, S. Quillin, and P. Smirniotis, "Influence of the synthesis method on the

structure and CO2 adsorption properties of Ca/Zr sorbents," *Energy and Fuels*, vol. 28, no. 5, pp. 3292–3299, 2014, doi: 10.1021/ef402573u.

[19] K. S. Sultana, D. T. Tran, J. C. Walmsley, M. Rønning, and D. Chen, "CaO Nanoparticles Coated by ZrO2 Layers for Enhanced CO2 Capture Stability," *Ind. Eng. Chem. Res.*, vol. 54, no. 36, pp. 8929–8939, 2015, doi: 10.1021/acs.iecr.5b00423.

[20] Y. Hu, H. Lu, W. Liu, Y. Yang, and H. Li, "Incorporation of CaO into inert supports for enhanced CO2 capture: A review," *Chem. Eng. J.*, vol. 396, no. February, p. 125253, 2020, doi: 10.1016/j.cej.2020.125253.

[21] L. Habte, N. Shiferaw, D. Mulatu, T. Thenepalli, R. Chilakala, and J. W. Ahn, "Synthesis of nano-calcium oxide fromwaste eggshell by sol-gel method," *Sustain.*, vol. 11, no. 11, pp. 1–10, 2019, doi: 10.3390/su11113196.

[22] F. Munawaroh, L. K. Muharrami, T. Triwikantoro, and Z. Arifin, "Characterization of Limestone in Pamekasan Madura Island as Raw Material for Producing Nano Precipitated Calcium Carbonate (NPCC)," 2018, doi: 10.1088/1757-899X/395/1/012009.

[23] L. Lutterotti, "MAUD - Materials Analysis Using Diffraction (and more)," 2024. https://luttero.github.io/maud/ (accessed Jan. 22, 2024).

[24] N. Widiarti *et al.*, "CATALYTIC ACTIVITY OF CALCIUM OXIDE FROM FISHBONE WASTE IN WASTE
 COOKING OIL TRANSESTERIFICATION PROCESS," *J. Bahan Alam Terbarukan*, vol. 6, no. 2, pp. 97–106, 2017, doi: 10.15294/jbat.v6i2.8335.