



Preparation and characterization of calcium oxide from snail shell

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Abstract: This paper studied the synthesis of calcium oxide (CaO) from snail shells by calcination, crushing, and grinding. Then, the sample was analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), specific surface area (BET), and particle size. The XRD result showed obtained CaO content of 98.7%. FTIR spectrum analysis revealed a sharp band appeared at 3647 cm^{-1} due to the formation of $\text{Ca}(\text{OH})_2$ and the band at 1419 cm^{-1} was the characteristic peak of CaO. SEM images supplied a fairly uniform crystal structure and high porosity capillary. TGA analysis also gave a clear mass loss in two temperature ranges from $320\text{--}500^\circ\text{C}$ and $515\text{--}780^\circ\text{C}$. At the same time, our results are compared with previous related studies.

Keywords: Synthesis; calcium oxide (CaO); Physicochemical analysis; Snail shell.

1. Introduction

Calcium oxide (CaO), has many important applications in industrial fields and daily life. As a popular compound with a relatively reasonable price, Calcium Oxide is commonly used in industrial production. In aquaculture, Calcium oxide is often used at the end or beginning of the season to remove alum, improve soil, kill fungi, assist in killing pathogens, reduce pH, reduce acidity, etc. It is the starting material and cannot be used. It is lack to produce other chemicals and products such as bleaching powder, soda ash, etc. It is a compound that helps purify other chemicals such as Citric Acid, Glucose, dyes, etc. Some studies on materials used in the preparation. These materials in different substance sources are used as acids or bases in homogeneous and heterogeneous forms [1]. For acids, high reaction temperatures and times are needed, but for homogeneous liquid sources. Reaction time is lower than using acid [2]. However, homogenized

liquids exhibit some disadvantages such as being difficult to separate from the product and being unable to be reused. In addition, heterogeneous solids have many advantages over homogeneous liquids in that they are easy to separate and reuse, don't corrode [3].

In some studies, heterogeneous solids are considered to have a tendency to be used for polluted water treatment and some other fields. Materials used to produce acids and bases come from many sources. However, to reduce costs and make the most of waste from everyday life and business, a variety of heterogeneous basic substances are used to research a number of environmental fields. Some raw materials used to synthesize substances that participate in chemical reactions include seashells, oyster shells, and snail shells [4, 5]. These materials contain compounds CaCO_3 , CaO, etc.

Projects around the world have researched the production of materials from snail shells,

typically the research of author Roschat and his colleagues has synthesized materials from river snail shells. CaO contained in snail shells is heated at a temperature of 600-1000°C for 3 hours (h) [6]. In one study, Kaewdaeng et al. used heterogeneous fluids. The raw materials used are river snail shells, cleaned and dried at 105°C for 24 h. Next, it is heated at 800°C for 4 h. Then, the ingredients are ground into fine powder and filtered through a 60mm stainless steel sieve [7].

In addition, Kaewdaeng and Nirunsin synthesized CaO from river snail shells by heating at 700°C, 800°C, and 900°C for 4 h. The material was then analyzed using X-ray fluorescence (XRF), XRD, and SEM. XRF results gave the calcium oxide content was 59.5%; 70.1%, and 73.9% at heating temperatures of 700°C, 800°C, and 900°C, respectively [8].

Snail shells have been studied around the world. In 2016, the research team of authors Gupta and Agarwal tested snail shells as a substance for the transesterification reaction. The snail shells are calcined and denatured with potassium hydroxide (KOH) to obtain highly active substances. The KOH/snail shell material gave the highest yield of 96% when performing the cross-esterification reaction at 65°C, the methanol/soybean oil ratio was 9:1 with a sample volume of 6% [4]. Research on waste cooking oil using materials prepared from snails is carried out as follows: Snail shells containing CaCO₃ are converted into CaO after heating at 800°C for 4 h and CaO is the material participating in the reaction. Heterogeneity is considered effective in converting waste cooking oil [9]. Similar studies were also conducted by the author groups El-Gendy et al. and Laska et al. [10, 11].

In Vietnam, research into the use of snail shell materials is still very limited. Recently, the team of authors Tong Thi Minh Thu and Tong Thi Kim Oanh successfully made material of CaO, from scraps such as chicken eggshells, seashells, and coral. CaO-prepared materials were tested for their

properties using physicochemical analysis methods, XRD, FT-IR, SEM, and BET [12].

Thus, research into making calcium oxide from snail shell materials and solid waste from snail shells arises from people's daily lives and production activities.

Therefore, this study was conducted to prepare CaO from snail shells. The implementation of the Calcium oxide preparation process also takes advantage of waste generated from daily life, business activities and recovery of harmful animals. In this article, the research focuses on contents including introduction, materials and methods, results, discussion and conclusions in CaO preparation.

2. Materials and methods

2.1. Materials

The product of this study is a heterogeneous catalyst. They were snail shells collected from the Ha Dong area, Hanoi. After collection, the samples were gutted, cleaned many times with water, then dried in a drying oven, and synthesized in the next steps.

2.2. Equipment and tools

This paper used some devices to synthesize CaO at the Environmental Laboratory, Department of Chemistry - Environment, Faculty of Applied Science, University of Transport Technology, included: Desiccator (UN 160 Memmert/Germany); Furnace (LH 15/14 Nabertherm/Germany); Ball mill (PM 100 RETSCH/ Germany); Precision balance (Practum 2101-1S); Analytical balance (Practum 224-1S Sartorius - Germany) and other glassware. Privately, the agate mortar is used at the School of Chemistry and Life Sciences, Hanoi University of Science and Technology. In addition, the analytical equipment for CaO properties such as parameters of XRD, FT-IR, SEM, BET, and particle size were used at the Vietnam Academy of Science and Technology.

2.3. Synthesis method

a. Determination of CaCO₃ content in the collected snail shells

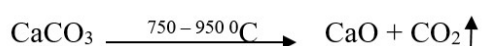
To check the calcium carbonate content (CaCO_3) in the investigated shell source, we used the method as follows: weighed m gram of the sample, whose surface had been cleaned and crushed. Put the sample in a glass beaker and add the HCl solution [13]. At that time, the CaCO_3 content in the sample was completely dissolved in the HCl solution according to the following reaction equation:



When there is no longer bubbling in the cup, filter out the insoluble portion, which may be impurities insoluble in the HCl solution. Then to determine the CaCO_3 content in the snail shell sample, we performed the following experiment: Weighed 5 g of crushed snail shell and dissolved it completely in 100 mL of 2.5M HCl solution. Filter the solution after the collection reaction and take 50 mL of this solution, add a few drops of phenolphthalein indicator and titrate with 0.1 M NaOH solution to find 37.6 ml.

b. Synthesis of CaO from CaCO_3 source in the collected snail shell

In theory, after being cleaned and dried, the shells are calcined at 750 – 950°C [8, 10] to remove carbon dioxide (CO_2) according to the following irreversible chemical reaction:



CaO material was produced by the calcination method. The dried snail shells were calcined at 750°C, 850°C, 900°C, and 950°C in air atmospheric pressure for 4 h, then crushed and ground to reduce the size. The resulting product was a white powder. The calcined sample was kept in a sealed vessel to avoid moisture absorption and the reaction with CO_2 .

For convenience in presenting and discussing the results, the raw material in this study is denoted as SSP, SSP-t is a symbol of the sample, calcinated at a temperature of t (°C), for example, SSP - 750, SSP – 850, and SSP – 900 are the samples after being fired at temperatures

of 750°C, 850 °C, and 900 °C, respectively.

The sample after calcination is analyzed with the physicochemical properties by the following methods:

- XRD: XRD is used to determine the crystal structure of the material, the X-ray diffraction (XRD) pattern for the SSP-900 sample was analyzed using XRD (D8 Advance - Bruker, Germany).

- FTIR spectra were recorded on an FTIR spectrometer (Nicolet 6700 FT-IR spectrometer) in the range 400 - 4000 cm^{-1} .

- SEM images and surface elemental analysis were recorded by a FESEMS system (Field Emission Scanning Electron Microscope S – 4800).

- BET was applied to determine the specific surface area of the material. This experiment was conducted on a Chem BET – 3000 and a Micromeritics Gemini VII 2390 V1.02.

3. Results and Discussion

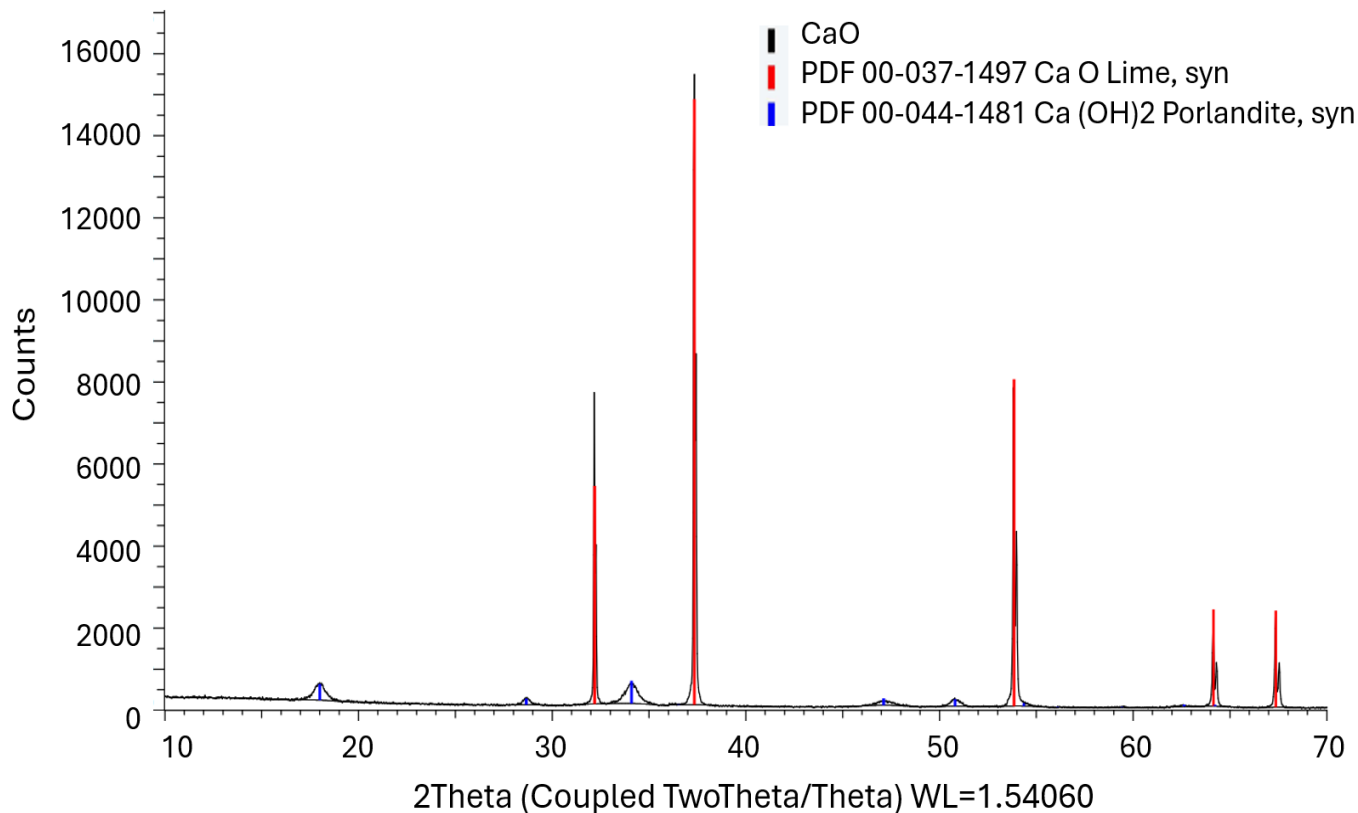
3.1. Results of CaCO_3 content in the snail shell

Experimental results to determine the CaCO_3 content in snail shells: after adding 5g of snail shell sample, 37.6 ml of 2.5 M HCl solution is needed for the reaction to occur completely and is based on the reaction equation in Section 2.3 calculate CaCO_3 content in snail shells reaches 94%.

The obtained data shows that the amount of CaCO_3 in snail shells is high, so using this source of raw materials to synthesize CaO will give high-efficiency.

3.2. Results of CaO content in the snail shell

Using the CaO distribution model on the XRD diagram (Fig 1) of the snail shell sample shows that the product after firing has the main component of CaO. The CaO content in our study is 98.7%, higher than the study using the same material as snails by Sani et al. with 95.186% [9], by Laskar et al. with 98.017% [10], and the material of coral shell by Tong Thi Minh Thu et al. with 92% [12]. Specific comparison data are given in Table 1. In addition, also from the XRD distribution diagram denoted that the $\text{Ca}(\text{OH})_2$ content is minimal, only 1.3%.



Pattern List : CaO

Index	Color	Scan	Compound Name	Formula	System	I/Ic DB	S-Q
1	■	CaO.brml #1	Lime, syn	Ca O	Cubic	(1)	98.7 %
2	■	CaO.brml #1	Portlandite, syn	Ca (O H)2	Hexagonal	2.900	1.3 %

Wavelength	Space Group
1.54060 Å	Fm-3m (225)
1.54060 Å	P-3m1 (164)

a
4.81059 Å
3.58990 Å

b	c	alpha	beta	gamma
4.91600 Å				

Volume	Density
111.33 Å ³	3.346 g/cm ³
54.87 Å ³	2.242 g/cm ³

Fig 1. The CaO distribution model on XRD pattern of the snail shell sample

3.3. The survey on the physicochemical properties

a. TGA analysis – DTG analysis

To determine the decomposition temperature of CaCO_3 in snail shells, the study carried out differential TGA analysis. In addition, through the sensory perception of calcinated sample color at different temperatures, the optimal calcination temperature was selected.

TGA analysis of the SSP in this study is shown in Fig 2. The results after calcination showed that there were two mass losses. The first loss in the temperature range of 320-500°C was due to the removal of $\text{Ca}(\text{OH})_2$ and the second loss in the temperature range of 515-780°C was due to the decomposition of CaCO_3 into CaO and CO_2 along with some inorganic impurities being lost. The mass losses of the two data were approximately 19.7% and 1.3%, respectively. Our TGA results were similar to those of Gupta and Agarwal with the weight losses of the two data being 12.27% and 1.60% [4].

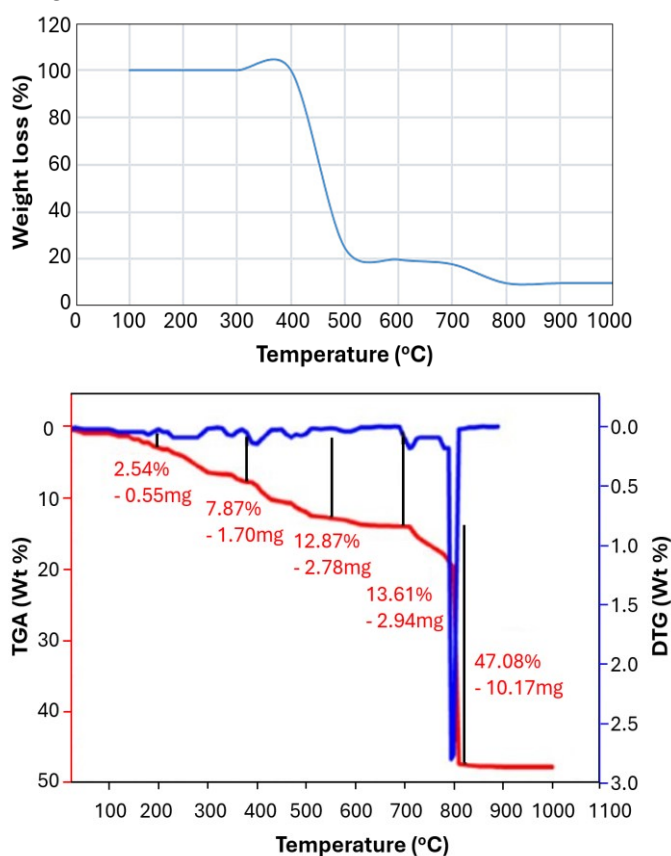


Fig 2. The TGA curves of SSP sample and TGA-DGT/DSC curve of Snail Shell

This study uses a differential scanning calorimeter (DSC) and thermogravimetric analysis by derivative thermogravimetry (TGA-DTG) to know the mass loss and heat flow during the phase transformation of snail shells at temperatures from 200°C to 1000°C. Fig 2 shows the obtained TGA-DTG/DSC thermogram. TGA shows the weight loss of SSP as a function of temperature.

We can see that from the thermogram includes many processes. The weight loss of SSP-900 is indicated by the TGA-DTG thermogram in milligrams and percent compared to the original mass. The first loss appears at about 193.85°C with a rate of 2.43% because the SSP-900 sample surface is initially dry but contains water molecules. In addition, at a temperature of 390°C, a loss rate of 8.2% was detected, which is due to the removal of organic compounds from the shell and water molecules bound to aragonite molecules.

According to authors Hu and colleagues [14] reported a significant weight loss of 41.3% in snail shells when the temperature increased from 631°C to 775°C. In addition, when the calcination temperature exceeded 800°C, the weight loss remained almost constant until reaching 835°C. The results show the decomposition of CaCO_3 to CaO by releasing CO_2 molecules.

Thus, when heated above 850°C, there is almost no decrease in mass, proving that the decomposition reaction of CaCO_3 to form CaO has completely occurred before 850°C.

For calcined powder samples at temperatures from 750 to 950°C and ground, through sensory perception of color and size, it can be seen that: Up to 750°C, the sample is still dark gray and difficult to grind, so most of it still exists in the form of small pieces that cannot be formed into fine powder; Up to 850°C, it has turned brighter and finer than the calcined sample at 750°C; It is improved at 900°C with a bright white color and much smoother and fluffier than the sample calcined at lower temperatures. When calcined at 950°C, the state of the sample does not change compared to the before sample (900°C). Thus, based on the results of TGA analysis and the actual

appearance, it can be confirmed that the calcinate sample at 900°C is a suitable value with both ensures complete decomposition and smooth grinding for the sample. Fig 3 shows the above-mentioned products.



Fig 3. The image of the snail shells calcined at 750°C, 850°C, 900°C and 950°C

b. XRD analysis

As mentioned, Fig 1 shows the XRD pattern

measured from the snail shell source after calcination at 900°C for 3h, mainly containing CaO. Strong sharp CaO peaks (red color) were observed at 2θ around 32.8°; 37.3°; 54.2°; 64.1° and 67.5°. The results are quite similar to the research results of Gupta and Agarwal with several sharp peaks of CaO observed at 2θ around 32.12°; 37.28° and 53.76°. In addition, the CaCO₃ peak is almost absent [4]. Other studies have similar results [8].

In XRD spectrum analysis, Ca(OH)₂ peaks marked by blue color also appeared at positions of 18°, 34°, 58°, and 61°. Ca(OH)₂ exists in the sample due to the humidity in the storage environment. However, the peak of Ca(OH)₂ is very small. Through the results of the functional groups appearing in the XRD spectrum, we can see that the CaO catalyst sample calcined from snail shells has high purity and the main component is CaO.

c. FTIR analysis

When the sample is heated at 900°C for 3 h, the FTIR spectrum of the sample SSP-900 is shown in Fig 4.

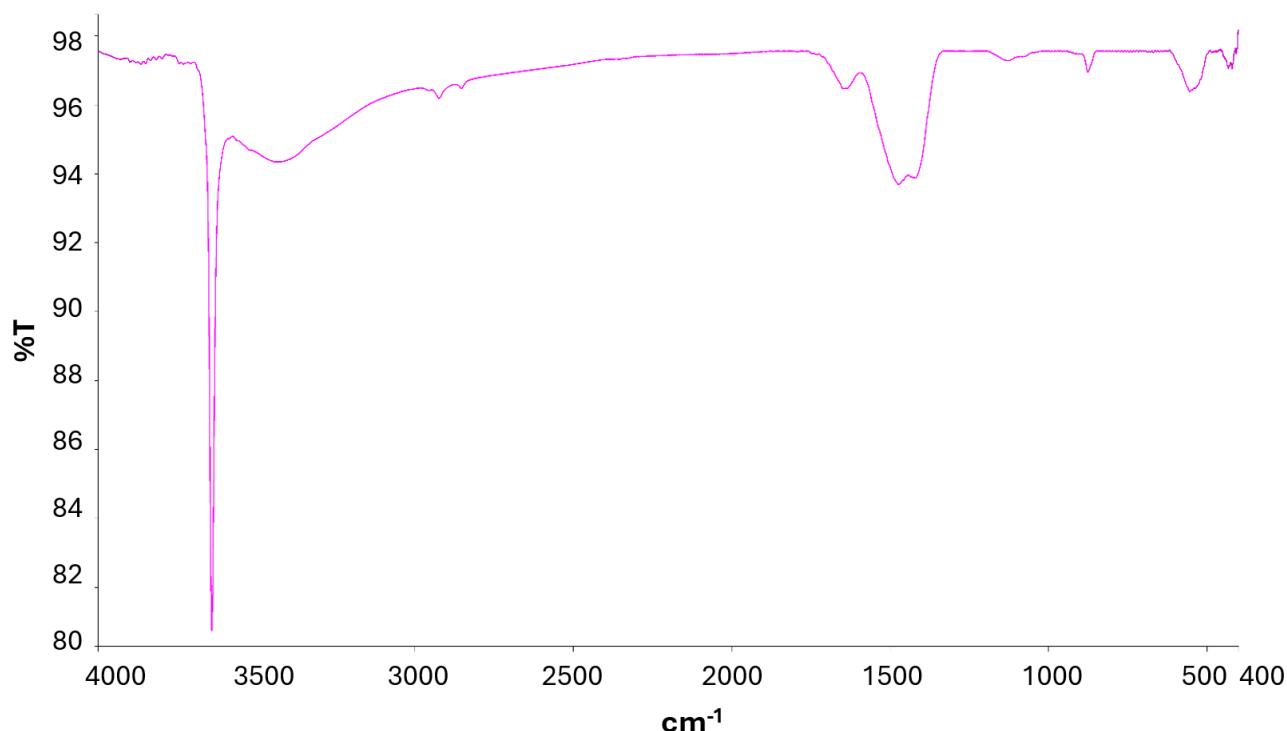


Fig 4. The FTIR spectrum image of sample SSP-900

Under this condition, due to the thermal decomposition of CaCO₃, CaO and Ca(OH)₂ were formed. Through FTIR spectrum analysis of the SSP-900 sample, a sharp band appeared at 3647

cm⁻¹ due to the formation of basic OH groups attached to calcium atoms, i.e. Ca(OH)₂, and the band at 1419 cm⁻¹ was the characteristic peak of CaO. At the peak of 876 cm⁻¹, a characteristic peak

of CaCO_3 appeared. It is also possible that CaCO_3 in the snail shell sample has not been completely thermally decomposed, so the peak appeared at this position. From the above analysis, it can be seen that in XRD analysis, CaCO_3 does not appear, but in FTIR analysis, it does, however, with a very low peak intensity, proving that its residual amount is very small. Thus, our research results show quite similar to a study using highly active solid base catalyst synthesized from snail shells to prepare biodiesel with a sharp peak at $3,640\text{ cm}^{-1}$ due to the presence of $\text{Ca}(\text{OH})_2$, a strong peak at 1471 cm^{-1} for CaO in the previous study [4].

d. SEM analysis

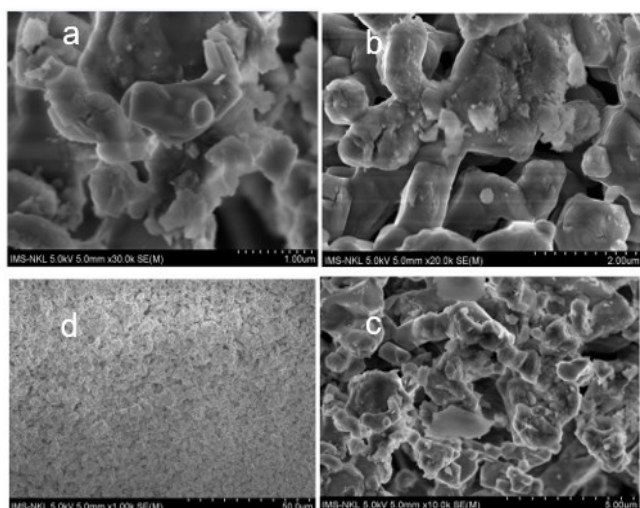


Fig 5. SEM image for SSP-900;

(a-d) with magnification of approximately $1\mu\text{m}$, $2\mu\text{m}$, $5\mu\text{m}$, and $50\mu\text{m}$, respectively

SEM was used to determine the external structure of the calcined snail shell, as illustrated in Fig 5 (a-d). Fig 5 (a-d), materials with particle sizes from $1\mu\text{m}$ to $50\mu\text{m}$. This image shows that the obtained sample has a fairly uniform crystal structure, is not sintered, does not cluster, and has high porosity because the calcination process due to the thermal effect affects the organic compounds in the ash of the snail shell after calcination [1]. In addition, combined with the image in Fig 3, it can be seen that at the firing temperature of 750°C and 850°C , the surface structure of the material is rougher. At the higher calcination temperature of 900°C , particles were small and agglomerated. The smaller particle size resulted in higher surface area for catalysis [8, 15]. However, calcination at

higher temperature thus fragile, easily brittle fractures can be easily crushed to calcination at a lower temperature.

e. BET analysis

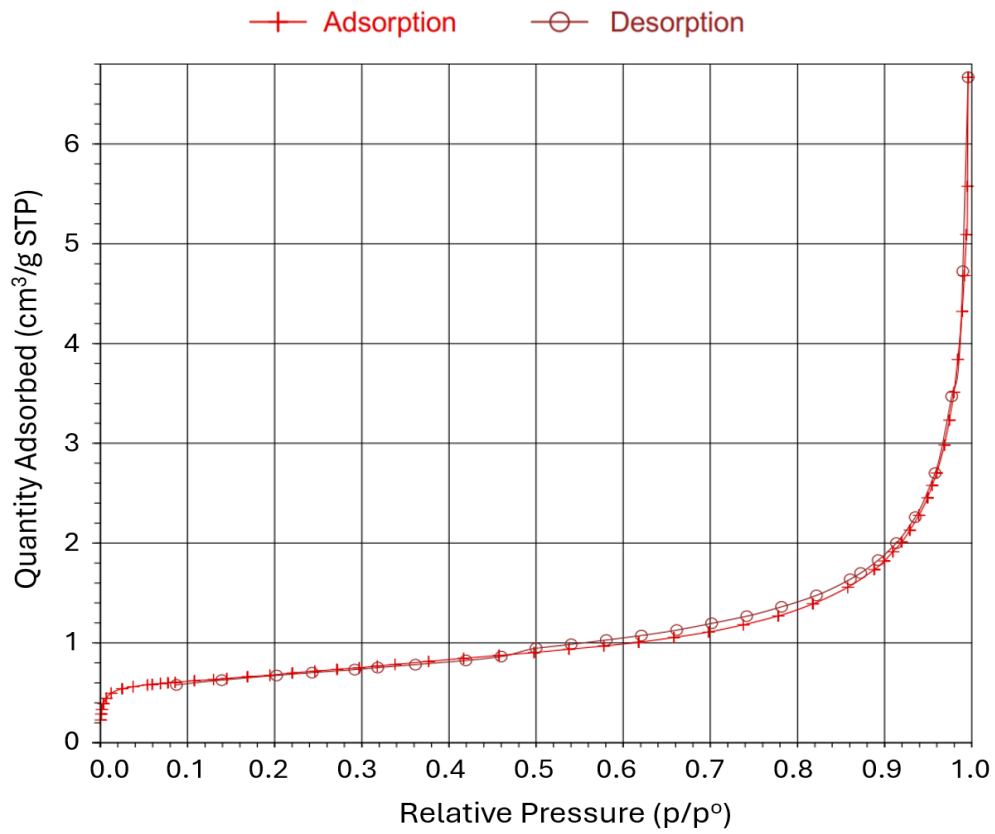
The BET analysis results of the SSP-900 sample are shown in Fig 6 (a, b). The SSP-900 sample has a surface area of $2.32\text{ m}^2/\text{g}$. The adsorption isotherm of the above sample has a sling shape, so it belongs to the medium capillary type. The safe diameter analysis diagram found that the sample after reaction has a tempered diameter of about 24.5945 \AA which is compatible with the CaO sample after heat activation and can measure an error of $0.007370\text{ cm}^3/\text{g}$ for uniform particle size. With this result, the synthesized sample achieved a similar specific surface area of $2.66\text{ m}^2/\text{g}$ (900°C) by Roschat et al. [8].

During the carbonization process, the CaCO_3 sample decomposes, releasing CO_2 , which acts as a trigger to activate the carbon materials, creating micropores and mesopores as well as increasing the pore size. The N_2 adsorption/desorption isotherm, capillary size distribution, and parameters of carbonized carbon materials at two critical temperatures, namely 900°C higher than the CaCO_3 pyrolysis temperature and 650°C lower than the CaCO_3 pyrolysis temperature. Our results show that the capillary size of SSP-900 has an average pore diameter of 12.7 nm and 14.5 nm for adsorption and desorption [16].

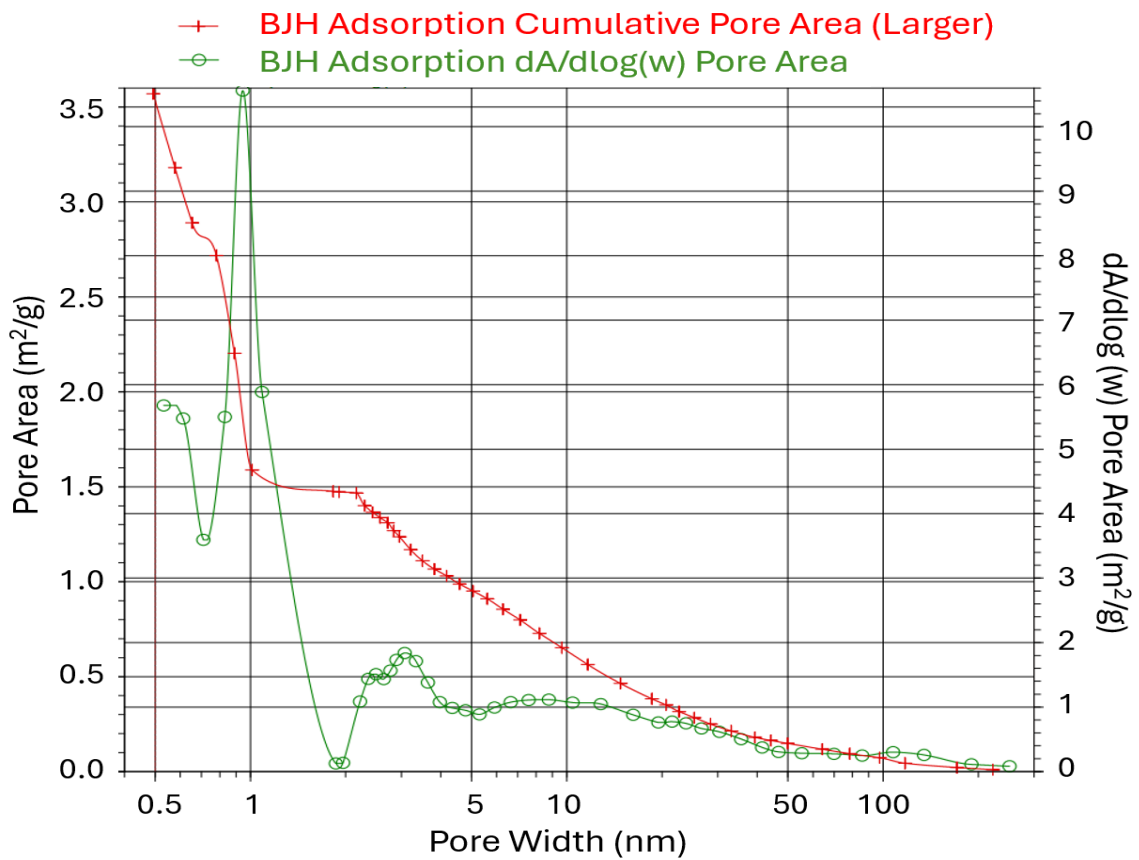
f. Particle size analysis

The results of particle size distribution of the sample are shown in Fig 7.

In addition, the particle size distribution of snail shell sample SSP-900 after being ground in a ball mill (PM 100 RETSCH/Germany) at a speed of 450 rpm , for 30 minutes and then the composite sample was taken Determined by laser scattering method on HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950 at the laboratory of the Institute of Chemistry and Materials under the Vietnam Academy of Science and Technology gives an average size of 658 nm . With this result, we can apply calcium oxide samples from snail shells in many fields [17].



a) Nitrogen adsorption-desorption isotherms of the SSP -900 samples



b) Capillary distribution curve of SSP-900

Fig 6. The Adsorption - Desorption Isotherm N₂ and Capillary distribution curve of SSP-900

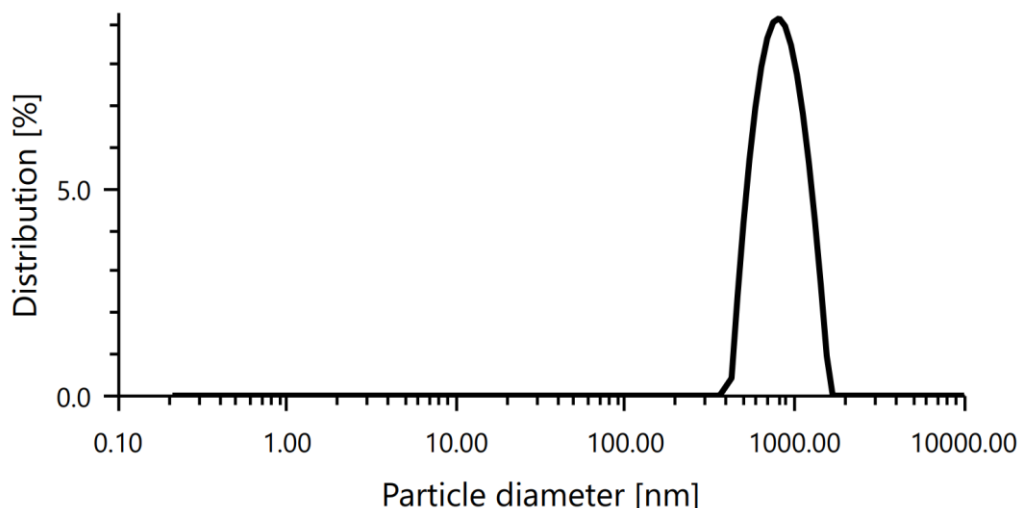


Fig 7. The particle size distribution results of SSP-900

4. Conclusion

The paper synthesized SSP-900 from a calcined snail shell at 900°C for 3h. SSP-900 was analyzed by XRD, FT-IR, SEM, and BET, and on that basis discussed and compared with samples released in previous related studies. The XRD results of SSP-900 denoted the obtained CaO content of 98.7%. This work has confirmed that the SSP-900 model can be applied in many different fields when using calcium oxide.

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