REPEATED EXTRACTION OF CALCIUM CARBONATE MICRO SIZED FROM CHERRY SHELL

Kanokwan Najai[a,b], Sunti Phewphong[a], Hassakorn Wattanasan[a], Sakda Sansupan[c], Tosawat Seetawan[a,b,c*]

[a]*Extraction Research Laboratory, Thermoelectrics Research Center, Research and Development Institution, Sakon Nakhon Rajabhat University, 680 Nittayo Road, Mueang District, Sakon Nakhon 47000, Thailand*
[b]*Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University,*
[c]*680 Nittayo Road, Mueang District, Sakon Nakhon 47000, Thailand*
Research and Development Institution, Sakon Nakhon Rajabhat University, 680 Nittayo Road, Mueang District, Sakon Nakhon 47000, Thailand

Received 24 July 2015; Revised 1 September 2015; Accepted 8 September 2015
Papers Selected from Sakon Nakhon Rajabhat University International Conference 2015 (SNRU- IC2015)

ABSTRACT

The calcium carbonate ($CaCO_3$) was extracted from *Pomacea Canaliculata Lamarck* (Cherry shell) by using hydrothermal method. Cherry shell was washed and crushed by DI water and mortar. The powder size was analyzed by particle (aperture size 63 μm). HCl and Na_2CO_3 were mixed with $CaCO_3$ powder from Cherry shell, autoclave was used for controlled temperature and pressure, filtering and annealing at 373.15 K for 20 h. The crystal structure was characterized by the x-ray diffraction patterns analysis. Fourier transform infrared spectroscopy (FTIR) analysis revealed the presence of aragonite and calcite. The morphological of Cherry shell and $CaCO_3$ powders were observed by using the scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). It found that the $CaCO_3$ showed the single phase of $CaCO_3$ crystal structure, and crystallite size about 0.4 μm. The methods adopted used in the synthesis of calcium carbonate are small crystals nearby the nanoscale

KEYWORDS: *Cherry shell, micro sized, hydrothermal process, calcium carbonate*

* Corresponding authors; e-mail: t_seetawan@snru.ac.th, Tel.&Fax +6642744319

INTRODUCTION

Calcium carbonate ($CaCO_3$) is a common substance which was found in rocks in all parts of the world, and it the main component of shells of marine organisms, snails, coal balls, pearls, and eggshells. The vast majority of $CaCO_3$ used in industry is extracted by mining or quarrying. The two crystalline forms are calcite and aragonite [1,2]. In the part, synthesis of $CaCO_3$ was followed by two basic synthetic routes: (1) the solution route, through a double decomposition reaction, where in aqueous $CaCl_2$ and Na_2CO_3, or $CaCl_2$ and $(NH_4)_2CO_3$, or $Ca(NO_3)_2$ and Na_2CO_3 are combined in an equal molar ratio; and (2) the carbonation method, in which CO_2 gas is bubbled through an aqueous slurry of $Ca(OH)_2$ [3,4].

In this paper, we are focused on the repeated extraction from $CaCO_3$ by hydrothermal method. The extracted powder $CaCO_3$ was analyzed for crystal structure, and crystallite size. The phase transformation of $CaCO_3$ was analyzed by Fourier transform infrared spectroscopy (FTIR). The morphology of Cherry shell and $CaCO_3$ powders were observed by using scanning electron microscope (SEM).

MATERIALS AND METHODS

The $CaCO_3$ was extracted from Cherry shell by using the hydrothermal method. Cherry shell was washed with DI water, and crushed to powder. The powder was reduced to smaller size with sieve (aperture size 63 μm). The Cherry shells powder was drying in an oven at 378.15 K for 2 h. The powder for 10 g was digested in 100 ml hydrochloric acid concentration 2 M which was $CaCl_2$ solution, filtered $CaCl_2$, and 100 ml sodium carbonate was mixed, obtained $CaCO_3$ solution, and then took into an autoclave

under controlled temperature and pressure. The crystalline $CaCO_3$ was rinsed with distilled water until nonionic residue by measuring the pH value of about 7, and then dried at 378.15 K for 12 h in an oven, we get the $CaCO_3$ powder. Eventually, the powder was extracted by once upper processes

The overall reactions for the $CaCO_3$ extracted step can be summarized from Eq.

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$CaCl_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + 2NaCl_{(aq)}$$

The crystalline phase of the synthesized $CaCO_3$ was characterized by X-ray diffraction with CuKα, λ = 0.15 nm (XRD-6100 Shimadzu, Japan). After thoroughly cleaning the sample holder, the $CaCO_3$ powder obtained from Cherry shells was spread on the sample holder. The sample was then placed inside the XRD machine and the sample was investigated to understand the phase(s) and size of the $CaCO_3$ micro powder.
The average crystallite size of the $CaCO_3$ was calculated using Scherrer's equation [5].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

D = shape factor, λ = X-ray wavelength, β = FWHM of diffraction peak, θ = Bragg angle.

The samples were measured by using FTIR spectroscopy analysis (FTIR-8900 Shimadzu, Japan) by the potassium bromide (KBr) pellet method. The sample pellets were prepared as follows: KBr and $CaCO_3$ were drying in an oven at 378.15 K and were stored in a desiccator. The $CaCO_3$ powder was mixed with KBr at the ratio of 1:100. The mortar and pestle was thoroughly cleaned with acetone, the mixture of $CaCO_3$ powder and KBr was crushed. The $CaCO_3$ powder and KBr mixture was then put into the disc which was placed on a holder placed inside the FTIR machine to investigate the unknown materials present in the sample.

The sample of $CaCO_3$ powder was affixed to a metallic stub which is placed on the sample holder. The sample holder was then fixed on a rotatable disc inside the machine and the $CaCO_3$ powders were ready for SEM. The surface morphological of the powder sample was observed on SEM (SEM JSM6301F JEOL, Germany) operated under low vacuum to get the sharp image of the sample. All sample were Au-coated prior to examination by SEM

RESULTS AND DISCUSSION

X-ray diffraction is a sensitive instrument used for the identification of crystalline phases of inorganic compounds. The data obtained from the X-ray diffraction patterns in Figures 1(a) and 1(b) demonstrates the crystalline nature and phase composition of both samples under analysis, The intensity of X-ray, 2θ and (h, k, l) indices of $CaCO_3$ powder show rhombohedral structure and agree with ICUD PDF number 00-047-1743. The crystallite size of $CaCO_3$ from extraction and $CaCO_3$ from repeating extraction were calculated by the Scherrer's equation yield of 0.54 μm and 0.4 μm, respectively for crystallite size.

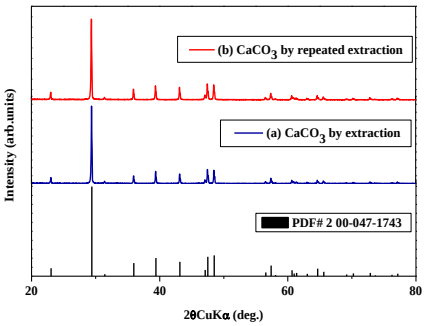

Fig. 1. X-ray diffraction patterns of Calcium carbonate powder for (a) $CaCO_3$ by extraction, (b) $CaCO_3$ by repeated extraction

FTIR spectra of the $CaCO_3$ are presented in Figures 2(a) and 2(b). FTIR spectroscopy is an important instrument used to identity different phases of organic and inorganic compounds and, specifically, $CaCO_3$ phases due to the differences in their carbonate ions (CO_3^{2-}). The spectral data obtained for the samples reveal a broad absorption peak of at ~1788.07 cm^{-1}, ~1082.10 cm^{-1}, ~875.71 cm^{-1}, ~862.21 cm^{-1}, ~713 cm^{-1}, and ~700 cm^{-1}, which have been reported to be the common characteristic features of the CO_3^{2-} in $CaCO_3$ and are the fundamental modes of vibration for this molecule [1,2,6]. The characteristic peak of calcite is ~1788.07 cm^{-1}, ~875.71 cm^{-1}, and ~713 cm^{-1} and those of aragonite are ~1082.10 cm^{-1}, ~862.21 cm^{-1} and ~700 cm^{-1} [7].

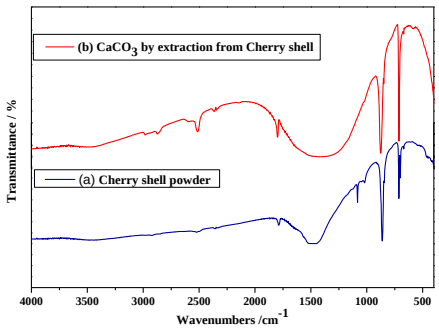

Fig. 2. FTIR spectra of (a) Cherry shell powder (b) Calcium carbonate has been extracted from Cherry shell

The morphological characteristics of the calcium carbonate micro-crystals presented in Figures 3(a) and 3(b). The images are shown calcium carbonate possess different crystal patterns and crystal structure. It can be seen that the product displays a calcium carbonate is hexagonal or Cube-like crystals. SEM images confirmed that the extracted calcium carbonate powder from Cherry shells have particle sizes 0.5 - 2 µm. The morphological analyzed by SEM of particle size was decreased with repeated extractions.

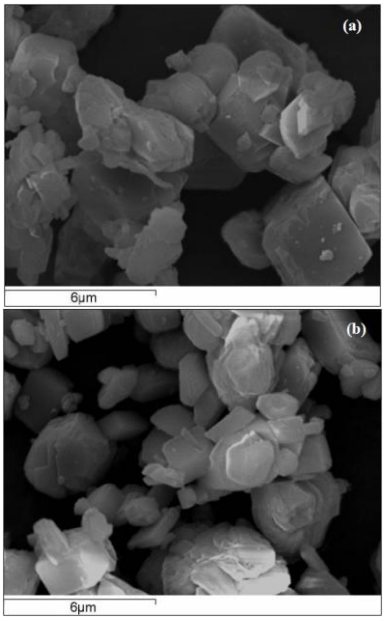

Fig. 3. SEM photograph of calcium carbonate from extraction (a) $CaCO_3$ by extracted, (b) $CaCO_3$ by repeated extracted

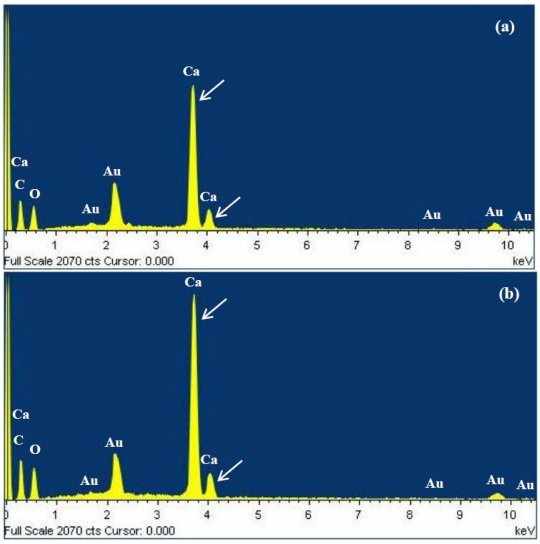

Fig. 4. EDS spectra and atomic (%) of the elemental contents of the $CaCO_3$ by extraction (a) $CaCO_3$ by extracted, (b) $CaCO_3$ by repeated extracted

The EDS analysis, an integrated feature of a SEM, has been conducted in order to evaluate the composition of $CaCO_3$. Figure. 4 depicts the EDS analyses which compare the elemental composition of $CaCO_3$ by extraction, $CaCO_3$ by repeated extraction. All the elements presented the $CaCO_3$ from extraction, Ca, Au, C, and O, can be recognized on the synthesized, the percentage of calcium has been increased significantly in the due to repeated extraction.

CONCLUSION

Calcium carbonate powder was extracted from shells by hydrothermal method. X-ray diffraction patterns of calcium carbonate showed a single phase and rhombohedral structure. The morphological analyses by SEM were confirmed have approximately with average size of 0.5 - 2 µm. Further experiments showed that by changing the repeated extraction repetition, different micro-crystals structure with different. The crystallite size by calculating from Scherrer's equation, equates 0.54 µm and 0.4 µm, respectively.

The methods adopted used in the synthesis of calcium carbonate are small crystals nearby the nanoscale. We applied this calcium carbonate with precursor powder such as cobalt oxide or manganese oxide to synthesis thermoelectric materials.

REFERENCES

[1] N.V. Vagenas, A. Gatsouli, C.G. Kontoyannis : *J. Talanta*. 59, **2003** 831-836.
[2] C. Wang, J. Zhao, X. Zhao, H. Bala, Z. Wang : *J. Powd. Tech.* 163, **2006** 134-138.
[3] S.Y. Park, W.S. Choi : *J. Adv. Powd. Tech*. 15(1), **2004** 1-12.
[4] O. Cizer, C.R. Navarro, E.R. Agudo, J. Elsen, D.V. Gemert, K.V. Balen : *J. Mater Sci.* 47, **2012** 6151-6165.
[5] P. Scherrer : *Math. Phys Class*. 26, **1918** 99-100.
[6] C. Wang, C. Piao, X. Zhai, F.N. Hickman, J. Li : *J. Powd. Tech*. 198, **2010** 131-134.
[7] R.C. Linga, K.V. Narasimhulu, N.O. Gopal, J.L. Rao, B.C.V. Reddy : *J. Mol. Struct*, 608 (2-3), **2002** 201-211.