

Characterization of Precipitated CaCO_3 Synthesized from Dolomite

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ABSTRACT. The precipitated CaCO_3 has successfully been synthesized from dolomite. The influence of various temperature and carbonation rate on the morphology, crystal size, phase and structure of the carbonation products were studied. The particles resulted from this process have the crystal size 400-800 nm. The calcite phase was formed in the synthesis at 30 °C with carbonation rate of 2 and 7 SCFH, and synthesis at 80 °C and 2 SCFH also produces calcite phase. Observations by SEM shows morphology of calcite as so-called schalenohedral.

1. Introduction

Calcium carbonate (CaCO_3) has widely been used in various industrial fields, such as papers, plastics, coatings, ink, paint and polymer products. Meanwhile, higher and special quality CaCO_3 has also been needed for ingredients from cosmetics [1], drug delivery [2], bioactive materials [3], to supplements of nutrition [4]. Calcium carbonate is used in the industry is the type of calcium carbonate precipitates. The precipitated CaCO_3 (PCC) is generally prepared by precipitation process using CO_2 , gas bubbling in the solution containing Ca ions, such as $\text{Ca}(\text{OH})_2$. The starting materials $\text{Ca}(\text{OH})_2$ may potentially be a limestone as natural resources with calcium content of around 98% [5].

In our previous study, the PCC has successfully been prepared from limestone employing a facile method of carbonisation, resulting in CaCO_3 with various phases and unique morphology [6]. However, the various processes which have been applied to prepare the PCC only produced powders having crystalline size $> 1 \mu\text{m}$. Several applications, in fact, need CaCO_3 with smaller crystal size to improve its better characteristics. A further study focusing the PCC with reduced crystal size is therefore a challenge. It was reported [7] that one way to reduce the crystal size in the preparation of CaCO_3 is to add other elements, such as Mg, which is close to Ca. The Mg^{2+} ion is effective in the synthesis of calcium CaCO_3 with aragonite (needle-like) structure. It was also reported [8] that the PCC with calcite and aragonite phases have successfully been synthesized from dolomite using poly (methyl methacrylate) (PMMA).

In this paper, the synthesis of CaCO_3 from the starting material containing Mg, namely dolomite, will be presented. The Dolomite is a carbonate mineral containing Mg, or $\text{CaMg}(\text{CO}_3)_2$. The use of dolomite, where Ca and Mg coexist, is expected to be more effective to produce CaCO_3 with smaller crystal size.



2. Experimental Method

The raw material was dolomite obtained from a quarry in Tuban (East Java, Indonesia). The elemental content and initial phases of dolomite were characterized by X-ray fluorescence (XRF) and diffractometry (XRD). The powdered dolomite was dissolved in a solution of 12 M HCl, and then stirred by using hot plate/magnetic stirrer with speed of 500 rpm for 30 minutes. Carbonation process was performed by flowing CO₂ gas into the solution by bubbling method. Synthesis process was performed in three different conditions, (i) CO₂ flow of 2 SCFH at 30°C, (ii) 7 SCFH at 30°C, and (iii) 2 SCFH at 80°C. The different synthesis conditions were applied to produce PCC with different morphologies. The solution that has been carbonated would form white precipitates as carbonation products, which were then filtered and dried at 80 °C- 90 °C for 24 hours. The white precipitates were finally characterized by XRD and scanning electron microscopy (SEM).

3. Results and Discussion

The elemental composition of dolomite as a result of by XRF measurement is shown in Tab. 1. The content of calcium is of 92.40% and magnesium 6.5%, while the others are impurity phases having content < 1%. The existence of magnesium in dolomite is expected to be the best alternative to produce PCC with a smaller size compared to using limestone doped with elements Mg. The characterization results of dolomite by XRD and diffraction patterns analysis using the "MATCH" Software are shown in Fig. 1. It is seen that all diffraction peaks are matched with dolomite phase without impurity. It means that Mg and Ca exactly form CaMg(CO₃)₂.

Table 1. The elemental content of dolomite by XRF.

Elemental content	Concentration (wt%)
Ca	92.40
Mg	6.50
Fe	0.45
Mn	0.055
Yb	0.54
Cu	0.073

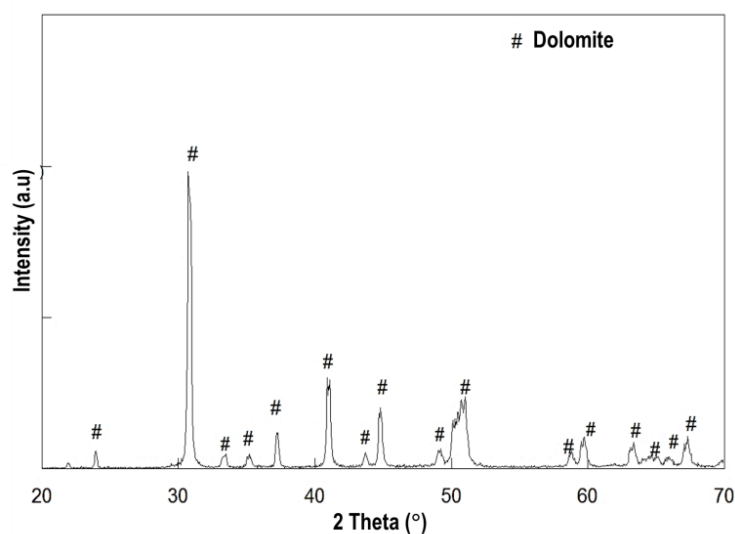


Figure 1. XRD patterns of samples of the limestone.

Fig. 2 shows the XRD patterns of the carbonation products. Three different synthesis conditions have produced the same CaCO_3 phase of calcite. This is certainly interesting, because in our previous study [6], these different conditions of synthesis have led to the different phases of CaCO_3 . The Dolomite has an ideal structure [9,10] consisting of ionic layers of Ca^{2+} and Mg^{2+} with strong bond. Calcination process is not carried out in this synthesis, because it induces decomposition. Dolomite bond is still strong to still obtain calcite phase during carbonation process. The calculation results of crystal size based on the XRD data in Fig. 2 using "MAUD" Software are shown in Tab. 2.

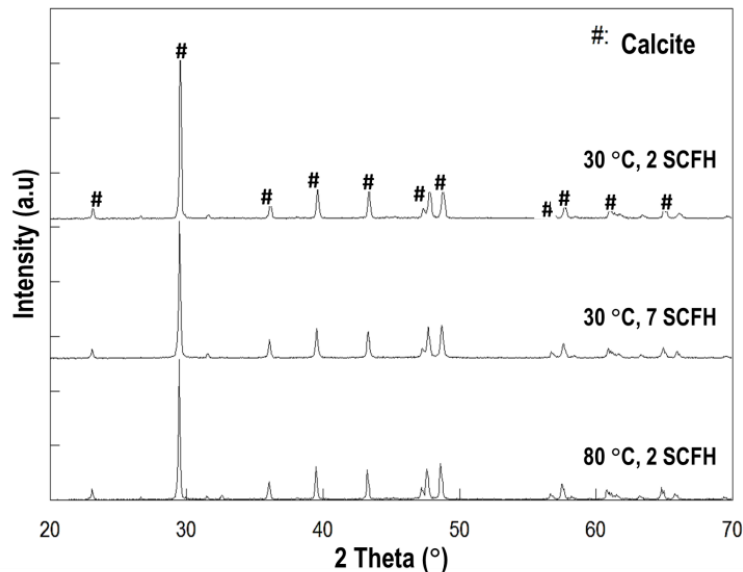


Figure 2. The XRD spectra of the carbonation products, with different processing parameters as specified.

Table 2. Crystal size of the carbonation products.

Synthesis condition	Crystal Size
30 °C, 2 SCFH	674.3±0.3nm
30 °C, 7 SCFH	417.7 ±0.4nm
80 °C, 2 SCFH	782.8 ±0.6nm

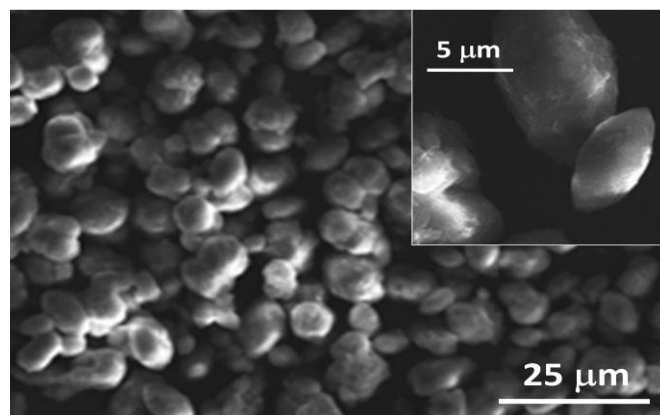


Figure 3. Morfologi of the carbonation products at 30 °C and carbonation rate of 2 SCFH with magnification of 1500 x and 7500x (inset).

Morphology of the PCC product synthesized at 30 °C and carbonation rate of 2 SCFH is given in Fig. 3. Morphology of the carbonation products in different synthesis condition also have calcite phase with the so-called scalenohedral. Scalenohedral calcite formed if the ratio of $[Ca]/[CO_3] > 1.56$ [11]. When the carbonation is conducted with a smaller flow rate as in this synthesis, the ratio of $[Ca]/[CO_3]$ will be greater, so that it will increase the formation probability of scalenohedral calcite morphology. Further, The phase of dolomite has the structure with a longer c-axis because of substitution of Mg. The Ca-O bond length is also much longer than that in the calcite phase [12]. Pokrovsky pointed out that in the case of homogeneous precipitation from supersaturated solutions, aragonite is the ubiquitous phase at Mg^{2+}/Ca^{2+} activity ratio higher than 3, while mostly calcite is formed at lower Mg^{2+}/Ca^{2+} ratio [13]. This in turn affects that the resulted calcite has morphology with slightly elongated shape. It is also observed in Fig. 3 that the particles shape and size are almost uniform at all points. Furthermore, the inset to Fig. 3 shows the rhombohedral calcite particles which are formed by a collection of calcite crystals with size in hundreds nanometer or in sub-micrometer.

4. Conclusions

The precipitated calcium carbonate with calcite phase has successfully been synthesized from dolomite by carbonation method with three different processing parameters. The product were observed with elongated shape morphology, as collection of calcite having crystalline size < 1 micrometer.

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References

- [1] Wang C, Tong H C, Liu Z and Zeng X F 2010 *Int. J. Pharmace* **308** 160
- [2] Peng C, Zhao Q and Gao C 2010 *Colloids Surf A: Physicochem Eng. Asp* **353** 132
- [3] Kumar G S, 2008 *J. Colloid Interf. Sci* **349** 56
- [4] Ghamgui H 2007 *Biochem. Eng. J* **37** 34
- [5] Arifin Z, Pratapa S, Tririkantoro and Darminto 2013 *AIP Conf. Proc.* **1554** 90
- [6] Arifin Z, Pratapa S, Tririkantoro and Darminto 2015 *Trans. Ind. Ceram. So* **74** 1
- [7] Park W K, Ko S J, Lee S W, Cho K H, Ahn J, Wand Han C 2008 *J Cryst Growth* **310** 2593
- [8] Mantilaka M M M G P G, Karunaratne D G G P, Rajapakse R M G, Pitawala H M T G A 2013 *Powder Tech* **235** 628
- [9] Land L S 1985 *J Geologedu* **33** 112
- [10] Warren J K 1985 *Am. Assoc. Petrol. Geol. Bull.* **69** 1013
- [11] Carmona J G, Morales J G, Clemente R R 2003 *J Colloid Interf Sci.* **261** 434
- [12] Titiloye J O, de Leeuw N H, Parker S C 1998 *Geochim Cosmochi Acta.* **62** 2637
- [13] Pokrovsky O S 1998 *J Cryst Growth* **186** 233