

# Synthesis of Mesoporous $\text{CaCO}_3$ Powder using Natural Limestone as Ca Ion Source with Solution Mixing Method

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**ABSTRACT.** In this study, the  $\text{CaCO}_3$  powder has successfully been synthesized by mixing  $\text{CaCl}_2$  derived from natural limestone and  $\text{Na}_2\text{CO}_3$  in the same molar ratio. The mixing process of two solutions was performed by employing the molar contents of 0.25, 0.5, 0.75 and 1 M at varying temperatures of 35, 50 and 80°C. The produced  $\text{CaCO}_3$  microparticles were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET). The highest content of vaterite phase of the samples is around 96 wt%, resulted from the process using solution of 0.25 M at 35°C. All the samples prepared show mesoporous solids with pore sizes of 3-4 nm and specific surface area of 81- 90  $\text{m}^2/\text{g}$ .

## 1. Introduction

The controlled synthesis of inorganic materials of specific size and morphology is a key aspect in fields as diverse modern materials, catalysis, medicine, electronics, ceramics, pigments and cosmetics [1–4]. The strategy of using organic templates or modifiers with complex functionalization patterns to control the nucleation, growth, and alignment of inorganic crystals has widely been adopted for the biomimetic synthesis of inorganic materials with complex form [4–8]. Several porous minerals have been used including synthetic zeolite [9], silica xerogel materials [10-13], porous hollow silica nanoparticle [14], porous hydroxyapatite [15], porous silica–calcium phosphate composite [16], porous calcium carbonate microparticle as a template for the assembly of polyelectrolyte layer by layer [17-18] and other porous ceramics.

In this work, we have successfully prepared the vaterite  $\text{CaCO}_3$  microspheres through the precipitation reaction of  $\text{CaCl}_2$  with  $\text{Na}_2\text{CO}_3$  at molar contents of 0.25, 0.5, 0.75 and 1 M at temperatures of 30, 50 and 80 °C. The effect of the solution concentration and temperature on the formation of vaterite phase, morphology, porous size and specific surface area will be investigated and discussed

## 2. Materials and Methods

### 2.1. Materials

The limestone from a quarry in Tuban (East Java, Indonesia), as the starting material, was calcined for 5 hours at 900 °C. The calcined limestone was then dissolved in a solution of 10 M HCl and stirred at a constant rate of 500 rpm for 30 minutes. Furthermore, the resulted  $\text{CaCl}_2$  solution was diluted to be of 0.25, 0.5, 0.75 and 1 M. Moreover, the as-received  $\text{Na}_2\text{CO}_3$  was dissolved in demineralized water to prepare  $\text{Na}_2\text{CO}_3$  solutions with the same molar content as  $\text{CaCl}_2$ .

### 2.2. Preparation of porous $\text{CaCO}_3$ powder

The  $\text{CaCO}_3$  particles were prepared by rapid mixing of equal volume of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  aqueous solutions with the same volume. Typically, 0.25 M  $\text{CaCl}_2$  was rapidly poured into 0.25 M  $\text{Na}_2\text{CO}_3$  solution and then agitated by stirring with a magnetic stirrer for 2 hours at 35 °C. The precipitate was filtered off, thoroughly washed with aquaest, and dried in air. The course of the reaction was observed with a light microscope. Other



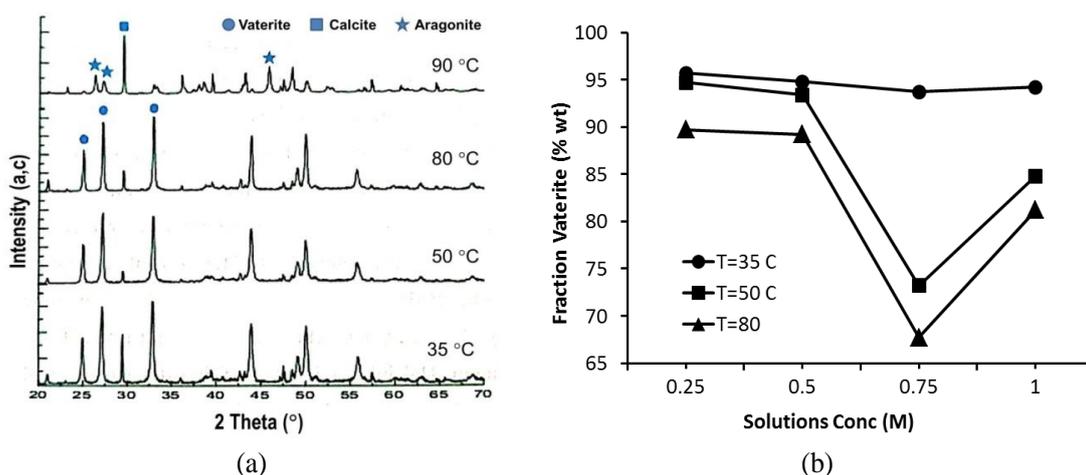
variations of the solution is proceeded in the same way with concentrations of 0.5, 0.75 and 1 M in temperatures of 35 °C, 50 °C dan 80 °C. This simple procedure results in highly homogeneous spherical CaCO<sub>3</sub> powders.

### 2.3. Characterization

The powder diffraction patterns were recorded using XRD (Philips X'Pert MPD system, monochromated Cu-K<sub>α</sub> radiation), employing record in the diffraction angle (2θ) range of 20 – 70°. The morphology of powder was observed using SEM (FEI Inspect S50, at the acceleration voltage of 15 kV), by dropping the particle suspension on a glass slide, drying overnight, then sputtering with gold-palladium in a vacuum evaporator (Emitech SC7620 *sputter coater*). The specific surface area, pore volume and size distribution of CaCO<sub>3</sub> powders were determined following the Brunauer–Emmett–Teller (BET) method of nitrogen adsorption/desorption at –196 °C with an ASAP-2010 surface area analyzer.

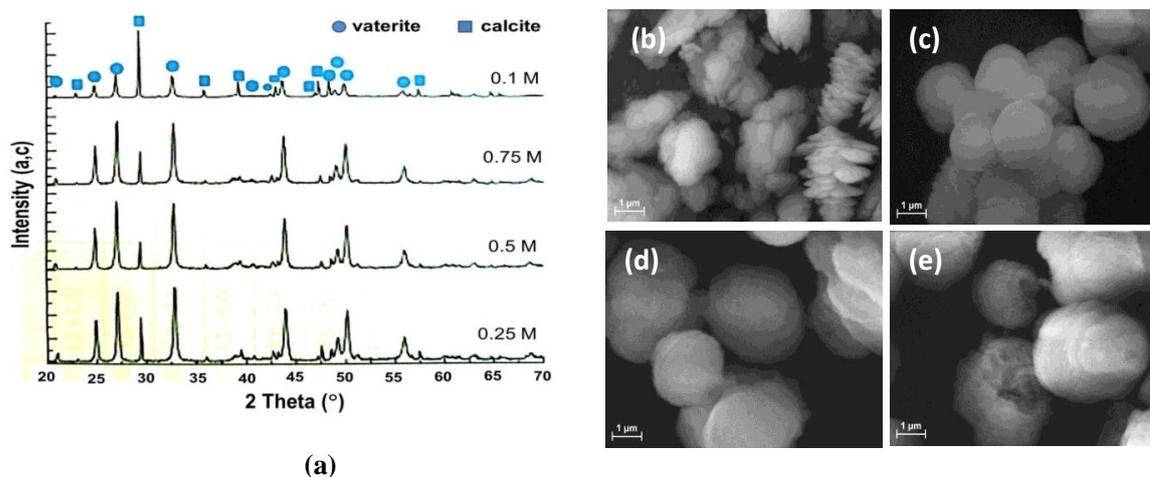
### 3. Results and discussion

The X-ray diffraction pattern of CaCO<sub>3</sub> precipitate with 0.25 M concentration at different temperature, as shown in Fig 1a. This figure shows calcite and vaterite phases at 35 - 80°C. For a comparison, we also included the powder processed at 90 °C showing an aragonite phase. The formation of vaterite phase was the highest of ~ 96 wt% and calcite phase of ~4 wt% which was achieved by the process at 35°C. Because the vaterite phase is only dominantly formed at 35 - 80 °C, then the reaction of vaterite CaCO<sub>3</sub> is only performed at this temperature with a solution concentration variation 0.25 M, 0.5 M, 0.75 M and 1 M.



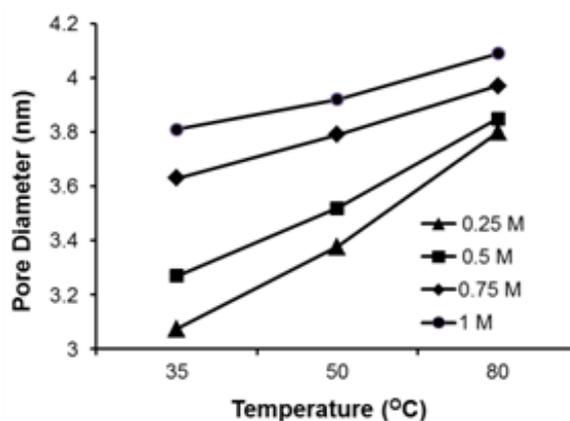
**Figure 1.** (a) The XRD spectra of the precipitated CaCO<sub>3</sub> prepared using solution of 0.25 M at different temperatures as specified. (b) The resulted vaterite phase fraction depending on solution content of all samples prepared.

The synthesis of CaCO<sub>3</sub> microparticles at low concentration, 0.25 M and low temperature, T = 35 °C shows ~ 97 wt% of vaterite phase. The fraction of vaterite phase was decreased with the increased of concentration and temperature, as exhibited in Fig. 1b. Calcite is solid particle with higher density than that of vaterite phase. Vaterite was composed by the aggregation of nano spheroid with large porous spheroid. The saturated formation of vaterite will be reached faster in the increasing temperature. Therefore, at higher concentration and temperature, vaterite can probably be re-transformed into calcite [19]. The formation rate of vaterite from amorphous particle is higher than the transformation rate of vaterite into calcite. The formation of vaterite will occur when the concentration of bicarbonate ion (HCO<sub>3</sub><sup>2-</sup>) in the solution is dominant. This condition was achieved by 1M solution at processing temperature of 35, 50 dan 80 °C. The Vaterite has a large surface area (porous), soluble particles and unstable thermodynamic properties. Hence, it is easy to transform into calcite with the increasing of solution concentration and temperature. At low concentration of 0.25 M, the weight fraction of vaterite phase was ~96 wt% and was decreased to 94.2% for 1 M solution. The increasing weight fraction of calcite phase was not significant and not observed in Fig. 1b. This indicates that the transformation of vaterite phase to calcite phase at 35 °C was very small.



**Figure 2.** (a) The XRD spectra of  $\text{CaCO}_3$  precipitates prepared at  $35^\circ\text{C}$  with solution molar content as specified. The SEM images of corresponding samples with molar contents of : (b) 0.25 M, (c) 0.5 M, (d) 0.75 M, (e) 1 M.

Fig. 2a shows the XRD spectra, exhibiting the effect of concentration at  $35^\circ\text{C}$  on the formation of vaterite phase, which is not significant and due to the formation of  $\text{CaCO}_3$  from  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  with the same molar content, 1:1. It was also confirmed by Kedra, et al. [20] and Montez, et al. [21], who reported that the size, phase and morphology of  $\text{CaCO}_3$  were affected by the amount  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions. Moreover, the morphology of the corresponding samples is given in Fig. 2b-2e. One may observe in those figures that the particle shape for all samples is generally spherical with aggregation. The pile of spheres may construct the bigger aggregates creating pores inside.



**Figure 3.** The pore size of  $\text{CaCO}_3$  powders prepared with varying processing parameters as specified.

The resulted hollow  $\text{CaCO}_3$  particles can be divided into three types, namely microporous, mesoporous, and macroporous with pore size are  $< 2$  nm,  $2 - 50$  nm and  $> 50$  nm, respectively. The BET measurement results show the pore size of  $\text{CaCO}_3$  particle using solution of 0.25 – 1 M at different temperature, as shown in Fig. 3. The pore size of  $\text{CaCO}_3$  microparticle was obtained to be 3 - 4 nm with the specific surface area of  $81 - 90$   $\text{m}^2/\text{g}$ . So, the prepared  $\text{CaCO}_3$  is a mesoporous powder. The pore size was increased with the increasing solution concentration and the mixing temperature.

#### 4. Conclusion

The  $\text{CaCO}_3$  powder has successfully been synthesized utilizing natural limestone as Ca ion source employing a solution mixing method with  $\text{Na}_2\text{CO}_3$  counterpart solution. The maximum weight fraction of the synthesized vaterite  $\text{CaCO}_3$  micro-sized powders is around 96 wt%, obtained from the mixing process at  $35^\circ\text{C}$

using solution with molar content of 0.25 M. The resulted CaCO<sub>3</sub> precipitate is mesoporous powder with the pore size of 3 – 4 nm and the specific surface area of 81 – 90 m<sup>2</sup>/g.

### Acknowledgements

This research was partially supported by "PUPT" Research Grant, DRPM, Kemenristekdikti, 2015 - 2016.

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