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Research paper



Effect of Methane on the Synthesis of Precipitated Calcium Carbonate via Carbonation Process

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Abstract

Precipitated calcium carbonate (PCC) is synthetic calcium carbonate that has high purity of more than 98 wt% of $CaCO_3$ content. Owing to its unique characteristic whereby its shape and size can be controlled to tailor to various applications, PCC has seen great demands in many industries such as paper, paint, plastic, food, ceramics, cosmetics, pharmaceutical, and many others. PCC can be synthesized via various methods and the most often used method in industry is via carbonation process. This process has caught interest of the oil and gas industry for utilizing existing carbon dioxide waste from plant processes. Precipitation of PCC is carried out using hydrated lime under various conditions at different gas purity (1 mol% CH_4 + 99 mol% CO_2, 40 mol% CH_4 + 60 mol% CO_2), different gas flowrate, and different stirring rate. All experiments are carried out using 1 litre of ionic solution at ambient conditions. All samples are characterized using Field Emission Scanning Electron Microscopy (FESEM), Particle Size Distribution, X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF). FESEM analysis shows different surface morphology for different methane content with calcite formation. The particle size for all PCC produced at different parameters are comparable at the range 5-9 microns depending on the mixing rate used whereas XRF results indicate very high purity of $CaCO_3$ of more than 99 wt%.

Keywords: *Precipitated Calcium Carbonate, Carbonation, Methane*

1. Introduction

Calcium carbonate is one of the most abundant naturally occurring minerals which has attracted considerable attention not only as an important building material in organisms but also as a starting material in many industries. High purity calcium carbonate has been acknowledged as a versatile additive, pigment, filler, or extender in industries such as rubber, ceramics, paper, plastics, ink, cosmetics and detergents [1]. As a specialty chemical, PCC is also used as a component of food and pharmaceuticals as well as having numerous uses in electronics and catalysis. The high purity of calcium carbonate is typically produced by means of chemical reaction. The final product known as Precipitated Calcium Carbonate (PCC) is conventionally produced through gas–solid–liquid carbonation route.

PCC production process is quite straight forward. Lime product (calcium oxide) is hydrated into calcium hydroxide through slaking process. This is an important step which provides the medium for CO_2 to be dissolved in the solution for carbonation process. Gaseous CO_2 will be bubbled through the concentrated aqueous $Ca(OH)_2$ slurry in a batch or semi-batch process. This process requires high purity mineral feedstock with certain purity of CO_2 as the starting material. For an integrated plant, CO_2 from the calcination of limestone is re-utilized to manufacture high purity PCC [2]. However, in most cases, the lime used in the PCC plant will be brought from lime producer within mining industry and not from the integrated plant.

Industrial PCC production aims at controlling the phase morphology and the physical properties of PCC such as particle size [3], aspect ratio, and specific surface area by adjusting the reactant concentration [4, 5]. The product purity is another critical factor to determine the quality and product sales in the market. Application of PCC in specialty chemicals – i.e. in food and pharmaceuticals require very high purity of more than 99 wt%. Therefore, presence of any impurities either from the mineral feedstock or CO_2 will have an impact on the final PCC quality.

With regards to impurities from mineral feedstock, a lot of studies have been conducted on utilizing industrial waste minerals such as alkaline ashes and steel slags as feedstock to produce high purity PCC [6 – 9]. This attractive path has the potential of becoming an alternative route for carbon sequestration [2, 10, 11]. For impurities study from gas feedstock, several studies reported for CO_2 fixation from flue gas stream – mainly CO_2 and air [12]. Works mostly testified on the effect of different concentration of CO_2 in the flue gas stream. So far, there is no report or study conducted for other gas impurities especially for CO_2 coming from natural gas separation process such as membrane or AGRU process.

In this study, the effect of methane on the morphology of PCC is investigated at different concentration based on CO_2 composition before and after membrane gas separation process. A simple approach was used to synthesis PCC through carbonation of an ionic solution – calcium rich solution at atmospheric condition with different gas flowrate and stirring rate.

2. Experimental

2.1. Materials

Industrial grade calcium hydroxide, $Ca(OH)_2$ with composition as per Table 1 and sucrose are purchased from Sigma Aldrich and

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used without further purification. Mixture of carbon dioxide/ methane gas at a ratio of 99: 1 and 60: 40 are bought from Air Liquide.

Table 1: Composition of industrial grade $Ca(OH)_2$, units in mol%.

CaO	Fe_2O_3	MnO	TiO_2	Al_2O_3	MgO
59.31	0.12	0.03	0.02	0.05	0.85

2.2. Preparation of ionic solution

To prepare the ionic solution, 100 g of sucrose is added to 1000 ml of filtered water in order to obtain 10 °Brix of solution. The sucrose solution concentration is checked using portable Brix meter (Atago, Pan-α). The Brix measurement is adjusted by adding more sucrose in order to achieve 10 °Brix ionic solution. For the addition of calcium ion in the sucrose solution, approximately 120 g calcium hydroxide powder is added into the sucrose solution. The mixture is stirred until all the powder is fully dissolved. The mixture is then filtered to remove unreacted $Ca(OH)_2$ and the filtrate is called the ionic solution.

2.3. Carbonation process of producing Precipitated Calcium Carbonate

1 litre of ionic solution is placed in a beaker and stirred using mechanical stirrer at 1500 rpm for a few minutes. The initial pH of the ionic solution is recorded to identify the pH of the solution prior to the start of experiment . For carbonation to occur, CO_2 gas is introduced at a flowrate of 4.0 L/ min into the ionic solution until the pH of the solution drops to pH 8.
The white PCC precipitate is later recovered by filtering the slurry solution and rinsing with hot water to remove sucrose and any unreacted $Ca(OH)_2$. The wet PCC cake is dried using an oven at 90 °C and weighted to determine the mass of PCC produced. The same process is repeated for different parameters and different gas purity.

2.4. Characterization of Precipitated Calcium Carbonate

For all samples, the morphological analysis are performed with Field Emission Scanning Electron Microscope (FESEM, Supra 40V Zeiss, Germany). For particle size measurement, Malvern Mastersizer laser diffraction is used to analysed the particle size distribution of the precipitated powder. X-Ray Diffraction (XRD) is used to identify the relevant phase of PCC product at ambient temperature using Bruker D8 ADVANCED powder diffractometer with Ni-filtered Cu-Kα radiation (λ = 0.15406 nm). For chemical composition and purity of PCC, X-Ray Fluorescence Spectrometer (XRF 1700, Shimazu) is utilised.

3. Results and discussion

Solid $Ca(OH)_2$ powder is dissolved in the sucrose solution during ionic solution preparation. The resulting ionic solution contains soluble Ca^{2+} and OH^- ions. The purpose of utilizing sucrose solution is to provide more binding sites for higher concentration of Ca^{2+} to be dissolved per litre of solution and also to remove some of the impurities in the feedstock [13]. CO_2 gas will be dissolved in the ionic solution to form weak acid H_2CO_3 and then forming H^+, HCO_3^- and CO_3^{2-}. Ca^{2+} ion will combine with CO_3^{2-} to form $CaCO_3$ and water –sucrose solution. This water – sucrose solution is recycled back for reaction in Eq. (1).

$$Ca(OH)_2(aq) \rightarrow Ca^{2+} + 2OH^- \quad (1)$$

$$CO_2(g) \rightarrow CO_2(aq) \quad (2)$$

$$CO_2(aq) + H_2O \rightarrow H_2CO_3(aq) \quad (3)$$

$$H_2CO_3(aq) \rightarrow H^+ + HCO_3^- \quad (4)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (5)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \quad (6)$$

3.1. Morphology of Precipitated Calcium Carbonate

Calcium carbonate exists as three anhydrous crystalline polymorphs namely calcite, aragonite and vaterite. Calcite is the most stable phase at ambient temperature and pressure. Even though calcite and aragonite have similar chemical composition, they differ in their crystal structure. Calcite displays a trigonal crystal structure whereas aragonite has orthorhombic crystal structure [14]. In terms of shape, calcite typically displays rhombohedral – cubic or scalenohedral geometry [4]. Synthesis of different morphologies of calcite PCC can be done by controlling process parameters such as temperature, gas flowrate and by introducing additives into the process. Modification of particle morphology can be attained by inducing different growth rate on crystal faces [15].
The SEM image of PCC at different gas impurities were shown in Figure 1 and 2. In the presence of low amounts of methane as impurities, the precipitated calcium carbonate is produced with the cubic – rhombohedral shape: a complete formation of stable calcite with flat surfaces. At higher methane content (40 mol%) , the crystals are in the scalenohedral shape with perforated surface .

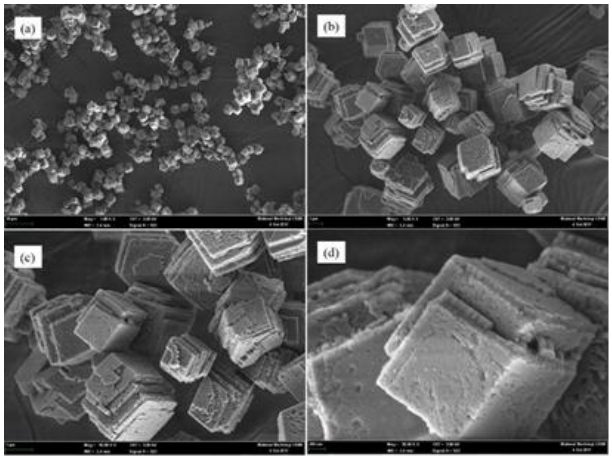

Fig. 1: FESEM image of precipitated calcium carbonate with 1% methane at magnification (a) 1kx, (b) 5kx, (c) 10kx and (d) 30kx.

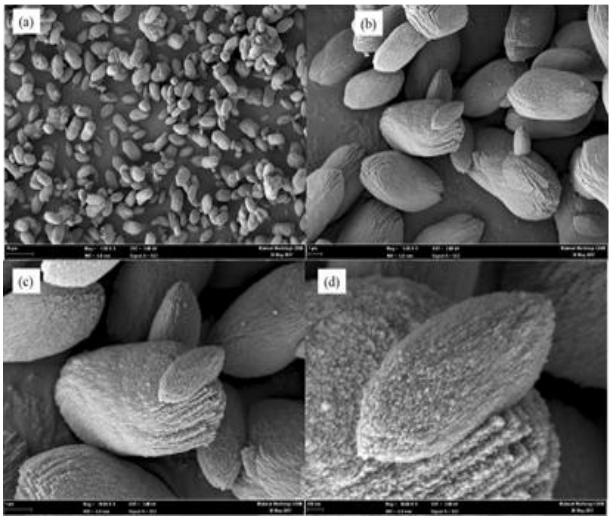

Fig. 2: FESEM image of precipitated calcium carbonate with 40 mol% methane at magnification (a) 1kx, (b) 5kx, (c) 1 0kx and (d) 30kx.

Similar observation is reported by Cizer et.al. [4], where amorphous calcium carbonate (ACC) transforms into cracked/ corroded scalenohedral calcite under carbonation in 20% CO_2 atmosphere . Under non-stoichiometric condition with $[Ca^{2+}] >> [CO_3^{2-}]$, scalenohedral faces which has polar characteristics will interact strongly as compared to the non-polar {104} rhombohedral faces [16]. This effect will ultimately favors the stabilization of scalenohedral shape of PCC. This perhaps explains why at high methane content in the gas stream, scalenohedral shape of PCC is favoured. Whereas, at low methane content, the impurities are not significant enough to 'disturb' the stoichiometry between calcium ion and carbonate ion for equimolar condition of Ca^{2+}: CO_3^{2-} . The stoichiometry between Ca^{2+} and CO_3^{2-} ions appears to favour the development of rhombohedral calcite irrespective of the supersaturation during crystallization [4, 17].

Similar perforated surfaces of PCC is obtained at higher gas flowrate of 4 L/min, as shown in Figure 3. Small and narrow pits/ pores can be seen clearly on the surface. These perforated surfaces are due to CH_4 gas molecules occupying and being trapped on the crystal surface during the slow crystallization process. This observation is also similarly reported by Cizer *et al*. for water molecules at different hydration study [4].

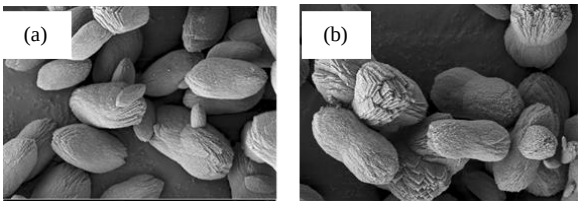

Fig. 3: FESEM images of Precipitated Calcium Carbonate with 40 mol% Methane and 200 rpm stirring rate at ambient condition. (a) Hydrated lime with 1 L/min gas flowrate (b) Hydrated lime with 4 L/min gas flowrate

3.2. Purity of Precipitated Calcium Carbonate

For the quality of the final product, the corresponding XRD patterns of the product were shown in Figure 4. All peaks are indexed by calcite formation (ICDD No 047-1743) at 40%, 5%, and 1% of methane content in the gas. The sharp narrow diffraction peaks indicated that the prepared PCC samples have good crystallinity characteristics in all morphologies of calcium carbonate.

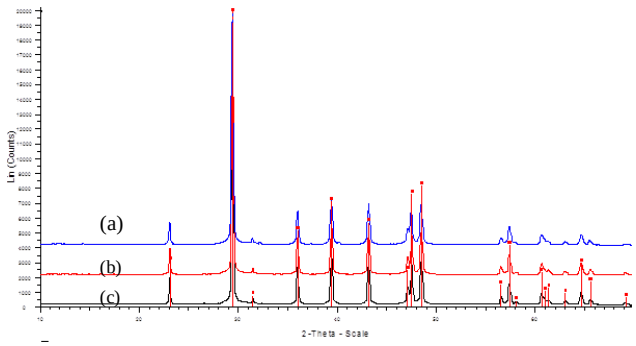

Fig. 4: XRD patterns of samples synthesized at different methane content at gas flowrate of 4 L/ min and stirring rate 1500rpm with a) 40 mol% methane, b) 5 mol% methane, and c) 1mol% methane.

Table 2 summaries the PCC product composition based on the XRF analysis. Based on the results, high purity PCC has been successfully produced. A few samples were also tested at 5 mol% of methane content for sensitivity study. Again, the results were similar with 1 mol% and 40 mol% of methane content in the CO_2 gas stream. There was no significant effect on the crystal phase at various concentration of methane due to its unreactive nature. Methane is a nonpolar hydrocarbon molecule with very limited solubility in water and the amount is highly dependent on the pressure applied [18]. Methane does not dissolve and dissociate in water directly to form any ionic solution. Hence, it is unable to take part in any reaction within the PCC as proven by the XRD and XRF results below.

Table 2: XRF analysis results for hydrated lime at 4 L/min and 1500 rpm stirring rate

Composition	Methane content (%)		
Composition	1%	5%	40%
CaO	56.14	56.45	56.48
$CaCO_3$	100.19	100.75	100.81
Fe_2O_3	0.10	0.08	0.09
MnO	0.02	0.03	0.03
TiO_2	0.02	0.02	0.02
K_2O	0.02	0.02	0.02
P_2O_5	0.02	0.02	0.02
SiO_2	0.06	0.04	0.06
Al_2O_3	0.02	0.02	0.02
MgO	0.26	0.24	0.24
Na_2O	0.15	0.10	0.09

3.3. Carbonation time and yield of Precipitated Calcium Carbonate

The effect of methane on the formation efficiency was also evaluated within this study. The carbonation time for high purity PCC was measured by varying the gas impurities at 1 mol%, 5 mol% and 40 mol% of methane. Figure 5 shows carbonation time of carbonation process at various flowrates and stirring rates.

Generally, higher methane content in gas stream will require longer carbonation time for a complete formation of PCC. This is perhaps due to smaller amount of CO_2 available for the reaction. High flowrate of gas stream has no significant effect to shorten the carbonation time unless the solution is well stirred. The results were in agreement in previous study on the dissolution of CO_2 as the limiting factor for the process [19, 20].

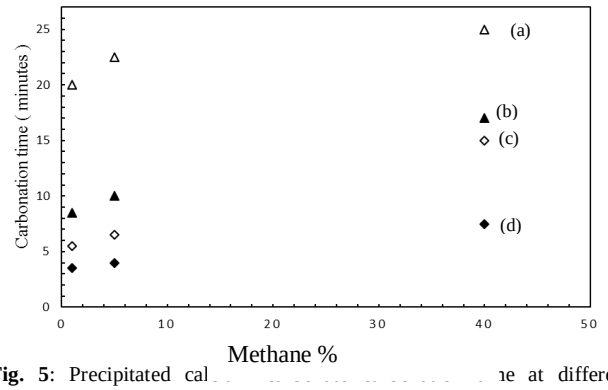

Fig. 5: Precipitated cal[illegible]ne at different flowrates and stirring rates: a) 1 L/ min at 200 rpm, b) 4 L/ min at 200 rpm, c) 1 L/ min at 1500 rpm, d) 4 L/ min at 1500 rpm

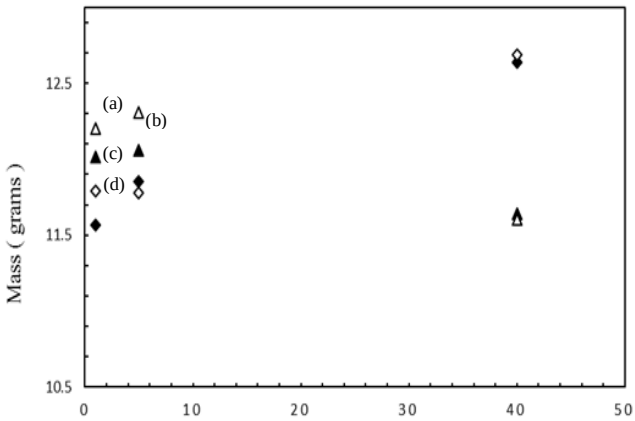

Fig. 6: Precipitated calcium carbonate carbonation time at different flowrates and stirring rates: a) 1 L/ min at 200 rpm, b) 4 L/ min at 200 rpm, c) 1 L/ min at 1500 rpm, d) 4 L/ min at 1500 rpm

For a litre of solution, the average yield of 11 – 13 g of PCC is obtained. Again, there is no significant effect on the influence of methane towards yield of PCC. The only slight difference can be attributed to the effect of mixing rate. At higher stirring rate with high methane content, the yield is slightly higher than 12.5 grams per litre. Figure 6 shows the average yield of PCC per litre of solution.

3.4. Particle Size of Precipitated Calcium Carbonate

Another important characterization of PCC is the particle size. Based on this analysis, the particle size range was in between 5 – 9 microns. The average particle size or the median diameter d50 and d90 at different gas impurities and gas flowrate were comparable to each other. This indicates that methane as a gas impurity has no influence on the particle size distribution. Based the study, the factor that clearly influence particle size is the stirring rate. Different stirring rates lead to different shear rates that in turn influence the aggregation and growth of PCC. At lower stirring rate, larger particle size of PCC was obtained and this finding is in agreement with other studies [21, 22] on how the stirring rate affects the size of the crystals. The overall results were summarized in Figure 7 and Figure 8.

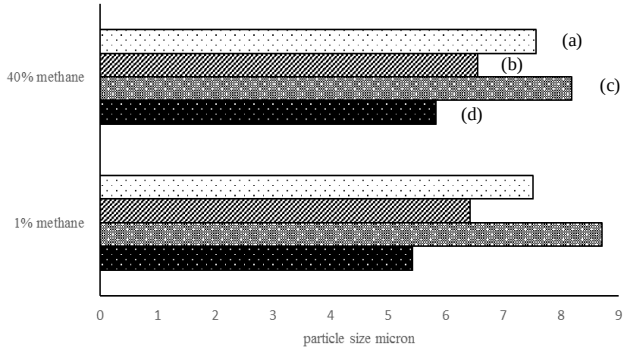

Fig. 7: Average particle size distribution at d50 in micron: a) Gas flowrate 4 L/ min with 200rpm stirring rate, b) Gas flowrate 4 L/ min with 1500 rpm stirring rate, c) Gas flowrate 1 L/ min with 200 rpm stirring rate, d) Gas flowrate 1 L/ min with 1500 rpm stirring rate.

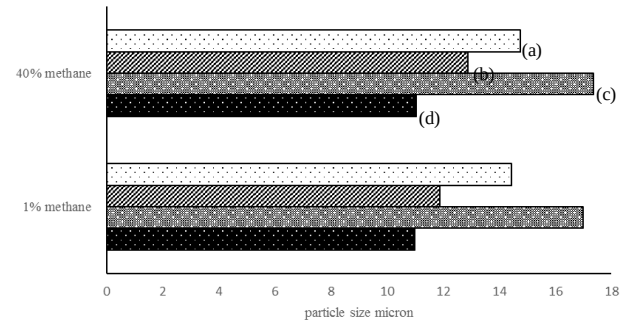

Fig. 8: Average particle size distribution at d90 in micron: a) Gas flowrate 4 L/ min with 200rpm stirring rate, b) Gas flowrate 4 L/ min with 1500 rpm stirring rate, c) Gas flowrate 1 L/ min with 200 rpm stirring rate, d) Gas flowrate 1 L/ min with 1500 rpm stirring rate.

4. Conclusion

The effect of methane in the production of Precipitated Calcium Carbonate was investigated at various gas concentration, gas flowrate, and stirring rate. In general, the gas impurities *i.e.* methane has no significant effect on the crystal phase, product purity, and the particle size of PCC product. At various impurities concentration, complete calcite phase with more than 99 wt% calcium carbonate purity was successfully synthesized. The average particle size is also comparable to each condition in the range of 5 – 9 microns depending the mixing rate used.

However, at high impurities content (40 mol% of methane), perforated crystal structure of PCC is obtained with scalenohedral shape. This is a special morphology which has a lot of potential especially as a filler with high surface area and light application. Therefore, the synthesis of PCC at various methane concentration in the gas stream does not compromise the final product quality. In fact, this condition is offering a promising application of PCC as specialty chemical.

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