J Mater Sci (2006) 41:4663–4667
DOI 10.1007/s10853-006-0037-4

Influence of initial $CaCl_2$ concentration on the phase and morphology of $CaCO_3$ prepared by carbonation

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Received: 17 May 2005 / Accepted: 20 September 2005 / Published online: 2 May 2006

Abstract Calcium carbonate particles were prepared by bubbling the mixed gas CO_2/N_2 into $CaCl_2$ solution. The effect of initial $CaCl_2$ concentration on the morphology and phase of $CaCO_3$ was discussed with the help of XRD and SEM measurements. The samples prepared at low $CaCl_2$ concentration composed mainly of spherical vaterite. With the increase of $CaCl_2$ concentration, more and more rhombic particles were formed and mixed with spherical particles. When the initial $CaCl_2$ concentration increased to 0.3 mol/L, only rhombic calcite was formed in the final product. The change of $CaCO_3$ morphology with the increase of $CaCl_2$ concentration was attributed to the excess of Ca^{2+}, which speeded the transformation of vaterite to calcite, thus more rhombic calcite was formed at higher $CaCl_2$ concentration.

Introduction

Calcium carbonate is a widely used chemical in various industries, such as plastics, textiles, rubbers, adhesives, paints and so on. Advanced applications of $CaCO_3$ are used as fillers in polyester films for the manufacture of magnetic tapes, coating of pigments used in the cosmetic industry or in the paper manufacturing [1]. The application of $CaCO_3$ particles is determined by a great number of strictly defined parameters, such as particles morphology, structure, size, specific surface area, brightness, oil adsorption, chemical impurity and so on [2]. One of the most important factors is particles morphology. The morphologies of crystal calcium carbonate particle are generally classified as rhombic calcite, needle-like aragonite and spherical vaterite. Calcite is the most stable phase at room temperature under normal atmospheric conditions, while aragonite and vaterite are metastable polymorphs which readily transform into the stable phase—calcite.

The morphology of calcium carbonate particles was mainly determined by the preparation conditions, such as reactants concentration, flowing rate, pH, temperature, and additives. Reactants concentration ($[Ca^{2+}]$ and $[CO_3^{2-}]$) is usually considered to be the basically important factor in controlling the morphology of calcium carbonate. There are many literatures reporting the influence of reactants concentration on the formation of calcium carbonate [3–5]. Their main concerns focused on the influence of the $[Ca^{2+}][CO_3^{2-}]$ ion product on the formation of calcium carbonate. There are a few literatures investigating the $[Ca^{2+}]$ and $[CO_3^{2-}]$ separately. Even through a few literatures were reported, some of the reporting results are contradictory or arguable. For example, Chen et al. [6] found that the concentration of calcium ion seems to be a minor factor in the determination of vaterite. While Yagi et al. [7] reported that the vaterite were preferably formed at low Ca^{2+} concentration. For complete and clear understanding the influence of each reactants concentration, it is necessary to investigate each of the species separately and systematically. The influence of $[CO_3^{2-}]$ on the formation of calcium carbonate has been discussed in another paper [8]. This paper will mainly focus on the effect of $[Ca^{2+}]$ on the formation of calcium carbonate.

The main purpose of this paper is to investigate the influence of $[Ca^{2+}]$ on the morphology and phase of

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precipitated calcium carbonate (PCC). The PCC particles were prepared by bubbling the CO_2/N_2 gas into $CaCl_2$ solution in an agitated conical flask. The effect of excess Ca^{2+} ion on the transformation and growth of calcium carbonate was discussed.

Experiments

Calcium chloride (Wako Pure Chemicals, Japan) and ammonia water (Wako Pure Chemicals, Japan) were mixed and diluted to form a solution. The freshly prepared solution reacted with the mixed gas (CO_2 + N_2) that was introduced to the bottom of the solution via a wood filter. The reaction temperature was kept 25 °C by a water bath. During the carbonation, the solution was continuously stirred at a constant rate by means of Teflon-coated magnetic stirring bar. The total volume of the working solution was 500 mL and the pH of the solution was measured by a pH meter (Cyberscan, made in Singapore). The pH value decreased continuously with the proceeding of precipitation. There was no more change in pH after the precipitation was completed. The prepared solids were collected by filtering through membrane filters (0.2 μm) and dried at 120 °C for at least 24 h, and used for measurements. SEM (JEOL JSM-6100) was used to observe the morphologies of samples. XRD (RINT, Rigaku, Japan) measurements were conducted using CuK_α radiation (40 keV, 30 mA) to identify the composition of products. The scanning step is 0.02° and the 2θ range from 20° to 60°. Figure 1 is the schematic illustration of the preparation procedure.

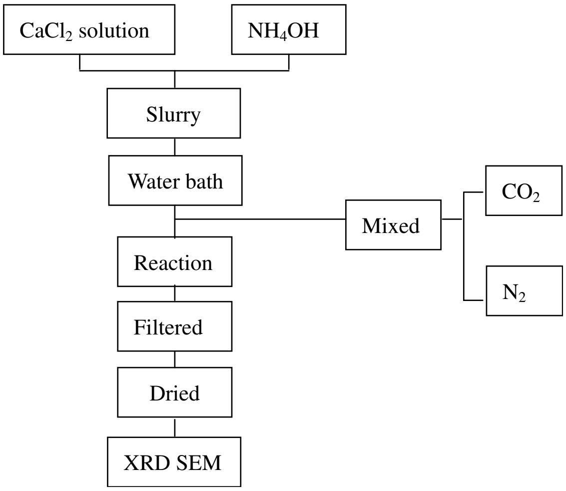


Fig. 1 Schematic diagram of preparation procedure

Results and discussion

Figure 2 shows the influence of the initial $CaCl_2$ concentration on the morphology of PCC particles. The morphology of PCC particles was quite sensitive to the variation of the initial $CaCl_2$ concentration. Spherical particles as the major polymorph were formed at the initial $CaCl_2$ concentration of 0.001 mol/L. With the increase of $CaCl_2$ concentration, more and more rhombic particles were formed with a mixture of spherical particles, as shown in the figure of 0.1 mol/L. Further increase of $CaCl_2$ concentration to 0.3 mol/L, the spherical particles disappeared and only rhombic particles were observed.

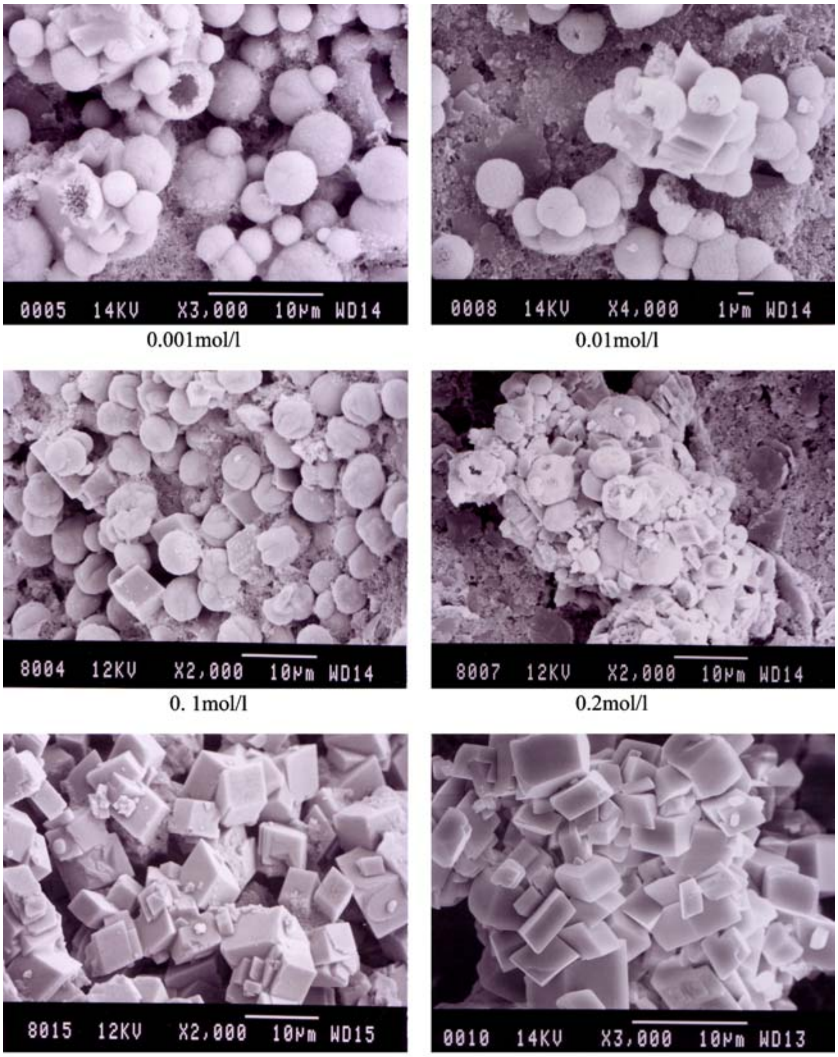
Figure 3 reveals the phase of PCC prepared at different initial $CaCl_2$ concentration. At the low initial $CaCl_2$ concentration, such as 0.001 mol/L, the samples contained two phases, namely vaterite and calcite. When the initial $CaCl_2$ concentration increased to 0.3 mol/L, only calcite was checked in the samples. This result is consistent with the observation of SEM. Because there is no signal for amorphous phase in XRD pattern, the Rao equation can be used here to express the relative fraction (fc) of vaterite in the crystalline phases [9]

$$\mathrm{fv} = (\mathrm{I}_{110\mathrm{v}} + \mathrm{I}_{112\mathrm{v}} + \mathrm{I}_{114\mathrm{v}})/(\mathrm{I}_{110\mathrm{v}} + \mathrm{I}_{112\mathrm{v}} + \mathrm{I}_{114\mathrm{v}} + \mathrm{I}_{104\mathrm{c}})$$

The subscripts v and c here indicate vaterite and calcite, respectively. The fraction of calcite is 1 − fv. The calculation results of fv at different initial $CaCl_2$ concentration were shown in Fig. 4. It is easy to conclude that the fraction of vaterite decrease with the initial $CaCl_2$ concentration.

In the carbonation process, the CO_2 gas is firstly dissolved into water and converted to H^+, HCO_3^- and CO_3^{2-} ions. Then the CO_3^{2-} reacts with Ca^{2+} to form amorphous calcium carbonate [10], which is an unstable form and is often described as spherical shapes. The initially formed amorphous $CaCO_3$ is quickly transformed to two crystalline phases, namely vaterite and calcite. The vaterite is not stable in its mother solution and ready to transform to the stable phase—calcite. The transformation of vaterite to calcite includes two steps. First is the dissolution of vaterite. Second is the growth of calcite, which is the rate-determining step for overall transformation of vaterite to calcite [11]. It was supposed that the growth of calcite was commenced with the formation of the ion pairs [$CaCO_3^0$] at the calcite surface [12].

Previous results [13] have allowed a clear and unambiguous identification that the calcite surface was adsorbed with the ions of Ca^{2+} and CO_3^{2-}. And the adsorption behaviors of Ca^{2+} and CO_3^{2-} on a calcite surface are different, reflecting in their Langmuirian adsorption coefficients ($K_{Ca^{2+}}$ and $K_{CO_3^{2-}}$): $K_{Ca^{2+}} = 10^6$ cm³/mol, $K_{CO_3^{2-}} = 3 * 10^7\ \mathrm{cm^3/mol}$ [14]. Compared with the Ca^{2+}



0.001mol/l 0.01mol/l

0. 1mol/l 0.2mol/l

0.3mol/l 0.5mol/l

Fig. 2 SEM image of $CaCO_3$ prepared at different initial $CaCl_2$ concentration

ion, the CO_3^{2-} is easy to be adsorbed on the calcite surface, which may be the result of the prevalence of positively charged species over calcite surface [15]. Since the growth of calcite is supposed to complete via the formation of ion pairs [$CaCO_3^0$] at the calcite crystal surface, it seems clear that the equivalent adsorption of Ca^{2+} and CO_3^{2-} is in favor of the formation of calcite on the crystal surface. With the increase of the initial $CaCl_2$ concentration, the possibility of Ca^{2+} adsorption on the calcite surface also increases due to the adsorption of ions on the particle surface is proportional to the ions concentration in solution [16]. It can be expected that the equivalent adsorption of Ca^{2+} and CO_3^{2-} on the calcite surface could be reached with the excess of Ca^{2+}. With the ignorance of the difference for CO_2 dissolution at various $CaCl_2$ concentrations, it is estimated that the $CaCl_2$ concentration for the stoichiometric reaction of calcium carbonate is 0.01 M. When the initial $CaCl_2$ concentration was greater than 0.01 M, the excess of Ca^{2+} appeared, which would lead to the equivalent adsorption of Ca^{2+} and CO_3^{2-} on the calcite surface and favor the formation of new calcite, speeding the transformation of vaterite to calcite. The higher the excess of Ca^{2+} leads to the faster the transformation of vaterite to calcite, resulting more vaterite transformation to calcite during the precipitation reaction. Hence, the fraction of vaterite in the final products decreased with the increase of $CaCl_2$ concentration, as shown in Fig. 4. When the $CaCl_2$ concentration amounted to 0.3 M, the equivalent of Ca^{2+} and CO_3^{2-} on the calcite surface may be reached. The transformation of vaterite to calcite is quiet quick, thus only calcite was formed in the final products.

On the other hand, the improvement of the calcite growth by the excess of Ca^{2+} can be explained by the electrokinetic's behavior of the synthetic calcite. Since the adsorption of excess Ca^{2+} on the particle surface is proportional to the $CaCl_2$ concentration, it can be expected

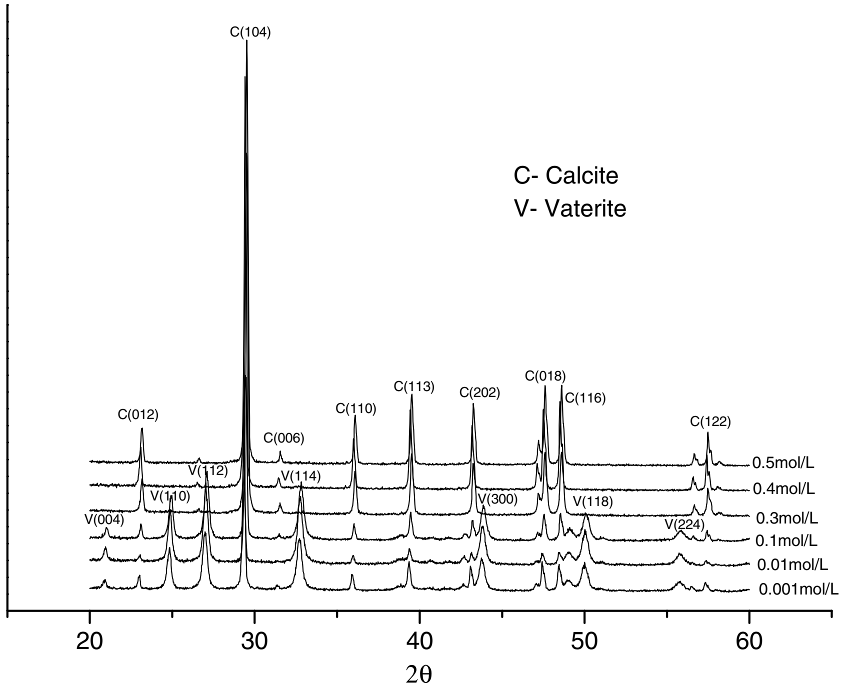


Fig. 3 XRD pattern of $CaCO_3$ prepared at different initial $CaCl_2$ concentration

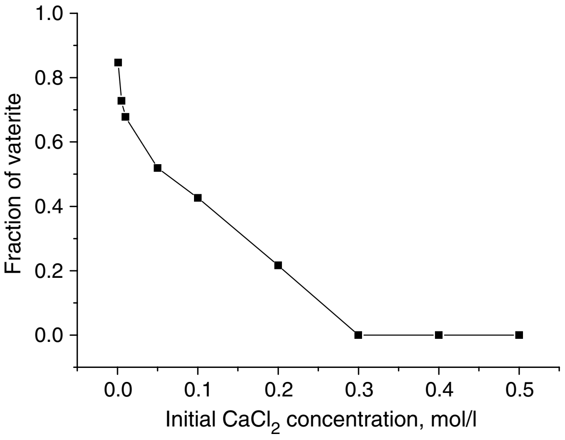


Fig. 4 Relative fraction of vaterite changing with the initial $CaCl_2$ concentration

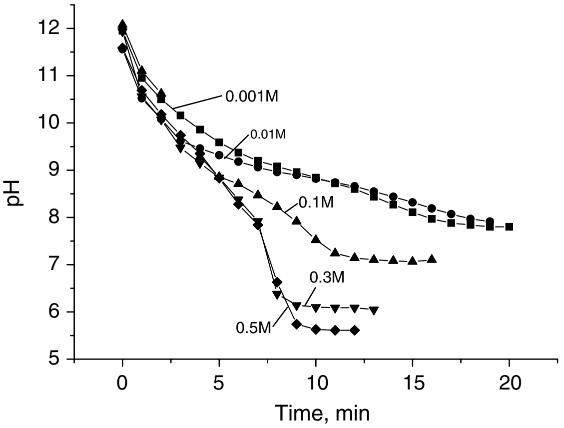


Fig. 5 pH of the solution changing with the process of precipitation

that more Ca^{2+} ions were adsorbed on the calcite surface at the higher $CaCl_2$ concentration. Under these conditions, the surface of calcite acts as a sink for CO_3^{2-} ions, thus the formation of ion pairs $CaCO_3^0$ was improved and the transformation of vaterite to calcite was enhanced.

It should be mentioned that the adsorption of Ca^{2+} and CO_3^{2-} on the vaterite surface is not stable because of the dissolution of vaterite. Even through the calcite and vaterite are in the same solution, the effect of the excess Ca^{2+} on the growth of vaterite is not evident.

Figure 5 shows the change of pH during the process of precipitation, which are step-like curves. The curves contained two decreasing steps and one flat step. At the beginning of reaction, the first step was characterized with the sharp reduction of pH, which corresponded predominantly to the spontaneous nucleation. The sharp reduction of pH was attributed to the induction course before nucleation. Following the first step was the flat step, which was obviously at the low initial $CaCl_2$ concentration. The flat step reflected the participation of two main progresses, namely new precipitation and the transformation of vaterite to calcite. Because the transformation process does not induce the decrease of pH and only the precipitation arises the decrease of pH, the pH decreased lightly in the second step. It could be concluded that the transformation process lasted a long time at the lower $CaCl_2$ concentration, such as 0.001 and 0.01 mol/L. While it took a short time at the higher $CaCl_2$ concentration, which could be ascribed to the increase of transformation rate resulting from the excess of Ca^{2+}, as discussed in previous part. The second decreasing step corresponded mainly to the growth of calcite [9]. At the high $CaCl_2$ concentration, this step was also characterization with the sharp reduction of pH, which can be attributed to the high growth rate of calcite.

Conclusions

PCC was prepared by bubbling the CO_2/N_2 mixture into $CaCl_2$ solution. The influence of the initial $CaCl_2$ concentration on the morphology and phase of $CaCO_3$ was discussed. With the increase of initial $CaCl_2$ concentration, more and more rhombic calcite particles were formed and mixed with the spherical particles. When the initial $CaCl_2$ concentration amounted to 0.3 mol/L, only rhombic calcite was formed. The change of morphology and phase of $CaCO_3$ with the initial $CaCl_2$ concentration was attributed to the excess of Ca^{2+}, which improved the formation of the ions pair $CaCO_3^0$, thus speeding the transformation of vaterite to calcite.

Acknowledgement This study has been supported by a grant from the NITECH 21st Century COE Program ''World Ceramics Center for Environmental Harmony'', and by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 15310052, 2003, Japan.

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