Proceedings of Symposium on Ultrasonic Electronics, Vol. 36 (2015)
5-7 November, 2015

Synthesis of calcite-type calcium carbonate using monoethanolamine and calcium chloride under ultrasound irradiation

超音波照射下におけるモノエタノールアミンと塩化カルシウムを用いたカルサイトの合成

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1. Introduction

Carbonate and carbon dioxide (CO_2) are used as sources of carbonic acid for synthesis of calcium carbonate in liquid phace. Currently, carbon capture and storage (CCS) is known as a technology for reducing CO_2 emission[1]. CO_2 is able to be recovered from the exhaust gas of coal fired power plant and it is injected into underground such as an aquifer. There are numerous studies to recover CO_2 from gases. Thus, the recovery methods of CO_2 using absorbents are improving. Monoethanolamine (MEA) is mainly used as a chemical absorbent in CCS technology because absorption amount of CO_2 mass per unit in MEA is large (0.43 g-CO_2/1.00 g-MEA). However, MEA has some drawbacks. Desorption of CO_2 from MEA is difficult without heating (about 120 °C). Therefore, a new recovery method of CO_2 without heating is desired.

We reported the method to desorb CO_2 from low concentration of MEA solutions at 25 °C using the ultrasound irradiation[2]. We also reported that the ratio of CO_2 desorbed was able to be improved by the addition of calcium chloride in the desorption process using ultrasound irradiation. Calcium carbonate was formed as calcite from calcium chloride and CO_2 desorbed from MEA. It is kown that calcium carbonate has three forms, calcite, aragonite and vaterite. Calcite is the most tharmally-stable in these three forms. We expect that calcite is able to be synthesized using calcium chloride and CO_2 desorbed from MEA (CO_2-MEA) with ultrasound irradiation.

In this study, we investigated the effect of the concentration of calcium chloride (Ca/MEA) on the morphology and size of calcite particles synthesized.

2. Experimental methods

The experimental apparatus is shown in **Fig.1**. Transducer was set on the bottim of water both. Ultrasound was irradiated to MEA solution indirectly from the bottom of flat-bottom-beaker.

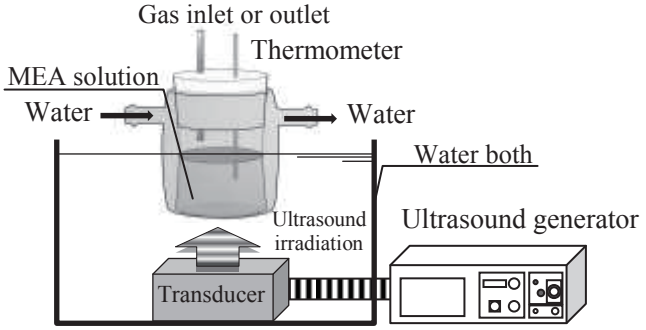

Fig. 1 Experimental apparatus using ultrasound irradiation

The ultrasound power was 11.6W which value was calculated by calorimetric method[3].

The reaction solution (CO_2-MEA) was prepared by absorbing CO_2 (0.16 M) into the MEA solution (0.2 M). The pH value of the solution was decreased from 11.2 to 7.2 by CO_2 absorption. After the preparation of CO_2-MEA solution, we added $CaCl_2$ into the solution and irradiated for 5 min. To confirmed the effect of ultrasound, we also investigated using stirring at 1500 rpm for 5 min (without ultrasound). Temperature during synthesis of calcium carbonate was kept at 25 °C using a circulation system of cooling water. Calcium carbonate synthesized was identificated using XRD and SEM.

3. Results and disscuss

Calcium carbonate was synthesized using calcium chloride solution (0.01, 0.05, 0.10, 0.20 M) and CO_2-MEA solutions. $CaCl_2$ was used as a source of Ca^{2+}. The effect of the molar ratio (Ca/MEA) on samples synthesized under ultrasound irradiation was investigated. Experiments were performed using ultrasound irradiation or stirring (1500 rpm) for 5 min at Ca/MEA = 0.5 condition. SEM images and XRD patterns of samples synthesized from Ca/CO_2-MEA are shown in **Fig.2** and **Fig.3** respectively. The morphology of particles synthesized under ultrasound irradiation was rhombohedral, and the size of particles was about

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2-3 μm evenly(Fig.2-a). This crystal structure was identified calcite by XRD analysis(Fig.3-a). On the other hand, the morphology of particles synthesized with stirring was spherical, the size of particles was about 5μm (Fig.2-b). This crystal structure was not a single phase and it was identified as a mixture sample of vaterite and calcite (Fig.3-b).

Next step, calcium carbonate was synthesized by changing the additional amount of $CaCl_2$. The initial pH of the MEA solution in the desorption process was 7.1. The yield of calcium, which is recovered as calcium carbonate, was calculated using the amount of calcium carbonate synthesized and that of $CaCl_2$ added. We also confirmed pH values of the solutions after the reaction at various Ca/MEA ratio (**Table I)**. The yield of calcium carbonate synthesized using ultrasound irradiation for 5min was much higher than that using stirring. In addition, the change of pH after the synthesis using ultrasound irradiation was larger than that using stirring. When the low ratio of Ca/MEA, the following reaction would be occured by a degasifying effect of ultrasound. As a result, pH was increasing.

$$HCO_3^- \rightarrow CO_2 \uparrow + OH^- \qquad (1)$$

When the high ratio of Ca/MEA, calcium carbonate was synthesized by a following reaction formula[4].

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \qquad (2)$$

The reaction of $CaCl_2$ and HCO_3^- decreases pH of the solution by the release of H^+ (Eq. 2). Equation (2) is more dominant than that Equation (1)[2]. The yield of $CaCO_3$ using ultrasound was larger than that using stirring, which may come from the nucleation effect of ultrasound. The samples synthesized under ultrasound irradiation were calcite form and uniform grain-shape. On the other hand, the sample synthesized under stirring was mixture of vaterite and calcite at all conditions of Ca/MEA. We also found out that as the ratio of Ca/MEA increases, the size of particles decreases. We considered that the size decreament of the particles comes from the increament of the number of nucleation at high concentration of $CaCl_2$.

4. Conclusion

We investigated the effect of ratio of Ca/MEA on the size, morphology and crystal structure of $CaCO_3$ synthesized under ultrasound irradiation or stirring. The ratio of Ca/MEA did not effect on the morphology and form of $CaCO_3$. Single phase of calcite was synthesized using ultrasound irradiation at all ratio of Ca/MEA. It was also found that the sample synthesized by stirring was a mixture of vaterite and calcite.

Acknowledgment

This study was supported by a Grant-in-Aid for Scientific Research (KAKENHI) 15K06638.

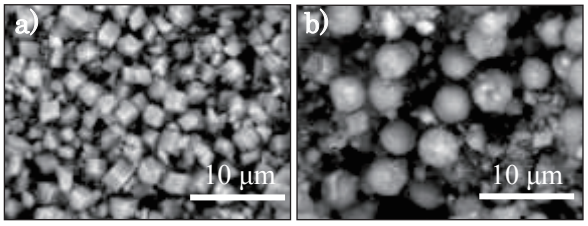

Fig.2 SEM images of calcium carbonate synthesized a) using ultrasound and b) using stirrer (Ca/MEA ratio = 0.5).

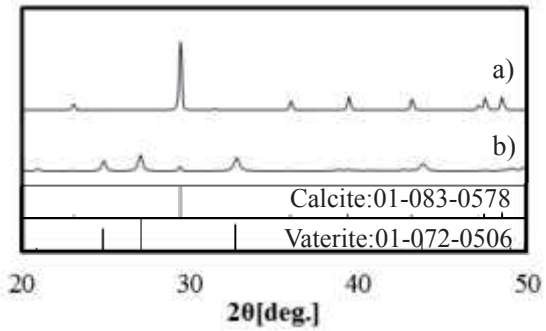

Fig.3 XRD patterns of calcium carbonate synthesized a) using ultrasound and b) using stirrer (Ca/MEA ratio = 0.5).

Table I pH and calcium yield of solutions after the reactions

Ca/MEA	Ca yield[%] (pH)*2	
	Ultrasound	Stirrer
0*1	- (7.6)	- (7.4)
0.05	72.5 (7.4)	36.6 (7.2)
0.25	79.7 (7.0)	40.0 (7.1)
0.5	80.1 (6.9)	47.6 (7.1)
1	53.0 (6.8)	46.8 (6.9)

*1 Without addition of $CaCl_2$
*2 pH value of solutions after reactions using ultrasound or stirring.

References

1. S. M. Richard, K. E. Jordan: Applied Energy. **108** (2013) 66.
2. K. Tanaka, T. Fujiwara, H. Okawa, T. Kato, K. sugawara: Jpn. J. Appl. Phys. **53** (2014) 07KE14.
3. S. Koda, T. Kimura, T. Kondo, H. Mitome: Ultrason. Sonochem. **10** (2003) 149.
4. Y. Kojima, K. Yoshitake, T. Umegaki. N. Nishimiya: Jour. Soc. Inorg. Mater. Jpn. **19** (2011) 104.