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Effect of orientation of CaO plate-like particle on CO_2 adsorption property

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ABSTRACT

The plate-like CaO particle with a highly (111)-plane orientation was synthesized, and its CO_2 adsorption property was investigated. Firstly, the $Ca(OH)_2$ powders were prepared from a saturated $Ca(OH)_2$ aqueous solution, and then the prepared $Ca(OH)_2$ powder was thermally decomposed to synthesize the CaO powder. The orientation degree of the (0001) plane of $Ca(OH)_2$ was increased by increasing the time for evaporating the solvent in the $Ca(OH)_2$ aqueous solution. The orientation degree of the (111) plane of CaO increased by increasing that of the (0001) plane of $Ca(OH)_2$. Increasing the orientation degree of the (111) plane of CaO was effective for suppressing the aggregation of CaO particles in the CaO powder. Consequently, it was found that the CO_2 adsorption rate was increased by increasing the specific surface area of the CaO powder. Furthermore, the (111) plane-oriented CaO powder maintained the CO_2 adsorption ratio even after the cycle of CO_2 adsorption and desorption at 700 °C.

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1. Introduction

Various methods of separating and collecting CO_2 from the source of emission, such as flue gas have been developed because of the recent increase in the concentration of CO_2 in the atmosphere, considered to be a factor contributing to global warming [1–5]. Calcium oxide, CaO, is a candidate material for capturing CO_2 because it exists abundantly in nature [6–10]. Especially, CaO is suitable for the efficient separation of CO_2 from hot gases because it readily absorbs CO_2 at temperatures up to approximately 900 °C to produce $CaCO_3$ [11–17].

It has been known that synthesizing CO_2-adsorbing materials with a higher specific surface area, such as fine and porous particles is an effective approach because the CO_2 adsorption capacity of CaO depends on its specific surface area [18–23]. However, the aggregation of CaO particles progresses when they react with CO_2 at high temperatures, and it lowers the CO_2 adsorption capacity of CaO particles. On the other hand, it has been reported that fabricating composite materials was effective for suppressing the aggregation of CaO particles [24–28]. However, the CO_2-adsorption capacity of the composite material was lower than that of the CaO powder because the mass of the composite material was larger than that of the CaO powder.

One of the approaches for developing CO_2 adsorption capacity is controlling the crystal plane of CaO. Several methods for the preparation of CaO with a highly (111)-oriented plane have been reported [29,30] because the (111) plane of CaO has a high surface energy. In this study, the CaO powder consisted of plate-like CaO particles was synthesized by the thermal decomposition of Ca(OH) plate-like particles and the CO_2 adsorption and desorption properties of the synthesized CaO powder were evaluated.

2. Experimental

Firstly, the saturated $Ca(OH)_2$ aqueous solution was prepared by dissolving a commercial CaO (99%, Wako Chemical). Then the $Ca(OH)_2$ particles were prepared by evaporating the solvent in the saturated $Ca(OH)_2$ aqueous solution in a glass vessel under N_2 gas flow, followed by drying at 120 °C for 12 h in air. Here the solvent was removed using a hot plate. Then, the prepared $Ca(OH)_2$ powder was heated in an electrical furnace to synthesize a CaO powder at 900 °C for 2 h at a heating rate of 1 to 10 °C/min under Ar gas flow.

As well as the orientation degrees of the (0001) plane of $Ca(OH)_2$ and the (111) plane of CaO, the crystalline phases of the CaO and $Ca(OH)_2$ powders were characterized by X-ray diffractometry (XRD; RINT2000, Rigaku, CuKα, 40 kV, 30 mA). The thermal decomposition behavior of $Ca(OH)_2$ powders and the CO_2 adsorption capacity of CaO powders were investigated by thermal gravimetry and differential thermal analysis (TG-DTA; ThermoPlus TG8120, Rigaku). The cycle property of CO_2 adsorption and desorption at 700 °C was investigated by TG-DTA. Firstly, the sample set in a Pt pan was heated to 600 °C under Ar gas flow at a heating rate of 200 ml/min. Then, the CO_2 adsorption at 700 °C was carried out under CO_2 gas flow at a flowing rate of 200 ml/min, and the CO_2 desorption at 700 °C was carried out under Ar gas flow at a flowing rate of 200 ml/min. The morphologies of the CaO and $Ca(OH)_2$ powders were examined by field emission scanning electron microscopy (FESEM; S4100, Hitachi). The specific surface areas of the CaO and $Ca(OH)_2$ powders were measured from the adsorption isotherm of

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nitrogen at −196 °C by the Brunauer-Emmett-Teller method (BET; NOVA-4200e, Quantachrome).

3. Results and discussion

3.1. Preparation of CaO with (111) orientation

3.1.1. Influence of evaporation time on CaO orientation

Fig. 1 shows the XRD patterns of the $Ca(OH)_2$ powders (PDF; 04-0733) obtained by evaporating the solvent in the saturated $Ca(OH)_2$ aqueous solution for the evaporation time of 2 to 12 h under N_2 gas flow. Two diffraction peaks of the (0001) and (0003) planes were clearly recognized for the $Ca(OH)_2$ powder prepared in the case of the evaporation time of 12 h (hereafter, $Ca(OH)_2$-12 h). The result indicates that the $Ca(OH)_2$ crystals were oriented in the [0001] direction by increasing the evaporation time because the (0001) plane of $Ca(OH)_2$ is thermodynamically stable compared to other planes of $Ca(OH)_2$. Fig. 2(a) and (b) show the XRD patterns of the CaO powders (PDF; 37-1497) obtained by decomposing the $Ca(OH)_2$ powder. Here, CaO-2 h and CaO-12 h represent the CaO powders obtained by decomposing $Ca(OH)_2$-2 h and $Ca(OH)_2$-12 h, respectively. The relative intensities of the diffraction peaks of the (111) and (222) planes of CaO-12 h were larger than those of other diffraction peaks, and those of CaO-2 h was relatively smaller compared to CaO-12 h. The result indicates that the (0001) orientation of $Ca(OH)_2$ gave rise to the increase of the orientation in the [111] direction of CaO.

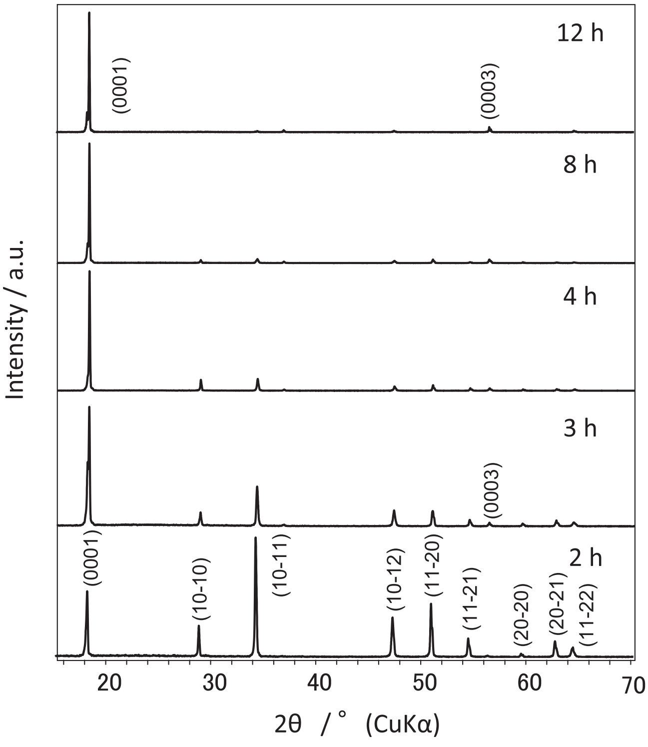

Fig. 1. XRD patterns of the $Ca(OH)_2$ powders prepared by evaporating the solvent in the saturated $Ca(OH)_2$ aqueous solution for the evaporation time of 2 to 12 h under N_2 gas flow.

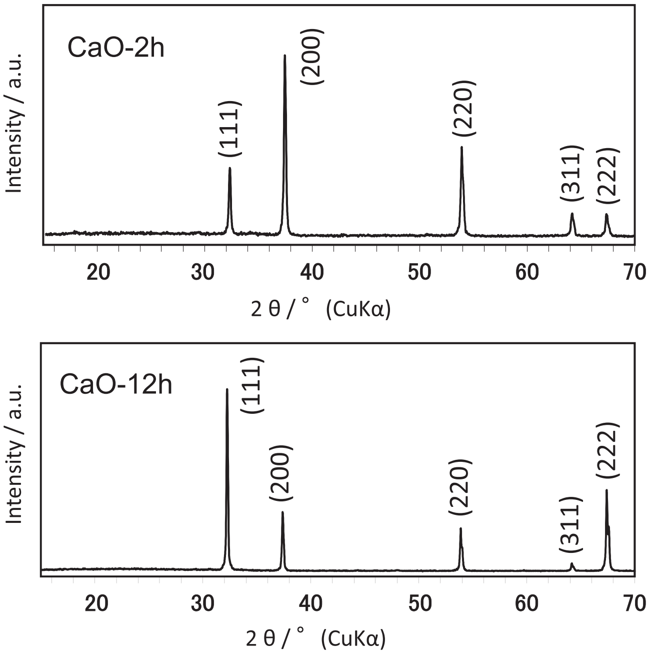

Fig. 2. XRD patterns of CaO-2 h and CaO-12 h powders synthesized by decomposing $Ca(OH)_2$-2 h and $Ca(OH)_2$-12 h powders, respectively.

Fig. 3 shows the relationship between the orientation degrees of the (0001) plane of $Ca(OH)_2$ and the (111) plane of CaO which was synthesized by thermally decomposing $Ca(OH)_2$-2 h and $Ca(OH)_2$-12 h at 900 °C for 5 h at a heating rate of 1 °C/min. Here, the orientation degree of the (0001) plane of $Ca(OH)_2$ was calculated as the ratio of the sum of peak areas of the (0001) and (0003) planes for the total peak areas. The orientation degree of the (111) plane of CaO was calculated as the ratio of the sum of peak areas of the (111) and (222) planes for the total peak areas. The orientation degree of the (111) plane of CaO increased by increasing that of the (0001) plane of $Ca(OH)_2$. This is because the atomic configuration of the (0001) plane of $Ca(OH)_2$ corresponds to that of the (111) plane of CaO [19]. Fig. 4(a) and (b) show the SEM photographs of $Ca(OH)_2$-2 h and $Ca(OH)_2$-12 h, respectively. The pillar-like and plate-like particles were mainly observed for the $Ca(OH)_2$-2 h and $Ca(OH)_2$-12 h powders, respectively. The (0001) plane in the hexagonal crystals of $Ca(OH)_2$-12 h was clearly larger compared to that of $Ca(OH)_2$-2 h. Fig. 4(c) and (d) show CaO-2 h and CaO-12 h, respectively. There was the difference in shape between the hexagonal particles of CaO-2 h and CaO-12 h. The powder of CaO-2 h mainly consisted of the pillar-like particles, while the powder of CaO-12 h mainly consisted of the plate-like particles. Thus, it was confirmed that the (0001) orientation of the $Ca(OH)_2$ particles influences the generation of the (111) orientation of the CaO particles, similar the other report [20]. The aggregation of CaO particles was remarkably observed for CaO-2 h and

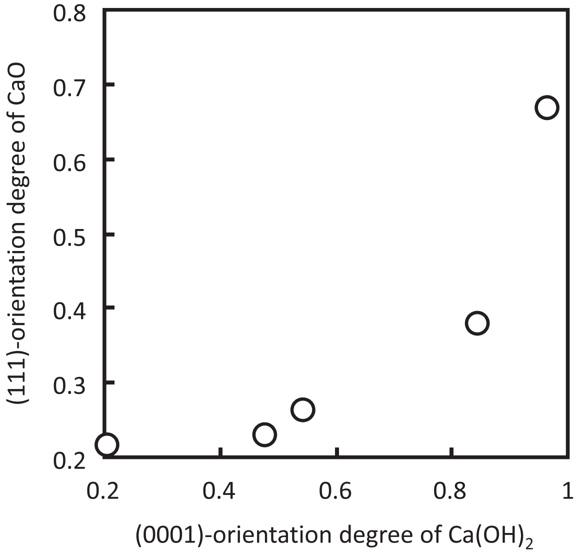

Fig. 3. Relationship between (001)-orientation degree of $Ca(OH)_2$ and (111)-orientation degree of CaO.

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