

Fabrication of Pollucite Porous Body for CO₂ Absorption

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CO₂ absorption behavior of CaO-coated aluminosilicate foam, Cs_{0.9}Al_{0.9}Si_{2.1}O₆, fabricated by utilizing a polyurethane foam and an amorphous Cs_{0.9}Al_{0.9}Si_{2.1}O₆ powder was investigated. Aluminosilicate foam was fabricated by two-step heat treatment at 873 K for 20 h and 1523 K for 5 h following the coating of aluminosilicate slurry on the polyurethane foam. CaO-coated foam was fabricated by coating Ca(NO₃)₂ slurry on the aluminosilicate foam at 1073 K for 5 h, which resulted in the formation of porous CaO particles on the foam. The CaO-coated foam showed a long lifetime for the cyclic process of CO₂ absorption and desorption.

Key words : Calcium oxide, Carbon dioxide, Foam, Pollucite, TG-DTA

1. INTRODUCTION

Calcium oxide (CaO) is suited to the efficient separation of CO₂ from hot flue gases because it readily absorbs CO₂ between approximately 773 and 1173 K to produce CaCO₃, and releases CO₂ at temperatures above 1173 K. On the other hand, the CO₂ absorption ability markedly decreases upon repeated absorption and desorption of CO₂ (hereafter CO₂ absorption-desorption cycles)^{1) - 4)} due to the agglomeration of CaO particles when CaO powder is used.

Composite materials containing CaO have been fabricated to suppress the decrease in the CO₂ absorption ability upon cyclic absorption and desorption.^{5) - 7)} Lu et al. attempted to enhance the cyclic absorption ability of CaO particles added to SiO₂¹¹⁾ and Liu et al. investigated the cyclic absorption ability of a porous composite material including CaO covered with a clay.⁸⁾ However, Lu's approach was not effective in suppressing the decreasing cyclic absorption ability of CO₂, and Liu's experiment did not clarify whether the specimen had superior cyclic ability of CO₂ absorption because the number of CO₂ absorption-desorption cycles was only 3. Thus, as described above, composite materials, including CaO, have been developed to suppress the agglomeration of CaO particles during CO₂

absorption-desorption cycles. However, the development of a suitable substrate for the enhancement of the CO₂ absorption-desorption ability of CaO has not been achieved.

From the reports described above, the fabrication of a porous material coated with CaO was considered to be effective for the development of a high-efficiency CO₂ absorbent. As a porous substrate, an aluminosilicate compound with cubic symmetry, Cs_{0.9}Al_{0.9}Si_{2.1}O₆ (hereafter, 9CAS), having a low thermal expansion coefficient of $2.0 \times 10^{-6} \text{ K}^{-1}$ in a temperature range of 298 to 1273 K, was selected.^{9), 10)} 9CAS is suitable because of its high thermal resistance due to its low thermal expansion.^{11), 12)} Furthermore, 9CAS does not have the serious disadvantage of oxidation at higher temperatures, as do nonoxides, and does not produce microcracks due to thermal stress from anisotropic thermal expansion, as does cordierite (Mg₂Al₄Si₅O₁₈) during heating and cooling.¹³⁾ In this study, a ceramic 9CAS foam coated with CaO was fabricated, and its CO₂ absorption ability and lifetime for CO₂ absorption-desorption cycles were investigated by thermal gravimetry and differential thermal analysis (TG-DTA). The morphology of the CaO-coated foam was also observed by scanning electron microscopy (SEM).

2. EXPERIMENTAL

CsNO₃ powder (99%; High Purity Chemical Co., Ltd.) was added to the fine powder consisted of γ -Al₂O₃ and amorphous SiO₂ fine powders⁹⁾ prepared by commercially available Al₂O₃ sol (Al₂O₃ sol 200; Nissan Chemical Co., Ltd.) and SiO₂ sol (Snotex O; Nissan Chemical Co., Ltd.), which was then mixed and ground in ethanol for 24 h by ball milling using Al₂O₃ balls. After removing the ethanol and drying, the mixed powder was heated at 873 K for 20 h to obtain a calcined powder of 9CAS with an amorphous phase. A slurry of 9CAS amorphous powder with a mass ratio of 9CAS / water = 1 / 1 was prepared and then coated on the surface of a commercially available polyurethane foam (HR30; Bridgestone Co., Ltd.). After drying the slurry on the foam, the polyurethane was removed by heating at 873 K for 2 h at a rate of 2 K / min under air with a flow rate of 200 ml / min, and then a heat treatment at 1523 K for 5 h was performed to prepare a ceramic foam (hereafter, 9CAS foam). Then, a slurry (hereafter, Ca(NO₃)₂ slurry) with a mass ratio of Ca(NO₃)₂ / water = 1 / 1, which was prepared by ball milling for 2 h in water, was coated on the surface of the 9CAS foam. After drying the Ca(NO₃)₂ slurry coated on the 9CAS foam, the as-dried foam was heated at 1073 K for 2 h at a rate of 5 K / min to fabricate the CaO-coated 9CAS foam (hereafter, CaO foam) under Ar gas flow to prevent CaO from

absorbing water.

Powder X-ray diffractometry (XRD) was used to investigate the crystalline phases of the specimens. FT-IR spectra of calcined powders were investigated by KBr method using FT-IR apparatus (Shimazu Co.,Ltd.).

The cyclic CO₂ absorption-desorption property of the CaO foam was investigated by TG-DTA (TAS-200, Rigaku Co., Ltd.) at 973 K for 30 min under CO₂ or Ar gases with a flow rate of 200 ml / min. Here, Ar gas was used to decarbonate the CaO foam effectively. The CO₂ absorption ability of the CaO foam was evaluated from the CO₂ absorption ratio of CaO in the foam. Here, CO₂ absorption ratio means carbonation ratio of CaO to CaCO₃. Weight of CaO in the CaO foam was calculated from a difference in weight between the CaO foam and the 9CAS foam. The morphologies of the specimens were observed by SEM (S4100, Hitachi Co., Ltd.).

3. RESULTS and DISCUSSION

XRD patterns of the powders calcined at 873 K for 20 h and at 1073 K for 20 h are shown in **Fig. 1 (a)** and **(b)**, respectively. Although a crystalline phase was clearly recognized in the powder calcined at 1073 K for 20 h, only an amorphous phase was recognized in the powder calcined at 923 K. **Fig. 1 (c)** and **(d)** show FT-IR spectra of the powders calcined at 923 K and 1073 K,

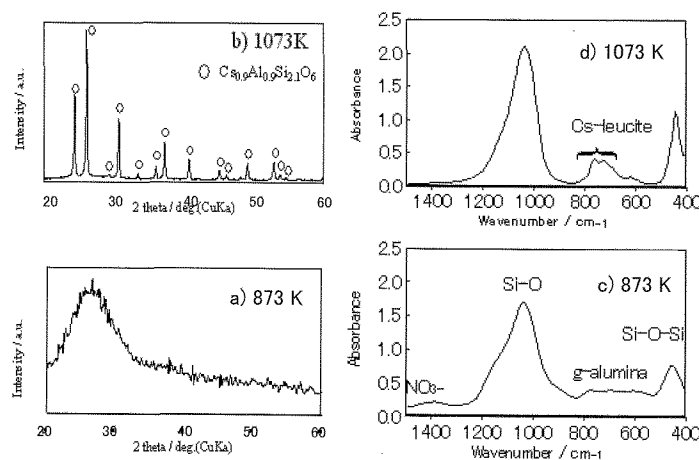


Fig.1 XRD patterns and FT-IR spectra of pollucite powders calcined at 873 K and 1073 K.

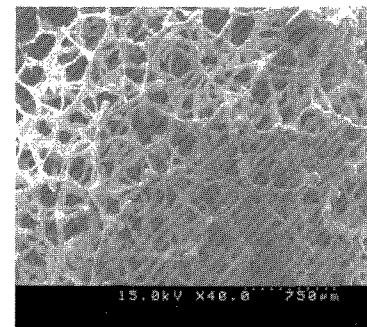


Fig.2 SEM morphology of 9CAS foam.

respectively. Judging from these spectra, the amorphous phase did not have an aluminosilicate framework of pollucite because absorption spectra in range of 600 to 800 cm^{-1} belong to pollucite structure was not recognized in the spectrum of the amorphous powder.

Frames of 9CAS foam sintered at 1523 K for 5 h are shown in Fig. 2 (a), had a similar shape to the polyurethane foam, indicating that the 9CAS slurry was sufficiently coated on the surface of the polyurethane foam before the fabrication of the 9CAS foam by sintering amorphous 9CAS particles. A frame of ca. 100

μm in width was observed in the three-dimensional structure of the 9CAS foam. The frame size of the 9CAS foam almost coincides with that of the polyurethane foam. The 9CAS foam had a porosity of about 90 %.

Surfaces of 9CAS foam coated with CaO prepared from $\text{Ca}(\text{NO}_3)_2$ slurry, observed by SEM, are shown in Fig. 3. Morphology of the surface changed according to amount of CaO coated on the foam. Plate-like CaO crystals were observed in case of 30 wt% of a coated ratio on the 9CAS foam and finally porous CaO particles were produced on the surface of the 9CAS foam. Figure 4 shows the XRD patterns of powder samples prepared by grinding CaO foam sintered at 1173 K for 2 h under Ar gas flow. Here Ar gas was used to prevent CaO from absorbing water during cooling. Although only CaO and 9CAS phases were recognized, Ca_2SiO_4 and CsAlSiO_4 phases were also recognized. These phases were produced by a

reaction of CaO and $\text{CsAlSi}_2\text{O}_6$. The reaction was caused at the surface of the frame as shown in Fig. 3. It was considered that the reaction of CaO with 9CAS was promoted by the increase in contact area due to $\text{Ca}(\text{NO}_3)_2$ melting at 834 K, which promoted the above reaction.

The CO_2 absorption-desorption behavior of the CaO foam was investigated by TG-DTA in the temperature range of R.T. to 1273 K under CO_2 gas flow with a rate of 200 ml / min at a pressure of 1 atm. Here, fragments of the CaO foam were used as a sample for TG-DTA measurement to investigate the effect of coating CaO on the frames of the three-dimensional aluminosilicate used for CO_2 absorption-desorption. The cyclic ability of the CaO foam to absorb and desorb CO_2 was investigated by TG-DTA at 973 K under CO_2 (absorption) or Ar (desorption) gas flow. The result is shown in Fig. 5. Here, the CO_2 absorption time at 973 K was fixed at 30 min. CaO particles on the CaO foam rapidly reacted with CO_2 at 973 K. Although the absorption ratio for CO_2 was about 45 %, the CaO foam maintained the CO_2 absorption ratio even after 15 CO_2 absorption-desorption cycles.

Figures 6(a) and (b) show morphologies of the CaO particles coated on the 9CAS foam before and after 15 CO_2 absorption-desorption cycles, respectively. The porous structure of the CaO particles coated at the surface of 9CAS foam before the CO_2 absorption-desorption cycles was hardly changed even after 15 CO_2 absorption-desorption cycles. Thus, CaO with the

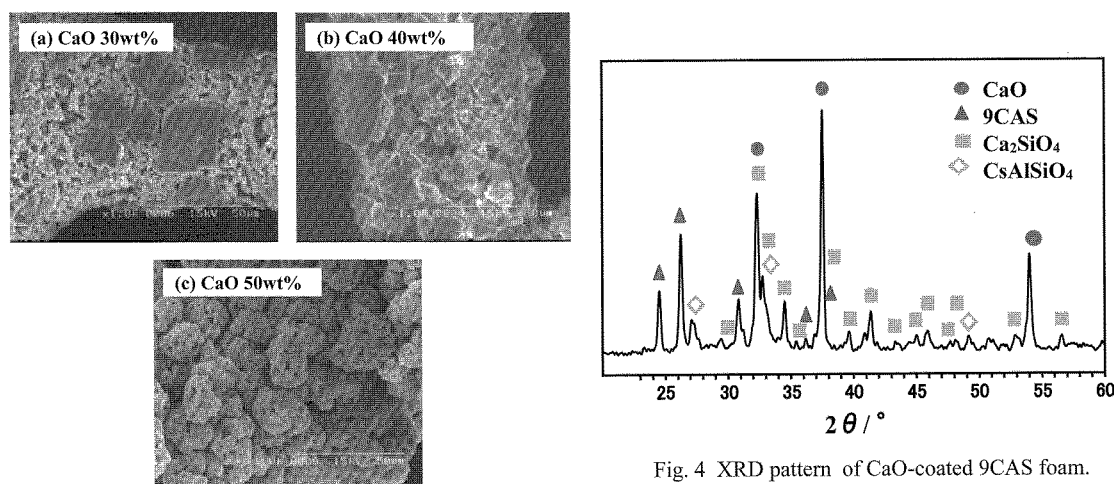


Fig. 4 XRD pattern of CaO-coated 9CAS foam.

Fig. 3 SEM morphology of CaO particles coated on 9CAS foam.

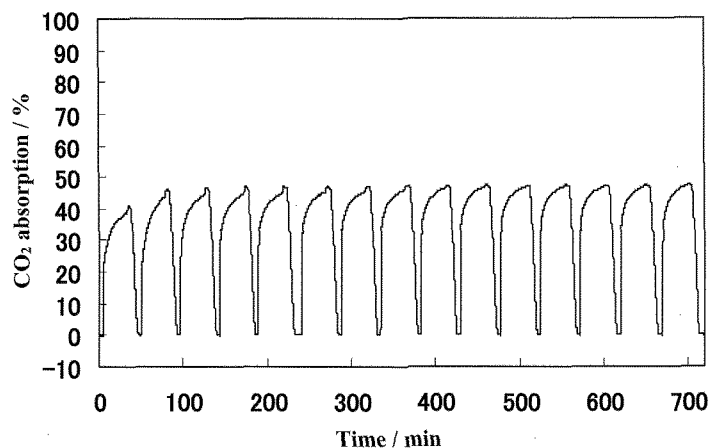


Fig. 5 CO₂ absorption-desorption behavior of CaO foam at 973 K under CO₂ (absorption) or Ar (desorption) flow.

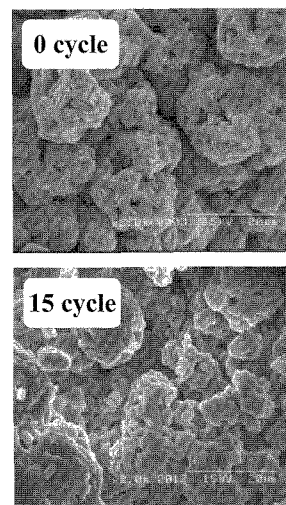


Fig. 6 SEM morphology of CaO particles before and after CO₂ absorption-desorption.

porous structure was considered to be effective for maintaining a CO₂ absorption ratio during the cyclic CO₂ absorption-desorption cycles. Such a low reaction ratio of CO₂ of the CaO foam was considered to be due to the formation of Ca₂SiO₄ and CsAlSiO₄ clearly decreases the amount of CaO on the foam acting as a CO₂ absorbent.

4. CONCLUSIONS

Ca(NO₃)₂ slurry was coated on the pollucite foam prepared by coating amorphous 9CAS slurry on commercially available polyurethane foam, followed by heat treatment at 1073 K for 5 h under Ar gas flow to fabricate CaO-coated pollucite foam. SEM observation revealed that the foam had a frame with a diameter of ca. 1 μm. The CaO-coated foam had superior absorption ability and a long lifetime for the cyclic process of CO₂ absorption and desorption, owing to its porous structure of CaO particles.

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