

Absorption of CO₂ on CaSiO₃

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Abstract. CaSiO₃ was prepared through solid chemical reaction of CaCO₃ and SiO₂ at 800°C and investigated as a CO₂ sorbent via X-ray diffractometry (XRD) and thermal gravimetric analysis (TGA) techniques. The results revealed that CaSiO₃ commenced to absorb CO₂ at 400°C and ended at 800°C with about 28.72% CO₂ sorption efficiency while using 15% CO₂, 85% N₂ as flow gases. About ten cycles of CO₂ sorption-desorption were also exhibited. CaSiO₃ can be regenerated by calcination at 800°C within 10 hours, furthermore, the cheap CaSiO₃ can also be used to capture CO₂ eternally.

Keywords: Carbon dioxide capture; Calcium silicate; Sorbent; Thermal gravimetric analysis.

1. Introduction

It is well-known that the rising emission of green-house gases are exacerbating the global environment, bringing on drought, desertification, hot weather, and sea level increase. In order to maintain a compatible living surrounding, mankind have to control CO₂ emission into atmosphere, which is the principal ingredient of green-house gases. Flue gases occupy ca. 30% among CO₂ emission sources. Collecting CO₂ from flue gases is essential for the reduction of CO₂ emission.

There are various methods to collect CO₂ such as absorption with a solvent (Mandal et al., 2006), membrane separation (Kanksha et al., 2007) and using zeolite (Wirawan et al., 2006). These techniques are costly and consume much energy, even pollute environment again. The improved technique is chemical absorption of CO₂ with solid sorbent. Those researches are attracting much attention in recent years. Yamaguchi et al. investigated separation performance of CO₂ absorbing material based on lithium silicate, 33 wt% of a CO₂ was absorbed on the material (Yamaguchi et al., 2007). Researches on lithium silicates are numerous (Pfeiffer et al., 1998; Bretado et al., 2005; Cruz et al., 2006). Lee et al. studied alkali metal-based solid sorbents with different support such as activated carbon (AC), TiO₂, Al₂O₃, MgO, SiO₂ and various zeolites (Lee et al., 2006). Their CO₂ capture capacities are lower than 12 wt% and cycle properties of CO₂ sorption-desorption are poor owing to formation of intermediates though the operating temperature was lower than 400°C. Martavaltzi et al. prepared CaO sorbent by using two kinds of precursors, Ca(OH)₂ and Ca(CH₃COO)₂, confirming the former precursor provided a higher tortuosity to yielded CaO and that CaO produced by Ca(CH₃COO)₂ exhibited higher CO₂ uptake up to 50% by weight. They also found

that using $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as framework in CaO sorbent enhanced stability of CO_2 sorption-desorption process, and the amount of CO_2 fixed on CaO- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ derived from $\text{Ca}(\text{CH}_3\text{COO})_2$ was higher than 6 mol/kg sorbent even after 45 cycles of sorption-desorption (Martavaltzi et al., 2008). Shtepenko et al. investigated the effect of CO_2 on β -dicalcium silicate and Portland cement, revealing amount of CO_2 which reacted with dicalcium and Portland cement was 48 and 37%, respectively, in a cycled process at 40°C , 3 bar for 60 min (Shtepenko et al., 2006).

Herein, we explored sorption-desorption property of CO_2 on homemade CaSiO_3 . CaSiO_3 is relatively cheap, thus it can be employed for CO_2 everlasting deposition. Moreover, the CO_2 sorption temperature is lower than that of CaO. Researches concerning CaSiO_3 have been rare so far.

2. Experimental

CaCO_3 (analysis purity) and SiO_2 (analysis purity) were weighed according to chemical stoichiometric ratio (molar ratio, 1:1), and then ball-milled with an instrument, SPEX 8000 Mixer/mill. The homogeneous admixture was pressed in a die via a pressing instrument into a disc shape with a diameter of 1 cm at 50 Mpa. The discs were calcined in a chamber furnace at 800°C for 10 h. The chemical reaction of CO_2 absorption/desorption should be as follows;



The forward process is CO_2 desorption, and the reverse process belongs to CO_2 fixed process. Thus the reaction is reversible according to the thermodynamics. After that, the calcined specimen was ball-milled again. The powder was measured through XRD together with TGA (METTLER TOLEDO, Model TGA 851). A mixture of 15 vol % CO_2 with 85 vol % N_2 was purged during the TGA process. The ratio of CO_2 is the same as that of flue gas. XRD was measured with a Siemens D500 diffractometer employing Cu/ $K\alpha$ radiation.

3. Results and discussions

3.1 Characterizations of specimens

Comparing curves 1 and 2 in Fig.1, new peaks denoting CaSiO_3 occurred in curve 3, whereas most peaks from curve 1 and 2 vanished, indicating CaSiO_3 was synthesized via chemical reaction of SiO_2 and CaCO_3 . Since CaSiO_3 is amorphous, its XRD reflection peaks are not distinct (Shtepenko et al., 2006).

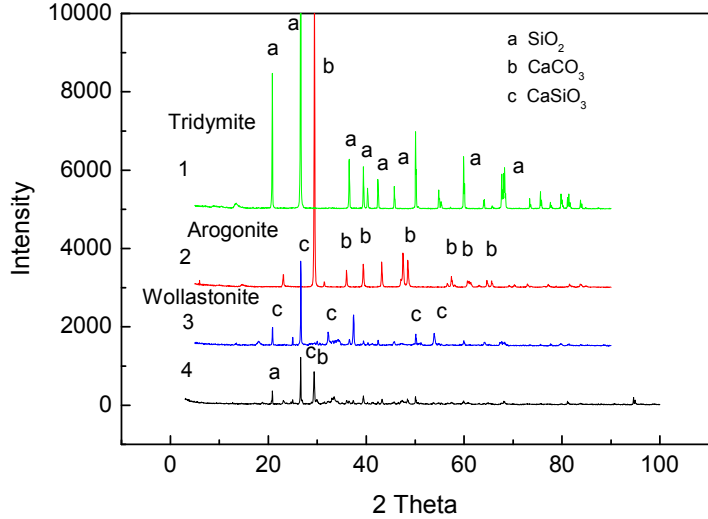
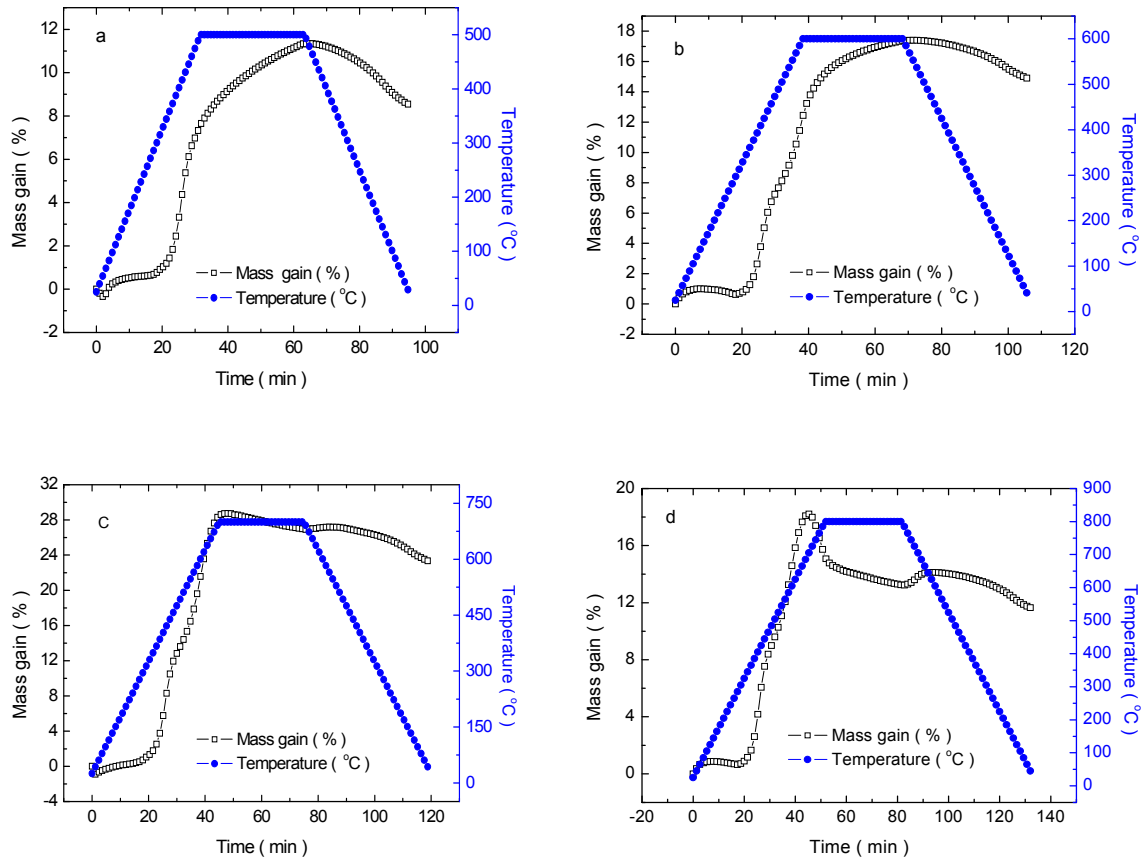


Fig.1 XRD patterns of calcium silicates at various states. 1 SiO_2 raw material; 2 CaCO_3 raw material; 3 synthesized CaSiO_3 at 800°C ; 4 CaSiO_3 after CO_2 absorption at $400\text{-}700^\circ\text{C}$.

Advantage of employing CaCO_3 other than CaO as feedstock lies in that the former can release CO_2 during the reaction, therefore, the product, CaSiO_3 , is incompact. Sintering of product must be prevented, which provide larger specific surface area and are beneficial for latter reaction.

3.2 Effect of temperature on CO_2 capture capacity

It can be seen from Fig.2 that the mass gain of CaSiO_3 due to CO_2 absorption increased with increasing temperature. CaSiO_3 absorbs CO_2 sharply when temperature reached to 400°C . The highest CO_2 absorption ratio attained to be 28.72%, however, CO_2 absorption ratio decreased to 18.21% when measuring temperature reached 800°C and a valley appeared in mass gain curve. The temperature of 800°C was so high that newly produced CaCO_3 via CO_2 absorption reaction began to partially decompose, therefore, mass gain decreased until temperature descended. CaSiO_3 absorbed CO_2 , mass gain ascended slightly again. The absorption process proceeded intensively that highest mass gain can be achieved within 45 minutes.



a Temperature range of 20-500°C; b 20-600 °C; c 20-700 °C; d 20-800 °C

Fig.2 Mass gain of CaSiO_3 during CO_2 absorption process

The highest CO_2 absorption ratio is 28.72%, obtained at 700°C, accordingly, 700°C is the optimal temperature for CO_2 absorption as CaSiO_3 is sorbent.

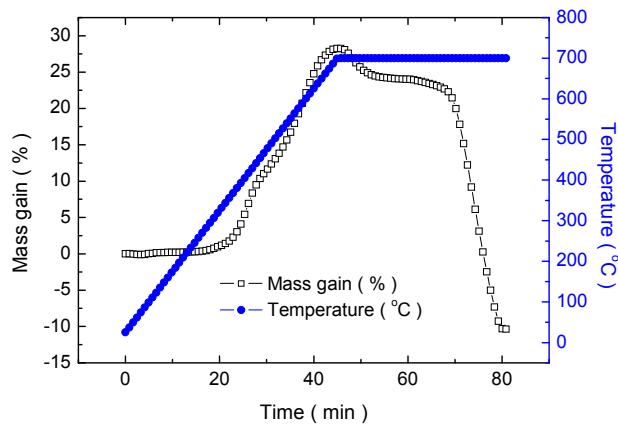


Fig.3 CO_2 sorption-desorption cycle

Experiments in Fig.2 were performed at CO₂/N₂ atmosphere all along, hence, mass dropped slowly because the temperature was decreased after mass gain reached the highest point. In order to perform desorption process, atmosphere alteration is essential. In Fig.3, CO₂/N₂ were changed into pure N₂ shortly after the highest mass gain was obtained, and then, mass dropped sharply to be even lower than the original value, releasing the adverse process of reaction (Mandal et al., 2006), namely CO₂-desorption process, could also proceed. The specimen derived from the CO₂-desorption process was characterized via XRD (curve 4, Fig.1). The peak in curve 4 at about 30 degree was attributed to CaCO₃, the feedstock, proving that the whole reaction is reversible. Hence, the adverse process can be achieved by atmosphere alteration at 700°C.

3.3 Cycle property of CO₂ sorption-desorption

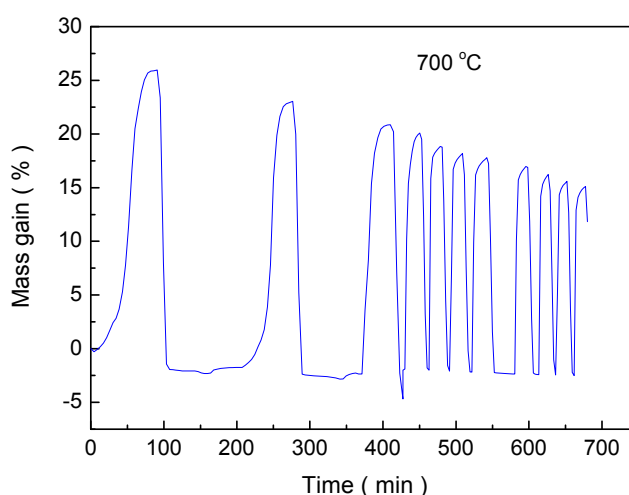


Fig.4 Cycle property of CO₂ sorption-desorption on CaSiO₃ at 700°C.

Capacity of CO₂ sorption/desorption descended drastically from 26.09%, 23.04% to 15.28% with the increasing cycle time (Fig.4). The decay rate is about 3%. Fig.4 showed certain cycle capacity though it is much inferior to that of CaO (Martavaltzi et al., 2008). The figure also indicated that CO₂-desorption reaction required long time, which decreased the whole cycle efficiency. We observed that the specimen after cycle experiment became more rigid than before. It was sintered additionally, which resulted in decrease of reaction specific area, consequently, low reaction activity.

On the other hand, the spent sorbent can be regenerated via sintering at 800°C for 10 hours to ensure the reaction of CaCO₃ with SiO₂ completely like that have been done during CaSiO₃ preparation process. About 95% of CO₂ sorption-desorption efficiency can be resumed by the above process. Regardless of the low cycle capacity, CaSiO₃ is a principal ingredient as wollastonite that is widely existing in the earth with cheap, thus it can be employed to deposit CO₂ everlasting since CO₂ utilization ratio is so low even less than 1% of emission quantity (Yang, 2005), which is also superior to Li₄SiO₄ (Yamaguchi et al., 2007).

4. Conclusions

In the present work, CaSiO_3 was investigated as a CO_2 sorbent via XRD and TGA techniques, releasing that CaSiO_3 commenced to absorb CO_2 at 400°C and ended at 800°C with about 28.72% CO_2 sorption efficiency while using 15% CO_2 , 85% N_2 as flow gases. The ten cycles of CO_2 sorption-desorption were also exhibited well. CaSiO_3 can be regenerated by the calcination at 800°C , furthermore, the cheap CaSiO_3 can also be applied to deposit CO_2 eternally.

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