IMPROVING CO₂ SORPTION PERFORMANCE OF CaO/Ca₃Al₂O₆ SORBENTS BY STEAM HYDRATION PRETREATMENT

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ABSTRACT

CaO-based CO₂ sorbents play a significant role in sorption enhanced methane steam reforming process for hydrogen production and CO₂ emission reduction. In this work, pretreatment of CaO/Ca₃Al₂O₆ sorbents in steam atmosphere at different temperatures was investigated for its influence on CO₂ sorption capacity and cyclic stability. The sorbents were synthesized to contain a CaO to Al₂O₃ mass ratios of 9:1, and then subjected to cycling tests with repeated carbonation and calcination process. Results showed that the sorbents pretreated by steam at 250 °C obtained a minimum CaO grain size of 37.9 nm and a maximum surface area of 17.4 $m^2 \cdot g^{-1}$. This resulted in an increase in CO₂ sorption capacity, up to 8.53 mmol $CO_2 \cdot g^{-1}$ sorbent. After 50 cycles, the CO₂ sorption capacity decreased, but still remained 10% above those for the original (no pretreatment) sample. The mechanism about the improved CO₂ sorption performance of the pretreated sorbents was also postulated.

Keywords: CO₂ capture; CaO; steam pretreatment; sorption performance; mechanism

NONMENCLATURE

Abbreviations	
SEMSR	sorption enhanced methane steam reforming
C9A1	CaO/Ca₃Al₂O₆ sorbent with CaO to Al₂O₃ mass ratios of 9:1

1. INTRODUCTION

Sorption enhanced methane steam reforming (SEMSR) is a desirable route to economically provide H₂ and reduce CO₂ emission [1]. In the SEMSR process, a key widely investigated material is the appropriate CO₂ sorbent because it determines the extent of the equilibrium shift. To date, CaO-based sorbents have been one of the most promising candidates for their sorption capacities under the conditions for steam reforming, and it is believed to be thermodynamically the best candidate among metal oxides for CO₂ capture in zero emission power generation systems [2]. Currently, the major challenge is to overcome the loss of CO₂ sorption capacity during the repeated cycling. To counteract this, promising strategies have been proposed to improve the durability of CaO sorbents, involving thermal pretreatment [3]; hydration treatment [4]; modification of precursors [5]; and incorporation of supports or dopants [6]. In our previous studies, CaO/Ca₃Al₂O₆ sorbent was successfully synthesized, and an initial sorption capacity of 4.85 mmol $CO_2 \cdot g^{-1}$ sorbent was achieved at 500 ºC when the mass ratio of CaO to Al₂O₃ is 9:1 (correspondingly, the active CaO content is 73.53% and its theoretical sorption capacity should be 13.13 mmol $CO_2 \cdot g^{-1}$ CaO/Ca₃Al₂O₆). Though the synthesized CaO/Ca₃Al₂O₆ sorbent shows 5%-10% higher CO₂ absorptivity than the other Al-doped sorbents reported in the literature [7-9], it should be noticed that there is still a gap between the theoretical value and the current level. Thus, to improve the CaO/Ca₃Al₂O₆ sorbents sorption performance at lower sorption temperature (500 °C) and provide guidance for future

work to accelerate its industrial application, it is reasonable to modify the $CaO/Ca_3Al_2O_6$ sorbents so as to enhance its CO_2 sorption performance.

Steam hydration is a promising way to improve CO_2 sorption capacity of CaO-based sorbents during the carbonation/calcination process [4, 10, 11]. However, it is usually employed either in carbonation process or calcination process at high temperature (600-900 °C), and different mechanisms were reported by researchers.

In this study, steam hydration is applied to pretreat the $CaO/Ca_3Al_2O_6$ sorbents in the preparation process at low temperature (200-300 °C) with the aim of generating self-reactivation to improve its CO_2 sorption performance. The mechanism about the improved CO_2 sorption performance of the pretreated sorbents was also postulated.

2. EXPERIMENTAL

2.1 Synthesis of $CaO/Ca_3Al_2O_6$ sorbent

The $CaO/Ca_3Al_2O_6$ sorbents with CaO to Al_2O_3 mass ratios of 9:1 were prepared via a modified sol-gel method we reported [12,13]. Sorbent synthesized in this way is marked as C9A1.

2.2 Pretreatment of $CaO/Ca_3Al_2O_6$ sorbents

The obtained C9A1 sorbent was pretreated in a 10% H_2O-N_2 atmosphere at different temperatures for 1 h followed by calcination in N_2 atmosphere at 700 °C for 30 min prior to the cyclic tests. Sorbents treated at 200 °C, 250 °C and 300 °C were denoted as C9A1-200, C9A1-250 and C9A1-300, respectively.

2.3 Sorbent characterization

The crystallographic structure of the sorbent was determined by a Rigaku powder X-ray diffraction (XRD) with Cu Kα radiation (λ= 0.154 nm) and the scanning angle was in the range of 10~90 ° at a rate of 8 °/min; the accelerating voltage and current were 40 kV and 40 mA, respectively. The textural properties of the sorbent, such as Brunauer-Emmett-Teller (BET) surface area and pore volume were measured by nitrogen adsorption-desorption analysis at -196 °C on an automatic instrument (JW-BK). The surface morphologies of the sorbents before and after carbonation reaction were examined using TM-3000 scanning electron microscopy (SEM, HITACHI, Japan).

2.4 Sorbent cyclic sorption performance

The CO_2 sorption capacity and cyclic stability of the sorbents were evaluated by using a small fixed-bed quartz reactor coupled with thermal conductivity detector. A 15 mg sorbent sample was pretreated as described in section 2.2. The sample was then cooled down to carbonation temperature and subsequently was carbonated in 10% CO_2-N_2 atmosphere (50 mL·min^{-1}) at 500 °C for 30 min (the carbonation conditions simulated the SEMSR conditions.). After the carbonation process, the sorbent was purged in helium (50 mL·min^{-1}) to 800 °C for 10 min to get complete decomposition. The CO_2 amount produced was analyzed online by TCD to determine the CO_2 capture amount. For the cyclic performance tests, the carbonation-calcination cycle was repeated 50 times.

3. RESULTS AND DISCUSSION

3.1 Properties of the pretreated $CaO/Ca_3Al_2O_6$ sorbents

3.1.1 Crystallographic structure of the pretreated sorbents

The XRD patterns of C9A1 and the sorbents pretreated in steam atmosphere at different temperatures were presented in Figure 1. It was obvious that all the obtained sorbents only had two phases, CaO (JCPDS 48-1467) and $Ca_3Al_2O_6$ (JCPDS 38-1429). No Al_2O_3 crystal or $Ca(OH)_2$ were found in all specimens. This indicated that $Ca(OH)_2$ could be completely decomposed into CaO after it was calcined at 700 °C for 30 min, and the thermal pretreatment in steam atmosphere did not change the crystallographic structure of C9A1 sorbents. However, compared to C9A1, the pretreated sorbents possessed lower diffraction peak height, which related to the variation in the crystalline degree of CaO grains. Based on the calculation from Scherrer's formula for the strongest diffraction peak (200), the grain sizes of these samples were shown in Table 1. It was found that the grain size of CaO decreased with the increasing steam pretreated temperature, and the C9A1-250 obtained a minimum grain size of 37.9 nm.
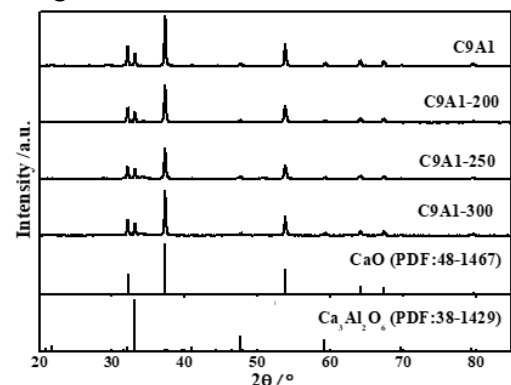

Fig. 1. The XRD patterns of C9A1and the sorbents pretreated

Table 1. CaO grain size in C9A1 and the sorbents pretreated in steam atmosphere at different temperatures

Sorbents	C9A1	C9A1-200	C9A1-250	C9A1-300
Grain size / nm	47.7	38.3	37.9	41.1

3.1.2 Textural and surface properties of the pretreated sorbents

The textural properties of C9A1 and the sorbents pretreated in steam atmosphere at different temperatures were summarized in Table 2. It was observed that the sorbents pretreated at higher temperature led to a higher surface area, and 250 °C is the optimum temperature. The C9A1-250 possessed a highest surface area of 17.4 $m^2·g^{-1}$, which would enable more CaO to be exposed. Moreover, it is clear in Figure 2 that all the samples present villiform porous structures, the abundant existing pore with larger pore volume (Table 2) were beneficial to the CO_2 diffusion through product layer and the increase of CO_2 sorption capacity.

Table 2. BET surface area and pore volume of C9A1 and the sorbents pretreated in steam atmosphere at different temperatures

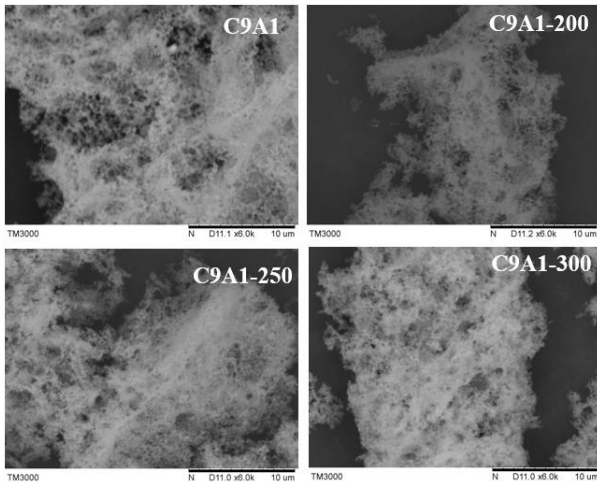| Sample	BET surface area / $m^2·g^{-1}$	Pore volume / $cm^3·g^{-1}$	Pore radius / nm
C9A1	8.9	0.030	38.2
C9A1-200	16.9	0.123	21.9
C9A1-250	17.4	0.089	1801
C9A1-300	17.3	0.128	21.0

Fig. 2. SEM images of C9A1 and the sorbents pretreated in steam atmosphere at different temperatures

3.2 CO_2 sorption performance of the pretreated sorbents

The CO_2 sorption capacity and cyclic sorption stability of the pretreated C9A1 sorbents were shown in Figure 3. It was seen that the initial CO_2 sorption capacity of the C9A1-200, C9A1-250 and C9A1-300 were greatly enhanced. For instance, C9A1 had an initial CO_2 sorption capacity of 4.85 mmol·g^{-1}, while that of C9A1-200, C9A1-250 and C9A1-300 were 7.81, 8.53 and 7.25 mmol·g^{-1}, respectively. On the other hand, as described above, the theoretical sorption capacity of C9A1 should be 13.13 mmol $CO_2·g^{-1}$ sorbent. Accordingly, the C9A1-250 had the maximum reactive CaO ratio of 65.0%. Even though the initial CO_2 sorption capacity decreased to 7.25 mmol $CO_2·g^{-1}$ sorbent when C9A1 was pretreated at 300 °C in steam atmosphere, it was still higher than that of C9A1. This phenomenon was due to the smaller grain size of CaO existing in the pretreated C9A1 samples. In the pretreated process, temperature would determine the amount of generated $CaCO_3$ in the carbonation stage [7]. Since the calcination temperature of the pretreated C9A1 (700 °C) was lower than that of the C9A1 (900 °C) in the preparation process, and the calcination time of the pretreated C9A1 (30 min) was also shorter (1.5 h for C9A1), both of which were beneficial to the production of smaller CaO grain size. Moreover, there were abundant CO_2 in the calcination process, which would accelerate the generation of larger pore volume. The mechanism might be described as Figure 4.
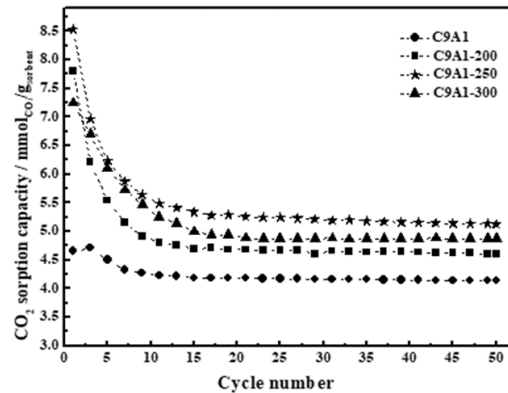

Fig.3 CO_2 sorption performance of C9A1 and the sorbents pretreated in steam atmosphere at different temperatures
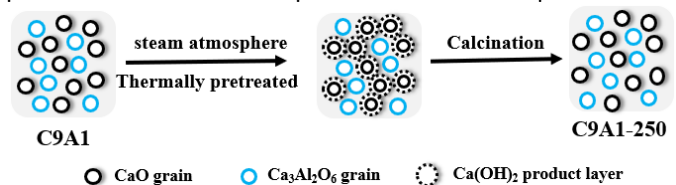

Fig. 4. The mechanism of CO_2 pretreatment for sorbents

The cyclic sorption stability of the pretreated C9A1 sorbents could also be obtained from Figure 3. Compared to the C9A1 sorbent, though the cyclic sorption stability of pretreated C9A1 decreased, the CO_2 sorption capacity was still higher than that of C9A1. For instance, the CO_2 sorption capacity of C9A1-250

decreases from 8.03 mmol·g^{-1} to 4.62 mmol·g^{-1} after 50th run, which was still 10% higher than that of C9A1. The main decrease in CO_2 sorption capacity occurred mainly before 15th cycling. This could be attributed to the instability of the pretreated C9A1. When C9A1 was thermally pretreated in steam atmosphere, the CaO grain size became smaller and the surface area increased, which was prone to suffer sintering, because they contain more surface free energy and are more instable. As the carbonation-calcination process proceeded, the surface area and porosity of the powder would decrease gradually, but it is difficult to remove the pores in grains and particles entirely with the decreasing of the original surface free energy. In the end, the surface area and porosity of sorbents become steady, which was contributed to the cyclic sorption stability of pretreated C9A1.

4. CONCLUSION

CaO/Ca$_3$Al$_2$O$_6$ sorbents with mass ratio of CaO to Al$_2$O$_3$ of 9:1 were pretreated in steam atmosphere at different temperatures for its influence on CO_2 sorption capacity and cyclic stability. It is found that the sorbents pretreated by steam at 250 °C possessed 8.53 mmol·g^{-1}, and showed 5.12 mmol·g^{-1} after 50th run, which was still 10% higher than that of the original (no pretreatment) sample. The higher CO_2 sorption capacity was ascribed to the smaller grain size of CaO and its higher surface area. The gradual decreased cyclic stability was attributed to the decreasing of the original surface free energy.

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