Applied Energy 220 (2018) 419–425

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Self-activation of $CaO/Ca_3Al_2O_6$ sorbents by thermally pretreated in CO_2 atmosphere☆

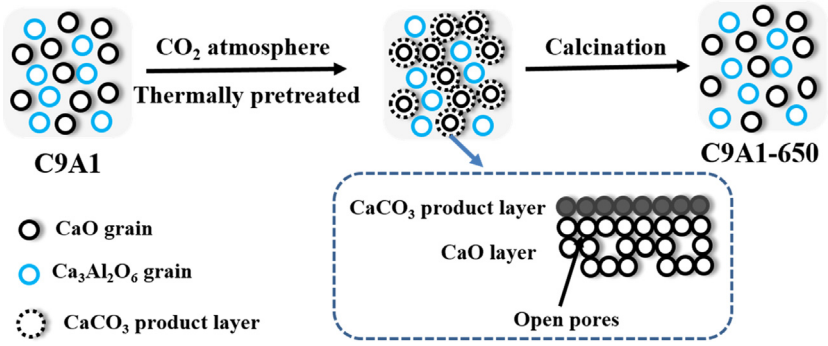
Jie-ying Jing*, Xue-wei Zhang, Qing Li, Ting-yu Li, Wen-ying Li*

Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education and Shanxi Province, Taiyuan 030024, PR China
Training Base of State Key Laboratory of Coal Science and Technology Jointly Constructed by Shanxi Province and Ministry of Science and Technology, Taiyuan 030024, PR China

HIGHLIGHTS

- C9A1-650 obtained the best cyclic sorption performance.
- Self-activation provided smaller grain size and higher surface area.
- Self-activation gave sorbents high absorptivity.
- The cyclic sorption stability was due to the small original surface free energy.
- C9A1-650 provided 98.9% H_2 concentration in SEMSR process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
$CaO/Ca_3Al_2O_6$
Thermal pretreatment
Self-activation
Sorption capacity
Cyclic sorption stability

ABSTRACT

$CaO/Ca_3Al_2O_6$ sorbents have been proved to be a promising sorbent for CO_2 sorption. However, the sorbents still suffer from low CO_2 sorption capacity. In this work, self-activation was generated via thermally pretreating $CaO/Ca_3Al_2O_6$ sorbents in CO_2 atmosphere at various temperatures to enhance the CO_2 sorption capacity of $CaO/Ca_3Al_2O_6$ sorbents. Results showed that the thermally pretreated temperature plays an overwhelming role in the CO_2 sorption capacity and stability of the $CaO/Ca_3Al_2O_6$ sorbents. Superior CO_2 sorption capacity (8.01 mmol g^{-1} for C9A1-650 at 500 °C) is achieved, which is 72% higher than that of C9A1 (no pretreatment sample). After 50 carbonation-calcination cycles, the CO_2 sorption capacity of C9A1-650 still remained 20% higher than that of C9A1. The high CO_2 sorption capacity is ascribed to the smaller CaO grain size (37.1 nm) and the higher surface area (13.1 $m^2 g^{-1}$), resulting from the self-activation process. Meanwhile, the CO_2 cyclic sorption stability is due to the small original surface free energy. Furthermore, the C9A1-650 sorbent is employed to use in sorption enhanced methane steam reforming process. It provides a H_2 concentration of 98.9% and CH_4 conversion of 98.7%, presenting greatly potential in practical application.

☆ The short version of the paper was presented at ICAE2017, Aug 21-24, Cardiff, UK. This paper is a substantial extension of the short version of the conference paper.

* Corresponding authors at: Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education and Shanxi Province, Taiyuan 030024, PR China.
E-mail addresses: jingjieying@tyut.edu.cn (J.-y. Jing), ying@tyut.edu.cn (W.-y. Li).

https://doi.org/10.1016/j.apenergy.2018.03.069
Received 9 January 2018; Received in revised form 26 February 2018; Accepted 25 March 2018
Available online 30 March 2018

1. Introduction

Hydrogen (H_2) is a promising clean, efficient energy and could be used as a potential alternative for conventional fossil fuel which is associated with greenhouse gases emission. It is desirable that H_2 can be produced from renewable sources such as wind power or solar energy. However, due to the current technical and economical limitations, methane steam reforming (MSR) process has been most widely used to produce H_2 in chemical industry [1,2]. Because of the strong endothermic characteristics of MSR, a high temperature is usually required to achieve a high CH_4 conversion, which would result in high-energy consumption. Moreover, in order to obtain high pure H_2 (higher than 99.9%), pressure swing adsorption (PSA) has to be employed to separate H_2 from the product mixture of H_2 and CO_2, and this separation process accounts for around 50% energy cost in the whole process. Sorption enhanced methane steam reforming (SEMSR) has been recently regarded as a desirable route to economically provide hydrogen (H_2) and reduce carbon dioxide (CO_2) emission [3]. Compared to the MSR process, the CO_2 produced in the SEMSR process could be removed in-situ to produce high concentration of H_2 in a single step through integrating catalysts with CO_2 sorbents in the system. More importantly, after CO_2 was in-situ removed, the reaction equilibrium would be shifted and the reaction temperature would decrease from 800–900 °C to 500–600 °C, which could not only greatly reduce energy consumption and simplify technology process, but also decline the requirements for the apparatus.

As a key part of the SEMSR, CaO-based CO_2 sorbents are widely used because of its high theoretical sorption capacity (17.86 mmol g^{-1}), extensive sources and inexpensive cost [4,5]. However, the CO_2 sorption capacity and cyclic stability of the CaO-based sorbents still remain to be improved for the loss of CO_2 sorption capacity during the repeated carbonation-calcination cycles, which is derived from the sintering of CaO grains [6–8].

In order to prevent the sorbent grains from sintering during the carbonation-calcination cycles so as to provide higher surface area and proper pore structure, promising strategies have been proposed to improve the cyclic sorption performance of CaO sorbents, involving thermal pretreatment [9,10], incorporation of supports or dopants [11], modification of precursors [12,13], and hydration treatment [14–16]. Among these approaches, the addition of dopants shows the most promising stable behavior. A variety of materials have been extensively tested as supports or dopants for CaO-based sorbents recently, such as: (1) $Ca_{12}Al_{14}O_{33}$, $Ca_3Al_2O_6$, $CaZrO_3$, MgO, ect. which formed during preparation process when doped the third element into CaO [17–19]; (2) attapulgite [20], mineral rejects [21], etc. Due to its prospective performance and low cost, Al-doped materials were greatly investigated. Li et al. first incorporated Al into CaO sorbents and synthesized CaO/$Ca_{12}Al_{14}O_{33}$ sorbents to improve the cyclic stability of CaO sorbents [22]. Zhou et al. investigated the influence of calcium and aluminum precursors and produced different forms of calcium aluminate inert supports. They reported that the CaO/$Ca_9Al_6O_{18}$ sorbent prepared by calcium citrate and aluminum nitrate exhibited the best performance for CO_2 capture [11]. In our recent studies [23], we successfully modified CaO sorbents by incorporating Al to obtain CaO/$Ca_3Al_2O_6$ sorbents. It was found that the CO_2 sorption capacity and stability were greatly affected by the relative quantity of CaO to Al_2O_3. When the mass ratio of CaO to Al_2O_3 is 9:1 (the obtained sorbent was denoted as C9A1), an initial CO_2 sorption capacity of 4.85 mmol g^{-1} was achieved at 500 °C, and 84.5% sorption capacity was retained even after 100 carbonation-calcination cycles. Though the synthesized CaO/$Ca_3Al_2O_6$ sorbent (C9A1) shows 5–10% higher CO_2 sorption capacity than the other Al-doped sorbents reported in the literature [24,25], it should be noted that there is still a gap between the theoretical value (13.13 mmol g^{-1} for C9A1) and the current level (4.85 mmol g^{-1}). Thus, to further improve the CaO/$Ca_3Al_2O_6$ sorbents sorption performance at lower sorption temperature (500 °C) and provide guidance for its industrial application, it is reasonable to modify C9A1 sorbent so as to enhance its CO_2 sorption performance.

It is well-known that the reaction between CaO and CO_2 is a gas-solid non-catalytic reaction. In the calcination process, as the reaction proceeded, the unreacted CaO was gradually packed by the product layer, therefore, a very fast kinetically-controlled stage turns to a slow diffusion-controlled stage [26]. It has been proved that 40–70% CO_2 sorption capacity was contributed by the kinetically-controlled stage, which was closely related to the surface area and pore structure of CaO sorbents; while the slow diffusion-controlled stage was mainly controlled by the CO_2 diffusion through the product layer. In order to obtain a higher CO_2 sorption capacity, it is essential to simultaneously improve the structure of C9A1 sorbent and enhance the CO_2 diffusion rate.

Thermal pretreatment of CaO sorbent was an amazing approach, which sometimes showed the self-activation with increasing cycle number and has been elucidated by the formation of a hard and stable skeleton during the pretreatment which increased the solid-state diffusion carbonation in the first cycle. A renovated porous skeleton with increased surface area could be achieved via a quick calcination process [27,28]. Currently, self-activation has been proved to be affected by many experimental variables, including temperature, pretreated duration, presence of impurities/additives, and looping-carbonation conditions etc. [27–30]. It was reported that Al addition, a prolonged duration could significantly enhance self-reactivation at higher temperature (800–1300 °C) [29,30]. However, it should be noted that the CaO sorbents were generally pretreated at 800–1300 °C in the reported literatures, and it did not present the potential merit of SEMSR, which would decrease the reaction temperature from 800–900 °C to 500–600 °C. Too high temperature would cause more energy consumption and increase the requirements for the apparatus.

In this work, based on our previous investigation, thermal pretreatment is employed to treat CaO/$Ca_3Al_2O_6$ sorbents with the aim of generating self-reactivation to improve its CO_2 sorption performance. The pretreatment occured in CO_2 atmosphere at lower temperature (500–700 °C), not N_2 atmosphere at 800–1300 °C as reported previously [27–30]. The effect of various pretreated temperature on the structure, morphology and CO_2 sorption performance were investigated to obtain superior CO_2 sorption capacity and stability. The self-activation mechanism of CaO/$Ca_3Al_2O_6$ sorbents by thermally pretreated in CO_2 atmosphere was also proposed. Furthermore, the resultant pretreated CaO/$Ca_3Al_2O_6$ sorbents was used in SEMSR process to evaluate its catalytic performance when it was combined together with Ni/CeO_2-ZrO_2 catalyst.

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 ratio of 9:1 (C9A1) were prepared via a modified sol–gel method according to our previous study [23]. In a typical process, 13.28 g calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), 2.57 g aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), and 13.26 g citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) were dissolved in 50 mL distilled water, and then the pH value of the solution was adjusted to 1 by the addition of ammonia ($NH_3{\cdot}H_2O$). The mixture was then stirred vigorously for 1 h to obtain a uniform sol. The condensation reaction was followed and performed at 80 °C for 6 h. The resulting compound was placed at room temperature for 18 h to form a wet gel and dried at 100 °C for 10 h, then dried at 120 °C for another 10 h, and eventually at 140 °C for 5 h until a low density foam was formed. Finally, the foam was crushed to powder and calcinated at 900 °C for 1.5 h. The prepared sorbent was marked as C9A1.