

Enhanced CO₂ sorption performance of CaO/Ca₃Al₂O₆ sorbents and its sintering-resistance mechanism



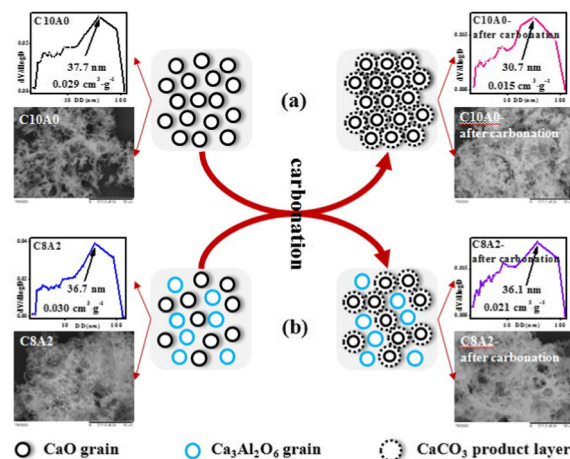
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HIGHLIGHTS

- Sorbent with CaO/Al₂O₃ mass ratio of 8:2 obtained the best cyclic sorption performance.
- Ca₃Al₂O₆ reduced CO₂ diffusion resistance and gave sorbents high absorptivity.
- The cyclic sorption stability is due to the small original surface free energy.

GRAPHICAL ABSTRACT



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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. However, the sorbents suffer from decreasing CO₂ sorption capacity and stability due to the sintering of CaO grains. In this study, we modified CaO sorbents by incorporating Al to obtain CaO/Ca₃Al₂O₆ sorbents via a modified sol-gel method. CO₂ sorption evaluation shows that the relative quantity of CaO to Al₂O₃ plays an overwhelming role in the CO₂ sorption capacity and stability of the CaO/Ca₃Al₂O₆ sorbents. Superior CO₂ sorption ratio (51.92% for sorbent C8A2 at 500 °C) is achieved, which is 5 times higher than that of the as-synthesized pure CaO sorbent. The high CO₂ sorption ratio is due to the existence of inert Ca₃Al₂O₆, which decreases the diffusion resistance of CO₂ through product layer during the carbonation reaction. Meanwhile, the superior CO₂ cyclic sorption stability is ascribed to the small original surface free energy of the as-synthesized sorbents.

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1. Introduction

Hydrogen (H₂) is an increasingly important clean, efficient energy now and probable the primary energy in future, since the greenhouse gases emission caused by fossil fuel has become a

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growing environmental problem. Currently, around 96% H₂ is produced from fossil fuel, and methane steam reforming (MSR) process accounts for about 50% of the H₂ production in the chemical industry [1,2]. However, this H₂ production process involves a strong endothermic reaction (high temperature), CO shift reaction, and the separation and purification of by-products carbon dioxide (CO₂) and H₂. All these factors finally result in a high-energy consumption, especially the reaction and separation process, which contributed to around 50% energy cost in the whole process.

Sorption enhanced methane steam reforming (SEMSR) is a potential approach to economically provide H₂ and reduce CO₂ emission. It has recently raised widespread concerns due to the advantages of its reducing energy consumption and simplifying technology compared to the traditional process (methane steam reforming, MSR). According to the Le Chatelier's principle, the CO₂ produced in SEMSR process could be removed in-situ to produce high concentration of H₂ in a single step through integrating catalysts with CO₂ sorbents in the system. Moreover, the reaction equilibrium would be shifted and the reaction temperature will be decreased from 800–900 °C to 500–600 °C [3–7]. In this process, the CO₂ sorbent plays a greatly important role because it determines the extent of the equilibrium shift. Due to its high theoretical sorption capacity (17.86 mmol CO₂·g⁻¹ CaO), inexpensive cost and extensive sources, calcium oxide (CaO) is frequently used in this process to capture CO₂ [8–11]. In a typical sorption process, the carbonation production of CaO, CaCO₃, would always decompose to give CaO for cyclic CO₂ absorption processes. However, most natural CaO sorbents, for example, limestone, suffer from the rapid loss of reactivity in cyclic utilization.

Many researches have proved that the main reason of sorbents deactivation derived from the sintering of CaO grains, which would result in the decrease of sorbents surface area and pore volume, and finally the decay of CO₂ sorption capacity [12–16]. It is reported that the CO₂ sorption capacity of natural CaO sorbents always dropped to a residual value of 7–8% after long cycles of carbonation-calcination [17], which would greatly increase the cost of CO₂ capture technology. Thus, it is urgent to develop new materials that possess high and stable sorption performance to accelerate the industrial application of CaO sorbents.

In order to enhance the cyclic sorption performance of CaO-based sorbent, there are many strategies proposed, such as thermal pretreatment [18–20]; hydration treatment [21–23]; modification of precursors [24,25]; and incorporation of supports or dopants [26]. Regrettably, none of these technologies is effective and suitable for industrial production scale. For instance, Manovic et al. examined the thermal activation of different types of CaO-based sorbents and observed that the pretreated sorbents showed better conversions than the original sorbents over a longer series of CO₂ cycles [20]. Nevertheless, plenty of researches had proved that the sorbents would lose a lot of initial sorption capacity after thermal retreatment due to the reduction of pore volume [18,26]. Blamey et al. employed steam hydration to reactivate the spent CaO-based sorbents. It is found that a higher CaO conversion were obtained after the steam hydration treatment [21]. However, the reactivated sorbents from this method appeared to become mechanically fragile, and the mass loss of sorbents in fluidized bed was increased [27,28]. Liu et al. studied the CO₂ capture capability of sorbents derived from different precursors and observed that the CaO derived from calcium D-gluconate monohydrate exhibited the best capacity [24]. Nevertheless, the use of organic-salts would raise the cost of sorbents preparation, which must be concerned in industrial production scale.

Considering both the sorption performance and the cost for industrial production, the most promising technology is the incorporation of CaO into inert materials. These materials included Al₂O₃ [29–32], MgO [30,33], ZrO₂ [34], TiO₂ [35], attapulgite [36],

and minerals in tailings [37] etc., among which Al-containing materials were greatly investigated due to its remarkable performance and low cost. Li et al. first doped CaO by Al and obtained the sorbents CaO/Ca₁₂Al₁₄O₃₃, in which Ca₁₂Al₁₄O₃₃ was the inert compound. They discovered that the as-synthesized sorbents had significantly improved cyclic stability [38]. After the study, a large number of works about Al-doped sorbents had been investigated, involving different synthesis methods [39], different operation conditions [40] and the utilizations in SEMSR process [41,42]. Zhou et al. prepared CaO-based sorbents incorporated with Al using a wet mixing method with different calcium and aluminum precursors, and prepared different forms of calcium aluminate inert supports. They reported that the CaO/Ca₉Al₆O₁₈ sorbent derived from calcium citrate and aluminum nitrate possessed the best performance for CO₂ capture [43]. Radfarnia et al. prepared an Al-stabilized CaO sorbent by using a citrate-assisted sol-gel technique. The sorption capacity of the optimal sorbent remained on 12.95 mmol CO₂·g⁻¹ sorbent after 31 cycles without deactivation under 100% N₂ atmosphere [44].

In these previous studies, most of the obtained Al-doped sorbents possessed enhanced sorption capacity and cyclic sorption stability. A large number of researches referenced the effect of catalyst support on active metal and proposed that the inert support can inhibit the sintering of CaO grains in the CaO-based sorbents [38,44]. However, some researchers indicated that the prevention effect of inert support on CaO grains sintering was not observed [45]. Moreover, a part of studies observed that impurities increased the rate of sintering of CaO grains [46]. To the best of our knowledge, the question whether the inert material had prevention effect on CaO grains sintering and the real theory of the enhanced sorption performance of Al-doped sorbents had never been in-depth discussed. In addition, it should be noted that the sorption performance of sorbents were usually conducted at a high sorption temperature (650–900 °C), which did not present the potential merit of SEMSR (decreasing the reaction temperature from 800–900 °C to 500–600 °C). If the SEMSR was conducted at 500–600 °C, it will not only save considerable energy in real application, but also decline the requirements for the apparatus. Thus, in order to improve the sorbents sorption performance at lower sorption temperature (500 °C) and provide guidance for future work to accelerate its industrial application, it is urgent to know the mechanism about the enhanced sorption performance of Al-doped sorbents.

In this work, we doped the CaO with Al to get CO₂ sorbents with strong cyclic sorption capacity and stability at 500 °C. The effects of the relative quantity of CaO to Al₂O₃ on the structure, morphology and CO₂ sorption performance were investigated to obtain superior CO₂ sorption capacity and stability. The mechanism about the enhanced cyclic sorption performance of Al-doped sorbents was also postulated.

2. Experimental

2.1. Sorbents preparation

The CaO/Ca₃Al₂O₆ sorbents with varying mass ratios of CaO to Al₂O₃ were prepared via a modified sol-gel method. In a typical process, the predetermined amounts of calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O), and citric acid monohydrate (C₆H₈O₇·H₂O) were dissolved in distilled water, with a metal ion to water molar ratio of 1:40 and a metal ion to citric acid molar ratio of 1:1. Subsequently, the pH value of the solution was adjusted to 1 by the addition of ammonia (NH₃·H₂O). The mixture was then stirred vigorously for 1 h to obtain a uniform sol. Then the condensation reaction was performed at 80 °C for 6 h. The resulting compound was placed

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