Fuel 235 (2019) 1070–1076

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Development of Ca/KIT-6 adsorbents for high temperature CO_2 capture

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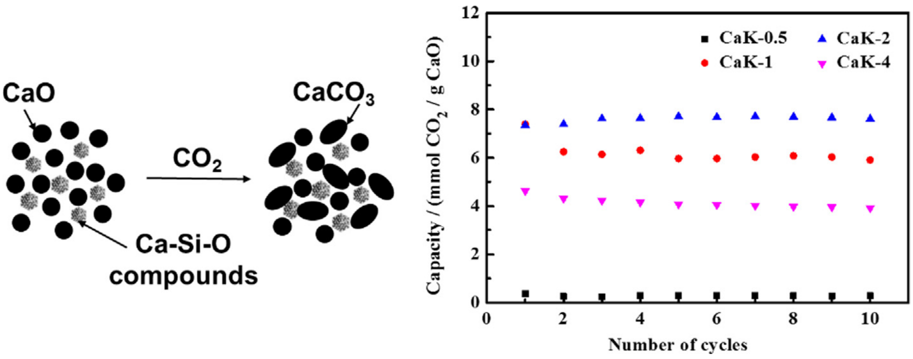
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
CaO
Mesoporous silica
KIT-6
CO_2 capture
Adsorbent

ABSTRACT

The incorporation of CaO into an inert porous solid support has been identified as an effective approach to improve the stability of adsorbents for CO_2 capture. In this work, we focus on enhancing the capacity of carbon capture and cyclic stability of CaO by impregnating CaO particles into a three-dimensional mesoporous silica (KIT-6) support. At a low CaO loading, the three-dimensional mesoporous support was filled with CaO nanoparticles. The further increase of CaO loading resulted in the aggregation of CaO particles on the external surface of the support material, as identified by electron microscopy analysis. These CaO/KIT-6 adsorbents show excellent high-temperature CO_2 carbonation/calcination stability over multiple cycles of CaO carbonation and calcination. The enhancement of the performance of carbon capture is attributed to the interaction between CaO and the silica skeleton of KIT-6 through the formation of interfacial $CaSiO_3$ and Ca_2SiO_4 which enhanced the resistance of CaO sintering.

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https://doi.org/10.1016/j.fuel.2018.07.044
Received 16 March 2018; Received in revised form 6 July 2018; Accepted 9 July 2018

1. Introduction

CO_2 emissions are major contributions to climate change and ocean acidification [1,2]. Natural concentration of atmospheric CO_2 ranges from 180 to 300 ppm [3]. However, the current concentration of CO_2 is over 407 ppm owing to the combustion of fossil fuels [4,5]. With global economic growth, especially for developing countries, the atmospheric CO_2 concentration is likely to be further increased. Thus technologies for carbon capture are gaining worldwide interest [6–8]. At high temperature (~700 °C), CaO-based adsorbent can be used for carbon capture and for sorption-enhanced hydrogen reaction [9]. In addition, the production of synthetic natural gas could be directly produced from the captured CO_2 using multifunctional catalytic adsorbents [10].

Calcium oxide is a promising high-temperature CO_2 adsorbent, due to its high theoretical capacity of carbon capture (17.8 mmol CO_2 g^{-1} CaO), and its low cost and high abundance [11–13]. The major limitation of CaO-based adsorbents, in particular at high temperature, is their intrinsic low resistance to particle sintering during the multicycle operation [14–16]. Thus a poor carbonation/calcination reversibility is obtained due to the inhibition of CO_2 diffusion through $CaCO_3$, a product formed on the surface of CaO during carbon capture. Several methods have been reported to enhance the capacity of CO_2 uptake and to reduce the sintering of CaO particles for carbon capture using CaO-based adsorbents. One of these methods is called controlled precipitation which can produce small and uniform porous CaO particles [17]. Furthermore, the pre-treatment of adsorbents through steam hydration [18,19] and acid modification [20] has been investigated to introduce cracks within the CaO particles to reduce the blockage of pores during carbon capture [19]. Manovic et al. [15] investigated steam reactivation of a spent adsorbent. It was reported that both the reversibility and the capacity of CO_2 capture were enhanced for the reactivated adsorbent compared to the parent material. In addition, the pre-treatment of limestone using acetic acid, conducted by Li et al [20], significantly decreased the crystallite size of CaO, enhancing the resistance to CaO sintering.

The addition of a second metal oxide represents another alternative strategy to improve the sintering resistance of CaO-based adsorbents [21,22]. Metal oxides such as MgO [21], Y_2O_3 [23] and CeO_2 [24] can act as a discrete second phase or react with CaO producing a mixed oxide material such as $Ca_{12}Al_{14}O_{33}$ [22], $CaTiO_3$ [25], $CaZrO_3$ [26] and $CaSiO_3$ [27]. Albrecht et al. introduced 20 wt% MgO into a CaO-based adsorbent, which enhanced the stability of the adsorbent owing to the finely dispersed MgO species [21]. Zhang et al. [23] synthesized a series of Y_2O_3-modified CaO adsorbents via a sol-gel method. With the introduction of Y_2O_3, the carbonation of CaO was significantly improved. In addition, a mixed oxide ($Ca_{12}Al_{14}O_{33}$) was produced via the addition of $Al(NO_3)_3{\cdot}9H_2O$. The authors reported a high CO_2 capture capacity of 10.2 mmol g^{-1} over 13 cycles carbonation and calcination using the $Ca_{12}Al_{14}O_{33}$) enhanced adsorbent [22]. However, the addition of expensive oxides, e.g. Y_2O_3, CeO_2 and TiO_2, will reduce the economic viability of the carbon capture process.

SiO_2 represents a cost-effective and widely available sinter-resistant metalloid oxide. Zhao et al. described a sol-gel method to synthesize a porous SiO_2 supported CaO, with an optimal Si:Ca ratio possessing a capture capacity of 7.5 mmol g^{-1} [27]. The material displayed an excellent stability over 50 cycles of carbonation and calcination due to the presence of Ca-O-Si and specific porosity of the adsorbent. Mesoporous silicas, MCM-48 modified with organosilane amines [28] and CaO/SBA-15 [29], have shown high capacities of CO_2 capture, revealing the feasibility of using both three-dimensional Ia3d and two-dimensional P6mm architectures as the support materials for CaO particles. KIT-6, a mesoporous SiO_2 combining the Ia3d architecture akin to MCM-48 but with larger pore diameters, has attracted attention in recent years due to its optimal physicochemical properties that enhance metal dispersion and subsequent accessibility of reactants [30,31].

Here we applied KIT-6, a highly stable CO_2 inert silica framework, as a support for CaO which was employed for high-temperature CO_2 carbonation. To our knowledge, this is the first time to use the mesoporous silica KIT-6 in CaO based CO_2 capture system. Its physicochemical properties could enhance the stability of CaO, potentially via the formation of interfacial Ca-rich mixed oxide phases, whilst simultaneously allowing superior carbonation/calcination reversibility due to the reduced effect of pore blockage arising from its three-dimensional pore structure. The effect of CaO doping concentration and the resulting influence on CO_2 capture were studied within a fixed bed reactor, with characterisations by in-situ X-ray diffraction (XRD), nitrogen adsorption-desorption, scanning electron microscopy (SEM) coupled to an energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM).

2. Experimental sections

2.1. Materials preparation

Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, 99.0% purity, Sigma-Aldrich) was used as the CaO precursor, with the KIT-6 mesoporous silica support synthesized by a non-ionic surfactant templating approach according to the procedure reported by Kleitz et al. [32].

The KIT-6 supported CaO-based adsorbents were synthesized using wet impregnation method. In a typical experiment, 4.217 g $Ca(NO_3)_2{\cdot}4H_2O$, corresponding to 1 g CaO, was dissolved in 25 mL distilled water. After the precursor was completely dissolved under continuous stirring at 80 °C, 0.5 g KIT-6 was then added to the calcium nitrate solution. The solution was kept static for 24 h at room temperature, prior to the evaporation of water at 80 °C. The solid product was calcined in a muffle furnace at 500 °C for 6 h with a heating rate of 2 °C min^{-1}. The resulting adsorbents are donated as CaK-x, where x represents the weight ratio of CaO to KIT-6, which was varied to give values of 0.5, 1, 2 and 4. A commercial CaO (Sigma-Aldrich, 99.99%), dried overnight at 130 °C, was used as a reference adsorbent.

2.2. Cyclic CO_2 capture tests

The performance of the CaK-x adsorbents for carbon capture was measured using an SDT Q600 thermogravimetric analyzer (TGA). The adsorbent (~10 mg) was loaded in an alumina crucible and activated by heating to 850 °C at a ramp rate of 15 °C min^{-1} under pure N_2 flow (1 bar, 100 mL min^{-1}) with the sample held at temperature for 10 min. The carbonation was performed under 15% CO_2 in N_2 (1 bar, 100 mL min^{-1}) at 600 °C for 30 min. The atmosphere was then switched to pure N_2 (1 bar, 100 mL min^{-1}) and the sample was heated to 800 °C at 15 °C min^{-1} and held for 10 min. The cycles of CaO carbonation/calcination were repeated 10 times.

In order to compare the performance of CO_2 capture using the CaK-x adsorbents, the capacity of CO_2 capture and the carbonation conversion are used.

The capacity of CO_2 capture was calculated according to the following formula:

$$\text{Uptake capacity (mmol g}^{-1}\text{)} = \text{mmol of CO}_2\text{/g of CaO} \tag{1}$$

The carbonation conversion of the sample was calculated using Eq. (2).

$$X_N\,(\%) = \frac{m_N - m_1}{m_0\text{Â}{\cdot}b}\text{Â}{\cdot}\frac{M_{CaO}}{M_{CO_2}}\text{Â}{\cdot}100\% \tag{2}$$

where X_N is carbonation conversion of sample, N is the number of cycles, m_0 is the initial mass of sample, b is the content of CaO in the synthesized sample, m_N is mass of the carbonated sample after N cycles, m_1 is mass of sample after calcination (mass of sample after each calcination is the same), and M_{CaO} and $M_{CO_2}$are mole mass of CaO and CO_2, respectively.