



Experimental study on CO₂ capture mechanisms using Na₂ZrO₃ sorbents synthesized by soft chemistry method



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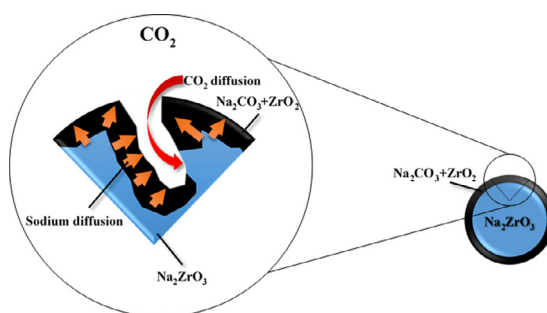
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HIGHLIGHTS

- Na₂C₂O₄-derived Na₂ZrO₃ sorbents by heated and freeze dryings were firstly reported.
- Freeze drying and resulting superior porosity did not favor CO₂ sorption.
- CO₂ diffusion and Na diffusion were two major mechanisms for CO₂ sorption.
- Sintering inhibited CO₂ diffusion but favored Na diffusion enhancing CO₂ capture.
- 800 °C was identified as the most favorable temperature for Na₂ZrO₃ to capture CO₂.

GRAPHICAL ABSTRACT



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ABSTRACT

The CO₂ capture performances were demonstrated for Na₂ZrO₃ sorbents prepared by soft chemistry using varied sodium precursors and drying methods. It was found that 'Na₂C₂O₄ precursor + heated drying' enabled superior sorption capacity (e.g. 22.77 wt% CO₂ uptake within 10 min at 800 °C in a 15 vol% CO₂ stream balanced by N₂) to the other precursor-drying combinations. The as-identified strongest sorbent was further investigated at a series of carbonation temperatures (400–800 °C) in N₂-balanced purging streams with 15 vol% and 50 vol% CO₂, corresponding post- and pre-combustion CO₂ capture scenarios, respectively. The analysis of the resulting sorption capacity, stability and kinetics suggests that sodium diffusion is a more efficient driver than CO₂ diffusion for the capture of CO₂. Sintering and the subsequent densification inhibits CO₂ diffusion but enhances sodium diffusion, which leads to a positive overall effect on the sorption performance. Hence, unlike other high-temperature solid sorbents such as CaO, sintering resistance during cyclic sorption is not a necessity for Na₂ZrO₃. In addition, higher CO₂ fractions in the feed gas improve the sorption kinetics and stability by promoting sodium diffusion as well as CO₂ diffusion.

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1. Introduction

The growing concern of global warming has been seriously raising the demand of carbon capture technologies. The heat from

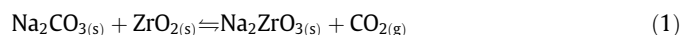
burning of fossil fuel is still the major energy source for current world's economy. About 75% of carbon dioxide (CO₂) emissions are from fossil fuel combustion in the past several decades [1]. The feasible strategies to capture CO₂ include pre-combustion and post-combustion processes, which remove CO₂ from the gas streams before and after the consumption of feedstock, respectively. A number of techniques have been used to remove CO₂, such as membrane separation [2–7], amine-scrubbing [8–11], cryogenic

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distillation [12–14], and solid sorbents [15–17]. Among these technologies, solid sorbents are of great interests for its compatibility to not only post-combustion but also pre-combustion processes. A typical application for the latter is to use sorbents along with catalysts in so called sorption-enhanced steam reforming (SESR) realizing in-situ CO₂ capture and enhancement in H₂ selectivity. For this purpose, the sorbents should be able to work at high-temperature zones (>400 °C) where both reforming and sorption happen simultaneously.

One such sorbent which has been intensively examined is CaO due to its high theoretical sorption capacity and abundance on earth. However, it was well known that CaO-based sorbents suffer from rapid decays over multiple cycles due to sintering deactivation, which has yet to be well addressed so far [18,19]. In view of this, sorbents with decent cyclic stability are of great interest for CO₂ capture. Alkali metal zirconates such as Li₂ZrO₃ and Na₂ZrO₃ seem as promising options in multiple carbonation-calcination cycles over a wide range of temperatures (room temperature up to 800 °C) [20–22]. Especially, Na₂ZrO₃ is economically and technically favorable over Li₂ZrO₃ and attracting emerging attention as CO₂ captor. Na₂ZrO₃ can be synthesized by a simple solid-state reaction from Na₂CO₃ and ZrO₂ (Eq. (1)) [20–23].



The reported capacity of CO₂ capture using Na₂ZrO₃ sorbents ranged from 17 to 23.8 wt% [20–26]. Despite the lower capacity of Na₂ZrO₃ than that of CaO, the constant performance of Na₂ZrO₃ during repeated cycles of carbonation-calcination is advantageous in industrial perspective [22]. However, only a few works regarding Na₂ZrO₃ as CO₂ captor have been reported. According to the limited number of literature, soft-chemistry method was mostly used for synthesis of Na₂ZrO₃ due to its superiority over solid-state method [24–29]. But, to our knowledge, further studies are still needed to systematically investigate the effects from precursor, drying method, and carbonation conditions such as temperature and CO₂ partial pressure. In this paper, sodium oxalate for the first time was utilized as Na₂ZrO₃ precursor and the CO₂ capture performance was compared against the sorbents made from sodium citrate which is currently the best precursor in open literatures. For the synthesis process, freeze drying (FD) was employed to compare the CO₂ sorption with samples prepared by conventional soft-chemistry synthesis route.

2. Experimental

2.1. Soft chemistry synthesis

Sodium oxalate (abbreviated as NaOX), Na₂C₂O₄, and sodium citrate (abbreviated as NaCA), Na₃C₆H₅O₇·2H₂O, were used as Na precursors; zirconium nitrate, Zr(NO₃)₄, was as Zr precursor. In order to approach 100% purity of the Na₂ZrO₃ product, stoichiometric molar ratio of Na and Zr (2:1) was adopted. To uniformly mix the Na and Zr species, precursors were co-dissolved in a solution instead of dry mixing. 0.03 mol Zr(NO₃)₄ was dissolved in 100 ml DI water and the obtained solution was equally divided into two batches, i.e. two 50-ml solutions containing 0.015 mol Zr²⁺, respectively. Meanwhile, two Na⁺ solutions were prepared by dissolving 0.015 mol NaOX and 0.01 mol NaCA in 50 ml DI water, respectively. Then, the Na solutions were added into the Zr ones, with flocculent precipitates observed, which resulted in cloudy solutions. Additional 50 ml oxalic acid (0.4 mol L⁻¹) and citric acid (0.4 mol L⁻¹) were dropwisely added into the NaOX-Zr(NO₃)₄ and NaCA-Zr(NO₃)₄ solutions, respectively, until clear solutions are re-formed [30]. Magnetic stirring for 1 h was performed to guarantee the homogeneity of these solutions. Then each solution was

divided into two batches. The first batch was dried by freeze drying method, i.e. freezing the liquid precursor at –86 °C followed by 24 h sublimation under vacuum; the other batch was directly dried in a fan oven, evaporating moisture at 60 °C within 24 h. 4 as-synthesized samples were referred to as: NaOX_HD, NaOX_FD, NaCA_HD and NaCA_FD, indicating oxalate (OX) and citrate (CA) Na precursors, and heated-drying (HD) and freeze-drying origins (FD), respectively.

2.2. Carbonation-and-calcination cycles

CO₂ capture performance was examined by TA50 Thermo-gravimetric Analyzer (TGA). The dried precursor powders obtained from the above mentioned soft-chemistry method were loaded into TGA with a sample size of 20 ± 0.1 mg, subject to a complete calcination in pure N₂ at 900 °C for 10 min prior to the carbonation-calcination cycles. The solid-state reaction (Eq.(1)) eventually happened during calcination with formation of Na₂ZrO₃. Following a cooling to target temperatures (varied from 400 to 800 °C), five cycles were repeated starting from carbonation for 10 min and ending with calcination at 900 °C for 10 min. A total gas purging rate was fixed at 100 ml min⁻¹, and during carbonation, two volumetric fractions of CO₂ were adopted, i.e. 15 vol% and 50 vol% with a purpose to simulate post-combustion (flue gas decarbonization) and pre-combustion (SESR) CO₂ capture scenarios, respectively. N₂ was fed at the same time as the balancing gas. During calcination, CO₂ gas was switched to N₂ enabling a pure N₂ purging stream. To ensure the precision of the tested results, each condition was repeated twice.

2.3. Sorbents characterization

The prepared samples were characterized by N₂ physisorption using a Quantachrome autosorb iQ-C instrument to measure the Brunauer–Emmett–Teller (BET) surface area, and Barrett–Joyner–Halenda (BJH) pore size and pore volume. Prior to the measurement, the as-prepared samples were subject to outgassing at 300 °C until successfully passing a leak test, i.e. pressure increment in the outgassing chamber less than 25 mtor min⁻¹ with the pumping system off. Powder X-ray diffraction (XRD, D/Max 2500 V+/PC) was performed to search and match the detected phases to the International Centre for Diffraction Data (ICDD) PDF2 database. The microstructure of the prepared sorbents was also characterized by scanning electron microscopy (SEM, Zeiss MERLIN VP Compact).

3. Results and discussion

3.1. Screening of sodium precursors and synthesis methods

Fig. 1 shows the CO₂ uptakes using the 4 as-synthesized samples over the five cycles with the carbonation temperature at 800 °C (detailed conditions can be found in Section 2.2; similarly hereinafter). It can be observed that, for the 1st cycle, the Na₂ZrO₃ sorbent made from NaOX precursor by heated drying presented the highest capacity (22.78 wt%) and fastest sorption rate. Using NaCA as precursor caused a bit drop in CO₂ capture capacity for the heated-drying samples, i.e. 20.49 wt%. Nevertheless, this performance is notably superior to those of previously reported sorbents synthesized in the same method such as 17 wt% [25], 17.5 wt% [26] and 19.6 wt% [24]. This is probably due to the addition of citric acid which improves the homogeneity of the mixed solutions (refer to the observation of cloudy solutions in Section 2.2). The sorbent made from NaCA by freeze drying

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