Alkaline zirconates as effective materials for hydrogen production through consecutive carbon dioxide capture and conversion in methane dry reforming

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ABSTRACT

In this work, H_2 production was evaluated using different carbonation conditions and two alkaline zirconates. For this purpose, Li_2ZrO_3 and Na_2ZrO_3 were synthesized, characterized and tested on a consecutive process composed of initial CO_2 capture, followed by methane dry reforming (MDR). Thermogravimetric results showed that under the four gas mixtures tested (diluted and saturated CO_2, CO and CO-O_2), both ceramics are able to chemisorb CO_2, with Na_2ZrO_3 having the highest capture with saturated CO_2. In catalytic tests, ceramics carbonated with saturated CO_2 or CO-O_2 gas flows were able to act as sorbents and catalysts, producing H_2 at T > 750 °C through the partial oxidation of methane. This reaction was produced because CO_2 desorption did not occur, thus avoiding the MDR process. On the other hand, carbonated ceramics under a CO-O_2 gas mixture presented an outstanding catalytic performance. Between 450 and 750 °C, H_2 was formed through the MDR process promoted by CO_2 desorption from both ceramics. This result is in line with CO_2 desorption results, where a weaker CO_2–solid interaction was observed in comparison with saturated CO_2. Afterward, both ceramics presented a similar catalytic behavior, good regeneration and cyclability after the double process proposed (CO_2 capture-MDR reaction). Lithium zirconate also presented high thermal stability during cycle tests; meanwhile, sodium zirconate showed an important H_2 production increase as a function of cycles. Finally, both materials are feasible options for producing a clean energy source in a moderate temperature range through the catalytic conversion of two greenhouse gases (CO_2 and CH_4).

1. Introduction

Twenty years ago, Nakagawa and Ohashi [1] published the first report about CO_2 chemisorption on alkaline ceramics (lithium zirconate, Li_2ZrO_3) at high temperatures. Since then, several authors have reported many other alkaline ceramics as possible CO_2 chemisorbents, including sodium zirconate (Na_2ZrO_3) [2–5].

Focusing on lithium [1,6–9] and sodium [10–15] zirconates, the lithium version has a theoretical CO_2 capture capacity of 6.5 mmol of CO_2 per gram of ceramic (mmol$_{CO2}$/g), although it presents moderate CO_2 capture efficiency and kinetic properties between 400 and 600 °C. Accordingly, different studies have reported Li_2ZrO_3 structural or microstructural modifications to improve some of their CO_2 capture properties [7,16–18]. For example, Radfarnia and Iliuta [16]

synthesized porous Li_2ZrO_3 nanoparticles, producing microstructural changes. They observed better CO_2 sorption rates and efficiencies on porous nanopowders than those obtained with Li_2ZrO_3 prepared by traditional methods (solid-state reaction). On the other hand, Peltzer et al. [17] prepared K-doped Li_2ZrO_3, implying a chemical modification. In that case, a K-doped Li_2ZrO_3 sample presented significant CO_2 capture improvements with respect to undoped Li_2ZrO_3, even after 30 CO_2 sorption-desorption cycles. In contrast, Na_2ZrO_3 has a slightly lower theoretical CO_2 capture capacity (5.4 mmol CO_2/g) in comparison to lithium zirconate, but it presents higher CO_2 capture kinetics in a wide temperature range (250–800 °C) [15,19–21]. For example, a recent work published by Zhao et al. [20] showed that Na_2ZrO_3 has a rapid CO_2 sorption when it is prepared by the spray-dried method, enhancing CO_2 sorption-desorption cyclic stability.

Moreover, in recent years, both zirconates and other alkaline ceramics have been proposed for different catalytic processes as catalysts or bifunctional materials [22–29]. Li_2ZrO_3 and Na_2ZrO_3 have been tested as possible basic heterogeneous catalysts for transesterification reactions of different molecules [25,26]. Recently, some alkaline zirconates have been used in the CO oxidation reaction, showing complete conversions to CO_2 between 450 and 600 °C and subsequent capture of CO_2 that was produced [30]. Correspondingly, among the possible bifunctionality of these ceramics, they have been tested as catalysts and CO_2 sorbents for different processes involving hydrogen production or purification [31–37]. For example, Zhao et al. [31] tested Na_2ZrO_3 as bifunctional catalyst-sorbent using cellulose as a biomass source under pyrolytic conditions, where Na_2ZrO_3 showed an important catalytic influence during pyrolysis catalyzing tar cracking and reforming reactions. Na_2ZrO_3 positively enhanced hydrogen production from cellulose, removing the CO_2 that was produced. In a different work, Wang et al. [35] described the use of Ni-based sorbents in a sorption-enhanced glycerol steam reforming process, showing H_2 production up to 85% and CO_2 removal on multi-cycle processes. This outcome was achieved due to the Ni species evolved to form stable Ni species, avoiding coke formation during the reforming reaction. Finally, Mendoza-Nieto et al. [34] proposed a modified process for H_2 production by two consecutive steps in the presence of Na_2ZrO_3: CO_2 capture over alkaline ceramics, followed by a catalytic reaction using CO_2 captured previously as a reagent in methane dry reforming (MDR). NiO-containing Na_2ZrO_3 samples were able both trap CO_2 chemically in a wide temperature range (200–900 °C) and produce hydrogen from 500 to 900 °C, depending on the NiO load used. The H_2 production and temperature reaction were importantly improved as a function of NiO content. Thus, 10% of H_2 at 900 °C was the highest amount observed with pristine Na_2ZrO_3; meanwhile, H_2 production of 27% was obtained using the sample with the highest NiO content (10%wt.). Additionally, that work showed the possibility of cycling the entire process using a re-oxidized sample, positioning NiO-doped sodium zirconate as a potential bifunctional material with good performance during H_2 production through a modified MDR process. This process was proposed considering that methane dry reforming is typically performed at temperatures between 700 and 900 °C, as this reaction is an endothermic process. Ni-based catalysts are the most common materials used for DRM, considering their low cost in comparison with noble metal catalysts, including Ru-, Rh- and Pt-based catalysts. Nevertheless, problems with carbon deposition may damage Ni catalyst performance [38].

Based on all previous reports described above, the aim of the present work was to analyze the possibility of using free-nickel alkaline ceramics, such as Li_2ZrO_3 and Na_2ZrO_3, as bifunctional materials in the following modified process: CO_2 capture continued by a subsequent MDR process. Thus, the influence of two variables (ceramic type and gas mixture used in CO_2 capture) over H_2 production was analyzed. For this purpose, different gas mixtures were employed (CO_2, CO or CO-O_2).

2. Experimental section

2.1. Synthesis and characterization of alkaline zirconates

Li_2ZrO_3 and Na_2ZrO_3 were synthesized by the well-known procedure of solid-state reaction as previously reported [14,26,30]. Zirconium oxide (ZrO_2, Aldrich) and lithium carbonate (Li_2CO_3, Aldrich) or sodium carbonate (Na_2CO_3, Aldrich) were used as reagents without any further treatment. Precursor salts were mechanically mixed and calcined in an air atmosphere at 900 °C for 12 h with a heating rate of 5 °C/min. Due to the high tendency of lithium and sodium to sublimate at temperatures higher than 700 °C, 10 wt% of carbonate excesses were considered [39,40].

Alkaline zirconates were structural and microstructurally

characterized by powder X-ray diffraction (XRD) and N_2 adsorption-desorption. XRD patterns were recorded in the $10° \leq 2\Theta \leq 80°$ range with a goniometer speed of 2°(2Θ) min^{-1} using a Siemens D5000 diffractometer coupled to a cobalt anode ($\lambda = 1.789$ Å) X-ray tube. Then, nitrogen adsorption-desorption isotherms were measured with Bel-Japan Minisorp II equipment at 77 K using a multipoint technique. Prior to physisorption experiments, samples were degassed at room temperature for 12 h in vacuum (p < 10^{-1} Pa). The specific surface area (S_{BET}) of each material was calculated according to the BET model.

2.2. CO_2 capture and CH_4 reforming process

CO_2 sorption ability was evaluated by performing different thermogravimetric analyses (TGA) with a TA Instruments Q500HR thermobalance. Both zirconates, Li_2ZrO_3 and Na_2ZrO_3, were heat-treated from room temperature up to 900 °C with a heating rate of 3 °C/min. These experiments were performed with ~50 mg of sample and a total flow rate of 60 mL/min under the following gas mixtures using nitrogen (N_2, Praxair grade 4.8) as balance gas: i) saturated CO_2 ($P_{CO2} = 1.0$, Praxair grade 3.0), ii) diluted CO_2 ($P_{CO2} = 0.05$), iii) diluted CO ($P_{CO} = 0.05$, Praxair certificate standard) and iv) CO-O_2 mixture ($P_{CO} = P_{O2} = 0.05$, Praxair grade 2.6 for O_2). The aim of using different gas mixtures was to evaluate if CO_2 obtained through different sources affects carbonation behavior of these ceramics. Additionally, it has to be pointed out that the CO experiments were performed considering that CO oxidation can occur with alkaline ceramics producing CO_2 that is subsequently captured [30]. Additionally, some isothermal experiments were performed at 600 °C during 3 h. In these tests, the samples were heated up to 600 °C (5 °C/min) using N_2 (40 mL/min) as the carrier gas. Once the desired temperature was achieved, the flow gas was switched to a saturated CO_2 or CO-O_2 mixture. Afterward, isothermal products were analyzed by CO_2 Temperature-Programmed Desorption (CO_2-TPD) with a chemisorption analyzer (Belcat, Bel-Japan) to obtain information about the desorption abilities of each material. CO_2-TPD analyses were performed by heating each sample up to 850 °C (heating rate of 2 °C/min) in a He flow of 30 mL/min. The data were quantified by a thermal conductivity detector (TCD).

To understand and complement the experimental results obtained during the capture process, *ab initio* thermodynamic calculations were performed by combining density functional theory (DFT) with the lattice phonon dynamics approach [41]. For this purpose, capture reactions of both solids were normalized by one mol of carbon monoxide or carbon dioxide (CO_x) and expressed as follows in Eq. (1):

$$\sum_{Ri} n_{Ri} solid_{Ri} + CO_x \leftrightarrow \sum_{Pj} n_{Pj} solid_{Pj} \tag{1}$$
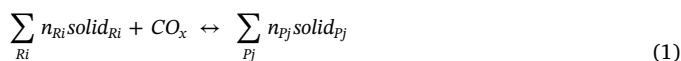
where n_{Ri} and n_{Pj} represent the moles of reactants (R_i) and products (P_j), respectively, involved in each reaction. The gas phase was treated as an ideal gas. By assuming that difference between chemical potentials ($\Delta\mu°$) of reactants (R_i) and products (P_j), the value can be approximated by the difference in their total energies (ΔE^{DFT}), obtained in DFT calculations; by their vibrational free energies of phonon dynamics; and by ignoring the PV contribution terms for solids. Thus, the variation in the Gibbs free energy (ΔG) as a function of temperature and CO_x pressure can be written as follows (Eq. (2)):

$$\Delta G(T, P) = \Delta\mu^0(T) - RT Ln\left(\frac{P_{COx}}{P_0}\right) \tag{2}$$

where

$$\Delta\mu^0(T) \approx \Delta E^{DFT} + \Delta E_{ZP} + \Delta F^{PH}(T) - G^0_{COx}(T) \tag{3}$$

Here, ΔE^{DFT} is the DFT energy difference between the reactants and products. ΔE_{ZP} is the zero point energy difference between the reactants and products obtained directly from phonon calculations. ΔF^{PH} is the phonon free energy change excluding zero-point energy (which is