



## Research Paper

# Nickel-doped sodium zirconate catalysts for carbon dioxide storage and hydrogen production through dry methane reforming process



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## ABSTRACT

NiO-doped sodium zirconate ceramics with different amounts of NiO (between 0 and 10 wt%) were synthesized and characterized by powder XRD, SEM-EDS and N<sub>2</sub> physisorption. Structural and microstructural characteristics of a Na<sub>2</sub>ZrO<sub>3</sub> based-ceramic were maintained in all NiO-containing samples. These materials were tested for CO<sub>2</sub> capture (TGA), desorption processes (TPD) and dry CH<sub>4</sub> reforming (DMR, catalytic tests). Initially, samples were dynamically tested for CO<sub>2</sub> chemisorption; these tests showed a slight inhibition for CO<sub>2</sub> capture due to the presence of NiO, which partially blocked Na<sub>2</sub>ZrO<sub>3</sub> surface sites where CO<sub>2</sub> can be chemisorbed. Then, NiO-doped samples were carbonated and exposed to a CH<sub>4</sub> flow in order to perform DMR reaction, using carbonate samples as CO<sub>2</sub> source. In all cases, NiO addition resulted in greater production of H<sub>2</sub> than that of pure Na<sub>2</sub>ZrO<sub>3</sub>. Additionally, a drastic reduction in the reaction temperature was observed, especially for NiO-doped Na<sub>2</sub>ZrO<sub>3</sub> containing 10 wt% of NiO. Additionally, regeneration and cyclic behavior showed that it is possible to accomplish consecutive cycles of CO<sub>2</sub> capture-DMR with considerable Na<sub>2</sub>ZrO<sub>3</sub> regeneration. On the other hand, cyclability was affected due to a partial NiO reduction after DMR steps. However, if a pre-oxidation step was performed, the catalytic activity and H<sub>2</sub> production were recovered. Hence, it was established that NiO-doped Na<sub>2</sub>ZrO<sub>3</sub> materials can be used as bifunctional materials as (i) CO<sub>2</sub> captors and then as (ii) catalytic materials during DMR reaction.

## 1. Introduction

In recent decades, methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) emissions have been responsible for climate change and global warming, as both gases are the major contributors to the greenhouse effect [1]. Although the concentration of methane in the atmosphere is much lower than that of CO<sub>2</sub>, methane more effectively absorbs infrared radiation, and thus, its contribution to planet warming is significantly higher than that of CO<sub>2</sub> [2]. However, carbon dioxide emissions are the main contaminants and contribute almost 60% for enhancing greenhouse effect each year, whereas methane is the primary component of natural gas and is responsible for 15% of global warming [2–4]. One option for limiting greenhouse effects is to reduce the emission of both gases by converting them into an alternative and cleaner energy source. In this regard, hydrogen (H<sub>2</sub>) production through the use of greenhouse gases would be a viable option [6–8]. Among H<sub>2</sub> production processes, the most commonly used are dry methane reforming (DMR) [9–12],

steam methane reforming (SMR) [13,14], sorption-enhanced methane reforming (SEMR) [15–17], water-gas shift reaction (WGSR) [18–20] and ethanol-steam reforming (ESR) [21–23]. These processes all produce synthetic gas (syngas), which is composed of H<sub>2</sub> and carbon oxides (CO or CO<sub>2</sub>), depending on the process utilized and reaction conditions. Hence, CO or CO<sub>2</sub> removal is usually a key step to purify H<sub>2</sub>. Thus, different technologies have been developed over the past few years to accomplish this necessity [24].

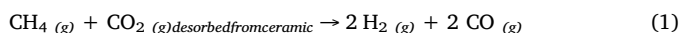
In particular, dry CH<sub>4</sub> reforming does have some disadvantages: (1) the reforming reaction is highly endothermic; (2) high temperatures are required to obtain high conversions, which leads to catalyst deactivation by coke formation; and (3) the H<sub>2</sub> purity from this process is low, and additional operations, such as purification, separation and compression techniques, must be used [25,26]. To achieve this goal, it has been necessary to use two different materials: one acting as a catalyst and a suitable chemical sorbent to eliminate the remaining CO<sub>2</sub> [16,17].

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In this sense, Ni-based materials supported over different metal oxides are the most used materials for performing DMR, e.g., Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [9], Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [10] or Ni/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> [11]. On the other hand, CO<sub>2</sub> capture and storage (CCS) [5,27,28] can be achieved using different alkali (Li, Na and K) and earth-alkaline (Be, Mg and Ca) metal-based ceramics as chemical sorbents [29–34], as these CCS materials present high superficial basicity, good sorption-desorption kinetics, thermal stability, high regeneration ability, mechanical strength and selective CO<sub>2</sub> sorption [35].

Recently, sodium zirconate (Na<sub>2</sub>ZrO<sub>3</sub>) [36] and NiO-CaO composites [37] were synthesized, characterized and tested as possible bifunctional materials, acting as both CO<sub>2</sub> sorbents and then as catalysts for dry CH<sub>4</sub> reforming to obtain a consecutive CO<sub>2</sub> capture and DMR processes. Those results clearly showed that both materials capture CO<sub>2</sub>, store it and then supply CO<sub>2</sub> during the DMR process (reaction (1)), thereby producing H<sub>2</sub> at T > 800 °C with Na<sub>2</sub>ZrO<sub>3</sub>; however, NiO-CaO showed a better catalytic behavior (~500 °C). With these results in mind, the aim of this work was to determine whether NiO addition modifies the CO<sub>2</sub> chemisorption on Na<sub>2</sub>ZrO<sub>3</sub> as well as the catalytic activity for H<sub>2</sub> production through the DMR process.



## 2. Experimental section

### 2.1. Synthesis and characterization of NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> materials

Sodium zirconate doped with different nickel oxide loadings were synthesized *via* acetate decomposition. Hereinafter, NiO-doped materials are labeled NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub>, where x represents the NiO loading used (x = 0.0, 2.5, 5.0, 7.5 and 10 wt%). Sodium acetate (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, Aldrich), zirconium acetate solution in acetic acid (Zr(C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)<sub>4</sub>, 16.1 wt% Zr, Aldrich) and nickel acetate tetrahydrate (Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, 98%, Aldrich) were used as reagents. Due to the likelihood of Na sublimation at temperatures higher than 800 °C, a 15.0 wt% excess of NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> was considered [35,38]. Acetate precursors were dissolved in water and heated at 60 °C until a paste was obtained. A solid product was obtained after two stages of calcination in static air: (1) first, acetate decomposition was carried out *via* heating at 400 °C for 6 h, then (2) the sodium zirconate crystalline structure was obtained *via* heating at 900 °C for 12 h.

NiO-containing catalysts were structurally and microstructurally characterized by powder X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption and analytical scanning electron microscopy (SEM-EDS). XRD patterns were recorded in the 10° ≤ 2θ ≤ 70° range with a goniometer speed of 1° (2θ) min<sup>-1</sup>, using a Siemens D5000 diffractometer coupled to a cobalt anode (λ = 1.789 Å) X-ray tube. Once the NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> crystalline structures were determined, nitrogen adsorption-desorption isotherms were measured with a 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<sup>-1</sup> Pa). The specific surface area (S<sub>BET</sub>) for each material was calculated with a BET model. CO<sub>2</sub> temperature-programmed desorption (TPD) analyses were performed using a chemisorption analyzer (Belcat, Bel-Japan). Before each analysis, approximately 50 mg of sample was introduced into a quartz cell and pretreated at 850 °C under a He flow (30 mL/min). Each sample was then cooled to 200 °C and saturated with a 60 mL/min flow of CO<sub>2</sub> for 60 min. Afterwards, CO<sub>2</sub>-TPD analyses were performed by heating each sample up to 850 °C (heating rate of 2 °C/min) in a He flow, and the data were quantified by a thermal conductivity detector (TCD). Finally, scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectroscopy (EDS) measurements were recorded on a FE-SEM JEOL JSM 7800F electron microscope equipped with an energy dispersive analysis detector Oxford 50 mm<sup>2</sup> X-Max. The acceleration voltage used was 20 kV and a

backscattered electron detector.

### 2.2. CO<sub>2</sub> capture and DMR processes

Carbon dioxide capture tests were performed in a Q500HR thermobalance from TA Instruments. NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> samples were heat-treated dynamically from room temperature to 950 °C (heating rate of 3 °C/min). These experiments were performed using ~40 mg of sample and a carbon dioxide (CO<sub>2</sub>, Praxair grade 3.0) flow rate of 60 mL/min. After CO<sub>2</sub> capture analysis, NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> catalysts were tested in the dry reforming reaction (DMR) following a previously published procedure [36], using 200 mg of sample in a Bel-Rea catalytic reactor from Bel-Japan. First, NiO-doped samples were carbonated dynamically from 30 to 600 °C (heating rate of 5 °C/min) and then isothermally treated at 600 °C for 0.5 h. Finally, samples were cooled to 200 °C, using a gas mixture composed of 60 vol% CO<sub>2</sub> and 40 vol% N<sub>2</sub> (Praxair grade 4.8). Once samples were carbonated and partially cooled down to 200 °C, the dry methane reforming (DMR) process was performed from 200 to 900 °C (heating rate of 2 °C/min) using 100 mL/min of a gas mixture composed of CH<sub>4</sub> (5 vol%, Praxair grade 5.0) and N<sub>2</sub> balanced. In addition, cyclic experiments of CO<sub>2</sub> capture and subsequent DMR tests were performed with the NiO(10)-Na<sub>2</sub>ZrO<sub>3</sub> catalyst. This procedure was performed using the same experimental conditions described above during 5 cycles, adding a sixth cycle, where CO<sub>2</sub> capture and DMR processes were performed after a previous oxidation step under 30 mL of O<sub>2</sub> at 600 °C for 2 h. Reforming gas products were analyzed every 15 °C up to 900 °C (dynamic experiments), or every 8.3 min (isothermal experiments), using a Shimadzu GC-2014 gas chromatograph with a Carbonex-1000 column. After DMR isothermal experiments, some materials were re-characterized by XRD.

## 3. Results and discussion

### 3.1. Characterization of NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> materials

Powder XRD patterns for NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> samples (0 ≤ x ≤ 10) are shown in Fig. 1. As expected, Na<sub>2</sub>ZrO<sub>3</sub> crystalline planes were observed (PDF file 35-0770) in the pure sample (x = 0.0). X-ray patterns for Na<sub>2</sub>ZrO<sub>3</sub> materials doped with different NiO amounts showed the same sodium zirconate crystalline structure. However, Na<sub>2</sub>ZrO<sub>3</sub> reflections shifted as a function of nickel oxide content, which indicate some changes in the crystalline unit cell. In addition to Na<sub>2</sub>ZrO<sub>3</sub> crystalline variations, these XRD patterns presented three other reflections located at 43.8, 50.9 and 74.6°, in 2θ scale, which increased as a function of the

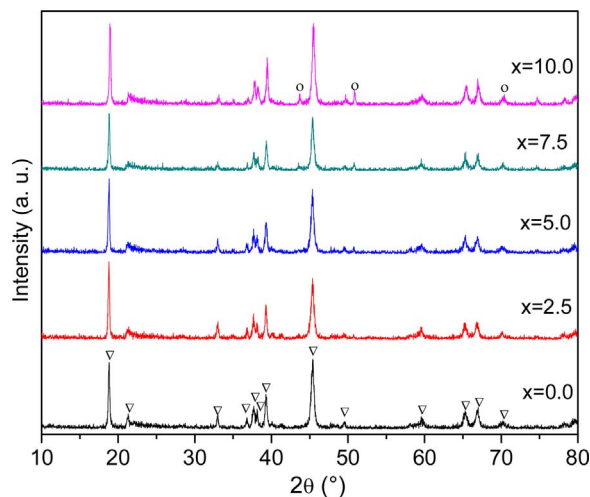


Fig. 1. NiO(x)-Na<sub>2</sub>ZrO<sub>3</sub> XRD patterns. Crystalline phases were labeled as; (▽) Na<sub>2</sub>ZrO<sub>3</sub> and (○) NiO.

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