



# Effect of reflux digestion treatment on the catalytic performance of Ni–CaO–ZrO<sub>2</sub> nanocomposite catalysts for CO<sub>2</sub> reforming of CH<sub>4</sub>



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## ABSTRACT

Ni–CaO–ZrO<sub>2</sub> nanocomposite catalysts with high activity and low coke formation for CO<sub>2</sub> reforming of CH<sub>4</sub> are developed by the co-precipitation method followed by a reflux digestion (aging) process. The effects of hot water treatment of the Ni–Ca–Zr containing precipitates on the structures and catalytic performance of the catalysts are systematically investigated. Results indicated that reflux temperature and time dramatically affect the textural properties, crystal phases, metal dispersion, and the metal–support interaction of the catalysts as indicated by the N<sub>2</sub> adsorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), chemisorption, and temperature programmed reduction (TPR) results. The reflux digestion with a higher temperature and a longer time substantially increases the surface areas of the catalyst, decreases the particle size in the mixed oxides, and also enhances the metal–support interaction, thus giving a higher activity and stability of the catalyst. The Ni–CaO–ZrO<sub>2</sub> nanocomposite catalyst refluxed at 100 °C for 24 h exhibits a stable activity over 800 h without deactivation at a GHSV of 79,000 ml/(h g) at 850 °C due to the restriction of Ni particle sintering and less coke formation. The relationship between the reflux treatment and catalytic performance is discussed.

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## 1. Introduction

Methane is expected to take a more important role in the future energy system. Recently, the exploration and utilization of non-traditional natural gases (such as shale gas, coal-bed methane) which are widely discovered all over the world, is considered as a near-term solution to the depletion of oil and gas and the increase of energy demand [1]. Developing an efficient CO<sub>2</sub> reforming of methane (dry reforming) process for synthesis gas production is highly interesting for many downstream uses where a lower H<sub>2</sub>/CO ratio is required [2–4]. In addition, the CH<sub>4</sub> and CO<sub>2</sub> coexist in some cases, such as biogases, field gases and tail gases in coal to chemical industries [5,6]. Furthermore, both CO<sub>2</sub> and CH<sub>4</sub> are considered as the main contributors to the 'global warming effect', their chemical utilization has been becoming more and more important in reducing the direct emission to atmosphere. As a consequence, catalytic CO<sub>2</sub> reforming of CH<sub>4</sub> has been proposed as one of most effective routes for utilization of these two most abundant gases with green house effect.

Great efforts have been made on developing the catalysts with high activity and stability for CO<sub>2</sub> and CH<sub>4</sub> reforming reaction. Noble metals such as Pt [7,8], Ru [9], Rh [10] et al. exhibit high activities and carbon resistance properties, but their utilization in large scale was limited by high cost and scarcity. Nickel-based catalysts present a comparable activity to noble metals for CO<sub>2</sub> and CH<sub>4</sub> reforming [11–13]. However, Ni-based catalysts tend to be deactivated by the sintering and carbon deposition [2,4,13,14].

Various methods to improve the activity and stability of Ni-based catalysts have been addressed. Firstly, decreasing Ni particle size is found effectively to inhibit the coke deposition [15,16], which can be achieved by forming a solid solution [12,17,18], spinel [19] or perovskite-typed catalysts [20,21], and nanocomposite catalysts [15,22–24]. Secondly, using basic supports or promoters (such as MgO, CaO, K<sub>2</sub>O, etc.) to promote the reaction between CO<sub>2</sub> and carbon, thus decreasing the carbon deposition on the surface of catalysts [25–27]. Thirdly, using redox supports or promoters (such as CeO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, etc.) can also reduce carbon deposition on catalysts by the reaction between carbon and the lattice oxygen formed in these redox oxides [28–30]. Lastly, a stronger interaction between Ni and support can stabilize the Ni particles, thus simultaneously reducing the sintering and carbon deposition on the catalysts [31–33]. Obviously, if a catalyst has a basic promoter, redox support, smaller Ni particles and strong metal–support interaction together, it might present a high activity

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and stability for CO<sub>2</sub>–CH<sub>4</sub> reforming. Consequently, base promoted Ni/ZrO<sub>2</sub> catalysts have been reported as a promising catalyst for CO<sub>2</sub>–CH<sub>4</sub> reforming [23,27,34]. However, the final catalyst structure is highly dependent on the preparation procedure, and a clear structure–performance relationship of Ni–CaO–ZrO<sub>2</sub> for CO<sub>2</sub>–CH<sub>4</sub> reforming is still absent.

In this work, Ni–CaO–ZrO<sub>2</sub> nanocomposite catalysts were developed by the coprecipitation method, followed by a reflux digestion process (aging in hot water for a certain time). We herein emphasized the importance of this reflux-digestion step on the final catalytic performance. The textural properties, crystalline structures, morphology, and metal–support interaction of the formed catalysts under different reflux-digestion treatments were well characterized. Moreover, the formed catalysts were tested by co-feeding CO<sub>2</sub> and CH<sub>4</sub> at high temperature using a quartz reactor. It is found that reflux-digestion treatment at a higher temperature with a longer time plays a key role in the formation of a catalyst with a high activity and less coke formation. These observations are confirmed by the N<sub>2</sub> adsorption–desorption measurement, XRD, TPR, TEM, chemisorption, thermogravimetric analyzer (TGA). Finally, the mechanism of reflux digestion treatment on the catalytic performance is discussed.

## 2. Experimental

### 2.1. Preparation of the catalysts

The Ni–CaO–ZrO<sub>2</sub> nanocomposite catalysts were prepared by a coprecipitation method using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (molar ratio  $n_{\text{Ni}}:n_{\text{Ca}}:n_{\text{Zr}}=0.4:0.2:1$ ) as precursors, and NaOH as a precipitate agent. After precipitation at a pH 12, the formed slurry was aged at room temperature overnight, filtrated, and washed by de-ionized water for several times till the pH of the water was close to 7. Subsequently, the resulted solid was refluxed in de-ionized water at elevated temperatures for a certain time, and then filtered, dried at 120 °C for 24 h. The dried samples prepared under different reflux digestion conditions were assigned as NC–X–Y, where X and Y were denoted as the reflux temperature and time, respectively. The dried sample prepared without reflux was denoted as NC-0. The dried solids were then calcined at 600 °C in the static air for 5 h to obtain the nanocomposite catalysts, which are denoted as NC–X–Y–C. The NC–X–Y–C reduced at 700 °C in 5% H<sub>2</sub>/Ar mixture flow for 1 h is denoted as NC–X–Y–R.

### 2.2. Characterization

The pore structures of the nanocomposite catalysts were measured using a Micromeritics Tristar II 3020 instrument. Prior to the tests, the catalysts were degassed at 200 °C for 5 h under vacuum conditions. The specific surface areas ( $S_{\text{BET}}$ ) were obtained by the Brunauer–Emmett–Teller (BET) method, and pore volumes were calculated by a Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction (XRD) patterns were recorded by a Rigaku D/max-A X-ray diffractometer using a nickel-filtered Cu K $\alpha$  ( $\lambda=0.15418$  nm) radiation source at room temperature from 20° to 80° with a step rate of 6°/min. Assignment of XRD peaks was based on the Joint Committee Powder Diffraction Standard Card (JCPDS Card).

The morphology and microstructure of the samples were examined by a transmission electron microscope (JEOLJEM-2100F, 200 kV Field Emission, 0.14 nm lattice resolution). Prior to the examination, very small amounts of powder samples were dropped into the pure ethanol (99.99%), and treated in the ultra-sonic bath for 10 min to form suspension. Then a drop of the suspension was dispersed on the copper grid covered with a holey carbon film.

The reducibility of samples was studied by H<sub>2</sub> TPR. 50 mg of the sample was loaded in a U-shaped fixed-bed quartz reactor on a Micromeritics Autochem 2920 II. The calcined sample was flushed with Ar at 120 °C for 1 h, and then cooled down to 25–30 °C. Then the sample was heated (5 °C/min) from 25 to 1000 °C in 5% H<sub>2</sub>–Ar mixtures. H<sub>2</sub> consumption was monitored by a thermal conductivity detector throughout the reduction process. In addition, to confirm that NiO in the catalysts are fully reduced, another reduction program is used as follows: the sample was firstly treated in pure H<sub>2</sub> flow at 450 °C for 3 h, and flushed with Ar for 1 h, and then cooled down to 35 °C. Finally, the sample was heated at a ramp rate of 5 °C to 1000 °C in 5% H<sub>2</sub>–Ar mixture, and H<sub>2</sub> consumption was also recorded by the thermal conductivity detector.

The Ni dispersion in the reduced catalysts was performed by the static method on a Micromeritics ASAP-2020C instrument. Prior to measurement, the weighed catalyst (0.2 g) was treated in the pure hydrogen flow (50 ml/min) at 450 °C for 3 h or 700 °C for 1 h, followed by degassing treatment at the same temperature for 1 h in high vacuum conditions (10<sup>-1</sup> Pa) to eliminate chemisorbed H<sub>2</sub> and water. The isotherms were measured at 35 °C. The H/Ni ratios were based on the amounts adsorbed at zero pressure found by extrapolation of the linear part of the isotherm. Estimated dispersion was based on spherical geometry and an adsorption stoichiometry of H/Ni = 1. Using the different reduction temperature for oxide composites prior to the measurement is to check the dispersion variation during the high-temperature treatment.

Thermogravimetric analysis (TGA) measurements were carried out on a NETZSCH STA 449F3 thermogravimetric analyzer from room temperature to 1000 °C with the rate of 10 °C/min under air flow (50 ml/min).

### 2.3. Activity tests of the catalysts

The CH<sub>4</sub>–CO<sub>2</sub> reforming reaction was carried out at 850 °C (inlet temperature of reactor) in a quartz fix-bed reactor at atmospheric pressure. The reaction mixture of CO<sub>2</sub> and CH<sub>4</sub> (molar ratio 1.2:1) without dilution was fed with a gas hourly space velocity (GHSV) of 79 500 ml/(h·g). The weighed catalyst samples (0.1 g, 80–100 mesh) were diluted with inert acid-washed quartz powders (0.9 g, 80–100 mesh). Prior to the reaction, the calcined catalysts were reduced at 700 °C for 1 h using 50% H<sub>2</sub>–Ar mixture (120 ml/min), and were heated to 850 °C under the same H<sub>2</sub>/Ar flow. The effluent of the reactor was analyzed with on-line MicroGC (Inficon 3000) equipped with TCD. The conversion of CH<sub>4</sub> and CO<sub>2</sub>, and H<sub>2</sub>/CO ratio are calculated based on the flow rate measurement at outlet of reactor by a soap flow meter and the results from MicroGC. The spent catalysts after the reaction of CO<sub>2</sub> and methane reforming are designated by an additional letter, E, in their name (such as NC–X–Y–C–E).

## 3. Results

### 3.1. Pore structures of the NiO–CaO–ZrO<sub>2</sub> nanocomposites

The N<sub>2</sub> adsorption isotherms of the typical NiO–CaO–ZrO<sub>2</sub> nanocomposites with different reflux-digestion treatments are shown in Fig. 1b, whereas the comparison between the dried and calcined samples is shown in Fig. 1a. The corresponding pore structure parameters are collected in Table 1.

From Fig. 1a, we can find, for both samples, the N<sub>2</sub> adsorption capacity decreases after the sample is calcined at 600 °C for 5 h. The dried sample of NC-100 °C-24 h gives a much higher N<sub>2</sub> adsorption capacity (slightly over 250 cm<sup>3</sup>/g(STP) at 1 bar) than the NC-0 sample (about 125 cm<sup>3</sup>/g(STP) at 1 bar), indicating that after reflux digestion treatment, both surface areas (from 317 to 423 m<sup>2</sup>/g)

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