



Highly active and stable Ni-based bimodal pore catalyst for dry reforming of methane



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ABSTRACT

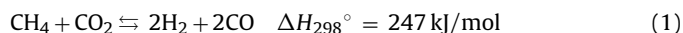
Bimodal pore NiCeMgAl catalysts were synthesized via the refluxed co-precipitation method. Methane reforming using carbon dioxide over this bimodal pore NiCeMgAl catalyst for syngas production was systematically studied by optimizing the active component NiO-loading, calcination temperature, reduction temperature and gas hourly space velocity (GHSV). The Ni₁₅CeMgAl sample with 15 wt% NiO loading, was found to be active enough at 750 °C with a high CH₄ conversion of 96.5%. The proper reduction temperature for the NiCeMgAl catalyst is either 550–650 °C or 850 °C. Higher calcination temperature favors the formation of NiAl₂O₄ and MgAl₂O₄ spinel structures. The Ni active sites derived from the NiAl₂O₄ spinel structure had longer stability than those from the free NiO. Compared with non-bimodal pore NiCeMgAl catalyst, bimodal pore NiCeMgAl catalyst has a longer stability in the feed gas without dilution. The large pores in the bimodal pore Ni₁₅CeMgAl catalyst were supposed to contribute to the quick molecule transfer during the dry reforming of methane (DRM) reaction when the GHSV was less than 96,000 h⁻¹. The evolution of the Ni₁₅CeMgAl catalyst before and after the DRM reaction was investigated by BET, XRD, TEM, and TGA techniques. A schema of the DRM reaction on the bimodal pore Ni₁₅CeMgAl catalyst was proposed, and the correlation between the structure evolution and catalytic performance change was also discussed.

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1. Introduction

Methane reforming with carbon dioxide, also called dry reforming of methane (DRM), is an endothermic reaction that occurs under the influence of a catalyst to generate synthesis gas (Eq. (1)), which can be applied in the Fischer–Tropsch (F–T) process to produce valuable products, such as hydrocarbons and oxygenates [1–4]. Growing attention has been paid to the F–T synthesis because of limited crude oil resources combined with increasing reveal of natural gas, shale gas or biogas from anaerobic digestion [5]. The importance of DRM lies not only in producing value-added chemicals through the gas-to-liquids process, but also in its ability to reduce emissions of CH₄ and CO₂, both greenhouse gases [6]. In addition, the DRM reaction can be applied to store energy via the conversion of solar to

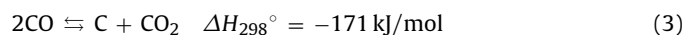
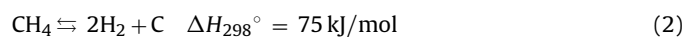
chemical energy, due to its highly endothermic characteristic [7,8].



Noble metal-based (Ru, Rh, Pt) and nickel-based catalysts are generally applied in the DRM reaction. Compared to the noble metal-based catalysts, nickel-based catalysts are more economic and suitable for industrial scale-up of the DRM process due to its low cost and high activity [9,10]. However, the use of nickel-based catalysts have been encountering a significant challenges due to active metal sintering and coke deposition, which leads to catalyst deactivation, and consequently poor stability [11,12]. The coke formation is mainly caused by methane decomposition (Eq. (2)) and the Boudouard reaction (Eq. (3)). However, it has been reported that the deactivation of nickel-based catalysts can be suppressed by adding promoters, such as strong Lewis bases (e.g. MgO, CaO) enhanced with chemisorb of CO₂, resulting in the reduction of coke deposition via the reaction with C to form CO. Similar effects have been reported for lanthanide elements, such as CeO₂ and La₂O₃, with the capacity to store and release oxygen, leading to carbon

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removal by the reaction between the deposited carbon and the lattice oxygen formed in these redox oxides [13]. Aluminum oxide is a commonly applied catalyst carrier in industrial steam reforming of methane due to its good pore size dispersion, and high specific surface area and mechanical strength. Ce-incorporated NiMgAl oxide catalysts, synthesized via a hydrotalcite precursor by the carbonate co-precipitation [14], thermo decomposition [15], reconstruction [16,17], and self-combustion method [18], exhibited high activity and selectivity and reduced coke formation during the DRM reaction. These studies revealed that the preparation method plays an important role in the performance of the promising CeNiMgAl catalyst.



For a NiCaZr catalyst, Chen et al. [13] reported that reflux treatment of the precipitate in hot water led to the formation of NiO and ZrO₂ with smaller particle size, giving more interfaces between NiO and ZrO₂, which was beneficial to the stabilization of Ni particles at high temperature treatment and resulted in long stability in the DRM reaction. The reflux method allows intimate mixing of corresponding species in a homogeneous state under atmospheric pressure and at the solvent's boiling point [19]. A bimodal pore structure has shown advantages in application in a few heterogeneous catalytic reactions [20–22]. The large pores ensure the fast transportation of reactant and product molecules, and small pores provide high specific surface area for active sites.

In this research, a series of bimodal pore NiCeMgAl composite oxide catalysts were synthesized by using a co-precipitation method followed by the reflux aging process and their catalytic properties were systematically investigated under a wide range of reaction conditions. The goals were not only to obtain and optimize efficient Ni catalysts suitable for industrial applications but also to understand the fundamentals of the DRM reaction and process.

2. Experimental methods

2.1. Catalyst preparation

Bimodal pore NiCeMgAl catalysts were prepared via co-precipitation method followed by a refluxing process that used NaOH (99%, Sigma–Aldrich) aqueous solution (1 M) as the precipitant. The metallic nitrates (Sigma–Aldrich), Ni(NO₃)₂·6H₂O (98.5%), Ce(NO₃)₃·6H₂O (99%), Mg(NO₃)₂·6H₂O (99%), and Al(NO₃)₃·9H₂O (98%), were dissolved in distilled water to achieve a 0.2 M reagent solution. The precipitant and nitrate reagent were added drop-wise into a beaker previously loaded with 25 mL distilled water at 40 °C, 600 rpm stirring, and a pH of 11.00. After the precipitation ended, the mixture suspension was filtered and washed thoroughly, and then transferred into a round-bottom flask and refluxed at 100 °C for 24 h, followed by filtration to recover the precipitate, which was subsequently dried at 110 °C for 12 h and calcined at 650–850 °C in air for 4 h. The sample was tableted, ground, and sieved into particle sizes of 40–60 mesh. Four catalysts with different nickel contents were prepared, all nominally containing 5 wt% MgO, 5 wt% CeO₂, and varying NiO amounts, from 5 wt% to 20 wt% in step of 5 wt%. The remaining content was balanced with aluminum oxide. The prepared catalysts were designated as Ni₅CeMgAl, Ni₁₀CeMgAl, Ni₁₅CeMgAl, and Ni₂₀CeMgAl, correspondingly.

2.2. Characterization

The X-ray diffraction (XRD) data was collected on an Ultima III XRD (Rigaku Americas, The Woodlands, TX) using CuKα (λ = 0.1548 nm) radiation, operated at 40 kV and 44 mA at a rate

of 4° min⁻¹ and 2θ range of 10–90°, to study the structural phase and crystallinity of the prepared samples.

The N₂ adsorption/desorption analysis were performed with a Quantachrome Autosorb-1 (Quantachrome Instruments, Boynton Beach, FL) analyzer at –196 °C. The catalyst sample (100–150 mg) was degassed at 300 °C before the adsorption/desorption experiment. The Brunauer–Emmett–Teller (BET) surface areas were calculated from the BET equation at a relative pressure range of 0.05–0.30. Total pore volume was calculated based on the amount of N₂ vapor adsorbed at a P/P₀ of 0.99. Pore size distributions were plotted using the Barrett–Joyner–Halenda (BJH) method on desorption branch.

Hydrogen temperature programmed reduction (H₂-TPR) analysis was applied to evaluate the reduction properties of prepared catalysts on a Quantachrome ChemBET Pulsar TPR/TPD apparatus (Quantachrome Instruments, Boynton Beach, FL). In the H₂-TPR experiment, 30 mg of catalyst was heated from 50 °C to 1000 °C (10 °C/min) in a gas mixture of H₂/Ar (4/96) at a flow rate of 70 mL/min. Prior to the H₂-TPR measurement, the samples were purged with 70 mL/min N₂ gas at 300 °C for 1 h. H₂ consumption during the reduction was measured using a thermal conductivity detector (TCD).

Morphology of the catalyst was observed with a JEOL JEM-2100 transmission electron microscope (TEM, Waterford, VA) operated at 200 keV. The catalyst sample was dispersed in ethanol and sonicated for 20 min in an ultrasonic bath to attain a suspension, 1–3 drop(s) of which was dropped onto a copper grid (300 mesh) coated with formvar and carbon layers. The grid was then dried on a filter paper under an infrared lamp, followed by inspection with the TEM.

The type and amount of carbon deposited on the used catalyst was determined by calculating the weight loss of the sample after combustion of the carbon components in a thermo gravimetric analyzer (Shimadzu TGA-50, Columbia, MD). The curves of thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) were obtained at the following conditions. About 7 mg of the used catalyst was heated with a ramping rate of 10 °C/min from room temperature to 900 °C, with an airflow of 50 mL/min. The decomposition behavior of the catalyst precursor was also conducted at the same conditions.

2.3. Activity measurement

The DRM was performed at 101 kPa in a quartz tube continuous fixed-bed reactor with an inner diameter of 8 mm (Fig. 1). A 0.1 mL (~80 mg) sample of catalyst particles (40–60 mesh) were sandwiched between two pieces of quartz wool and located in the center of the reactor, and a thermocouple covered with a bottom-end closed quartz sheath was put into the middle of the catalyst bed to monitor the central temperature of the DRM reaction, i.e. the reaction temperature. The sample was reduced in situ at 550–850 °C in a 50% H₂/N₂ flow of 100 mL/min for 2 h. Methane and carbon dioxide were then fed into the reactor controlled by two calibrated mass flow controllers (MFC, Brooks instrument, Bartlett, TN). The feed gas was produced by adequate mix of pure methane and pure carbon dioxide in a mixer before it entering the reactor (see Fig. 1). The CO₂/CH₄ ratio was kept constant at 1.04. The gas hourly space velocity (GHSV) varied from 24,000 to 120,000 h⁻¹. Catalytic activity tests were carried out at stepwise temperatures from 650 to 800 °C in step of 50 °C. Stability of the selected catalysts in the DRM reaction were tested at 750 °C for 100 h, after the initial evaluation from 650 to 800 °C. The feed gas and tail gas were analyzed online using an Agilent 7890 gas chromatograph (Santa Clara, CA). Helium and nitrogen were used as the carrier gases. CH₄, CO₂, CO, and H₂ were analyzed using a molecular sieve-packed column with a TCD.

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