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Highly stable barium zirconate supported nickel oxide catalyst for dry reforming of methane: From powders toward shaped catalysts

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ARTICLE INFO

Article history:

Received 4 December 2017

Received in revised form

20 February 2018

Accepted 23 March 2018

Available online xxx

Keywords:

Barium zirconate

Dry reforming of methane

Temperature-regulated chemical

vapor deposition

Self-decoking

Shaped catalysts

ABSTRACT

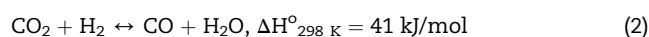
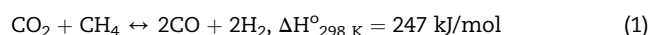
We report the barium zirconate supported NiO_x catalysts (NiO_x/BZO) for dry reforming of methane and feasibility test for their industrial application by using temperature-regulated chemical vapor deposition together with extrusion. Nickel oxide nanoparticles are well deposited and dispersed on BZO powders as well as structures in a gear form, showing high catalytic activity and extraordinary stability even at relatively lower temperature and higher space velocity. The NiO_x/BZO catalyst are highly coke resistant for 50 h operation with almost negligible agglomeration of NiO_x nanoparticles. Judging from XPS and high ion conducting properties of BZO supports, the –OH or –O species are expected to play an important role in promoting the self-decoking of surface carbon species to form CO and CO₂.

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Introduction

Carbon dioxide (dry) reforming of methane (DRM) offers much of benefits industrially, yielding a syngas with a H₂/CO ratio close to 1, which is suitable for the synthesis of liquid hydrocarbons and oxygenated chemicals by Fischer-Tropsch reaction [1–5]. And this process has attracted lots of attention because of environmental aspects which simultaneously removes two greenhouse gases. DRM is an endothermic

reaction (Eq. (1)) and takes place between 600 °C and 800 °C depending on the catalysts or experimental conditions. The main side reaction involved is the simultaneous occurrence of RWGS reactions (Eq. (2)) that produces more CO. The steam produced plays an important role in gasifying carbon species deposited in the reaction (Eq. (3)):

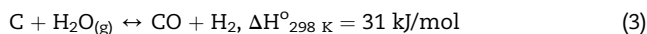


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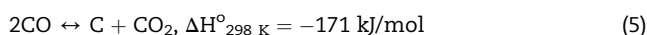
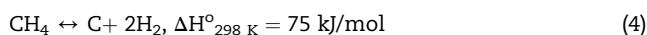
<https://doi.org/10.1016/j.ijhydene.2018.03.181>

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Transitional metals (Fe, Ni, Co and Cu) and noble metals (Ru, Rh, Pd and Pt) have widely been reported for the DRM reaction. Noble metals show higher efficiency than transition metals; however, the use of noble metals is generally limited for industrial application due to higher cost [6,7]. Among transition metals, the Ni-based catalyst is one of the most studied candidates because of its high activity and relatively low cost, aside from a great amount of carbon deposition which results in the deactivation of catalysts [8–10]. Therefore, catalytic stability is the key issue in the selection of catalyst components such as catalyst supports and promoters, as well as catalyst architectures.

The dominant carbon formation reactions on Ni based catalysts, including methane cracking and CO decomposition are thermodynamically more favorable than syngas production, in the lower temperature reaction regime (500–700 °C) [11,12].



To alleviate the carbon formation on Ni based catalysts, several studies encompass the control of Ni particle size, the conformal dispersion of metal species over catalysts or supports and structured catalysts [13–15]. Above all, well-controlled smaller particles have been reported to be more effective to alleviate carbon formation, because carbon formation is a structure sensitive reaction, and thus all catalyst particles should be below a critical size [16]. Chen et al. found that the size of the nickel crystal has an influence on both the coking rate and the ability of initiation or nucleation of carbon nanofibers during methane decomposition [17]. With smaller particles, high dispersion of metal species over catalysts may reduce coke formation [18].

Along with the chemical properties and structures of the catalyst components, the preparation method is another essential feature in the development of effective catalysts. Conventional supported catalysts are usually prepared by wet impregnation of different supports. This method is not fully reproducible and may give rise to some inhomogeneity in the distribution of the metal on the surface. Also, it is difficult to control the size of the active metals. In our previous studies, much simpler and effective chemical vapor deposition was developed to improve atomic layer deposition method, which is not so efficient due to lower productivity [19–21]. NiO_x nanoparticles were deposited on mesoporous Al₂O₃ by way of temperature regulated chemical vapor deposition (TR-CVD) method, which is a one-pot strategy for the incorporation of catalytically active metal oxide nanoparticles into the pre-formed mesoporous media. The NiO_x particle size on the surface of Al₂O₃ by TR-CVD is well controlled and ranges 4–5 nm with conformal deposition.

When it comes to catalyst supports, a strong metal-support interaction created during the catalyst preparation exhibits much higher stability, thermal resistance and coke resistance [22]. Also, ion-conducting ceramics are new and promising catalyst supports of finely dispersed and stabilized metallic

nanoparticles for the improvement of their performance [23,24]. The barium zirconate (BaZrO₃) has excellent thermal stability and has been studied for practice as catalytic materials for high temperature reaction. It is because that barium zirconate possesses intrinsic properties, such as high dielectric constant, high proton conductivity with rare-earth doping and capability to generate hydrogen by water catalytic reaction [25–29]. In particular, the role of Ba in BaZrO₃ catalysts is known to increase the density of basic sites, which provide CO₂ adsorption sites. Also, with an optimal arrangement of a high oxygen vacancy and basicity induced by Ba, the CO₂ reduction of the catalytic cycle is accelerated. In previous study, we reported a significantly improved conversion and selectivity for the reverse water gas shift (RWGS) reaction over BaZrO₃ based catalysts [30]. In addition, BaZrO₃ as a proton conductor can be used for hydrogen separation as well as DRM reaction.

In the present work, we investigate the conversion efficiencies and resistance against carbon formation of dry reforming of methane using BZO supported NiO_x catalysts prepared by TR-CVD. In addition, the feasibility for structured technical catalysts is also tested by shaping the catalyst powders into gear-type form.

Experimental

Synthesis of catalysts

The BaZrO₃ (BZO) powders are prepared by a conventional solid-state reaction method as described in our previous study [30]. Starting materials are BaCO₃ (Aldrich, 99.9%), ZrO₂ (Aldrich, 99.9%), and acetone. All materials are ground together in acetone, dried at 110 °C, and then calcined in air at 1150 °C for 5 h. Finally, the calcined materials are crushed into uniform powders by attrition milling.

The gear-type BZO structure is fabricated by an extrusion method. BZO powders and YB-132A (Yuken, Japan) as an organic binder are mixed uniformly firstly, and then deionized water is added into the mixture and kneaded on extruder without shaping mold. After aging overnight, the mixture is placed into the inlet end of the mold, then uniaxially compressed. The obtained gear-type BZO structure is dried at 60 °C overnight, and then sintered at 1000 °C (3 °C/min) for 3 h.

The Ni/BZO catalysts are synthesized by the TR-CVD method as described in our previous study [20]. Bis(cyclopentadienyl)nickel (Ni(Cp)₂, Aldrich) and oxygen/water vapor in air are used as precursors for NiO_x deposition. Firstly, the Ni(Cp)₂ solid powder precursor is located at the bottom and side of the SUS chamber (diameter = 130 mm, height = 110 mm), and the reaction chamber is sealed tightly. And then, the temperature of reaction chamber is raised and maintained to 100 and 250 °C for sublimation and deposition, respectively. The dosage of Ni(Cp)₂ controls 5, 10, 20, 30 wt% of BZO support, respectively. Physical properties of the prepared catalysts are summarized in Table 1.

Characterization of the catalysts

The Ni content of the catalysts are analyzed by X-ray fluorescence spectroscopy (XRF-1800, Shimadzu) after pelletizing

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