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Template-free preparation of bimetallic mesoporous Ni-Co-CaO-ZrO₂ catalysts and their synergetic effect in dry reforming of methane

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ABSTRACT

Mesoporous Ni-Co based nanocomposites with varied compositions were prepared without addition of a template. The physicochemical properties of Ni-Co catalysts were characterized extensively using techniques such as N₂ adsorption, ICP, XRD, H₂ chemisorption, TPR, TEM and TGA. The obtained results demonstrated that the addition of different amounts of Co could affect the metal support interactions, thus influence the synergetic effect between Ni and Co species, which affects the formation process of Ni-Co intermetallic particles. Among all the bimetallic catalysts, 50Ni50Co sample was characterized by better developed intermetallic alloy as well as metal-support interaction which in turn led to the best match of carbon intermediate formation and elimination rates during methane dry reforming reaction, therefore the 50Ni50Co sample showed the most excellent catalyst activity and stability with the mildest carbon deposition.

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1. Introduction

With the depletion of traditional fossil fuels, the worldwide energy crisis gradually emerging, and new energy development as well as low carbon economy have drawn more and more attention. As a potential alternative of petroleum and coal, natural gas (shale gas or biogas) may become a main energy resource and further stimulate the use of CH₄ as a chemical feedstock in the near future [1]. Meanwhile, as the main contributor of greenhouse effect, CO₂ is a universal waste gas in energy and chemical industries, its direct utilization is a potential method to mitigate the carbon emission. As a result, carbon dioxide (dry) reforming of methane (DRM) to produce synthesis gas is becoming more attractive due to the renewable interests in both the efficient utilization of natural gas and the low carbon recycle in the framework of Carbon Capture, Utilization and Storage.

Ni-based catalysts were investigated mostly for this reaction and are highly potential for industrial application in the future. However, one of the main obstacle of Ni-based catalysts encountered is the coke deposition on catalyst surface which can cause

deactivation of catalyst. Modification of the catalyst support with alkaline earth or redox oxide has been reported to improve both the activity of the catalyst and suppression of carbon formation. Yamazaki et al. [2] and Bachiller-Baeza et al. [3] reported that the CaO-promoted catalyst showed high affinity for chemisorption of CO₂ which could enhance thermal stability of the catalyst and suppress carbon deposition. The addition of redox oxides as a promoter has also been investigated in view of increasing the available O species. ZrO₂ was frequently reported as a candidate due to its ability to release lattice oxygen and quickly reoxidize in the presence of oxidative agents during reforming reaction [4,5]. As proved by our previous work [6–8], the prepared redox ZrO₂ supported Ni catalyst which processed strong metal support interaction (SMSI) was beneficial for the conversion of carbon intermediate during dry reforming.

An additional way to improve the anti-coking property of catalyst is by alloy formation between Ni and other metals [9–11]. For example, bimetallic Ni-Co catalysts derived from different preparation methods have been reported to show improved catalytic performance, such as methane partial oxidation [12,13], biomass steam reforming [14] and dry reforming [15,16] reactions. Koh et al. [12] prepared impregnated Ni-Co/CaAl₂O₄/A₂O₃ catalysts and found the bimetallic catalysts exhibited superior catalytic performance than monometallic Ni catalyst in methane partial oxidation. Chen et al. [13] also prepared a series of Ni-Co bimetallic aerogel

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catalysts which possessed high surface area larger than $300 \text{ m}^2 \text{ g}^{-1}$, these samples exhibited high and stable activity during methane Oxy- CO_2 reforming with less carbon deposition.

Furthermore, probably due to the similar electronic configuration, synergetic effect of alloy formation between Ni and Co has been widely proposed in reforming reactions [17–20]. Zhang et al. [21,22] found that Ni/Co bimetallic catalyst had superior performance in terms of activity and stability as compared to other Ni/Me combinations. Wang et al. [14] also reported that the interaction between Ni and Co is stronger than that between Ni and additive oxides because Ni and Co can be mixed on an atomic level by alloy formation. Yu et al. [23] revealed that the interaction between Ni and Co improved the metal particle dispersion and resulted in smaller Ni size, thus increasing the catalytic activity and coke resistance. You et al. [24] attributed the excellent performance of the bimetallic Ni-Co catalyst to its high metal dispersion, SMSI and formation of stable solid solution. Above all, we could commonly conclude that the addition of cobalt into Ni-based catalysts can lead to superior synergetic effect, which changed the catalyst properties such as particle size, metal nature, metal support interaction, and catalyst structure [25]. As a result, the different synergetic effect could in turn influence the catalytic performance or coking behavior. However, to the best of our knowledge, the application of mesoporous bimetallic Ni-Co during DRM has not been thoroughly investigated, and their synergetic interaction effecting on catalyst properties, especially mesoporous structure, as well as catalytic performance may deserve further elucidation.

In our previous work, a mesoporous nano-crystalline Ni-CaO-ZrO₂ catalyst showed high and stable activity during CH₄-CO₂ reforming [26]. Due to the high stability under severe operation condition, the catalyst is believed to be more suitable for industrial application. However, the as-prepared ordered mesoporous catalyst is generally prepared with the addition of a structure-directing template, which will raise the preparation cost. In our opinion, the catalytic importance of the mesoporous framework was mainly to increase the active surface area and inhibit the Ni particle growth via a confine effect. Since the mesoporous ordering had less influences on such a confine effect, we attempted to prepare a disordered meso-structure catalyst with large surface area and strong metal support interaction under a template-free condition. In this way, the prepared catalyst can preserve excellent catalytic performance, and this method can thus effectively decrease the preparation cost and wastes with little compromise on the textual properties and catalytic performance. Furthermore, inspired by synergetic effect of dual metal, in the present paper, template-free bimetallic Ni-Co-CaO-ZrO₂ catalysts with various Ni/Co contents were prepared by one-pot synthesis method without template and tested in long term DRM reactions. In order to clarify the synergetic effect between dual metal as well as the metal support interaction, the structural properties and coking behavior of Ni-Co catalysts were characterized extensively using the techniques of BET, XRD, H₂ chemisorption, TPR, TEM and TGA, etc.

2. Experimental

2.1. Preparation of the mesoporous Ni-Co catalysts

The template-free mono- and bimetallic Ni-Co-CaO-ZrO₂ mesoporous catalysts were prepared by co-precipitation method with a refluxing process. The preparation route was listed below: Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O and Zr(NO₃)₄·5H₂O (Sinopharm Chemical Reagent Co., Ltd.) were used as precursors and dissolved in de-ionized water, the green solution without surfactant template was co-precipitated by a NaOH aqueous solution (1 mol L^{-1}) at pH = 11–12. The obtained

slurry was aged under stirring for 2 h at ambient conditions, and then washed, refluxed in de-ionized water for 48 h, filtered, dried and calcined at 700 °C for 5 h. In order to study the synergetic effect of Ni-Co catalysts, the ratio of Ni and Co was varied but the atomic ratio of (Ni+Co):Ca:Zr was kept at 2:1:5. The obtained catalysts were nominated as 100Ni, 80Ni20Co, 50Ni50Co, 20Ni80Co and 100Co according to their Ni/Co ratios.

2.2. Characterization of catalysts

The mesoporous framework and surface area of the Ni-Co catalysts were measured by the BET method (N₂ adsorption) using a Micromeritics TriStar 3000 instrument. Prior to the test, the catalyst was degassed at 200 °C overnight. Pore size distributions of the samples were calculated from the analysis of the desorption branch of the isotherm via the conventional Barrett-Joyner-Halender (BJH) model.

The bulk chemical compositions of as-prepared catalysts were determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES, AtomScan 16, Thermo Scientific). The samples were acid digested with H₂SO₄ and HCl (3 M) at 50 °C for 2 h before analysis.

X-ray diffraction (XRD) experiments were carried out on a Panalytical X'Pert Pro X-ray diffractometer with monochromatized Cu K α radiation ($\lambda = 0.15406 \text{ nm}$) at a setting of 40 kV and 70 mA in the step mode (0.0167° , 10 s) over the calcined, reduced and used catalysts. The patterns recorded were referred to the Joint Committee Powder Diffraction Standard Card (JCPDS Card) for identification.

H₂ chemisorption was measured with a Micromeritics ASAP 2020 system to analyze the metal dispersion for different Ni-Co catalysts. Typically, 0.08 g catalyst was first reduced in a 50 mL min^{-1} 10% H₂/Ar gas mixture flow at 750 °C for 2 h and then allowed to cool until room temperature in pure Ar flow, where a pulse of 10% H₂/Ar was introduced after each 2 min interval till the area of successive hydrogen peaks was found to be identical.

Temperature programmed reduction (TPR) was conducted in a quartz tube reactor with an i.d. of 4 mm. 0.08 g of catalyst was loaded and heated in Ar flow from room temperature to 400 °C to remove surface contaminants, the temperature was then cooled down to room temperature and a 10% H₂/Ar mixture was fed with a flow rate of 30 mL min^{-1} . The reduction process was started from 60 °C to 850 °C at a heating rate of $10^\circ \text{C min}^{-1}$. TCD was used for the collection of the H₂ consumption signal.

The morphology of the particle distribution and carbon accumulation of used catalysts was observed by a JEM 2010 high-resolution transmission electron microscope (TEM) operated at 200.0 kV.

Thermal decomposition of carbon deposition was studied by thermogravimetric analysis (TGA) method by using STA-409 (NET-ZSCH Co.). Measurements were performed in the temperature range of 30–900 °C with linear temperature program rate of $10^\circ \text{C min}^{-1}$ in continuous flow of air (50 mL min^{-1}). Before each test, the loaded sample was first heated in N₂ at 120 °C for 1 h to remove adsorbed contaminants and then cooled down to room temperature before the start of the thermogravimetric measurement.

2.3. Reaction evaluation

The CH₄-CO₂ reforming reaction was carried out in a fix-bed quartz tube reactor (i.d. 6 mm) at atmospheric pressure. 0.10 g catalyst (average particle size 0.31 mm) diluted with 0.30 g quartz sand was used, reactant gases with desired compositions were fed via mass flow controllers under the condition that the gas hour space velocity (GHSV) equaled $32 \text{ L g}^{-1} \text{ h}^{-1}$. Prior to reaction, the catalysts were reduced at 750 °C with a 25% H₂/N₂ mixture (80 mL min^{-1}) for 2 h. After reduction, the reactor was purged with N₂ for 10 min and

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