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Fabrication of CeZrO₂ on Ni/SiO₂ and promoted catalysis for methane autothermal reforming in a fluidized bed reactor

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Abstract: The methane autothermal reforming in the presence of oxygen was studied over cerium- and zirconium-promoted Ni/SiO₂ catalysts in a fluidized bed reactor. The addition of CeZrO₂ resulted in a significant improvement in the initial activity of the catalysis as well as an increase in the stability. The long-term activity of the promoted catalyst was dependent upon the rapid redox properties between the oxidative zone and the reductive zone in a fluidized bed reactor. H₂ temperature-programmed reduction (H₂-TPR) and temperature-programmed surface reaction (TPSR) studies demonstrated that addition of the CeZrO₂ resulted in an increase in the reducibility and oxygen transfer ability of the support. Ni/Ce_{0.5}ZrO_{0.5}O₂-SiO₂ showed improved redox properties compared with Ni/SiO₂ due to a low-temperature reduction. X-ray diffraction (XRD) of the fresh and spent catalysts showed that the promoter enhanced the nickel dispersion and retarded metal particle growth during reaction at high temperature, and surface Ni was gradually oxidized by remaining O₂, leading to Ni deactivation.

Keywords: methane; reforming; Ni/Ce-ZrO₂-SiO₂ catalyst; fluidized bed reactor; rare earths

CO₂ conversion and utilization are an important element in chemical research on sustainable development. The transformation of methane and carbon dioxide into more valuable compounds has attracted the attention of researchers. Among published results, the catalytic CO₂ reforming and partial oxidation of CH₄ to synthesis gas have been investigated comprehensively over the past few years, as have been well summarized in recent reviews^[1-5]. Challenges in CO₂ reforming are the highly endothermic nature of the reaction and the rapid deactivation of nickel-based catalysts by carbon deposition. Partial oxidation of methane, which is exothermic, consists of methane combustion and successive reforming with the production of CO₂ and H₂O. Therefore, a serious temperature gradient is caused in the catalyst bed.

Addition of oxygen to the reforming reactants is an effective method to supply heat. Combined with CO₂ reforming and partial oxidation of methane, also called methane autothermal reforming [MATR], it has drawn significant interest in recent years in alternative routes for the conversion of methane to synthesis gas. Tomishige's^[6-9] and Ross's^[10,11] group have made significant contributions to the studies of MATR reaction over Ni catalysts in both experimental and theory. MATR involves a coupling of methane oxidation

with CO₂ reforming of methane in the same reactor. It is suggested that MATR is carried out in two separate reaction zones in the fixed-bed reactor, usually, a significant temperature gradient formed in the catalyst bed, which ultimately resulted in the thermal sintering and deactivation of catalyst^[6,9,10].

Several studies about the MATR process in a fluidized bed reactor has been reported by Tomishige et al.^[6-9] and Zheng et al.^[12-14]. They suggested that the high rates of heat transfer and high stability of operation be obtained. The fluidized bed reactor provides a close idealization in gas-solid contactors for high heat transfer rates, which is needed to ensure isothermal operation in a reactor^[15]. The use of solid catalysts as internal heat carriers will provide a more homogeneous temperature distribution in the fluidized bed reactor. Moreover, catalyst can maintain a suitable level of reducibility during fluidization that enhances the conversion of methane^[8,9,15,16].

Previous reports from our laboratory have shown that the Ni/SiO₂ catalysts modified by alkaline earth oxide are active and stable for the combined reaction in fluidized bed reactor^[12-14,17,18]. It has been reported that the catalysts consisting of Ce(Zr)O₂ exhibited exciting effects in oxygen storage ca-

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capacity, structural stability and carbon resistance for methane conversion reaction with O_2 input^[16,19-21]. In this paper, we reported synthesis gas production from the combined reaction in a fluidized bed reactor, using Ni/SiO₂ catalysts promoted by CeZrO₂. The correlation of the reducibility of Ni with its catalytic performance in a fluidized bed reactor was studied. MATR at different catalysts, methane and CO₂ activation, initiative reaction of MATR were determined on pure Ni/SiO₂ and Ce(Zr)O₂ promoted catalysts.

1 Experimental

1.1 Catalyst preparation

Ni/SiO₂ and Ni/CeZrO₂/SiO₂ catalysts were prepared by the incipient-wetness impregnation method. Nitrate salts were used as precursors, and the spherical SiO₂ (special support for fluidized reactor, $S_{BET}=364 \text{ m}^2/\text{g}$, average diameter 0.28–0.45 mm, Qingdao, China) was used as support. After impregnation, the samples were dried at 353 K in vacuum and subsequently calcined at 773 K for 4 h in stagnant air. The prepared catalysts were designated as Ni/Ce_{0.5}Zr_{0.5}O₂-SiO₂. The loading amount of Ni and Ce-Zr (the mole ratio of Ce:Zr=1:1) were controlled at 5wt.% and 10wt.% of the catalyst, respectively.

1.2 X-ray diffraction (XRD)

XRD patterns were obtained on a Rigaku-D/max-B (Rigaku, Japan) automated power X-ray diffractometer using Cu K α radiation at 45 kV and 40 mA. Diffraction data were recorded using continuous scanning at a rate of 2°/s, step 0.02°. The obtained X-ray diffraction patterns were employed to identify the major phases present.

1.3 Hydrogen-based temperature-programmed reduction (H₂-TPR)

H₂-TPR experiments were carried out on the AMI-200 characterization system (Zeton Altamira, USA). Before TPR experiment, 100 mg of sample was pretreated at 573 K for 30 min in Argon ambience. After cooled down to 303 K, the furnace was heated linearly to 973 K at a rate of 20 K/min in 5% H₂/Ar stream (30 m/min).

1.4 Temperature-programmed surface reaction (TPSR-MS)

Before these experiments, 100 mg catalysts were reduced in H₂ flow at 973 K for 1 h, after that, each sample was treated in Ar atmosphere at 973 K for 30 min to remove the adsorbed H₂, and then cooled to 323 K. CO₂ reforming of CH₄ was carried as a probe reaction to determine the initiative activity of CH₄ and CO₂ on different catalysts. CH₄/CO₂-TPSR was performed in 50 ml CH₄ and 50 ml

CO₂ diluted by 100 ml Argon, from 323 K to 1073 K at a constant rate of 15 K/min. All gases in effluent were detected by a mass analyzer (OmniStar GSD301, Switzerland) and recorded as a function of temperature.

1.5 Carbon deposition determination

The carbon deposition on the catalysts was measured using a thermogravimetric analysis (TGA) on a Perkin-Elmer model PE TAC7/DX instrument. Before the TG analysis was conducted, each sample was treated in a N₂ atmosphere at 573 K for 30 min and then cooled to ambient temperature. Finally, the Ar/O₂ (5%) was introduced while increasing temperature to 1073 K, at a ramp rate of 20 K/min.

1.6 Continuous flow experiments

MATR reactions were performed in a fluidized bed quartz reactor ($ID=12 \text{ mm}$; $H=750 \text{ mm}$) at atmospheric pressure. A reactant mixture with CH₄:CO₂:O₂=10:4:3 were introduced into the reactor controlled by three sets of mass flow controller (Brooks 5850E), and a flow rate of 300 ml/min. Prior to the reaction, 2 ml catalyst was first reduced in H₂ at 973 K for 1 h. The effluent gas was cooled in an ice-water trap and analyzed using a gas chromatograph (Shimadzu, GC-8A) equipped with a thermal conductivity detector and a packed column (TDX-01).

2 Results and discussion

2.1 MATR over different Ni catalysts

The durability of the pure and Ce(Zr)O₂ modified Ni/SiO₂ catalysts for MATR in a fluidized bed reactor are presented in Fig.1. All the nickel-based catalysts exhibit very high initial activities, confirmed that the nickel metal is the suitable catalyst for the MATR reaction. However, the CH₄

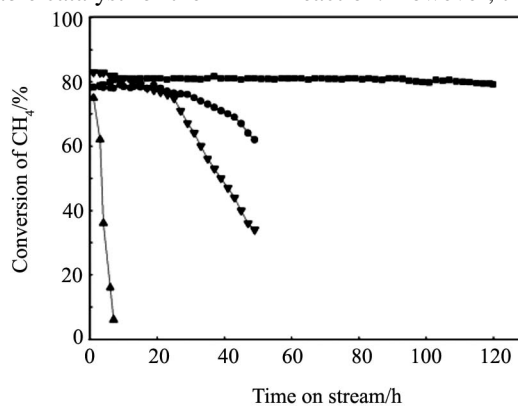


Fig.1 Durability of the different Ni catalysts for MATR in fluidized bed reactor (973 K)

(■) Ni/Ce_{0.5}Zr_{0.5}O₂-SiO₂; (●) Ni/ZrO₂-SiO₂;
(▼) Ni/CeO₂-SiO₂; (▲) Ni/SiO₂

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