



Effect of promoter Ce on the structure and catalytic performance of Ni/Al₂O₃ catalyst for CO methanation in slurry-bed reactor



Fanhui Meng, Zhong Li^{*}, Jun Liu, Xiaoxi Cui, Huayan Zheng

Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

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ABSTRACT

Catalysts Ni/Al₂O₃ modified with promoter Ce were prepared by wet impregnation method, and used for CO hydrogenation to synthetic natural gas production in a slurry-bed reactor. The effect of impregnation sequence of Ni and Ce, and the calcination temperature on catalyst structure and catalytic methanation has been investigated. Characterization of different catalysts was carried out using BET, XRD, TEM, TPR and XPS. The results showed that catalyst Ni–Ce/Al₂O₃ prepared by coimpregnation of Ni and Ce possessed larger specific surface area, higher Ni species dispersion, smaller Ni particle size, lower reduction temperature, and higher catalytic activity for catalytic methanation of CO than catalyst Ni/Al₂O₃, or catalyst Ce/Ni/Al₂O₃ impregnated with Ni firstly then Ce, or catalyst Ni/Ce/Al₂O₃ impregnated with Ce firstly then Ni. With the increase in calcination temperature, the interaction between Ni species and γ -Al₂O₃ support strengthened. Catalyst Ni–Ce/Al₂O₃, calcined at 350 °C, obtained the moderate interaction and exhibited the optimum catalytic activity under the reactions of 280 °C and 1.0 MPa, the CO conversion and CH₄ selectivity reached up to 95.4% and 90.7%, respectively. Further increase in calcination temperature decreased the catalyst reducibility and catalytic performance.

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1. Introduction

The production of synthetic natural gas (SNG) from coal or biomass has been investigated extensively due to the increasing demand for natural gas and the high energetic conversion efficiency (Zhang et al., 2013; Vannice, 1976; Kopyscinski et al., 2010). SNG production proceeds through the following steps: gasification, gas cleaning, conditioning and methanation. Among them, methanation of syngas ($3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) is an essential step (Li et al., 2013). A thermodynamic analysis shows that CO methanation reaction is a highly exothermic reaction (Gao et al., 2012), for every 1% CO, the temperature rise for a typical methanator gas composition in an ammonia plant was 74 °C (Zhang et al., 2013; Mills and Steffgen, 1974), the large potential temperature increase may cause the catalyst sintering and carbon formation, and the increase of reaction temperature resulted in the decrease of CO equilibrium conversion. Thus, one of the major challenges in developing the methanation reactor is to remove in time the highly

exothermic heat effectively and to improve the catalytic performance. Due to the poor heat transfer of fixed bed reactor and high amount of CO in the syngas, most commercial fixed bed methanation reactors are connected in series with intermediate gas cooling components or the product gas is recycled, which resulted in the complex process and high energy consumption (Kopyscinski et al., 2010). The slurry-bed reactor suspends the catalyst in an inert liquid medium and can be maintained at a uniform temperature, which is inherently suitable for the highly exothermic reaction, and now, it has been widely used in F-T synthesis (de la Peña O'Shea et al., 2007; Botes et al., 2013) and methanol synthesis (Salehi et al., 2014; Li et al., 2013). Recently, a few studies on methanation of CO in the slurry-bed reactor have been done (Zhang et al., 2014; Meng et al., 2014a; Kopyscinski et al., 2010; He et al., 2012).

Numerous metal based catalysts have been studied for CO methanation reaction in fixed bed reactor, such as Ni (Rahmani et al., 2014; Hwang et al., 2011, 2013; Hu et al., 2012), Ru (Urasaki et al., 2010; Chen et al., 2010), Rh (Karelovic and Ruiz, 2013) and Co (Zhou et al., 2013) on various supports (Al₂O₃ (Ma et al., 2011; Hu et al., 2012), SiO₂ (Yan et al., 2013), ZrO₂ (Zhu et al., 2013), TiO₂ (Karelovic and Ruiz, 2013) and MCM-41 (Zhang et al., 2013), etc.). Among these, Ni-based catalysts, especially supported on Al₂O₃,

^{*} Corresponding author. No. 79 Yingze West Street, Taiyuan, Shanxi 030024, China.

E-mail address: lizhong@tyut.edu.cn (Z. Li).

have been investigated extensively for industrial purposes because nickel is inexpensive and readily available, as well as it is highly active and selective for methane formation (Zhao et al., 2012; Mills and Steffgen, 1974). Despite these advantages, the traditional Ni-based catalysts are easily deactivated in fixed bed reactor as a result of being prone to sintering and/or carbon deposition at high temperatures (Zou et al., 2010). In addition, the Ni/Al₂O₃ catalyst exhibited poor catalytic activity for CO methanation in slurry-bed reactor (Zhang et al., 2013; Meng et al., 2014b), because the slurry solvent prevents the use of high temperatures. To further improve the catalytic activity and stability of Ni-based catalyst, many studies have focused on the addition of second metal (Hwang et al., 2012), such as La (Zhi et al., 2011; Cui et al., 2014), Ce (Qin et al., 2015; Liu et al., 2014), Fe (Tian et al., 2013) and Zr (Zhang et al., 2014) etc.. Previous studies have shown that La and Ce are better promoters at low temperatures than the others are (Zhi et al., 2011; Senanayake et al., 2011; Liu et al., 2014).

Our previous work have optimized the Ce content of Ni–Ce/Al₂O₃ catalyst for CO methanation in slurry-bed reactor (Meng et al., 2014c). However, the catalyst preparation procedure is one of the major contributing factors that determine the physical as well as chemical properties of Ni-based catalysts. For examples, Zhang et al. found that the Zr promoted catalyst Ni/Al₂O₃ showed high CO conversion and CH₄ selectivity under the reaction conditions of 325 °C and 1.5 MPa in slurry-bed reactor, which was as high as 91.2% and 87.5%, respectively, and the catalyst 25N3ZA prepared by impregnation coprecipitation shows higher activity of methanation than that of impregnation (Zhang et al., 2014). He et al. found that calcination temperature was a very important factor for Ni–SiO₂ catalyst in slurry-bed reactor, the particle size of active Ni increased and the specific surface area decreased with the increase in calcination temperature, and the optimum temperature of Ni–SiO₂ catalyst was 450–550 °C, the higher or lower than that would reduce the catalytic activity (He et al., 2012). Therefore, it is essential to study the effect of preparation conditions on structure and catalytic performance of Ce promoted Ni/Al₂O₃ catalyst for CO methanation in slurry-bed reactor.

In this work, Ni/Al₂O₃ catalyst and Ce-promoted Ni/Al₂O₃ catalyst were prepared by the incipient–wetness impregnation method using γ -Al₂O₃ support, and the purpose of this work is to undertake a comprehensive investigation on the catalyst preparation processes, including impregnation sequences of Ni and Ce and the calcination temperatures, on catalytic performance of Ni-based catalysts for CO methanation in slurry-bed reactor. Combined with catalyst characterizations, the structures and catalytic behaviors of Ni-based catalysts were studied in detail so as to optimally design a highly active catalyst for the application of CO methanation in a slurry-bed reactor.

2. Experimental

2.1. Catalyst preparation

The commercial γ -Al₂O₃ (supplied by Shandong Alumina Company, China) precalcined in air at 550 °C for 6 h was used in this study. Analytical grade chemicals nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification. The samples with the nickel loading of 16 wt% and the cerium loading of 4 wt% were prepared by the incipient–wetness impregnation method. First, 7.9 g of Ni(NO₃)₂·6H₂O and 1.2 g of Ce(NO₃)₃·6H₂O were dissolved in 10.0 mL deionized water in a 50 mL flat bottom beaker, followed by the addition of 10.0 g of γ -Al₂O₃, the resulting mixture was sealed with plastic film to prevent the evaporation of

water and stirred continuously at room temperature for 24 h, and then dried at 120 °C for 12 h. The obtained solid was ground to powder (100–140 mesh) and then calcined in air at 450 °C for 4 h to form 16NiO–4CeO₂/Al₂O₃, which was denoted as Ni–Ce/Al₂O₃.

The Ni and Ce were loaded consecutively. Firstly, the Ce was loaded on γ -Al₂O₃ support and calcined in air at 450 °C for 4 h to form CeO₂/Al₂O₃ solid, and then Ni was loaded on the CeO₂/Al₂O₃ sample, finally, the catalyst was calcined again in air at 450 °C for 4 h to form NiO/CeO₂/Al₂O₃ solid, which was denoted as Ni/Ce/Al₂O₃. The Ce and Ni were also loaded consecutively, and the obtained catalysts were denoted as Ce/Ni/Al₂O₃. Ni/Al₂O₃ catalyst without Ce-promotion was used a reference.

Catalyst Ni–Ce/Al₂O₃ calcined at various temperatures was denoted as Ni–Ce/Al₂O₃-X, where X represents calcination temperature, and X = 250 °C, 350 °C, 450 °C, 500 °C, and 550 °C.

2.2. Catalyst characterization

X-ray diffraction (XRD) data were obtained with Rigaku D/max 2500 diffractometer (Cu K α radiation, λ = 0.154056 nm) at 40 kV and 30 mA, the samples were scanned with Bragg's angles between 10° and 85° at a rate of 4°/min, the phase identification was determined by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS), the crystallite diameter of the samples were estimated from XRD patterns applying the Scherrer equation.

Temperature-programmed reduction of H₂ (H₂-TPR) experiments were carried out with Micrometrics Autochem II 2920 model multifunctional adsorption instrument by using the reduction gas (10% H₂ diluted in Ar, purchased from South Beijing Industry and Trade Co. Ltd., China). Prior to the TPR measurement, 20 mg of the sample was pretreated at 350 °C for 0.5 h in flowing He (50 mL/min, 99.999%, purchased from South Beijing Industry and Trade Co. Ltd., China) to remove any moisture and other adsorbed impurities, after cooling the reactor to room temperature, a 10%H₂/90%Ar (50 mL/min) gas mixture was introduced, and the sample was heated to 800 °C at a rate of 10 °C/min, and the consumption of H₂ was monitored by TCD.

The specific surface area, pore volume and the average pore diameter of samples were calculated from N₂ physisorption isotherms using the BET method. The N₂ adsorption–desorption isotherms were obtained using liquid nitrogen (purchased from Taiyuan Iron & Steel (Group) Co., Ltd., China) at –196 °C over the whole range of relative pressure using a Micrometrics ASAP 2100 automatic device. Before the measurement, the sample was degassed at 250 °C for 3 h under vacuum.

X-ray photoelectron spectroscopy (XPS) data were collected on Thermo Fisher ESCALAB 250Xi with Al K α radiation to obtain the information of chemical composition and oxidation state. The binding energy was corrected using C 1s at 284.8 eV.

Transmission electron microscopy (TEM) experiment of the catalyst was performed on JEOL JEM-2100F microscope operated at 200 kV. Prior to TEM measurement, the samples were dispersed in ethanol, ultrasonicated and deposited on a sample holder.

2.3. Catalytic activity evaluation

Before the catalytic activity test, the catalyst was reduced at 550 °C for 6 h in a flow of 25% H₂ diluted with nitrogen. In each experiment, 2.0 g of reduced catalyst (100–140 mesh particle) and 120 mL of liquid paraffin (boiling point higher than 350 °C, Tianjin Kemiou Chemical Reagent Co., Ltd., China) were added into a 250 mL slurry-bed reactor vessel and rotated at a speed of 750 r/min. The slurry-bed reactor was heated by an electric furnace, and the temperature was controlled by K-type thermocouples placed in

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