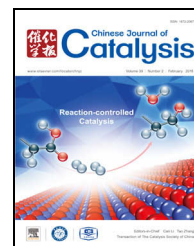


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Article

ZrO₂-modified Ni/LaAl₁₁O₁₈ catalyst for CO methanation: Effects of catalyst structure on catalytic performance



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ABSTRACT

We report Ni/LaHA@ZrO₂ catalysts prepared by a facile modified successive adsorption and reaction method for CO methanation. N₂ adsorption, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, thermogravimetric analysis, H₂ temperature-programmed reduction, H₂ temperature-programmed desorption, X-ray photoelectron spectroscopy, thermogravimetric analysis, and inductively coupled plasma atomic emission spectrometry were used to characterize the samples. The results indicated that the ZrO₂ nanoparticles were distributed over the surface of the Ni/LaHA@ZrO₂ catalyst and even partially covered some Ni particles, resulting in the coating exerting a confinement effect. The excess ZrO₂ had an adverse effect on the enhancement of CO conversion because of the coverage of the surface Ni particles; however, the Ni/LaHA@ZrO₂ catalyst displayed much higher CH₄ selectivity than Ni/LaHA because of the activation of the byproduct CO₂ molecules by ZrO₂ species. Therefore, even though 20Ni/LaHA@ZrO₂-5 exhibited similar CO conversion as 20Ni/LaHA, the use of the former resulted in a higher CH₄ yield than the use of the latter. A 107-h-lifetime test revealed that the Ni/LaHA@ZrO₂ catalyst was highly stable with superior anti-sintering and anti-coking properties because of its coating structure and the promoter effect of ZrO₂.

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1. Introduction

The CO methanation reaction from syngas has attracted intensive attention from both academia and industry, especially in coal-rich regions and countries such as China [1–4]. This reaction is strongly exothermic and thermodynamically feasi-

ble ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -206.1 \text{ kJ mol}^{-1}$), leading to high demand for methanation catalysts. Ideal catalysts should be highly active at low temperatures ($\sim 300 \text{ }^\circ\text{C}$) and highly stable at high temperatures ($\sim 600 \text{ }^\circ\text{C}$). Some transition metals such as Ru, Rh, Pt, Ni, Fe, and Co have been used in the methanation reaction [5–9]. Among them, Ru-based catalysts

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are the most active; however, the limited resources and high cost of Ru restrict the large-scale industrial application of these catalysts [10]. In addition, both the activity and CH₄ selectivity of Fe- and Co-based catalysts are still relatively low [4]. Hence, Ni is the most favorable choice for CO methanation because of its relatively high activity and low cost [11]. Moreover, many supports such as Al₂O₃ [11], SiO₂ [12], SiC [13], TiO₂ [14], and ZrO₂ [15] have been investigated for Ni catalysts; however, these catalysts often suffer from Ni sintering and coke formation on the surface of the Ni particles during the methanation process. Therefore, considering that the methanation process is generally performed at high temperatures (≥ 400 °C) [1,3,16], together with its strongly exothermic nature, the control of the thermally induced sintering of Ni particles and supports as well as coke formation is critical for maintaining the catalyst activity.

Hexaaluminate (HA) materials are highly stable at high temperatures because of their unique layered structure of alternately stacked spinel blocks separated by mirror planes [5,17] and have been used as catalysts or catalyst supports for high-temperature reactions such as methane catalytic combustion [18,19], methane reforming reaction [20], and CO methanation [5,17]. In addition, the rare-earth oxide La₂O₃ has been widely used as an excellent promoter for various catalysts because of its unique properties, such as neutralization of acid sites [21], stabilization of the support [22–24], enhancement of the catalytic performance [25], and suppression of carbon deposition by activating adsorbed H₂O and CO₂ [26,27]. Lanthanum hexaaluminate (LaAl₁₁O₁₈)-supported Ni catalysts are thus expected to be promising CO methanation catalysts.

To prevent both the sintering of Ni particles and coke formation, several strategies have been employed in the literature, such as the addition of an inorganic oxide via atomic layer deposition [28,29], encapsulation using the precipitation–deposition method [11], or the use of core–shell [30,31], core–sheath [32], or ordered mesoporous structures [33,34]. Although partial success has been achieved, these approaches still have drawbacks, such as poor control of the shell thickness [30], the need for special equipment [28], costly raw materials [33], and complicated and harsh preparation processes [30], which limit their wide and large-scale applications. Recently, we prepared ZrO₂-modified Ni/ α -Al₂O₃ catalysts using a facile modified impregnation method for CO methanation with the construction of a ZrO₂-on-metallic Ni surface coating structure, yielding significant enhancement of the catalytic activity and anti-sintering of Ni particles [35]. However, the anti-coking property was poor and thus required further improvement.

Following our previous works on catalysis [6,35–40], in this work, ZrO₂-modified Ni/LaAl₁₁O₁₈ catalysts were prepared using a modified successive adsorption and reaction method to overcome the technical barriers of sintering and coking. To the best of our knowledge, no reports on this type of CO methanation reaction route are available in the literature. To better understand the effect of the catalyst structure on the catalytic activity and stability, a series of tests and characterizations were performed. The results revealed that the coating of ZrO₂ nanoparticles over the Ni/LaAl₁₁O₁₈ catalyst could suppress

both Ni sintering and coke formation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of LaHA support

The LaHA support was prepared using a coprecipitation method with carbon black as the hard template, similar to a method previously described in the literature [17]. First, 0.165 mol Al(NO₃)₃·9H₂O and 0.015 mol La(NO₃)₂·6H₂O were dissolved in 300 mL of deionized water at 60 °C; then, 10 g carbon black was added, and the mixture was stirred for 5 h to obtain a precursor slurry. Next, a (NH₄)₂CO₃ aqueous solution (3 mol L⁻¹) was heated to 60 °C and added to the above precursor slurry while controlling the pH at approximately 8.0. After vigorous stirring for 4 h, the mixture was filtered and dried at 100 °C. The calcination process was divided into two parts. First, the mixture was calcined in an Ar flow at 1350 °C for 12 h at a heating rate of 5 °C min⁻¹. During this process, the inclusion of carbon black prevented the agglomeration of LaHA particles at high temperature. Second, the carbon black was removed in air at 900 °C for 3 h to obtain the LaHA support.

2.1.2. Preparation of 20Ni/LaHA catalyst

The 20Ni/LaHA catalyst was prepared using the wet impregnation method [11]. Stoichiometric amounts of polyethylene glycol (average MW = 20000) and Ni(NO₃)₂·6H₂O were dissolved in deionized water, followed by the addition of LaHA powder; then, the slurry was vigorously stirred at room temperature overnight. During this process, polyethylene glycol was used as the dispersant for Ni²⁺ ions in the aqueous solution, with a mass ratio of polyethylene glycol:Ni(NO₃)₂·6H₂O of 1:10. After evaporation of the solvent at 80 °C, the mixture was calcined at 350 °C for 2 h in air to obtain the 20Ni/LaHA catalyst with a NiO loading of 20 wt%.

2.1.3. Preparation of ZrO₂-modified 20Ni/LaHA catalyst

The ZrO₂-modified 20Ni/LaHA catalyst (20Ni/LaHA@ZrO₂) was prepared using a modified successive adsorption and reaction method [35,41]. First, 0.05 mol L⁻¹ zirconium *n*-butoxide (Zr(OBu)₄) anhydrous toluene solution and 0.1 mol L⁻¹ ethanol aqueous solution were prepared. For each cycle, the milled 20Ni/LaHA (1.00 g) was first spread into a thin layer in a sand core funnel and immersed in a Zr(OBu)₄ anhydrous toluene solution (5 mL, 0.05 mol L⁻¹) for 1 min to allow adsorption of Zr(OBu)₄ onto the surface of 20Ni/LaHA. After being filtrated and washed twice with anhydrous toluene, the powder was dried at 150 °C for 10 min. Then, 5 mL ethanol aqueous solution (0.1 mol L⁻¹) was added sequentially, and the powder was immersed in the solution for 1 min. During this process, the pre-adsorbed Zr(OBu)₄ on the surface of 20Ni/LaHA could react with H₂O to form the desired ZrO₂ precursor. The powder was then filtrated and dried at 150 °C in an oven. To obtain the desired amount of ZrO₂, the above modification cycle could be repeated several times (Fig. 1). Finally, to control the crystalline phase of ZrO₂ [35], the obtained samples were calcined at 400

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