



Catalysis, Kinetics and Reaction Engineering

Catalytic methanation of syngas over Ni-based catalysts with different supports



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ABSTRACT

Co-precipitation method was selected for the preparation of Ni/Al₂O₃, Ni/ZrO₂ and Ni/CeO₂ catalysts, and their performances in methanation were investigated in this study. The structure and surface properties of these catalysts were characterized by BET, XRD, H₂-TPD, TEM and H₂-TPR. The results showed that the catalytic activity at low temperature followed the order: Ni/Al₂O₃ > Ni/ZrO₂ > Ni/CeO₂. Ni/Al₂O₃ catalyst presented the best catalytic performance with the highest CH₄ selectivity of 94.5%. The characterization results indicated that the dispersion of the active component Ni was the main factor affecting the catalytic activity and the one with higher dispersion gave better performance.

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1. Introduction

As an effective technology to synthesize the substitute of natural gas, methanation has aroused extensive attention of researchers [1–3]. At present, researches of syngas methanation mainly focus on the methanation catalyst including active components, auxiliaries and supports. Mills *et al.* [4] found that the methanation catalytic activities of the metals were in accordance with the following order: Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag. Precious metals such as Rh, Ir and Ru have better catalytic activities, however the cost is pretty high [5–8]; Co has better catalytic activity at low temperature and can avoid coking deactivation [9], while the selectivity of CH₄ is poor. Fe-based catalyst has extensive sources with lower price but it is easy to cause carbon deposition [10]. Compared with the catalysts mentioned above, Ni-based catalyst for CO methanation has a broad research prospect.

The activity of Ni-based catalyst can be affected by the supports, preparation methods and auxiliaries. The common supports of Ni-based catalysts include Al₂O₃, SiO₂ and ZrO₂ *etc.*, and these supports can affect the catalytic activities of Ni-based catalyst through changing the particle size of active components [11]. Al₂O₃ as support [12] can interact with the superficial NiO species to form ionic bonds promoting the dispersion of NiO species over the surface, which exhibited higher catalytic activity during the research of syngas methanation [3,13]. ZrO₂ has been studied widely in recent years [11,14]. ZrO₂ with the properties of N type semiconductor can generate strong interaction with the metal loaded on its surface, and occurs negative charge

absorption with oxygen easily [15]. Under the condition of less oxygen, the existence of redox pair Ce³⁺/Ce⁴⁺ makes Ce move fast between CeO₂ and Ce₂O₃ thus forming unstable oxygen vacancy and generate strong interaction with oxygen atoms of CO molecules, which makes C–O bonds easily break to form activated carbon over the surface of support. CeO₂, as an important rare earth oxide with special property, shows more potential in the study of support [16].

As a consequence, Al₂O₃, ZrO₂ and CeO₂ were employed to be catalyst supports for the research of methanation. Catalytic activity of catalysts for methanation is also affected by preparation method. Wang *et al.* [17] found that the particle size of catalyst was smaller prepared by co-precipitation, and the active components evenly dispersed over the support, which led to better catalytic performance. Therefore this paper adopted co-precipitation method to prepare Ni/Al₂O₃, Ni/ZrO₂ and Ni/CeO₂. The catalytic activities of these catalysts were compared in order to find out the most optimal catalyst which could display higher CO conversion and better selectivity to CH₄. Meanwhile the effect of different supports on Ni-based catalysts was investigated. In addition, the catalyst with the best result of methanation was taken to life test in aim to study the stability of the catalyst at high temperature.

2. Experimental

2.1. Catalyst preparation

Ni/Al₂O₃, Ni/ZrO₂ and Ni/CeO₂ catalysts were prepared by co-precipitation method with the nominal Ni loading of 15 wt%. The reagents were purchased from Sinopharm Chemical Reagent Co.

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Ni/Al₂O₃ catalyst was prepared through the following steps: 3.7 g Ni(NO₃)₂·6H₂O and 15.6 g Al(NO₃)₃·9H₂O were added to 125 mL deionized water to get the uniform aqueous solution after continuous stirring. Then 1 mol·L⁻¹ K₂CO₃ solution was dropwise added as a precipitant to the Ni(NO₃)₂ and Al(NO₃)₃ solution until the pH value reached 9–10, followed by stirring for 2 h at 70 °C. After that, the suspension was filtered and washed using deionized water to neutral state. The obtained precipitate was dried at 120 °C overnight and calcined at 500 °C in air for 4 h.

For the preparation of Ni/ZrO₂ and Ni/CeO₂ catalysts, 15.6 g Al(NO₃)₃·9H₂O was replaced by 14.8 g Zr(NO₃)₃·5H₂O and 10.7 g Ce(NO₃)₃·6H₂O respectively, while other procedures were the same as that for the preparation of Ni/Al₂O₃ catalyst.

2.2. Catalyst characterization

The surface area (*S*_{BET}) and pore structures of the catalysts were measured by N₂ physical adsorption (Quadrasorb SI). Before this measurement, the sample was degassed at 300 °C for 3 h. N₂ adsorption–desorption isotherms were recorded at –196 °C. The surface area was obtained via Brunauer–Emmett–Teller (BET) method while the pore size and volume were calculated from Barrett–Joyner–Halenda (BJH) model. The real content of nickel in the catalyst was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES), using a Thermo iCAP 6000 device.

Powder X-ray diffraction (XRD) patterns were characterized on a PANalytical X'Pert PRO X-ray diffractometer with a CuK_α radiation source at 40 kV and 30 mA. The diffraction angle 2θ ranged from 10° to 90° and the scan speed was 5(°)·min⁻¹. The crystallite size was calculated according to the Scherrer equation.

The active metal as well as its distribution of the catalysts was observed by transmission electron microscopy (TEM) using Philips-FEI Tecnai G2F30 apparatus. The metal size was calculated as follows: $d = \sum w_i d_i^3 / \sum w_i d_i^2$, where w_i was the specific metal particle size and d_i was the corresponding particle number [18].

Reduction feature of the catalysts was analyzed through hydrogen temperature programmed reduction (H₂-TPR) on an AutoChem II 2920 instrument (Micromeritics Instrument Corp). The samples (20 mg) were purged by argon at 200 °C for 90 min and then cooled to 50 °C. Then, the reduction was carried out with a mixture of 10% H₂/Ar at a heating rate of 10 °C·min⁻¹ up to 900 °C. During the reduction, the consumption amount of H₂ was recorded with a thermal conductivity detector.

The amount of active sites on the reduced catalysts was measured according to the hydrogen adsorption capacity and adsorption strength by H₂-TPD (temperature programmed desorption) experiments using an AutoChem II 2920 instrument (Micromeritics Instrument Corp). Prior to the H₂-TPD measurement, 50 mg catalyst sample was initially reduced with a mixed stream of 10% H₂/Ar. After cooling the sample to 50 °C, purging for 90 min under H₂/Ar atmosphere and then purging under argon for another 90 min to remove the physisorbed hydrogen, the temperature was increased from 50 °C to 800 °C at a heating rate of 10 °C·min⁻¹. The desorbed hydrogen was detected by using a thermal conductivity detector (TCD).

2.3. Test of catalytic activity

The catalytic test was conducted in a fixed-bed reactor. In the experiment, 1 g catalyst was packed in a stainless steel tube reactor and sandwiched by silica wool on the top and at the bottom. A thermocouple was centered in the catalyst layer to measure reaction temperatures. Before reactions, the catalysts were reduced by hydrogen (50 ml·min⁻¹) at 470 °C for 2 h with a heating rate of 5 °C·min⁻¹. After reduction, the catalyst bed temperature was decreased to the reaction temperature (200–440 °C) and the pressure was maintained at 1 MPa. The syngas had a composition of $n(\text{H}_2)/n(\text{CO}) = 3$ and the

gas hourly space velocity (GHSV) was at 20000 ml·h⁻¹·g⁻¹ controlled by the mass flowmeter (Brooks, 5850E). The production gas flow was measured via soap film flowmeter (GLIBRATOR-2). The product gases were analyzed with an online gas chromatograph (Agilent 7890A). The hydrocarbon was separated by HP-PLOT Q capillary column and detected by a hydrogen flame ionization detector (FID). H₂, CO, and CO₂ in the gas were separated by Porapak Q and carbon sieve packed columns and then measured by TCD. Under each reaction condition, several groups of data were obtained to get an average value. The molecular CO conversion (*X*_{CO}) and product selectivity were presented in Eqs. (1) and (2) as follows:

$$X_{\text{CO}} = \frac{n_{\text{CO}_{\text{in}}} - n_{\text{CO}_{\text{out}}}}{n_{\text{CO}_{\text{in}}}} \times 100\% \quad (1)$$

$$S_{\text{C}_m} = \frac{m \times n_{\text{C}_m}}{n_{\text{CO}_{\text{in}}} - n_{\text{CO}_{\text{out}}}} \times 100\% \quad (2)$$

where $n_{\text{CO}_{\text{in}}}$ and $n_{\text{CO}_{\text{out}}}$ represented the CO molecular numbers in feed gas and product gas, respectively, and m stood for the carbon number of product C_{*m*}.

3. Results and Discussion

3.1. Catalyst characterization

N₂ physical adsorption of the three prepared catalysts was carried out to characterize their BET surface area and pore structure. As shown in Table 1, the BET surface area of Ni/Al₂O₃ catalyst is 266.3 m²·g⁻¹, which is much larger than the other catalysts, 13.4 and 32.9 m²·g⁻¹ for Ni/ZrO₂ and Ni/CeO₂ catalysts respectively. Meanwhile, the largest pore volume of 0.27 ml·g⁻¹ was found in Ni/Al₂O₃ catalyst. For catalyst of Ni/ZrO₂, its pore volume is only 0.02 ml·g⁻¹, indicating the less developed pore structure. Ni/Al₂O₃ and Ni/CeO₂ catalysts show the isotherms of type IV (Fig. 1(a)) and hysteresis loops of type H1, indicating the characteristic of particulate adsorbents with mesopores. However, the hysteresis loop in Ni/Al₂O₃ catalyst is not quite obvious due to its less porous structure. The BJH plots (Fig. 1(b)) reveal that compared with the other two Ni-based catalysts, the Ni/Al₂O₃ is a porosity catalyst with the most probable pore size of 3.8 nm.

Fig. 2 depicts the XRD patterns of reduced Ni-based catalysts. For the Ni/Al₂O₃ catalyst, the broad peaks at 2θ of 19.6°, 31.9°, 37.6°, 45.8°, 60.5°, 66.8°, 84.5° assignable to Al₂O₃ (JCPDS 29-0063) were found. The diffraction peak of Ni at 2θ = 44.5° (JCPDS 04-0850) was overlapped by the peak at 2θ = 45.8° assigned to Al₂O₃. It is indicated that Ni was highly dispersed on Al₂O₃ and was too small to be detected [19], which is in accordance with the result of TEM. For the catalyst of Ni/CeO₂, two weak diffraction peaks at 2θ of 44.5° and 51.8° which were characteristics of metallic Ni (JCPDS 04-0850) were detected, suggesting the increased crystalline size of Ni. The Ni crystallite size is 3.4, 6.3 and 12.1 nm for Ni/Al₂O₃, Ni/ZrO₂ and Ni/CeO₂ catalysts respectively. The results revealed that the Ni species could be highly distributed on the supports of Al₂O₃ and ZrO₂ though the Ni/ZrO₂ catalyst with low BET surface area and pore volume.

The characterization technology of TEM was applied to obtain the morphology of Ni catalysts. As shown in Fig. 3, the particles of active components are uniformly dispersed on the support with spherical

Table 1
Textural properties of the Ni-based catalysts after reduction

Catalysts	<i>S</i> _{BET} /m ² ·g ⁻¹	<i>V</i> _{Pore} /ml·g ⁻¹	<i>D</i> _{Pore} /nm	<i>d</i> _{Ni} /nm	Ni loading [Ⓛ] /wt%
Ni/Al ₂ O ₃	266.3	0.27	4.0	3.4	15.2
Ni/ZrO ₂	13.4	0.02	6.4	6.3	14.9
Ni/CeO ₂	32.9	0.13	13.3	12.1	14.8

[Ⓛ] Measured by ICP-AES.

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