



A comparison of Ni/SiC and Ni/Al₂O₃ catalyzed total methanation for production of synthetic natural gas

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ABSTRACT

Ni/SiC and Ni/Al₂O₃ catalysts were prepared by impregnation method for total methanation. The 120 h stability tests of the catalysts were conducted at 500 °C and 3 MPa with a syngas of H₂/CO = 3. The catalysts before and after reaction were characterized by N₂ adsorption–desorption, H₂-TPR, XRD, TPO, TG-DSC, SEM, and TEM. The results show that the Ni/SiC catalyst is more stable than the Ni/Al₂O₃ catalyst. Compared to the Ni/Al₂O₃ counterpart, the Ni/SiC catalyst is more resistant to sintering and carbon deposition and easier to regenerate in the methanation reaction due to the high thermal conductivity of SiC and the weak metal–support interaction.

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1. Introduction

In recent years, production of synthetic or substitute natural gas (SNG) from coal or biomass has attracted much interest due to the increasing demand for natural gas, the wish for enhancing domestic energy security, the opportunity of reducing CO₂ emission, and the high energetic conversion efficiency [1–3]. SNG production proceeds through the following steps: gasification, gas cleaning and conditioning, methanation, and subsequent gas upgrading. Among them, methanation of syngas is an essential step. Methanation for SNG production is extremely exothermic due to the high concentrations of carbon oxides. For every 1% CO and every 1% CO₂, the temperature rise for a typical methanator gas composition in an ammonia plant is 74 °C and 60 °C, respectively [4]. The large potential temperature increase may cause sintering of the catalyst and for some cases carbon formation [5], which requires the catalyst to be stable and resistant to carbon deposition at high temperature.

Nickel catalysts have been preeminently used for methanation reaction because of their relatively low cost, high activity, and the best selectivity to methane as compared to other metals [6]. Many studies have focused on improving the stability of nickel catalysts by varying support materials, promoters, and preparation methods [7–13]. Gao et al. prepared barium hexaaluminate (BHA) supported nickel catalyst for CO methanation and found Ni/BHA was more

stable and more resistant to carbon deposition than Ni/Al₂O₃ [8]. Bartholomew et al. reported that nickel was more thermally stable on NiAl₂O₄ than on Al₂O₃ and addition of Rh and Ru could enhance the thermal stability of nickel on alumina [9]. However, over the above-mentioned catalysts, the reaction heat would rapidly accumulate and hot spots can be easily generated due to the poor thermal conductivity of the catalysts. For the syngas of H₂/CO = 3 at 3 MPa with an inlet temperature of 300 °C, the adiabatic temperature rise would reach 623 °C [14], and the hot spot temperature would be higher, which may cause catalyst deterioration. One solution is to prepare stable and highly thermo-conductive catalysts to lower the hot spot temperature.

Silicon carbide (SiC) possesses many properties such as excellent mechanical strength, superior thermal stability, high heat conductivity, and chemical inertness. It is a very promising catalyst support in place of the traditional insulated supports in highly endothermic or exothermic reactions [15,16]. SiC has been proved to be a superior catalyst support in many different reactions, e.g., methane reforming [17–21], automotive exhaust treatment [22–24], methane combustion [25–27], butane oxidation [28], Fischer–Tropsch synthesis [29–31], oxidative coupling of methane [32], isomerization [33], and dehydrogenation [34]. However, to the best of our knowledge, SiC support is less employed in the methanation reaction. Vannice et al. [35] first used SiC support in CO methanation, but under a very mild reaction condition significantly different from that of total methanation. Yu et al. reported that Ni/SiC showed higher stability than Ni/TiO₂ in CO methanation [10]. But it is well known that Ni/Al₂O₃ catalysts are mostly used for

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methanation reaction both in academic study and industrial application. Thus, to further highlight the performances of SiC support in total methanation, alumina support should be used as a counterpart. In this work, we made a comparison between performances of Ni/SiC and Ni/Al₂O₃ catalysts in the total methanation reaction for the first time.

2. Experimental

2.1. Catalyst preparation

All chemicals were used as received without further purification unless otherwise clarified. The supports used here were in the granular form. Commercial silicon carbide fine powder (RS07, 99% purity), hydroxypropyl methylcellulose, tung oil, and deionized water were mixed and milled together. The mixture was extruded into small sticks (\varnothing 1 mm), dried at 110 °C for 24 h, and calcined in air at 800 °C for 4 h. The calcined sticks were crushed and screened to give a granulometric fraction between 0.7 and 0.9 mm. Commercial pseudoboehmite powder (99% purity) was molded under 10 MPa into cylindrical lumps (\varnothing 20 mm). The obtained cylinders were calcined in air at 550 °C for 8 h, crushed, and screened to the desired size (0.7–0.9 mm). The catalysts were prepared by wet impregnation of the prepared support materials using aqueous solutions of nickel nitrate with different concentrations (3 M for SiC, 1 M for Al₂O₃). After impregnation, the samples were dried at 110 °C for 4 h and then calcined in air at 500 °C for 2 h. The nominal nickel loadings of the prepared Ni/SiC and Ni/Al₂O₃ catalysts were 4.2 wt% and 5.3 wt%.

2.2. Catalyst characterization

BET surface area and pore volume were measured by nitrogen adsorption at the liquid nitrogen temperature on a Quantachrome NOVA2200e analyzer. Prior to analysis, the samples were degassed under dynamic vacuum at 300 °C for 2 h.

TPR tests were performed in flowing 10% H₂ in argon (30 mL min⁻¹) using a Quantachrome ChemBET Pulsar automated chemisorption analyzer. The catalysts were placed in a quartz reactor and heated from room temperature to 900 °C at a ramping rate of 10 °C min⁻¹. Before analysis, the samples were flushed with argon at 300 °C for 1 h to desorb moisture and impurities. After passing through a cold trap to remove water formed, the effluent gas was continuously monitored with a TCD detector. The reduction degree of the catalyst was defined as the ratio of H₂ uptake calculated by integrating the peak area under the TPR profiles to the theoretic H₂ consumption. The proportion between H₂ uptake and the peak area was calibrated by injecting accurately known amount of H₂ into the empty quartz reactor under the same testing conditions.

XRD measurements were carried out on a Rigaku RINTD/MAX-2500PC diffractometer with a monochromatic Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The scans were performed from 20° to 80° of 2θ angle with a step size of 0.02°. The crystalline phases were identified using JCPDS data files.

TPO analysis of the spent catalysts was performed using the same instrument as that in the TPR tests. The samples were purged with helium at 300 °C for 1 h. The helium flow was then replaced by 3% O₂ in helium (30 mL min⁻¹), and the sample temperature was raised from 100 °C to 900 °C at a heating rate of 10 °C min⁻¹.

TG-DSC analysis of the used catalysts was conducted under air flow (50 mL min⁻¹) from room temperature to 900 °C at a heating rate of 10 °C min⁻¹ on a NETZSCH STA 449 F3 thermoanalyzer.

SEM images were obtained on a FEI Quanta 200F microscope operated at 10–20 kV. The sample was fixed on a copper holder with conductive adhesives.

TEM observations were conducted using an FEI Tecnai G2 Spirit microscope operated at 100 kV. HRTEM images were obtained on an FEI Tecnai G2 F30 S-Twin microscope operated at 300 kV. The sample was dispersed in ethanol using an ultrasonic bath, and the obtained suspension was then dropped onto a holey carbon-coated copper grid.

To obtain fresh reduced catalysts for N₂ adsorption–desorption, XRD, SEM, TEM, and HRTEM analysis, the as-prepared catalysts were pretreated in pure H₂ at 500 °C for 4 h and passivated in CO₂ at room temperature for 4 h to prevent bulk oxidation of Ni particles. The used catalysts were characterized as obtained without further treatments.

2.3. Catalyst test

Methanation reaction was performed in a fixed bed flow reactor located inside a tubular resistance furnace. The reactor section included a stainless steel reactor and an inner lined corundum tube (\varnothing 15 mm \times 2 mm \times 600 mm). The reaction temperature was measured in the middle of the catalyst bed with a thermocouple. High purity H₂ (99.99%) and CO (99.99%) were used as reactants, and CO was subjected to additional purification to remove possible carbonyl compounds. The gas flow rates were controlled by Brooks 5850E mass flow controllers. The feed and product gases were analyzed using an online Agilent 7890A gas chromatograph equipped with a TDX-01 packed column, a thermal conductivity detector, and a flame ionization detector. An ice-water trap was used to prevent water from entering the GC.

The catalyst was packed in the middle of the reactor in the same manner for all runs. Typically the reactor was first filled with inert silica sand (0.4–0.9 mm) and a layer of silica wool, followed by 2.7 mL of the catalyst (3.4 g for Ni/SiC, 2.7 g for Ni/Al₂O₃), and then another layer of silica wool and silica sand. Before the start of each test run, the catalyst was reduced in situ under flowing hydrogen (200 mL min⁻¹) at 500 °C for 4 h. The reactant gases consisted of 75.75 vol% H₂ and 24.25 vol% CO, and the total gas flow rate was ca. 227 mL min⁻¹, corresponding to a volume hourly space velocity of ca. 5000 h⁻¹. Catalyst tests were performed at 500 °C and 3 MPa for 120 h. A blank run only without the catalyst was also carried out under the same reaction conditions in order to check the activity of the evaluation system. Under these conditions, the evaluation system was negligibly active. Methane selectivity was calculated as the concentration ratio of methane to the sum of all detected carbon-containing products, viz. CH₄ and CO₂, without accounting for carbon deposits.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. N₂ adsorption–desorption

As summarized in Table 1, the BET surface area and pore volume of SiC-supported catalysts are much smaller than those of Al₂O₃-supported catalysts. The surface area of the Ni/SiC catalyst kept unchanged after reaction, highlighting the thermal resistance of the SiC support. For the spent Ni/Al₂O₃ catalyst, the surface area decreased by 22% of the original value and the average pore size increased by 26%, which may be attributed to thermal sintering of the alumina support and to blockage of the smaller pores by carbonaceous deposits (vide infra).

3.1.2. H₂-TPR

As can be seen in Fig. 1, TPR spectra of the two catalysts are obviously different. The spectrum of the NiO/SiC catalyst has two peaks centered at 430 °C and 770 °C, the former related to free and

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