Bimetallic Ni–Fe total-methanation catalyst for the production of substitute natural gas under high pressure

Dayong Tian [a], Zhihong Liu [a], Dandan Li [b], Huiliang Shi [a], Weixiong Pan [a], Yi Cheng [a],*

[a] Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China
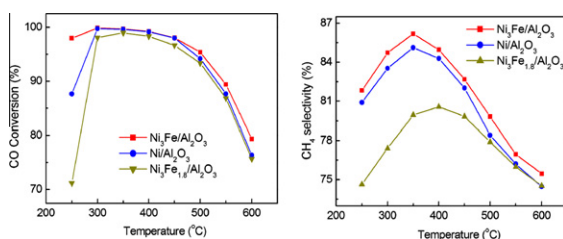[b] School of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

HIGHLIGHTS

► Bimetallic Ni–Fe catalysts were prepared for total-methanation process, showing excellent catalytic performance.
► High activity of Ni–Fe catalysts was attributed to the quality of Ni–Fe alloy.
► Silicon content in catalyst support as an impurity played a negative role in CH$_4$ selectivity.

GRAPHICAL ABSTRACT

The bimetallic Ni–Fe catalysts used in CO total-methanation reaction were prepared by the impregnation method on γ-Al$_2$O$_3$ support for the production of substitute natural gas (SNG). The methanation performance under the industrial total-methanation conditions (0.1–3.0 MPa, H$_2$/CO = 3.0–3.1) was studied in detail using Ni–Fe/γ-Al$_2$O$_3$ as a heterogeneous catalyst. The results showed that the addition of Fe to the catalyst can effectively improve the catalytic activity of Ni/γ-Al$_2$O$_3$, while the high activity of bimetallic Ni–Fe catalyst was attributed to the quality of Ni–Fe alloy in the catalyst in terms of the experimental results of H$_2$-TPR.

ABSTRACT

The bimetallic Ni–Fe catalysts used in CO total-methanation reaction were prepared by the impregnation method on γ-Al$_2$O$_3$ support for the production of substitute natural gas (SNG). The catalysts were characterized by N$_2$ physisorption measurements, field-emission scanning electron microscopy (FE-SEM), and H$_2$ temperature-programmed reduction (H$_2$-TPR). The methanation performance under the industrial total-methanation conditions (0.1–3.0 MPa, H$_2$/CO = 3.0–3.1) was studied in detail using Ni–Fe/γ-Al$_2$O$_3$ as a heterogeneous catalyst. The results showed that the addition of Fe to the catalyst can effectively improve the catalytic activity of Ni/γ-Al$_2$O$_3$, while the high activity of bimetallic Ni–Fe catalyst was attributed to the quality of Ni–Fe alloy in the catalyst in terms of the experimental results of H$_2$-TPR. The sample with appropriate Ni/Fe molar ratio of about 3 exhibited the highest CO conversion (near 100% at 225–550 °C) and the highest CH$_4$ selectivity (over 99% at 300–450 °C) under the reaction pressure of 3.0 MPa. Furthermore, based on the systematic study of catalyst components, MgO in the catalyst can increase the reduction temperature of nickel oxide on the support. The silicon species as an impurity in the support play a negative role in the catalytic activity, especially for the CH$_4$ selectivity.

1. Introduction

Methanation (CO + 3H$_2$ = CH$_4$ + H$_2$O) is an important process in the chemical industry, including removal of trace amounts of CO from H$_2$–rich feed gas, purification of the reformate gas for fuel cell, and processes in relation to Fischer–Tropsch synthesis [1–4]. Recently, the production of substitute natural gas (SNG) from coal or biomass is becoming of interest, especially in the areas which are lack of the natural gas resource [5]. Total-methanation is the main reaction that converts the syngas produced from gasifier to SNG. Here, the total-methanation refers to the methanation

* Corresponding author. Tel.: +86 010 6279 4468; fax: +86 010 6277 2051.
E-mail address: yicheng@tsinghua.edu.cn (Y. Cheng).

reaction with pure syngas (CO and H_2) as the feedstock, where the mole ratio of H_2 to CO is about 3.0. As a comparison, the partial-methanation indicates the conversion of little amount of CO in the feedstock, which is used to increase the heat-value of city gas. A distinct difference in these two processes is the amount of heat released from the reaction. In the former case (i.e., the total-methanation), the reactor design and the catalyst activity meet more challenges due to the much higher exothermicity than the partial-methanation. Except for the total-methanation reaction in the SNG production process, the water–gas shift (WGS) reaction ($CO + H_2O = CO_2 + H_2$) must be suppressed as a side reaction which reduces the selectivity of methane. In the industrial SNG production, the mole ratio of H_2/CO in the feed gas is 3.0–3.1, slightly higher than the stoichiometry. Moreover, the acceptable CO conversion and CH_4 selectivity in the product gas are more than 99% and 97%, respectively. Thus, the activity of the catalyst in promoting CO methanation versus water–gas shift reaction is of paramount importance.

In general, the methanation is carried out on the metal catalysts, which rest on the metals of Group VIII, on Mo or on Ag, often containing expensive noble metals, supporting on the carriers of Al_2O_3, SiO_2, CeO_2, etc. Based on the studies of Mills and Steffgen [6], the methanation activity of various metals follows the order: Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag. From the comprehensive analysis of raw material sources, cost, and activity, the current methanation catalysts are almost based on Ni. However, a problem with nickel-based catalysts is the dissatisfactory selectivity between the CO methanation and the water–gas shift reactions. In the past few decades, several approaches have been developed to promote the catalytic activity of the methanation catalyst. Studies show that the barrier for CO dissociation and the stability of the main intermediates on the metal crystal surface are the main factors determining the activity of the methanation catalyst [7–9]. Through the combination of two metals, the surface active sites could be constructed to get the optimal dissociative adsorption energy of CO on the metal surface [8,10]. Furthermore, many studies for the CO hydrogenation reactions have been conducted with bimetallic catalysts. For example, by adding copper, the activity of iron catalyst is increased in the Fischer–Tropsch synthesis [11]. Other bimetallic Fe–Co, Co–Ni, Ni–Cu and Ni–Fe Fischer–Tropsch catalysts appear to be more active than the monometallic ones [12–16]. To the best of our knowledge, there has no report on the performance of bimetallic catalyst in the total-methanation reaction under the industrial condition (3.0–4.0 MPa, H_2/CO = 3.0–3.1).

In the present study, the supported bimetallic Ni–Fe catalysts were developed in order to improve the methanation reaction performance, i.e., the CO conversion and CH_4 selectivity. Besides, the influences of catalyst components such as the molar ratio of Ni/Fe, loadings of MgO, and property of the catalyst support on the catalytic performance have also been studied. This study aimed to provide a general method to prepare high activity total-methanation catalyst.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the successive impregnation method. All the reagents used for the catalyst preparation were in analytical grade (AR) and used as received without further purification: $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and deionized water. The γ-Al_2O_3 support (BET surface area: 140 m^2/g) was aged at 550 °C for 5 h before the impregnation. Typically, the γ-Al_2O_3 was first impregnated with an aqueous solution

of cerous nitrate and magnesium nitrate, and dried at 60 °C. The impregnated sample was heated at 100 °C for 10 h and calcined in air at 550 °C for 5 h. Then the sample was impregnated with a solution of nickelous nitrate and ferric nitrate as the same way with the cerous nitrate and magnesium nitrate. After calcined in air at 550 °C for 5 h, the catalysts loading NiO, Fe_2O_3, CeO_2 and MgO were obtained.

2.2. Catalyst characterization

The BET surface areas and pore sizes were measured on a Quantacerome AUTOSORB-1C automated chemisorption/physisorption surface area and pore size analyzer at 77.3 K using N_2 as the adsorbate. The average pore sizes were calculated from the adsorption isotherm branch by BJH method. The electron micrographs were taken on a JEOL JSM-7401F field-emission scanning electron microscopy (FE-SEM). The composition of the support surface was tested by energy-dispersive X-ray spectrometric microanalysis (EDS) with SEM. The reducibility of the catalysts was studied by H_2 temperature-programmed reduction (H_2-TPR) using a catalyst characterization system equipped with a TCD detector. In H_2-TPR, 0.5 g sample loaded in a quartz tube (i.d. 8 mm) was kept under a nitrogen flow of 25 ml/min at 120 °C for 0.5 h. Each run was carried out at a heating rate of 5 °C/min from 25 °C to 880 °C in a reductive gas flow (10% H_2/N_2) of 25 ml/min.

2.3. Reaction tests

The evaluation of methanation performance was carried out in a fixed-bed reactor at an industrial operation pressure of 0.1–3.0 MPa. Before each test, 0.5 g catalyst was reduced with a reductive gas flow (20% H_2/N_2) of 40 ml/min at 800 °C for 1 h. Then H_2 and CO was introduced with the purity of 99.999%. The feed rate was controlled by the mass flow controllers (MFCs) with the total flow rate varying from 80 to 130 ml/min. Two thermocouples were used in the catalytic tests. One was inserted into the furnace chamber to control the environmental temperature around the reactor. The other was placed at the end of the catalyst bed to monitor its real temperature. The product gases were analyzed by an on-line Shimadzu GC-2014 gas chromatograph equipped with a TCD detector and a TDX-01 packed column (3 m in length). The generated water was separated from the reaction system by a water-cooled condenser. Thus, the CO conversion and CH_4 selectivity were calculated in terms of Eqs. (1) and (2). The experimental data reported in this paper was stable at least 1 h at each temperature to reflect the exact catalyst performance.

$$C_{CO} = \frac{\text{moles of CO converted}}{\text{moles of CO introduced}} \tag{1}$$

$$S_{CH_4} = \frac{\text{moles of } CH_4 \text{ produced}}{\text{moles of CO converted}} \tag{2}$$

3. Results and discussion

3.1. Catalyst characterization

The metal oxide loadings of different catalysts and BET surface areas are listed in Table 1. The surface areas of Ni/γ-Al_2O_3, Ni_3Fe/γ-Al_2O_3, NiFe/γ-Al_2O_3, and $Ni_3Fe_{1.8}$/γ-Al_2O_3 are from 73.6 to 85.7 m^2/g. Fig. 1 shows the BJH adsorption pore distribution of the bimetallic Ni–Fe catalysts.

The morphology and dispersion of the metal particles on the surface of the γ-Al_2O_3 support were characterized by SEM. All of the samples were reduced at a reduction gas (20% H_2/N_2) for 1 h.