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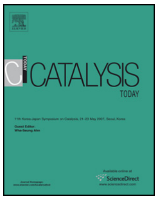

Production of hydrogen by steam reforming of methane over alumina supported nano-NiO/SiO_2 catalyst

Barnali Bej, Narayan C. Pradhan*, Swati Neogi

Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721302, India

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ABSTRACT

Steam reforming of methane (SRM) was carried out over alumina supported nano NiO catalyst in silica synthesized using sol–gel method. The crystallite size of NiO in $NiO–SiO_2$ catalysts was found to vary with the calcination temperature and the extent of Ni loading in the catalyst. The NiO crystallite size was found to be 9–15 nm in the Ni loading range of 5–15% and calcinations temperature range of 350–500 °C studied. Catalyst containing 10% Ni was found to be the best one for steam reforming reaction in terms of methane conversion. The catalyst was found to be very active and stable in the temperature range of 500–700 °C. The most favorable reaction condition was established at a temperature of 700 °C, steam to methane molar ratio of 3.5 and a space–time of 11.31 kg cat h/kmol of inlet methane. At this optimum condition, the conversion of methane was 95.7% and the yield of hydrogen was about 3.8 moles of hydrogen per mole of methane reacted.

1. Introduction

Hydrogen contains highest energy per unit weight (120.7 kJ/g) and is, therefore, considered as the energy carrier of the future. Moreover, hydrogen as a fuel is clean, non-polluting and renewable. Advances in fuel cell technology make hydrogen more important as a new energy source for both stationary and vehicle applications. As such, the demand for hydrogen in fuel cell application and also in chemical industry is continuously increasing [1]. However, development of feasible production method for hydrogen is necessary as most of the hydrogen is available in nature in bound form (as water or hydrocarbons). A number of catalytic reforming technologies, such as steam reforming, partial oxidation, and autothermal reforming, have been used for the production of hydrogen from various hydrocarbons [2–11]. Among these, catalytic steam reforming of natural gas, which contains mainly methane, is probably the most important and economic process for the production of hydrogen and synthesis gas on a large scale [12].

Catalytic steam reforming of methane involves the reaction of methane with steam over a catalyst at elevated temperatures (400–900 °C) and pressures (1–30 atm). The reactions that take place during the catalytic steam reforming of methane are:

Methane steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H_{298}{}^{\circ} = 206\,\text{kJ/mol}) \tag{1}$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (\Delta \text{H}_{298}{}^{\circ} = 165\,\text{kJ/mol}) \tag{2}$$

Water–gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \quad (\Delta \text{H}_{298}{}^{\circ} = -41\,\text{kJ/mol}) \tag{3}$$

Carbon formation reactions:

$$CH_4 = C + 2H_2 \quad (\Delta \text{H}_{298}{}^{\circ} = 76\,\text{kJ/mol}) \tag{4}$$

$$2CO = C + CO_2 \quad (\Delta \text{H}_{298}{}^{\circ} = -173\,\text{kJ/mol}) \tag{5}$$

Nickel-based catalysts are widely studied for steam reforming of methane (SRM) [13–23]. In particular, Ni/Al_2O_3 is considered as promising catalyst for SRM due to its low cost and high catalytic activity [24–30]. The present work is concerned with the steam reforming of methane over a nickel based catalyst.

The catalytic activity of Ni/Al_2O_3 is closely related to both nickel content and nickel dispersion, but the effects of these two factors on the catalytic activity are opposite [11]. While the catalytic activity of Ni/Al_2O_3 increases with nickel content due to increased number of active nickel sites, the nickel dispersion decreases with increased nickel content due to the aggregation of nickel, thereby decreasing the catalytic activity. In general, nickel content of conventional Ni/Al_2O_3 catalysts used in steam reforming does not exceed 12 wt% to avoid severe aggregation or sintering of nickel particles during the reaction. Better dispersion could be obtained if the nickel particles were in the nanometer range with superior catalytic activity

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* Corresponding author. Tel.: +91 3222 283940; fax: +91 3222 255303.
E-mail address: ncp@che.iitkgp.ernet.in (N.C. Pradhan).

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when used as catalysts. The objective of the present study was to prepare nano-nickel dispersed on silica and supported on alumina by a suitable technique for steam reforming of hydrocarbon.

The preparation of nano-nickel oxide highly dispersed in silica has been reported in the literatures. Recently, a simple technique of sol–gel processing for formation of mesoporous Ni/SiO_2 with high Ni content (over 50 wt% in NiO form) and increased Ni dispersion has been reported [31,32]. Citric acid has been used as mesopore forming agent with TEOS as SiO_2 precursor, nickel nitrate hexahydrate as Ni precursor. The mesopores are formed by removing citric acid from the silica-Ni-citric acid composite and large shrinkage in pores occurs during calcination in air. High Ni dispersion is achieved in the Ni/SiO_2 by controlling large mesopores. Similar technique has been adopted for making nano-NiO/SiO_2 using different solvents [33–37]. Wu and Williams have discussed the hydrogen production from steam reforming of ethanol over a novel nano-Ni/SiO_2 catalyst [38].

It is evident from the above discussion that nano NiO/SiO_2 could be a good catalyst for reforming of hydrocarbon. Therefore, the present work was concerned with the preparation of nano-NiO/SiO_2 for the reforming of methane. The nickel loading in the catalyst was kept within 12 wt%. The activity of the prepared nano-catalyst was assessed in terms of methane conversion and hydrogen yield.

2. Experimental details

2.1. Catalyst preparation

A certain amount of tetraethyl ortho-silicate (TEOS) in ethanol solution was stirred using magnetic stirrer at room temperature. Nickel nitrate hexahydrate with intended Ni loading (say 10% in the catalyst) dissolved in the aqueous ethanol solution was added slowly to the silica sol with constant stirring. The final solution was stirred at room temperature for about 5–6 h and allowed to age for one week. The obtained gel was dried in hot air oven at 110 °C for 24 h to remove water and other volatile compounds. Then the dried gel was calcined at a particular temperature (350 °C, 400 °C, 450 °C and 500 °C).

To prepare alumina supported NiO–SiO_2 catalyst, alumina, NiO–SiO_2 and bentonite powder (as binder) were mixed in an appropriate proportion and the mixture was then transformed into extrudates. The extrudates were finally dried in hot air oven at 110 °C. The catalysts were prepared with different Ni loadings of 5, 7, 10 and 15 weight percent.

2.2. Catalyst characterization

XRD patterns were recorded on a PW1710 Phillips diffractometer using monochromatic CuKα radiation of wavelength 1.54 Å in the 2θ ranging from 10° to 90° operated at 40 kV and 20 mA. Crystalline phase identification of the catalyst was carried out by comparing the collected spectrum with the published files from the International Center for Diffraction Data (JCPDS files-1996).

TEM analysis was carried out in JEOL 2100 instrument operated at an accelerating voltage 200 kV. Specimen was prepared by ultrasonically dispersing the catalyst in acetone. A drop of the dispersion was then placed on clean carbon-coated copper grids and dried in air.

The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method using a Quantachrome AUTOSORB 1 instrument by adsorption of nitrogen at – 196 °C on 0.2 g of sample previously degassed at 200 °C for 2 h under high vacuum.

Scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) measurements were performed to observe the micro-structural surface morphology and elemental composition of the sample using EV060 ZEISS and Oxford instrument, respectively, with an acceleration voltage of 20 kV.

Temperature programmed reduction (TPR) profiles were recorded on a CHEMBET 3000 Quantachrome instrument equipped with a thermal conductivity detector (TCD). The samples (0.050 g) were loaded in a quartz tube, degassed at 200 °C and the temperature was raised at a rate of 10°/min up to 1005 °C, in a flow of 5% H_2/95%N_2 (flow rate 80 cm^3/min) while the TCD signal was recorded.

2.3. Experimental procedure

Steam reforming reaction was carried out in a fixed bed vertical tubular reactor (10 mm inner diameter) placed inside a cylindrical furnace. The reactor was loaded with catalyst (1.0 g) in such a way that the centre of the catalyst bed corresponded to the central heating zone of the furnace. The catalyst particles were mixed with inert particles so that the bed height was maintained at 80 mm. The catalyst was reduced as well as activated while it was heated to 500 °C with the flow of hydrogen (40 cm^3/min) for 4 h. The thermocouple inserted into the thermowell of reactor recorded the catalyst bed temperature. After catalyst activation, the reaction temperature was fixed at a desired value and catalytic steam reforming reaction was performed isothermally at atmospheric pressure. The reactor outlet stream was passed through a condenser for separation of condensable components in the gas–liquid separator. A schematic diagram of the experimental set-up is shown in Fig. 1.

The product gas stream flow rate was measured using a wet gas meter. The gas was periodically sent to a gas Chromatograph (Model: Chemito GC 1000 DPR) for analysis using a three-way valve. The gaseous products were analyzed using a thermal conductivity detector (TCD) with a Spherocarb column (3.175 mm diameter and 2.4 m length).

The conversion of methane, hydrogen content of the dry gas and hydrogen yield were calculated as follows:

$$\text{Conversion of methane}\,(\%) = \frac{F_{\mathrm{CH_4,in}} - F_{\mathrm{CH_4,out}}}{F_{\mathrm{CH_4,in}}} \times 100,$$

$$\text{Hydrogen content in dry gas}\,(\%) = \frac{F_{\mathrm{H_2,out}}}{F_{\mathrm{H_2,out}} + F_{\mathrm{CO,out}} + F_{\mathrm{CO_2,out}} + F_{\mathrm{CH_4,out}}} \times 100,$$

$$\text{Hydrogen yield} = \frac{F_{\mathrm{H_2,out}}}{F_{\mathrm{CH_4,in}} - F_{\mathrm{CH_4,out}}},$$

$$\text{CO selectivity}\,(\%) = \frac{F_{\mathrm{CO,out}}}{(F_{\mathrm{CH_4,in}} - F_{\mathrm{CH_4,out}})} \times 100,$$

$$\mathrm{CO_2}\ \text{selectivity}\,(\%) = \frac{F_{\mathrm{CO_2,out}}}{(F_{\mathrm{CH_4,in}} - F_{\mathrm{CH_4,out}})} \times 100,$$

where F terms are the molar flow rates of different components.

3. Results and discussion

3.1. Catalyst characterization

The structure and crystallinity of synthesized nickel oxide were revealed by XRD pattern as presented in Fig. 2. The existence of three strong and sharp diffraction peaks at 2θ values of 37.35, 43.35, and 63° corresponding to (1 1 1), (2 0 0) and (2 2 0) crystal reflection