Energy Conversion and Management 90 (2015) 218–229

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Co-production of hydrogen and carbon nanofibers from methane decomposition over zeolite Y supported Ni catalysts

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ARTICLE INFO

Article history:
Received 10 July 2014
Accepted 25 October 2014
Available online 29 November 2014

Keywords:
Coproduction
Hydrogen
Carbon nanofiber
Zeolite Y
Supported Ni
Methane decomposition

ABSTRACT

The objective of this paper is to study the influences of different operating conditions on the hydrogen formation and properties of accumulated carbon from methane decomposition using zeolite Y supported 15% and 30% Ni, respectively, at a temperature range between 500 and 650 °C in a pilot scale fixed bed reactor. The temperature ramp was showed a significant impact on the thermo-catalytic decomposition (TCD) of methane. An optimum temperature range of 550–600 °C were required to attain the maximum amount of methane conversion and revealed that at 550 and 600 °C, catalyst showed longer activity for the whole studied of experimental runs. Additionally, at 550 °C, the methane decomposition is two times longer for 30% Ni/Y zeolite than that for 15% Ni/Y zeolite catalyst, whereas it is almost three times higher at 500 °C. A maximum carbon yield of 614.25 and 157.54 g_c/g_{Ni} were reported after end of the complete reaction at 600 °C with 30% and 15% Ni/Y zeolite catalyst, respectively. From BET, TPD, and XRD analysis, we had reported that how the chemistry between the TCD of methane and metal content of the catalysts could significantly affect the hydrogen production as well as carbon nano-fibers. TEM analysis ensured that the produced carbon had fishbone type structures with a hollow core and grew from crystallites of Ni anchored on the external surface of the catalysts and irrespective of the metal loadings, the whisker types of nano filaments were formed as confirmed from FESEM analysis. Nevertheless, the effect of volume hourly space velocity (VHSV) on the methane conversion was also investigated and reported that the methane conversion increased as VHSV and nickel concentration in Ni–Y catalysts increased. Additionally, the initial methane decomposition rate increases with VHSV and it has reverse and non-linear relevancy to the weight of Ni/Y zeolite catalyst.

1. Introduction

The idea of co-production of hydrogen and carbon nanomaterials from thermo-catalytic decomposition (TCD) of methane has been having a great mettlesome attention among the Scientists and Engineers around the earth. This is because it produces environmentally –benign hydrogen and carbon nanomaterials that seem to be a clean, halcyon and officious product in foreseeable future [1–3]. Both of the products are derived from the TCD of methane, according to the following equation at low temperatures ranging from 400 to 700 °C when the process associated with the schemes of metal catalysts [4]:

$$CH_4 \rightarrow 2H_2(g) + C(s) \quad \Delta H^o = 75.6\ kJ/mol \tag{1}$$

Because of its lower cost selectivity, and much higher active site/carbon capacities, Ni has been broadly assessed in manufacturing of hydrogen from methane decomposition as compared with the cobalt or iron [5,6]. Regards to catalytic materials, the use of zeolitic materials has of both fundamental and practical significance due to their well-defined pore distributions, high surface area and unique catalytic features as compared to traditional catalyst supported on alumina, silica-alumina, CeO_2, peroviskite, active carbon, La_2O_3, and MgO [7]. The Y-zeolite has comparatively larger pores (Entry aperture of 0.74 nm, and a diameter of 1.3 nm) than the others such as HZSM-5 (0.51–0.55 nm; 0.51–0.55 nm) and zeolite A (0.41 nm 1.1 nm). Therefore, the introduction of nickel metals into Y zeolites by means of a suitable method such as impregnation or ion-exchange, etc., would make it suitable for TCD of methane. However, the research work on Y zeolite supported Ni catalysts in hydrogen and carbon nanomaterial's production from TCD of methane is still

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http://dx.doi.org/10.1016/j.enconman.2014.10.060
0196-8904/

very limited even though a great number of articles have already been disclosed the application of the metallic nickel catalysts on the activity of different support materials [2,6,8].

The degree of hydrogen and carbon nanomaterials production from TCD of methane depend as much on the reactor operating conditions such as feeding rate, reaction temperature and volume hourly space velocity (VHSV), as on the type of textural characteristics of support materials, catalyst's composition, and the additive concentration. Inaba et al. [9] have pointed out that the catalyst optimization using silica and several types of zeolite supported Ni catalysts for hydrogen yields from methane cracking at 650 °C. They described that USY-zeolite supported Ni catalysts showed higher catalytic longevity's (owing to active for around 6 h) as compared to silica supported Ni catalyst. The highest methane conversion was highlighted approximately 45%. They cited that the quantity of solid acidity in the support was tending to be lower if nickel particles have a smaller diameter. The accumulated carbon (AC) was estimated to be higher on the surface of Ni-supported catalysts even after complete deactivation when the supports have a larger external surface area. Very similar results were reported by Ashok et al. [8] who found that the highest activity subjected to Ni/HY catalyst (12 h) and higher activity of 955 mol_{H2}/mol_{Ni} compared to other tested support on HY, USY, SiO_2 and SBA-15 at 550 °C. At a temperature range between 750 and 900 °C and VHSV range between 3.0 and 18.0 $Lg^{-1}\,h^{-1}$ were set to investigate the methane decomposition for hydrogen yield using activated alumina and carbon as highlighted by Bai et al. [10]. At early of the decomposition reaction, the methane conversion was reflected maximum value around 25–35% for all types of used catalysts and thereafter, it started to decline progressively over the course of reaction stream (2 h). The catalytic activity took place primarily in the micropores that is confirmed from the change of pore size of activated carbon during the methane decomposition reaction. Apart from activated carbon textural properties, the activated alumina catalysts showed mesoporous nature that is subjected to the catalytic activity, resulting in a variation of carbon deposits and textural properties. Rely on the different precursors of activated carbon; two classes of AC can be appeared on the activated carbon either in the form of carbon filaments or agglomerates.

The work reported here emphasized at clarifying the influences of different operating conditions in a fixed bed reactor on hydrogen formation and properties of AC using two different Ni loading on the catalytic activity of Y zeolite catalyst. In addition, the structural and morphological features of the produced carbon and the textural features of the samples used are also examined for different operating parameters.

2. Experimental Methodology

2.1. Experimental view and operating conditions

Raw methane (99.9995%) purchased from Linde Compressed and nitrogen (99.999%) served by Air products were utilized in the experiment. The zeolite Y catalyst (surface area = 650 m^2/g, Si/Al = 10) purchased from Tosoh Corporation, Japan and used it as in the form of impregnation with nickel metals. The catalysts preparation methods and experimental apparatus used are described in details elsewhere [3]. In each experimental run, typically 3 g of Ni/Y zeolite catalyst was loaded into the reactor. Then the reaction started with the flow of 1 L/min of CH_4 over the catalyst bed using 15% and 30% Ni/Y zeolite catalysts at 500, 550, 600, and 650 °C, respectively. Before reaction, the catalyst is reduced by 20% hydrogen at 600 °C (heating ramp was 10 °C/min) in nitrogen for 2 h in order to obtain active metallic state in the catalyst and this is continued until system reached a set temperature. After that, a 1 L/min of nitrogen gas was thoroughly flushed for another 1 h within the reactor before feeding the set CH_4 flow rate. The reaction continued until the spontaneous hydrogen yield below 7%. The percentage of methane conversion calculated from data obtained from outflow gas that was analyzed by an online gas analyzer (GA). Using GA, other than hydrogen, no gaseous products detected. A flow of nitrogen was purged through the reactor to cool down it to ambient temperature after the reaction, and the total amount of solid carbon measured by using the following equation:

$$M_c\,(\%) = \left(\frac{w_{tot} - w_{cat}}{w_{cat}}\right) \times 100 \tag{2}$$

In Eq. (2), w_{tot} and w_{cat} represents the total and initial weight of the catalyst after and before reaction, respectively. This yield was also expressed in the form of g_{dep}/g_{Ni}.

2.2. Characterization techniques

In order to investigate the textural features of the catalysts and nanomaterials, the N_2 physisorption technique was done using nitrogen as adsorbent at 77 K from the Micromeritics ASAP 2020 sorptometer. A Micromeritics TPD/TPR 2720 analyzer was used to characterize how NH_3 molecules are strongly conjugated to the acid sites qualitatively. Firstly, a typical 0.50 g catalyst samples was heated in a flow system at a 30 mL/min helium flow rate with a temperature ramp of 10 °C/min increase to 25–780 °C, and at this temperature, the system stays for 30 min. Next, a helium flow of 20 mL/min was performed to reduce the catalyst until cool it to 210 °C. Thereafter, ammonia was streamed on the samples for 20 min. In order to reduce the physisorbed elements from the samples, a purging procedure was introduced with helium for another one hour. The chromatograms were obtained from the signal processing of thermal conductivity detector using the temperature ramp of 10 °C/min from 210 °C to 750 °C.

X-ray diffraction (XRD) patterns of the fresh and spent catalysts were determined on a Rigaku miniflex using Cu Kα radiation with a generator voltage and current of 45 kV and 40 mA, respectively. Using global Scherrer equation (based on the half-width of diffraction lines assigned to planes (111), (200), and (220) for NiO and Ni phase, respectively), the average crystallite size (D_{avg}) was obtained as follows [11]:

$$D_{avg} = \frac{0.9\lambda}{\beta \cos\theta} \tag{3}$$

where 0.9 is the Scherrer constant, β is the full width at half maxima (in radians) of a reflection located at 2θ.

The morphological structure and the diameter distribution of the catalysts and carbon nanomaterials were performed on a Field Emission Scanning electron microscopy, FESEM (QUANTA 450 FEG) and transmission electron microscopy, TEM (Hitachi HT-7700). Totally, more than 50 carbon nanofibers (CNFs) was measured on the TEM images, and the result reported as the arithmetic mean value of the data.

3. Results and discussion

3.1. Thermal decomposition of Methane over zeolite Y supported Ni catalysts

3.1.1. Effect of temperature ramp on TCD of methane

In Table 1, we report the reaction yields in terms of the three main conjugating reactions (initial H_2%, initial CH_4%, H_2 formation rate, and average carbon formation rate, ACFR) at the temperature range of 500–650 °C. In this experiment, the hydrogen formation rate (HFR) was presented in terms of average hydrogen formation