Thermo catalytic decomposition of methane over Cu - Al₂O₃ and 5 - 20wt% Ni - Cu - Al₂O₃ catalysts to produce hydrogen and carbon nanofibers

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Received: 16 March 2016, Revised: 25 September 2016 and Accepted: 31 November 2016

DOI: 10.5185/amp.2017/109
www.vbripress.com/amp

Abstract

Hydrogen is an environmental friendly fuel, which has the potential to significantly used of facil files; however several important challenges must defeat before it can be extensively used. Thermo catalytic decomposition of methane (TCD) is one of the most useful method, which will meet the future demand and hence an attractive route for CO₂ free production of hydrogen which is essential in fuel cell. In the present study, we made an attempt on hydrogen production with Cu-Al₂O₃ and 5, 10, 15 & 20wt% of Ni modified Ni/Cu-Al₂O₃ catalysts. It is also observed that, the conversion order is Cu-Al₂O₃ < 5 wt% Ni/Cu-Al₂O₃ < 20 wt% Ni/Cu-Al₂O₃ < 15 wt% Ni/Cu-Al₂O₃ < 10 wt% Ni/Cu-Al₂O₃ catalysts. It is observed that, while increasing the loadings of nickel in Ni/Cu-Al₂O₃ the efficiency of thermo catalytic decomposition of methane is also increasing. Among five catalysts prepared the 10wt% Ni/Cu-Al₂O₃ catalyst is showing good catalytic activity.SEM images of catalysts after thermo catalytic decomposition of methane shows the formation of carbon nanofibers. XRD patterns of the Cu-Al₂O₃ and 5,10,15 & 20wt%Ni/Cu-Al₂O₃ catalysts revealed, fairly crystalline peaks of which may responsible for the increase in the catalytic life and the formation of carbon nanofibers. The optimum hydrogen production of 70 volume % was observed with 10 wt% Ni/Cu-Al₂O₃ catalyst along with hydrogen carbon fibers were also found, which can be used as catalyst support. Copyright © 2016 VBRI Press

Keywords: Hydrogen, nickel, copper, alumina, thermo catalytic decomposition.

Introduction

The speedy enhance in the human population and the growth of various industrial areas worldwide has massively increased the consumption of energy. Presently, global energy production is based on the combustion of non-renewable fossil fuels, which are endlessly being depleted because of their extreme usage, further impacting the environment [1].

The combustion of fossil fuels mainly results in the generation of a huge quantity of green-house gases such as carbon, nitrogen and sulphur oxides. These gases harmfully influence the total global climate and lead to acid rain and global warming. To stay away from the above mentioned ecological impacts, strong efforts have been made to explore renewable and sustainable energy sources as well as energy carriers [2].

Hydrogen is considered as an ultimate energy carrier in the near future [3]. Presently, conventional methods of hydrogen production are based on steam methane reforming (SMR), coal gasification, electrolysis, biomass gasification and thermo chemical process. One of the drawbacks of the SMR process and methane partial oxidation is, it produces huge quantities of CO₂ which extensively contributes to the global warming. To avoid this, CO₂ - free hydrogen production by thermo catalytic decomposition of methane has been recommended. Since merely hydrogen and carbon are formed in the decomposition process, separation of products is not a problem. One more core benefit is the ease of the methane decomposition process as compared to conventional methods [4]. Furthermore, the hydrogen produced from this process can be used in proton exchange fuel cells (PEMFC) because it produces hydrogen without CO₂ contamination and it does not require any further purification and also useful for several other applications [5]. The other value added
carbon nanomaterials (carbon nanotubes, carbon nano fibers and graphitic carbon) are formed as by-products which has a lot of unique properties for example: high resistance to strong acids and strong bases, as a hydrogen storage material, in electronic switches, good mechanical strength and has high surface area makes them useful materials as a catalyst support in photocatalytic process and thermo catalytic process [6].

The catalysts used for thermo catalytic decomposition of methane are usually group vii transition metals like Ni [7-14], Fe [15-18] and Co [19-21]. Carbon materials like activated carbon, carbon black have been investigated as catalyst too, but they are less active than metals [22-24]. Predominantly the nickel based catalysts are active at low temperatures and provide higher H2 yield per unit mass of the active component [25-27]. Conversely, these catalysts are deactivated simply at high temperatures. Therefore, nickel based catalysts modification quicken a fascinating region to enhance the stability of catalyst and H2 yield at higher temperatures in thermo catalytic decomposition of methane [28]. In this view, second metal/metal oxide addition to a nickel catalyst implements considerable changes in the catalysts activity and catalysts stability [29]. However, further investigations discovered that doping of copper extensively improved the Nickel catalysts performance towards thermo catalytic decomposition of methane for superior yields of hydrogen [30-32]. The studies connected to thermo catalytic decomposition of methane reaction began in 1970s and investigations have been carried out with a focus on carbon deposition mechanisms, formation of carbon nanomaterials and kinetic studies using Ni, Ni-Cu based catalysts [6, 33-39]. As well Ni and Ni-Cu supported catalysts have too extensively studied and enormous progress in the stability of the Ni-Cu supported catalysts was usually observed and compared with Ni supported catalysts [25, 27, 31, 36-37, 40-44]. Muradov [45] and Parmon [46] reported at first on thermo catalytic decomposition of methane with Ni and Ni-Cu catalysts to produce hydrogen and carbon. For nickel based supported catalysts, we observed number of observations [47-51], it was concluded that with increasing temperature, the particle size decreased. This fashion is perhaps due to the fragile stability among the methane decomposition rate and the carbon diffusion rate. Particle size has a most important control on both reaction rates. It is possible that a self-establish scheme can control the proper particle size to adjust to the reaction states. Hence, Al2O3, SiO2 and MgO support materials used to control the particle size of catalyst and dispersion by physical connections (porous support) or chemical connections (charge transfer effect) [52]. Al2O3 is porous support material which will control the particle size of the catalyst and which is low cost, easily available material and also minimizes the coke formation. For this motive, Ni/Al2O3 catalyst composition have been competently investigated to decrease coke formation by preparing a nickel with other transition metals like Cu and Co. However, the Ni/Al2O3 catalyst durability drops rapidly with increasing reaction temperature [53]. To progress its durability and stop its deactivation at standard reaction temperatures, the third elements, as metals [25, 28, 30, 40, 41, 43, 53-55] and oxides [56-57] were introduced. The Cu doping was found extremely hopeful [4, 25, 42, 54]. It has been well-known that the Cu doping altered the state of nickel particles and modified the structure and morphology of the carbon formed [40, 54, 58-59].

Later Ni-Cu- Al2O3 catalysts were revealed many improvements over Ni/Al2O3 catalysts [60-61, 65]. Ni-Cu- Al2O3 catalysts with high metal loading required optimum temperature to achieve higher methane conversion. A co-precipitated Ni-Cu-Al2O3 catalysts were studied in fluidized bed reactor for thermo catalytic decomposition of methane at 715 and 740ºC. At 715ºC, catalyst deactivated in a time period of 65 min and at 740ºC, the catalyst durability improved and deactivates with in 65 min [62].

In the present study compares the performance of Cu-Al2O3 and 5-20 wt% Ni/Cu-Al2O3 catalysts in a fixed bed reactor at a reaction temperature 850 ºC for hydrogen and carbon nanofibers production in thermo catalytic decomposition of methane. The majority of this study has been focused on influence of nickel loading from 5, 10, 15 & 20 wt% and influence of bi metallic catalysts for hydrogen production and carbon nanofibers formation. Thus, in this present study, the role of varying nickel loading Ni-Cu/Al2O3 catalysts for hydrogen production and catalyst stability were observed. Apart from hydrogen, carbon nano fibers were also found, which can be used as catalyst support. This is the novelty of this study, where carbon dioxide emission free fuel was produced.

Experimental

Materials

Copper (II) nitrate, Aluminum nitrate nonahydrate, Sodium hydroxide, Sodium hydroxide and Nickel (II) nitrate hexahydrate was procured form Sigma Aldrich India Private Limited. These chemicals were used with analytical grade.

Methods

Catalyst preparation: preparation of Cu-Al2O3 catalyst

Cu-Al2O3 is prepared by co-precipitation method. In co-precipitation method, two solutions namely, solution (A) containing the desired amount of copper and aluminum nitrates and solution (B) containing the precipitating agents containing 2M NaOH and 1M Na2CO3 were added slowly and simultaneously into a beaker containing distilled water, while maintaining the pH ~ 9 under vigorous stirring at room temperature. Thus, produced precipitate was thoroughly washed with distilled water until the pH is adjusted to 7. The gel is filtered, dried at 100 ºC for
24 h and subsequently calcined in the presence of air at 550 °C for 5 h [54].

**Preparation of Ni/Cu-Al2O3 catalysts**

Ni/Cu-Al2O3 catalysts (Ni = 5, 10, 15 and 20 wt %) prepared by incipient wet impregnation method. The required amount of nickel nitrate solution dissolved in distilled water and mixed with the requisite amounts of Cu-Al2O3 to yield the wt% as mentioned above. These solutions were dried at 120°C and further calcined in the presence of air at 500°C for 5 h [66].

**Thermo catalytic decomposition of methane reaction for hydrogen production**

The hydrogen production studies carried out in a fixed bed quartz reactor (internal diameter =20 mm & length=950 mm) at a temperature of 850°C, flow rate of methane and nitrogen at 54 sccm and amount of catalyst used is 2.5 g, which are kept constant in order to check the influence of amount of impregnated Ni on the catalytic behavior of Cu-Al2O3 catalysts. The above prepared catalysts used for the evaluation of hydrogen production by TCD process.

Prior to the reaction, the catalyst sample was reduced at 725°C using flow rate of CH4= 54 sccm for 2 h. At the prescribed temperature (850°C), the feed was switched to the reactant stream with CH4/N2. The reaction is maintained from 15 min to 300 min and the collected the gas samples in Teddlar bags. The product composition was measured by Agilent Gas chromatography (GC) equipped with thermal conductivity detector (oven temperature 80°C; detector temperature 100°C; injector temperature 100°C) and Porapak Q column. Nitrogen has been used as carrier gas. The calibrated data of hydrogen and methane have been obtained using the standards—hydrogen (99.99 vol%, BOC Ltd, India) and methane (99.99 vol%, BOC Ltd, India). AIMIL GC data sheet was used in the analysis of GC data. The concentrations of hydrogen and unconverted methane have been determined using the calibrated data. The experiment carried triplicates to know the accuracy of the results.

**Characterizations**

Surface area of the catalysts were measured by surface area analyzer SMART SORB-93, crystallite size by Bruker-D8 Advanced X-ray diffractometer (using CuKα-radiation=0.154 nm) functioned at a voltage of 40kV and a current of 30mA with Cu Kα radiation (λ=0.154nm) between 2θ diffraction angles (20°-80°) for analyzing peak data and crystal structure and surface morphology by ZEISS scanning electron microscope Super (SEM) operating at an accelerating voltage of 15 kV.

**Results and discussion**

**BET surface area analysis**

The BET surface area of Cu-Al2O3 and Ni modified Ni/Cu-Al2O3 catalysts are reported in Table 1. The Cu-Al2O3 shows a surface area 35.30 m²/g (before the reaction) and 15.10 m²/g (after the reaction). The Ni/Cu-Al2O3 surface area significantly decreases with increase in nickel loadings from 5- 20 wt %. BET surface area of Cu-Al2O3 is 35 m²/g, which is almost equal to the 20 wt% Ni/Cu-Al2O3 sample.

**Table 1.** The BET surface area values of Cu-Al2O3 and 5, 10, 15, 20 wt% of Ni/Cu-Al2O3 catalysts.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Catalyst</th>
<th>Before reaction BET surface area (m²/g)</th>
<th>After reaction BET surface area (m²/g)</th>
<th>Before reaction pore volume (cm³/g)</th>
<th>After reaction pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu-Al2O3</td>
<td>35.30</td>
<td>15.10</td>
<td>0.61</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>5 wt% Ni/Cu-Al2O3</td>
<td>63.80</td>
<td>30.20</td>
<td>0.36</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>10 wt% Ni/Cu-Al2O3</td>
<td>84.10</td>
<td>41.00</td>
<td>0.58</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>15 wt% Ni/Cu-Al2O3</td>
<td>42.60</td>
<td>21.30</td>
<td>0.20</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>20 wt% Ni/Cu-Al2O3</td>
<td>34.30</td>
<td>16.15</td>
<td>0.16</td>
<td>0.04</td>
</tr>
</tbody>
</table>

It is observed that while increasing the nickel loadings on Ni/Cu-Al2O3, the surface area and pore volume decreases.

From Fig. 1, it is observed that the BET surface area altering due to the reaction. This variation is due to carbon encapsulation on the active sites of catalyst used.

From Fig. 2, it is observed that the pore volume is altering due to the reaction. This variation is due to carbon encapsulation on the active sites of catalyst used.
**X-ray diffraction (XRD) analysis**

The XRD pattern of fresh Cu-Al₂O₃ and Ni/Cu-Al₂O₃ catalysts were shown in Fig. 3. The peaks observed for CuO at 2θ = 37.2°, 67.2° and 68.9° is of monoclinic structure, peaks observed for NiO at 2θ = 37.28°, 48.1° and 75.4° is of cubic structure and peaks observed for Al₂O₃ at 2θ = 58.1°, 62.1° and 73.1° is of rhombohedra structure. These peaks were matched with JCPDS card numbers 80-12681, 01-12391 and 77-2135 for CuO, Ni and Al₂O₃, respectively.

X-ray diffraction system with Cu-Kα source radiation having wavelength 1.54 Å was used for characterizing the prepared catalysts. From the X-ray diffraction pattern the crystallite size is calculated by using Debye-Scherrer equation as follows:

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

where, \(D\) = average crystallite size, \(K\) = Scherrer coefficient, \(\lambda\) = wavelength of X-ray radiation, \(\beta\) = FWHM of diffraction peak and \(\theta\) = diffraction angle.

While varying weight % of Ni in Ni/Cu-Al₂O₃ catalysts i.e. 5 wt%, 10 wt%, 15 wt% and 20, the crystallite size is varying from 20 - 40 nm.

![Fig. 3](image1.png)

**Fig. 3.** The XRD patterns before reaction (a) Cu-Al₂O₃, (b) 5 wt% Ni/Cu-Al₂O₃, (c) 10 wt% Ni/Cu-Al₂O₃, (d) 15 wt% Ni/Cu-Al₂O₃ and (e) 20 wt% Ni/Cu-Al₂O₃ catalysts.

**Scanning electron microscope (SEM) analysis**

The surface morphology of Cu-Al₂O₃ and Ni/Cu-Al₂O₃ catalysts were analyzed by Scanning electron microscope. From Fig. 4, carbon nanofibers were observed from Cu-Al₂O₃ and Ni/Cu-Al₂O₃ catalysts. All the SEM images were taken at a magnification of 50 µm.

**Fig. 4.** SEM images of (a) Cu-Al₂O₃, (b) 5 wt% Ni/Cu-Al₂O₃, (c) 10 wt% Ni/Cu-Al₂O₃, (d) 15 wt% Ni/Cu-Al₂O₃, and (e) 20 wt% Ni/Cu-Al₂O₃ catalysts after test at 850°C.

**Hydrogen production studies**

After process optimization studies, reaction temperature (850°C), flow rate of feed (54 SCCM) and amount of catalyst (2.5g) were kept constant in order to check the influence of amount of impregnated Ni on the catalytic behavior of Cu-Al₂O₃ catalysts.

The hydrogen production results shown in Fig. 5, the 10 wt% Ni/Cu-Al₂O₃ has a high hydrogen production which is about 70 volume% obtained at 60 min. The catalytic activity rapidly decreased to 0 volume % at 300 min which is leading to complete deactivation of carbon. This deactivation is due to encapsulating carbon on the active metal sites which hinders access of the methane molecules to the active metal sites. This kind of hydrogen production is also seen in Douxi Li et al. 2009 [62] achieved 40 % hydrogen production in fluidized bed reactor. J.L. Pinilla et al. 2010 [64] performed the same work in fluidized bed reactor were 70% hydrogen production is observed at 60min and catalyst deactivated at 250min.

The low hydrogen production is about 50 volume% at 60 min for Cu-Al₂O₃. The catalytic activity rapidly decreases to 0 volume % at 300 min which is leading to complete deactivation.
Thus, suggests certain amount of Ni enhance the efficiency of Cu-Al2O3 catalyst towards thermo catalytic decomposition of methane. The hydrogen production for all the catalysts used in this study were following same trend. Among all tested catalysts the 10wt% Ni/Cu-Al2O3 is found to be a good catalyst for hydrogen production and formation of carbon nanofibers which is observed from SEM.

Fig. 5. Hydrogen production over Cu-Al2O3, 5 wt% Ni/Cu-Al2O3, 10 wt% Ni/Cu-Al2O3, 15 wt% Ni/Cu-Al2O3 and 20 wt% Ni/Cu-Al2O3 catalysts.

Conclusion

The results obtained in the present work reflected the simultaneous production of hydrogen and carbon nanofibers using Cu-Al2O3 and 5, 10, 15 & 20 wt% Ni loaded Cu-Al2O3 catalysts in a fixed bed reactor. 70% hydrogen production was achieved for 10 wt% Ni/Cu-Al2O3 catalyst at 60 min. The weight ratios of nickel content are influencing the morphology of the Ni/Cu-Al2O3 catalysts. With increasing nickel content, the catalyst activity had improved but further increase in the nickel content from 15 to 20 wt% led to decrease in catalyst activity. This was related to the morphology of the catalysts. When the nickel content was 10 wt%, the performance of activity is high among all. Carbon nanofibers formed are approximately 50-100 nm in diameter. The catalyst deactivation is observed due to carbon encapsulation. However, long duration studies may be required to assess its activity in the future.

Acknowledgements

The authors express sincere thanks to Ministry of New Renewable Energy – New Delhi for providing fellowship.

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