

Thermo Catalytic decomposition of methane on Ni/SiO₂ catalyst into pure hydrogen and carbon nanotubes

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Thermo-catalytic decomposition of methane is a promising approach to produce CO_x-free hydrogen and carbon nanotubes at a relatively low cost through a single-step process. Ni catalysts supported on silica as textural promoter prepared by wet impregnation and co-precipitation methods are studied to produce pure hydrogen and carbon nanofibers in a fixed-bed quartz reactor at 700 °C and at atmospheric pressure. The loading amounts of Ni in the Ni/SiO₂ catalyst were changed from 30 to 70 wt%. The catalytic activity is mainly influenced by the amount of metal loading, catalyst preparation method, reaction temperature and type of support material. It was observed that the catalytic activity and the yields of hydrogen and carbon nanofibers depended strongly on the loading amount of Ni and preparation method. 50% Ni/SiO₂ catalyst prepared by wet impregnation method found more suitable in terms of higher methane conversion and hydrogen yield compare to other catalyst.

Keywords: methane decomposition, catalyst, Ni/SiO₂, hydrogen generation

1. INTRODUCTION

Hydrogen is considered to be primarily energy source for the future, in terms of the most environmentally acceptable energy source. Nearly all(90% of total hydrogen production) of the present worldwide production of hydrogen is from steam reforming of methane and partial oxidation process. Reforming is an endothermic catalytic process which requires temperatures from 800 to 950 °C and a pressure of 3 to 25 MPa. However, the total CO₂ emissions from steam reforming process reach up to 0.43 moles CO₂ per mole of H₂ produced. Unlike steam reforming, partial oxidation process is carried out without the use of catalysts at higher temperatures between 1300-1500 °C and at a pressure of 3-25 MPa. After the partial oxidation process, a desulphurization and a CO-shift are necessary step for the production of pure hydrogen [1, 2]. Therefore a less severe and eco-friendly process is required that can reduce or eliminate CO₂ emissions in the production process. Thermo-catalytic decomposition of methane (TCD) has gain lot of attentions in the recent years which produce pure hydrogen without any associated of CO_x emission [3, 4]. Apart from this, TCD eliminate the need of water gas shift reaction and CO₂ sequestration step required by the conventional production process. Other additional advantages of this process over other by co-producing valuable carbon products

such as carbon nanotubes or graphite-like carbon and pure hydrogen in a single step without any gas purification. The TCD of methane was investigated over various transition metals (Ni, Co, Mo and Fe), support (Al₂O₃, SiO₂, TiO₂, MgO, MCM-41) with Cu, Pd and Zr promoter [5,6,7], showing that Ni based catalysts gave better results for hydrogen production with carbon nanotubes (CNTs) as the byproduct. However, Ni catalysts drastically deactivate and for continuous hydrogen supply regeneration process is required [8]. The present work deals with Ni/SiO₂ catalysts prepared by the impregnation and co-precipitation method. The influence of the metal loading, catalyst preparation method and reaction temperature on methane conversion and on the properties of the obtained carbon has been studied. The physico-chemical characteristics of the fresh and spent catalysts are evaluated using BET surface area, XRD, TGA, TPR, SEM and TEM analysis.

2. EXPERIMENTAL

2.1 Catalyst synthesis

Ni/SiO₂ catalysts were prepared by both wet impregnation and co-precipitation method. In wet impregnation, the required amount of nickel nitrate hexahydrate [Ni(NO₃)₂.6H₂O, Merck] was taken to give 30-70 wt% Ni loading on the catalysts. The powdery SiO₂ (Loba Chemie, India, particle size 40-150 mesh) was added to the solution of nickel nitrate hexahydrate and the solution were dried in a rotary vacuum evaporator for 2.0 h. All Ni samples were overnight dried at 110 °C, and calcined in a stream of air at 550 °C for 5 h. In co-precipitation method, required amount of NiNO₃.6H₂O salt precipitated with ammonia solution, the precipitated was the dried and calcined at 110 and 250 °C, respectively, for 5 h. Alcosol (TEOS, ethanol, water and HCl) was added with calcined precipitate and the mixing was done by magnetic stirrer for about 2 hours. After precipitation, the solid was filtered and washed with distilled water until the filtrate solution became neutral. Prepared all samples were dried and calcined at the above mentioned conditions.

2.2 Catalyst characterization

Temperature-Programmed Reduction (TPR) experiments were carried out in a conventional flow system (Micromeritics, Pulse Chemisorb 2720, USA) at a heating rate of 10 °C/min using a carrier gas (10% H₂/Ar) flow of 30 ml/min and a thermal conductivity detector. Thermo gravimetric analysis (TGA) was used to study the stability of

solids with respect to temperature changes using a TA Q600 Instrument (USA) at a heating rate of 10 °C/min, ranging 30–900 °C under air flow (100 ml/min). Powder X-ray diffraction (XRD) patterns of all the samples were obtained on a Philips X'pert Pro PW3040 diffractometer, using Cu K α radiation ($2\theta=10-80^\circ$, scan rate 1° min^{-1}) for the study of concentration of the crystalline species and calculate particle size using Scherrer's formula. The particle size was also confirmed by TEM (Fig. 6), which indicated the presence of particles size in the range of ~ 25-40 nm. The morphology of the fresh and spent catalysts was recorded by scanning electron microscopy (SEM) of ZEISS EVO-50 instrument. TEM observations were made by using a Philips CM12 operated at 120KV instrument equipped with a high-resolution camera.

2.3 Experimental set-up

Wet impregnated and co-precipitated catalysts were tested for the methane decomposition reaction with a quartz tube reactor (i.d. = 19 mm, length = 60 cm), at 700 °C and atmospheric pressure operated in a down flow mode. The reactor was kept in a tubular electric furnace controlled by temperature controller, connected to a thermocouple placed at the center of the reactor. Methane was fed with nitrogen as an inert to the reactor at 30 ml/min and regulated by a mass flow controller (Bronkhorst, Netherlands). A catalyst amount of 1.0 g was uniformly dispersed over quartz wool and loaded into the reactor. Prior to the activity tests, all catalysts were subjected to a reduction pre-treatment using a flow rate of 30 ml/min of pure hydrogen for 5 h at 550 °C. The composition of the outlet gases were analyzed by an online gas chromatography (Nucon, India) using carbosphere column and a TCD detector.

3.0 RESULTS AND DISCUSSIONS

3.1 Catalytic activity measurements

Catalytic activity of the catalysts were evaluated over variable Ni wt% samples of Ni/SiO₂ catalyst prepared by wet impregnation and co-precipitation method at 700 °C. All the experiments were carried out under similar conditions in order to observe the effect of Ni loadings on SiO₂. Fig. 1(a) shows the effect of time-on-stream on the methane conversion by wet impregnated catalyst. All the Ni/SiO₂ catalysts show high initial activity followed by a smooth decrease until the steady state [9]. The initial methane conversion on 30% Ni/SiO₂ catalyst was 54%, but the conversion dropped to 44% after 5 h. Similar results were obtained on 70% Ni/SiO₂ catalyst, where the initial conversion rate is 68%, and then decreases continuously up to 52%. On the other hand, Fig. 2 depicts co-precipitated Ni/SiO₂ catalysts which show higher deactivation rate than wet impregnated catalysts. The initial methane conversion was 37%, but dropped to 29% after 5 h for 30 wt% co-precipitated Ni/SiO₂ catalyst. The similar trends were also followed by other co-precipitated catalysts. After comparing and analyzing all the data, it can be easily concluded that

among all of the catalysts studied in this work, 50 wt% Ni/SiO₂ prepared by wet impregnation method was found to be the most effective catalyst for the production of hydrogen from the methane decomposition. Deactivation studies were also on carried out using this catalyst as shown in Fig. 1(b). It is expected that a catalyst will eventually deactivate due to the carbon deposition in the pores which was produced by methane decomposition. We have experimentally observed a significantly higher amount of carbon deposition on the Ni/SiO₂ catalysts before deactivation occurs after 14.5 h at 700 °C. The catalyst also noted slow deactivation rate in the first 3 h followed by a rapid loss of activity after 5 h. By the time the catalyst was completely deactivated (14.5 min), approximately 11.5 g of carbon had accumulated on the 1.0 g of the 50% Ni/SiO₂ catalyst sample. This was higher yield than the previously reported by Tiejun et. al [10] and Kuijpers et. al. [11] (50% Ni/SiO₂ catalyst at 623 K) who reported a fast catalyst deactivation due to active site blocking.

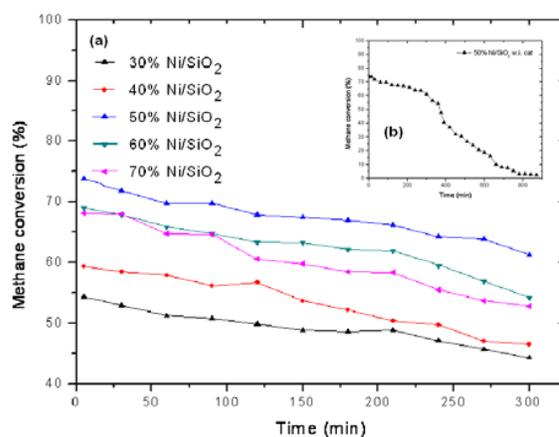


Fig. 1(a) Methane conversion during TCD over 30-70 wt% wet impregnated Ni/SiO₂ catalysts as a function of time (b) Deactivation of the 50 wt% wet impregnated Ni/SiO₂ catalyst at 700 °C

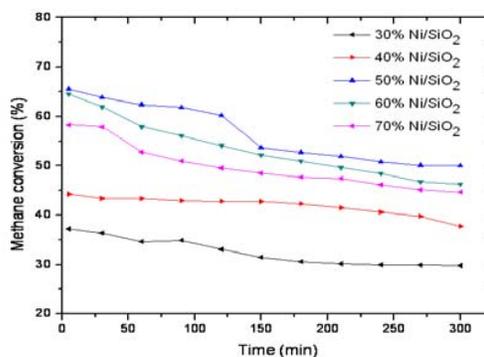


Fig. 2 Methane conversion during TCD over 30-70 wt% co-precipitated Ni/SiO₂ catalysts as a function of time

3.2 TPR studies

TPR measurements were carried out in order to determine the behavior of nickel metal in the reduction reactions and to investigate the metal–support interactions. Fig. 3 shows the reduction temperature and relative reduction peak, areas of NiO for each catalyst. One single phase of cubic NiO was observed between 420 and 480 °C of all the catalyst. It has been reported that the peaks between 400 and 500 °C represent the typical peaks for the reduced NiO species of low interaction with the SiO₂ support. It is also clearly evident from the patterns that with increase in Ni loading the H₂ uptakes were increased up to 70 wt% Ni/SiO₂.

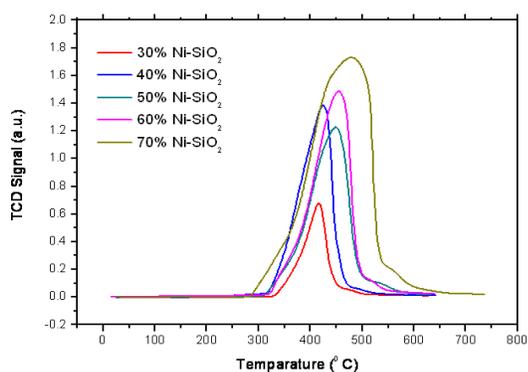


Fig. 3 TPR pattern of 30-70 wt% wet impregnated Ni/SiO₂ catalyst

3.3 Structure and composition

The calcined and spent Ni/SiO₂ catalysts were characterized by powder X-ray diffraction (XRD) technique. The XRD pattern of 30–70 wt% calcined Ni/SiO₂ catalysts shows the reflections at $2\theta = 37.2, 43.3, 62.8, \text{ and } 75.3^\circ$ are attributed due to the NiO phase [JCPDS, CAS No. 75-1523]. It is clearly observed from the XRD patterns that the intensity of the NiO phase is increased with increase in Ni loading and reflections due to SiO₂ phases could not be distinguish in all the Ni/SiO₂ catalysts. XRD pattern of the 30–70 wt% spent Ni/SiO₂ catalysts were also obtained after the methane decomposition reaction. X-ray diffractograms for spent catalyst at various stages of the reaction reveals the emergence of a peak at $2\theta = 26.3, 44.4, 54.1^\circ$ corresponding the value of (0,0,2), (1,0,1), (0,0,4) graphite phase [JCPDS, CAS No. 7782-42-5] with hexagonal structure. The XRD also exhibit three peaks at $2\theta = 44.4, 51.8 \text{ and } 76.3^\circ$ corresponding to (1,1,1), (2,0,0) and (2,2,0) planes of cubic metallic nickel in all the spent catalyst. The presence of pure metallic nickel phase in the spent catalysts reveals that the NiO phase is reduced during the reduction of the catalyst, which is active for the methane decomposition reaction. The highest intensity X-ray diffraction peak ($2\theta = 44.4^\circ$) has been further analyzed for all spent catalyst to yield the grain size of the metallic Ni particle by using the Scherer's formula. From the calculations it is found that crystalline size of the grain from 30 to 70% Ni are 25.7, 21.2, 25.2, 25.4 and 28.3

nm respectively. TEM analysis confirms the diameter of the nanofibers which vary from 25 to 40 nm.

3.4 TGA analysis

TGA analysis was carried out to examine the thermal stability of as grown CNTs on spent catalysts over wet impregnated Ni/SiO₂ catalyst. CNT has a different oxidation temperature than the other carbonaceous product. The oxidation temperature of amorphous carbon is in the range of 200–450 °C, while MWCNTs is oxidized from 500–650 °C in air [12]. Fig. 4 shows that the weight loss of all the catalyst started at approximately at 520 which continue till 680 °C. This characterizes the prepared carbon nanotubes as MWCNTs. The absence of any other further weight losses in the TGA graph after 680 °C indicates that the catalyst supports are thermally stable above this temperature. It was also observed that 70 wt% Ni/SiO₂ catalysts show amorphous carbon formation which is negligible with other catalysts in the temperature range of 200-500 °C. It was important to note that approximately 30% weight is in the form of residue for 50-70 wt% Ni/SiO₂ catalyst after performing TGA up to 900 °C. This residue remains mainly due to the presence of nickel found in between and within the inner walls of the CNTs.

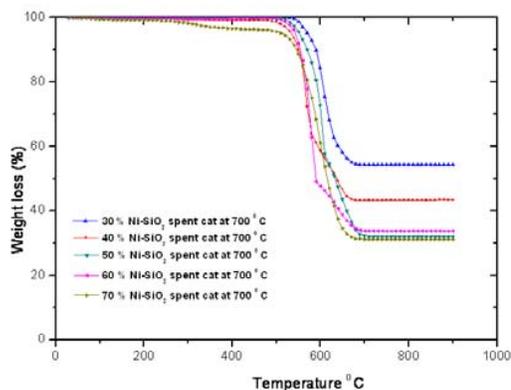


Fig. 4 TGA curves of wet impregnated Ni/SiO₂ spent catalyst at 700 °C

3.5 Morphology of spent catalyst

The morphology of deposited carbon nanofibers formed over Ni/SiO₂ is studied by SEM analysis and some of them are presented in Fig. 5 (a, b). It appears that wet impregnated Ni/SiO₂ catalysts leads to the formation of carbon nanofibers and the deposited carbon is filamentous in nature, but in case of coprecipitation catalyst nanofibers are not clearly distinguished. Micrographs of the wet impregnated spent catalysts showed that the surface is completely covered with filamentous carbon with relatively uniform diameters which shows consistent distribution of metal oxides on the surface of the SiO₂ support. The deposited carbon on spent catalyst was also examined by TEM, in order to get detail information of the carbon structure. Fig. 6 presents TEM

images of (a) 40% and (b) 50% Ni/SiO₂ spent catalyst at a reaction temperature of 700 °C.

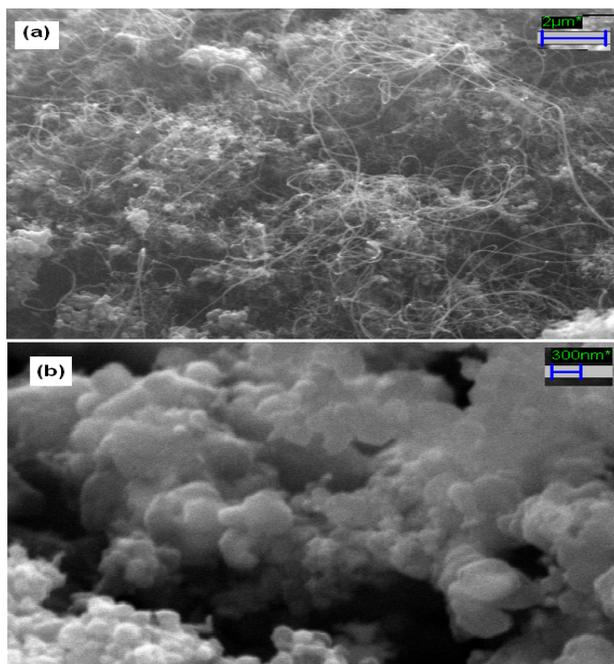


Fig.5 SEM images of “as grown” CNT on (a) 60% Ni/SiO₂ wet impregnated (b) 60% Ni/SiO₂ co-precipitated catalyst at 700 °C

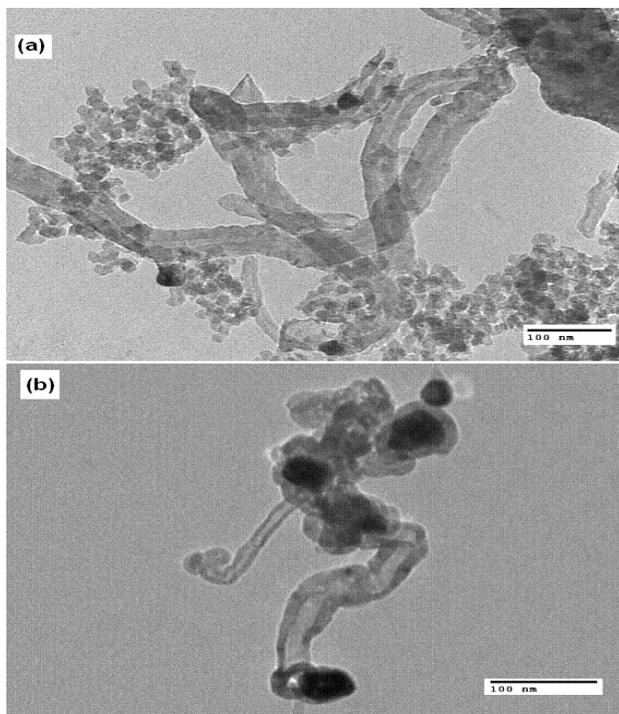


Fig. 6 TEM images of carbon nanotubes obtained from methane decomposition employing (a) 40% Ni/SiO₂ (b) 50% Ni/SiO₂ wet impregnated catalyst

It is evidenced that the methane decomposition over Ni/SiO₂ catalysts leads to the formation of carbon nanofibers that are a 500-600 nm in length and that are multiwall in nature. Nevertheless, it should be noted that the produced carbon fibers outer diameters are in the range of 25–40 nm and the particle size of the nickel catalysts are also in the same order of magnitude (20-30 nm).

CONCLUSIONS

Catalysts prepared by wet impregnation method are better than co-precipitation method in terms of both higher methane conversion and nanofibers production. Co-precipitated catalysts also show higher deactivation rate than wet impregnated catalysts. The catalytic activity and longevity of the catalysts were found to strongly depend on the loading of Ni metal. It was found that the 50 wt% Ni/SiO₂ catalyst synthesis by wet impregnation method demonstrated superior activity and longevity compared to other Ni loaded catalysts.

REFERENCES

1. T.V. Choudhary, D.W. Goodman, *Catal. Today* 77 (2002) 65–78.
2. J.N. Armor, *Appl. Catal. A: Gen.* 176 (1999) 159-176.
3. G. Bonura, O. Di Blasi, L. Spadaro, F. Arena, F. Frusteri, *Catal. Today* 116 (2006) 298–303
4. T.V. Choudhary, C. Sivadinarayana, C. Chusuei, A. Klinghoffer, D.W. Goodman, *J. Catal.* 199 (2001) 9-18.
5. A. Venugopal, S. Naveen Kumar, J. Ashok, D. Hari Prasad, V. Durga Kumari, K.B.S. Prasad, M. Subrahmanyam, *Int. J. Hydrogen Energy* 32 (2007) 1782– 1788
6. G. Li, L. Hu, J. M. Hill, *Appl. Catal. A: Gen.* 301 (2006) 16–24
7. J.C. Guevara, J.A. Wang, L.F. Chen, M.A. Valenzuela, P. Salas, A. Garcí'a-Ruiz, J.A. Toledo, M.A. Cortes-Ja'come, C. Angeles-Chavez, O. Novaro, *Int. J. Hydrogen Energy* 35 (2010) 3509 – 3521.
8. S. Takenaka, E. Kato, Y. Tomikubo, K. Otsuka, *J. Catal.* 219 (2003) 176–185.
9. R. Moliner, I. Suelves, M. J. Lázaro, O. Moreno, *Int. J. Hydrogen Energy* 30 (2005) 293-300.
10. T. Zhang, M.D. Amiridis, *Appl. Catal. A: Gen.* 167 (1998) 161-172
11. E.G.M. Kuijpers, J.W. Jansen, A.J. van Dillen, J.W. Geus, *J. Catal.* 72 (1981) 75-82.
12. V.Z. Mordkovich, E.A. Dolgova, A.R. Karaeva, D.N. Kharitonov, I.A. Maslov, A.A. Kamenev, V.F. Tretjakov. *Carbon* 45 (2007) 62-69.