

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

K. Srilatha¹, D. Bhagawan², V. Himabindu^{1*}

¹Centre for Alternative Energy Options, Institute of Science and Technology, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Hyderabad, Telangana, 500085, India

²Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Hyderabad-85, Telangana, 500085, India

*Corresponding author, Tel: (+91) 9959455674; E-mail: latha.hasini@gmail.com; drvhimabindu@gmail.com

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Abstract

Hydrogen is an environmental friendly fuel, which has the potential to significantly used of fossil fuels; however several important challenges must be defeated before it can be extensively used. Thermo catalytic decomposition of methane (TCD) is one of the most useful methods, which will meet the future demand and hence an attractive route for CO_x 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 be 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, CO_x - 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 CO_x 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 viii 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 740°C. At 715°C, catalyst deactivated in a time period of 65 min and at 740°C, the catalyst durability improved and deactivates with in 65min [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°C 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 from 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 °C 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 $\text{Cu-Al}_2\text{O}_3$ 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 2.5g, which are kept constant in order to check the influence of amount of impregnated Ni on the catalytic behavior of $\text{Cu-Al}_2\text{O}_3$ 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 $\text{CH}_4=54$ sccm for 2 h. At the prescribed temperature (850°C), the feed was switched to the reactant stream with CH_4/N_2 . 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 $\text{CuK}\alpha$ -radiation=0.154 nm) functioned at a voltage of 40kV and a current of 30mA with $\text{Cu K}\alpha$ radiation ($\lambda=0.154\text{nm}$) 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 $\text{Cu-Al}_2\text{O}_3$ and Ni modified Ni/Cu- Al_2O_3 catalysts are reported in Table 1. The $\text{Cu-Al}_2\text{O}_3$ shows a surface area $35.30\text{ m}^2/\text{g}$ (before the reaction) and $15.10\text{ m}^2/\text{g}$ (after the reaction). The Ni/Cu- Al_2O_3 surface area significantly decreases with increase in nickel loadings from 5- 20 wt %. BET surface area of $\text{Cu-Al}_2\text{O}_3$ is $35\text{ m}^2/\text{g}$, which is almost equal to the 20 wt% Ni/Cu- Al_2O_3 sample.

Table 1. The BET surface area values of $\text{Cu-Al}_2\text{O}_3$ and 5, 10, 15, 20 wt% of Ni/Cu- Al_2O_3 catalysts.

S. No	Catalyst	Before reaction BET surface area (m^2/g)	After reaction BET surface area (m^2/g)	Before reaction Pore volume (cm^3/g)	After reaction Pore volume (cm^3/g)
1	$\text{Cu-Al}_2\text{O}_3$	35.30	15.10	0.61	0.25
2	5 wt% Ni/Cu- Al_2O_3	63.80	30.20	0.36	0.12
3	10 wt% Ni/Cu- Al_2O_3	84.10	41.00	0.58	0.19
4	15 wt% Ni/Cu- Al_2O_3	42.60	21.30	0.20	0.06
5	20 wt% Ni/Cu- Al_2O_3	34.30	16.15	0.16	0.04

It is observed that while increasing the nickel loadings on Ni/Cu- Al_2O_3 , 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.

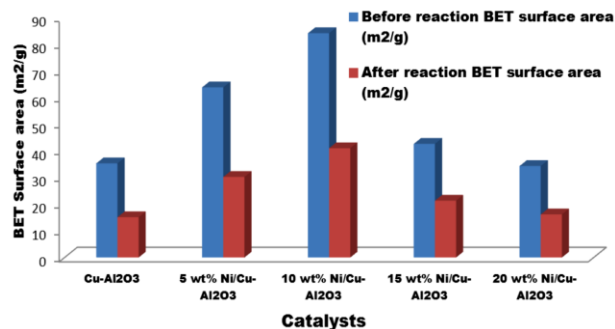


Fig. 1. BET surface area of (a) $\text{Cu-Al}_2\text{O}_3$, (b) 5 wt% Ni/Cu- Al_2O_3 , (c) 10 wt% Ni/Cu- Al_2O_3 , (d) 15 wt% Ni/Cu- Al_2O_3 and (e) 20 wt% Ni/Cu- Al_2O_3 catalysts.

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.

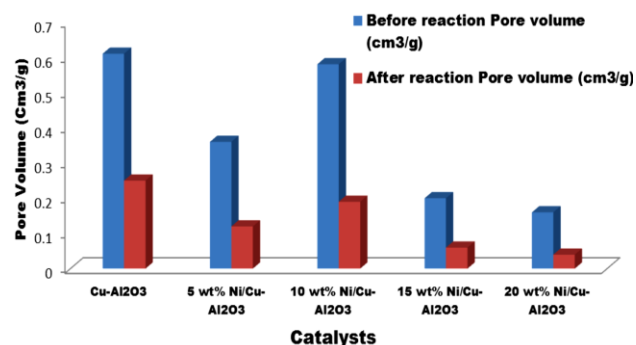


Fig. 2. Pore volume of (a) $\text{Cu-Al}_2\text{O}_3$, (b) 5 wt% Ni/Cu- Al_2O_3 , (c) 10 wt% Ni/Cu- Al_2O_3 , (d) 15 wt% Ni/Cu- Al_2O_3 and (e) 20 wt% Ni/Cu- Al_2O_3 catalysts.

X-ray diffraction (XRD) analysis

The XRD pattern of fresh $\text{Cu-Al}_2\text{O}_3$ and Ni/Cu- Al_2O_3 catalysts were shown in Fig. 3. The peaks observed for CuO at $2\theta=37.2^\circ$, 67.2° and 68.9° is of monoclinic

structure, peaks observed for NiO at $2\theta = 37.28^\circ$, 48.1° and 75.4° is of cubic structure and peaks observed for Al_2O_3 at $2\theta = 58.1^\circ$, 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 Al_2O_3 , respectively.

X-ray diffraction system with $\text{Cu-K}\alpha$ source radiation having wavelength 1.54\AA was used for characterizing the prepared catalysts. From the X-ray diffraction pattern the crystallite size is calculated by using Debye-Scherrer equation is as follows:

$$D = k\lambda / \beta \cos\theta \quad (1)$$

where, D = average crystallite size, K = Scherrer coefficient, λ = wavelength of X-ray radiation, β = FWHM of diffraction peak and θ = diffraction angle.

While varying weight % of Ni in $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts i.e. 5 wt%, 10 wt%, 15 wt% and 20, the crystallite size is varying from 20 - 40 nm.

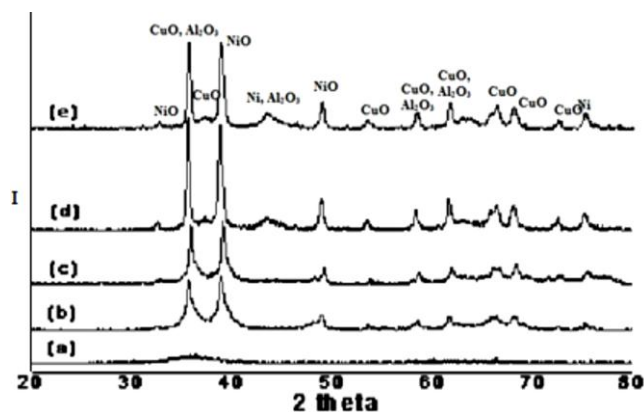


Fig. 3. The XRD patterns before reaction (a) $\text{Cu-Al}_2\text{O}_3$, (b) 5 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, (c) 10 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, (d) 15 wt% $\text{Ni/Cu-Al}_2\text{O}_3$ and (e) 20 wt% $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts.

Scanning electron microscope (SEM) analysis

The surface morphology of $\text{Cu-Al}_2\text{O}_3$ and $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts were analyzed by Scanning electron microscope. From **Fig. 4**, carbon nanofibers were observed from $\text{Cu-Al}_2\text{O}_3$ and $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts. All the SEM images were taken at a magnification of $50\ \mu\text{m}$.

Fig. 4 shows the presence of carbon nanofibers embedded and bounded by the carbon sooth deposited on the elements corresponding to $\text{Cu-Al}_2\text{O}_3$ and Ni loaded $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts. The carbon nanofibers are approximately 50-100 nm in diameter. From **Fig. 4(c)**, bulk carbon nanofibers were observed in 10 wt% $\text{Ni/Cu-Al}_2\text{O}_3$.

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 $\text{Cu-Al}_2\text{O}_3$ catalysts.

The hydrogen production results shown in **Fig. 5**, the 10 wt% $\text{Ni/Cu-Al}_2\text{O}_3$ 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 Douxing 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 $\text{Cu-Al}_2\text{O}_3$. The catalytic activity rapidly decreases to 0 volume % at 300 min which is leading to complete deactivation.

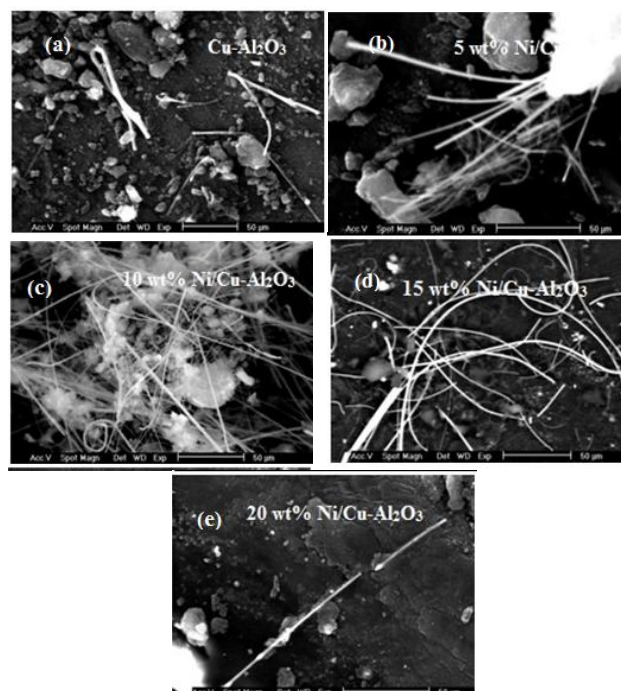


Fig. 4. SEM images of (a) $\text{Cu-Al}_2\text{O}_3$, (b) 5 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, (c) 10 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, (d) 15 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, and (e) 20 wt% $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts after test at 850°C .

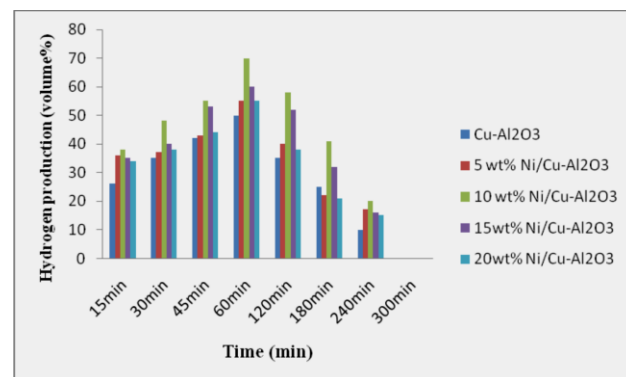


Fig. 5. Hydrogen production over $\text{Cu-Al}_2\text{O}_3$, 5 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, 10 wt% $\text{Ni/Cu-Al}_2\text{O}_3$, 15 wt% $\text{Ni/Cu-Al}_2\text{O}_3$ and 20 wt% $\text{Ni/Cu-Al}_2\text{O}_3$ catalysts.

It is observed from the literature [62-63], the copper doped catalyst; preparation technique plays significant role on hydrogen production and catalyst stability. The conversion is observed to be increased with increase in Ni content up to an optimum amount of 10 wt% at 60 min, further addition of Ni leads to the decrease in the conversion. However, almost all the Ni/Cu-Al₂O₃ catalysts showed high activity over Cu-Al₂O₃ catalyst.

It is also observed that, the conversion order is as follows:

Cu-Al₂O₃<5 wt% Ni/Cu-Al₂O₃ ~ 20 wt% Ni/Cu-Al₂O₃
<15 wt% Ni/Cu-Al₂O₃ < 10 wt% Ni/Cu-Al₂O₃ catalysts

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.

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.

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References

- Pinilla, J. L.; Suelves, I.; Utrilla, R.; Galvez, M. E.; Lazaro, M. J.; Moliner, R.; *Journal of Power Sources*, **2007**, 169, 103. DOI: [10.1016/j.jpowsour.2007.01.045](https://doi.org/10.1016/j.jpowsour.2007.01.045)
- Abanades, A.; Rubbi, C.; Salmieri, D.; *International Journal of Hydrogen Energy*, **2013**, 38, 8491. DOI: [10.1016/j.ijhydene.2012.08.138](https://doi.org/10.1016/j.ijhydene.2012.08.138)
- Muradov, N. Z.; *International Journal of Hydrogen Energy*, **1993**, 18, 211. DOI: [10.1016/0360-3199\(93\)90021-2](https://doi.org/10.1016/0360-3199(93)90021-2)
- Ashok, J.; Subrahmanyam, M.; Venugopal, A.; *Catal. Surv. Asia.*, **2008**, 12, 229. DOI: [10.1007/s10563-008-9054-4](https://doi.org/10.1007/s10563-008-9054-4)
- Choudhary, T V.; Goodman, D W.; *Catalysis Today*, **2002**, 77, 65. DOI: [10.1016/S0920-5861\(02\)00233-X](https://doi.org/10.1016/S0920-5861(02)00233-X)
- De Jong, K. P.; Geus, J. W.; *Catal. Rev: Science & Engineering.*, **2000**, 42, 481. DOI: [10.1081/CR-100101954](https://doi.org/10.1081/CR-100101954)
- Li, Y.; Chen, L.; Chang, L.; *Appl. Catal A: Gen.*, **1997**, 163, 45. DOI: [10.1016/S0926-860X\(97\)00116-6](https://doi.org/10.1016/S0926-860X(97)00116-6)
- Sakae, T.; Emi, K.; Yo, T.; Kiyoshi, O.; *Journal of Catalysis.*, **2003**, 219, 176. DOI: [10.1016/S0021-9517\(03\)00152-0](https://doi.org/10.1016/S0021-9517(03)00152-0)
- Kuvshinov, G. G.; Mogilnykh, Y. I.; Kushinov, D. G.; *Catal. Today.*, **1998**, 42, 357. DOI: [10.1010/S0920-5861\(98\)00115-1](https://doi.org/10.1010/S0920-5861(98)00115-1)
- Piao, L.; Li, Y.; Chen, J.; Liu, C.; Lin, J. Y. S.; *Catal. Today.*, **2002**, 74, 145. DOI: [10.1016/S0920-5861\(01\)00540-5](https://doi.org/10.1016/S0920-5861(01)00540-5)
- Zhao, N. Q.; He, C. N.; Ding, J.; Zou, T. C.; Qiao, Z. J.; Shi, C. S.; Du, X. W.; Li, J. J.; Li, Y. D.; *J Alloys & Compounds.*, **2007**, 428, 79. DOI: [10.1016/j.jallcom.2006.03.067](https://doi.org/10.1016/j.jallcom.2006.03.067)
- Bai, Z.; Chen, H.; Li, B.; Li, W.; *International Journal of Hydrogen Energy.*, **2007**, 32, 32. DOI: [10.1016/j.ijhydene.2006.06.030](https://doi.org/10.1016/j.ijhydene.2006.06.030)
- Venugopal, A.; Kumar, S. N.; Ashok, J.; Hari, P. D.; Kumari, D. V.; Prasad, K. B. S.; Subrahmanyam, M.; *International journal of Hydrogen Energy.*, **2007**, 32, 1782. DOI: [10.1016/j.ijhydene.2007.01.007](https://doi.org/10.1016/j.ijhydene.2007.01.007)
- Pinilla, J. L.; Suelves, I.; Lazaro, M. J.; Moliner, R.; Palacios, J. M.; *International Journal of Hydrogen Energy*, **2008**, 33, 2515. DOI: [10.1016/j.ijhydene.2008.02.041](https://doi.org/10.1016/j.ijhydene.2008.02.041)
- Takenaka, S.; Serizawa, M.; Otsuka, K.; *Journal of Catalysis*, **2004**, 222, 520. DOI: [10.1016/j.jcat.2003.11.017](https://doi.org/10.1016/j.jcat.2003.11.017)
- Ermakova, M. A.; Ermakova, D. Y.; *Catalysis Today*, **2002**, 77, 225. DOI: [10.1016/S0920-5861\(02\)00248-1](https://doi.org/10.1016/S0920-5861(02)00248-1)
- Shah, N.; Panjala, D.; Huffman, G. P.; *Energy Fuel*, **2001**, 15, 1528. DOI: [10.1021/ef0101964](https://doi.org/10.1021/ef0101964)
- Konieczny, A.; Mondal, K.; Wiltowski, T.; Dydo, P.; *International Journal of Hydrogen Energy*, **2008**, 33, 264. DOI: [10.1016/j.ijhydene.2007.07.054](https://doi.org/10.1016/j.ijhydene.2007.07.054)
- Avdeeva, L. B.; Kochubey, D. I.; Shaikhtudinov, S. K.; *Applied Catalysis A: Gen*, **1999**, 177, 43. DOI: [10.1016/S0926-860X\(98\)00250-6](https://doi.org/10.1016/S0926-860X(98)00250-6)
- Chen, J. L.; Zhou, X.; Cao, L.; Li, Y.; *Studies in Surface Science & Catalysis*, **2004**, 147, 73. DOI: [10.1016/S0167-2991\(04\)80030-2](https://doi.org/10.1016/S0167-2991(04)80030-2)
- Piao, L. Y.; Chen, J. L.; Li, Y. D.; *China Particuology*, **2003**, 1, 266. DOI: [10.1016/S1672-2515\(07\)60007-4](https://doi.org/10.1016/S1672-2515(07)60007-4)
- Muradov, N.; *Catalysis Communications*, **2001**, 2, 89. DOI: [10.1016/S1566-7367\(01\)00013-9](https://doi.org/10.1016/S1566-7367(01)00013-9)
- Dunker, A. M.; Kumar, S.; Mulawa, P. A.; *International Journal of Hydrogen Energy*, **2006**, 31, 473. DOI: [10.1016/j.ijhydene.2005.04.023](https://doi.org/10.1016/j.ijhydene.2005.04.023)
- Krzyzanski, S.; Kozlowski, M.; *International Journal of Hydrogen Energy*, **2008**, 33, 6172. DOI: [10.1016/j.ijhydene.2008.07.091](https://doi.org/10.1016/j.ijhydene.2008.07.091)
- Reshetenko, T. V.; Avdeeva, L. B.; Ismagilov, Z. R.; Chuvillan, A. R.; Ushakov, V. A.; *Applied Catalysis A: Gen*, **2003**, 247, 51. DOI: [10.1016/S0926-860X\(03\)00080-2](https://doi.org/10.1016/S0926-860X(03)00080-2)
- Ashok, J.; Subrahmanyam, M.; Venugopal, A.; *International Journal of Hydrogen Energy*, **2008**, 33, 2704. DOI: [10.1016/J.IJHYDENE.2008.03.028](https://doi.org/10.1016/J.IJHYDENE.2008.03.028)
- Ashok, J.; Reddy, P. S.; Raju, G.; Subrahmanyam, M.; Venugopal A.; *Energy & Fuels*, **2009**, 23, 5. DOI: [10.1021/EF8003976](https://doi.org/10.1021/EF8003976)
- Takenaka, S.; Shigeta, Y.; Tanabe, E.; Otsuka, K.; *Journal of Catalysis*, **2003**, 220, 468. DOI: [10.1016/S0021-9517\(03\)00244-6](https://doi.org/10.1016/S0021-9517(03)00244-6)
- Ashok, J.; Reddy, P. S.; Raju, G.; Subrahmanyam, M.; Venugopal A.; *International Journal of Hydrogen Energy*, **2008**, 33, 4809. DOI: [10.1016/J.IJHYDENE.2008.06.004](https://doi.org/10.1016/J.IJHYDENE.2008.06.004)
- Suelves, I.; Lazaro, M. J.; Moliner, R.; Echegoyen, Y.; Palacios, J. M.; *Catalysis Today*, **2006**, 116, 271. DOI: [10.1016/J.CATTOD.2006.05.071](https://doi.org/10.1016/J.CATTOD.2006.05.071)
- Echegoyen, Y.; Suelves, I.; Lazaro, M. J.; Moliner, R.; Palacios, J. M.; *Journal of Power Sources*, **2007**, 169, 150. DOI: [10.1016/J.JPOWSOUR.2007.01.058](https://doi.org/10.1016/J.JPOWSOUR.2007.01.058)

32. Lazaro, M. J.; Echegoyen, Y.; Suelves, I.; Palacios, J. M.; Moliner, R.; *Applied Catalysis A: General*, **2007**, 329, 22.
DOI: [10.1016/J.APCATA.2007.06.014](https://doi.org/10.1016/J.APCATA.2007.06.014)
33. Rostrup-Nielsen, J. R.; *Journal of Catalysis*, **1972**, 27, 343.
DOI: [10.1016/0021-9517\(72\)90170-4](https://doi.org/10.1016/0021-9517(72)90170-4)
34. Rostrup-Nielsen, J. R.; *Journal of Catalysis*, **1977**, 33, 184.
DOI: [10.1016/0021-9517\(74\)90263-2](https://doi.org/10.1016/0021-9517(74)90263-2)
35. Alstrup, I.; *Journal of Catalysis*, **1988**, 109, 241.
DOI: [10.1016/0021-9517\(88\)90207-2](https://doi.org/10.1016/0021-9517(88)90207-2)
36. Avdeeva, L. B.; Goncharova, O. V.; Kochubey, D. I.; Zaikovskii, V. I.; Plyasova, L. M.; Novgorodov, B. N.; Shaikhutdinov; *Applied Catalysis A: General*, **1996**, 141, 117.
DOI: [10.1016/0926-860X\(96\)00026-9](https://doi.org/10.1016/0926-860X(96)00026-9)
37. Yang, R. T.; Chen, J. P.; *Journal of Catalysis*, **1989**, 115, 52.
DOI: [10.1016/0021-9517\(89\)90006-7](https://doi.org/10.1016/0021-9517(89)90006-7)
38. Figueredo, J. L.; Bernardo, C. A.; Baker, R. T. K.; Huttinger, K. J. (Eds.); *Carbon Fibers Filaments and Composites*; Springer Netherlands: 1990.
DOI: [10.1007/978-94-015-6847-0](https://doi.org/10.1007/978-94-015-6847-0)
39. Li, Y. D.; Chen, J. L.; Ma, Y. M.; Zhao, J. B.; Qin, Y. N.; Chang, L.; *Chemical Communications*, **1999**, 12, 1141.
DOI: [10.1039/A902281C](https://doi.org/10.1039/A902281C)
40. Chen, J. L.; Li, Y. D.; Li, Z.; Zhang, X.; *Applied Catalysis A: General*, **2004**, 269, 179.
DOI: [10.1016/J.APCATA.2004.04.016](https://doi.org/10.1016/J.APCATA.2004.04.016)
41. Wang, H. Y.; Baker, R. T. K.; *Journal of Physical Chemistry B*, **2004**, 108, 20273.
DOI: [10.1021/jp040496x](https://doi.org/10.1021/jp040496x)
42. Dussault, L.; Dupin, J. C.; Guimon, C.; Monthieux, M.; Latorre, N.; Ubiato, T.; Romeo, E.; Royo, C.; Monzon, A.; *Journal of Catalysis*, **2007**, 251, 223.
DOI: [10.1016/J.JCAT.2007.06.022](https://doi.org/10.1016/J.JCAT.2007.06.022)
43. Monzon, A.; Latorre, N.; Ubiato, T.; Royo, C.; Romeo, E.; Villacampa, J. I.; Dussault, L.; Dupin, J. C.; Guimon, C.; Montieux, M.; *Catalysis Today*, **2006**, 116, 264.
DOI: [10.1016/J.CATTOD.2006.05.085](https://doi.org/10.1016/J.CATTOD.2006.05.085)
44. Muradov N.; Hydrogen production by catalytic cracking of natural gas. In: 11th world hydrogen energy conference, Stuttgart, Germany; 1996, 697.
45. Parmon V N.; Kuvshinov G G.; Sobyani V A; Innovative process for hydrogen production from natural gas and other hydrocarbons. In: Proceedings of the 11th world hydrogen energy conference. Stuttgart, 23-28 June 1996, 1996.
46. Ermakova, M. A.; Ermakov, D. Y.; Plyasova, L. M.; Kuvshinov, G. G.; *Catalysis Letters*, **1999**, 62, 93.
DOI: [10.1023/A:1019079929435](https://doi.org/10.1023/A:1019079929435)
47. Ermakova, M. A.; Ermakov, D. Y.; Kuvshinov, G. G.; *Applied Catalysis A: General*, **2000**, 201, 61.
DOI: [10.1016/S0926-860X\(00\)00433-6](https://doi.org/10.1016/S0926-860X(00)00433-6)
48. Takenaka, S.; Kobayashi, S.; Ogihara, H.; Otsuka, K.; *Journal of Catalysis*, **2003**, 217, 79.
DOI: [10.1016/S0021-9517\(02\)00185-9](https://doi.org/10.1016/S0021-9517(02)00185-9)
49. Pinilla, J.L.; Suelves, I.; Lázaro, M. J.; Moliner, R.; Palacios, J.M.; *Applied Catalysis A: General*, **2009**, 363, 199.
DOI: [10.1016/J.APCATA.2009.05.009](https://doi.org/10.1016/J.APCATA.2009.05.009)
50. Wang, H. Y.; Lua, A. C.; *Journal of Physical Chemistry C*, **2012**, 116, 26765.
DOI: [10.1021/jp306519t](https://doi.org/10.1021/jp306519t)
51. Dupuis, A. C.; *Progress in Material Science*, **2005**, 50, 929.
DOI: [10.1016/J.PMATSCI.2005.04.003](https://doi.org/10.1016/J.PMATSCI.2005.04.003)
52. Li, Y. D.; Chen, J. L.; Qin, Y. N.; Chang, L.; *Energy & Fuels*, **2000**, 14, 1188.
DOI: [10.1021/ef0000781](https://doi.org/10.1021/ef0000781)
53. Reshestenko, T. V.; Avdeeva, L. B.; Ushakov, V. A.; Moroz, E. M.; Shamkov, A. N.; Kriventsov, V. V.; Kochubey, D. I.; Pavlyukhin, Y. T.; Chuvil, A. L.; Ismagilov, Z. R.; *Applied Catalysis A: General*, **2004**, 270, 87.
DOI: [10.1016/J.APCATA.2004.04.026](https://doi.org/10.1016/J.APCATA.2004.04.026)
54. Li, Y. D.; Chen, J. L.; Chang, L.; Qin, Y. N.; *Journal of Catalysis*, **1998**, 78, 76.
DOI: [10.1006/jcat.1998.2119](https://doi.org/10.1006/jcat.1998.2119)
55. Li, J. Z.; Lu, G. X.; Li, K.; Wang, W. P.; *Journal of Molecular Catalysis A: Chemical*, **2004**, 221, 105.
DOI: [10.1016/J.MOLCATA.2004.06.015](https://doi.org/10.1016/J.MOLCATA.2004.06.015)
56. Chen, J. L.; Qiao, Y. H.; Li, Y. D.; *Applied Catalysis A: General*, **2008**, 337, 148.
DOI: [10.1016/J.APCATA.2007.12.007](https://doi.org/10.1016/J.APCATA.2007.12.007)
57. Lazaro, M. J.; Echegoyen, Y.; Alegre, C.; Suelves, I.; Moliner, R.; Palacios, J. M.; *International Journal of Hydrogen Energy*, **2008**, 33, 3320.
DOI: [10.1016/J.IJHYDENE.2008.03.050](https://doi.org/10.1016/J.IJHYDENE.2008.03.050)
58. Monthieux, M.; Noe, L.; Dussault, L.; Dupin, J. C.; Latorre, N.; Ubiato, T.; Romeo, E.; Royo, C.; Monzon, A.; Guimon, C.; *Journal of Materials Chemistry*, **2007**, 43, 4611.
DOI: [10.1039/B707742D](https://doi.org/10.1039/B707742D)
59. Zhao, N. Q.; He, C. N.; Jiang, Z. Y.; Li, J. J.; Li, Y. D.; *Materials Letters*, **2006**, 60, 159.
DOI: [10.1016/J.MATLET.2005.08.009](https://doi.org/10.1016/J.MATLET.2005.08.009)
60. Chesknov, V. V.; Zaikovskii, V. I.; Buyanov, R. A.; Molchanov, V. V.; Plysova, L. M.; *Kinetika I Kataliz*, **1994**, 35, 146.
61. Chesknov, V. V.; Prokudina, N. A.; Buyanov, R. A.; Molchanov, V. V.; USSR invention certificate 2042425, 1995.
62. Douxing, L.; Jiuling, C.; Yongdan, L.; *International Journal of Hydrogen Energy*, **2009**, 34, 299.
DOI: [10.1016/j.ijhydene.2008.09.106](https://doi.org/10.1016/j.ijhydene.2008.09.106)
63. Nosrat, I.; Ali, M. R.; Ahmad, Z.; Heshmatollah, V.; Maryam, R.; *International Journal of Hydrogen Energy*, **2014**, 39, 7765.
DOI: <http://dx.doi.org/10.1016/j.ijhydene.2014.03.036>
64. Pinilla, J. L.; Suelves, I.; Lazaro, M. J.; Moliner, R.; Palacios, J. M.; *International Journal of Hydrogen Energy*, **2010**, 35, 9801.
DOI: [10.1016/j.ijhydene.2009.10.008](https://doi.org/10.1016/j.ijhydene.2009.10.008)
65. Kang, D.; Lee, J. W.; Enhanced methane decomposition over nickel-carbon-B₂O₃-core-shell catalysts derived from carbon dioxide, *Applied Catalysis B: Environmental*, **2016**, 186, 41–55.
DOI: [10.1016/j.apcatb.2015.12.045](https://doi.org/10.1016/j.apcatb.2015.12.045)
66. Poncelet, G.; Jacobs, P.A.; Grange, P.; and Delmon, B.; *Studies in Surface Science and Catalysis*, 63,
ISBN: 9780444886163