The Production of CO_x-Free Hydrogen and Carbon Nanofibers from Direct Catalytic Decomposition of Methane

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Abstract

Direct decomposition of methane was carried out using a fixed-bed reactor at 700°C for the production of CO_x-free hydrogen and carbon nanofibers. The catalytic performance of NiO-M/SiO_2 catalysts (where M = AgO, CoO, CuO, FeO, MnO_x, and MoO) in methane decomposition was investigated. The experimental results indicate that among the tested catalysts, NiO/SiO_2 promoted with CuO gave the highest hydrogen yield. In addition, the examination of the most suitable catalyst support, including Al_2O_3, CeO_2, La_2O_3, SiO_2, and TiO_2, shows that the decomposition of methane over NiO-CuO favors SiO_2 support. Furthermore, the optimum ratio of NiO to CuO on SiO_2 support for methane decomposition has been determined. The experimental results show that the optimum weight ratio of NiO to CuO fell at 8:2 (w/w) as the highest methane conversion was obtained over this catalyst.

Keywords: Methane decomposition; hydrogen; carbon nanofibers; supported catalysts.

1.0   Introduction

The utilization of natural gas, one of the world's abundant resources, to produce valuable chemicals is one of the desirable goals in the current natural gas processing industry. In this regard, the production of hydrogen from natural gas has attracted the interest of industrialists and researches. The conventional options of hydrogen production from natural gas, such as steam reforming, partial oxidation, and autothermal reforming [1], involve CO_x production at some point at the technological chain of the process. Thus, the gas needs further treatment to separate hydrogen from the other gases such CO and CO_2. Hence, it is of importance to develop a simpler and less energy intensive method in producing hydrogen which is free of CO_x formation as this can reduce the capital cost with comparison to the conventional one. One of the ways to reach this objective is to use direct decomposition of methane over catalytic materials for the production of hydrogen [2-4].

Direct decomposition of methane, the main constituent of natural gas, offers the possibility of producing two valuable chemical commodities: pure hydrogen and carbon nanofibers. It is a technologically simple one-step process without energy and material intensive gas separation stages and shows the potential to be a CO_x-free hydrogen production process. The hydrogen produced from methane decomposition does not contain CO_x impurities. Undoubtedly, the produced hydrogen can be used directly without any removal of CO_x. Carbon nanofibers, a by-product which are produced from methane decomposition, are a predominantly mesoporous materials with high surface area [4]. Such properties make them a promising material for the applications in the areas of catalysis, adsorption and nanocomposites [5-7].

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Catalytic decomposition of methane has recently been receiving attention as an alternative route to the production of hydrogen at lower temperature. Many groups have studied methane decomposition of at moderate temperature such as at $550^{o}C$ because the catalysts possess high stability at this temperature [8-10]. However, the hydrogen yield from methane decomposition is low due to the thermodynamic limitation at temperatures of below $700^{o}C$ [11]. Decomposition of methane at higher temperatures attracts considerable interest today because of the conversion of methane is higher [12]. However, catalysts lose their activity and stability at higher temperature ($> 700^{o}C$) due to their fast deactivation. It has been proved that the deactivation of catalyst for methane decomposition is mainly caused by the formation of encapsulating coke on the active sites of the catalyst. Therefore, developing a catalyst, which is resistible for its deactivation at higher temperatures, is necessary.

In the previous studies, we have reported that NiO/TiO_2 catalyst is of efficiency for methane decomposition at high temperature with the activation energy calculated being one of the lowest ever reported in the literature for this process [12]. In addition, the examination of the catalyst promoters for NiO/TiO_2 catalyst indicated that MnO_x is the preferable promoter for the said catalyst [13]. We also reported that the metal in oxide form gave better conversion for methane during methane decomposition reaction [13]. In continuation of our investigation, in this paper we further examine different supported metal oxide catalyst for methane decomposition. This includes the investigations on the catalytic performance of NiO/SiO_2 catalysts promoted with other metal oxide species, the effect of catalyst supports for NiO-CuO alloys, the optimum weight ratio of NiO to CuO for methane conversion and the morphology of the carbon deposited on the used catalysts.

2.0   Materials & Method

Methane decomposition was studied using $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_2.H_2O$ $Cu(NO_3)_2.6H_2O$, $Mn(NO_3)_2.4H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ as metal sources for the preparation of the supported bimetallic catalysts. The Al_2O_3, MgO, CeO_2, TiO_2, La_2O_3, and SiO_2 (Cab-osil) were used as catalytic supports in this study. All the catalysts were prepared by a conventional impregnation method as reported elsewhere. The desired amounts of the transition metal oxides were dissolved in deionized water. The resulting paste was dried at $105^{o}C$ for 12 hours and was calcined in air at $600^{o}C$ for 5 hours. The catalysts were then sieved to a size of 425-600 μm. The production of CO_x-free hydrogen and carbon nanofibers via catalytic decomposition of methane were carried out in a fixed-bed reactor at $700^{o}C$. The detailed experimental setup and procedure have been reported earlier [14]. The activity tests for the catalysts in the decomposition of methane were conducted at atmospheric pressure in a stainless-steel fixed-bed reactor (length and diameter of the reactor were 600 and 20 mm, respectively). High purity methane (99.999% supplied by Malaysian Oxygen Sdn. Bhd.) was mixed with argon (99.999% purity, supplied by Sitt Tatt Industrial Gases Sdn. Bhd.) before entering the reactor and 0.2 g of catalyst was put in the middle part of the reactor for each run. The flow of methane was regulated using a mass flow controller (MKS) and the argon flow was regulated by mass flow controllers (Brooks, model 5850E). The product gases were analyzed using an on-line gas chromatograph (Hewlett-Packard Series 6890, USA). The schematic diagram of the experimental apparatus is given in Fig. 1. The carbon nanostructures deposited on the catalysts were analyzed using a transmission electron microscope (TEM) (Philips, CM12). In preparation for TEM experiments, a few samples of the spent catalyst were dispersed in acetone (100% purity), and then a drop was deposited on a coated copper grid. The conversion of methane and hydrogen yield are defined as follows:

$$\text{Methane conversion (\%)} = \frac{\text{Mole of methane reacted}}{\text{Mole of methane input}} \quad x \quad 100$$

$$\text{Hydrogen yield} = \frac{\text{Mole of hydrogen produced}}{\text{Mole of metal oxide in a fresh catalyst}}$$
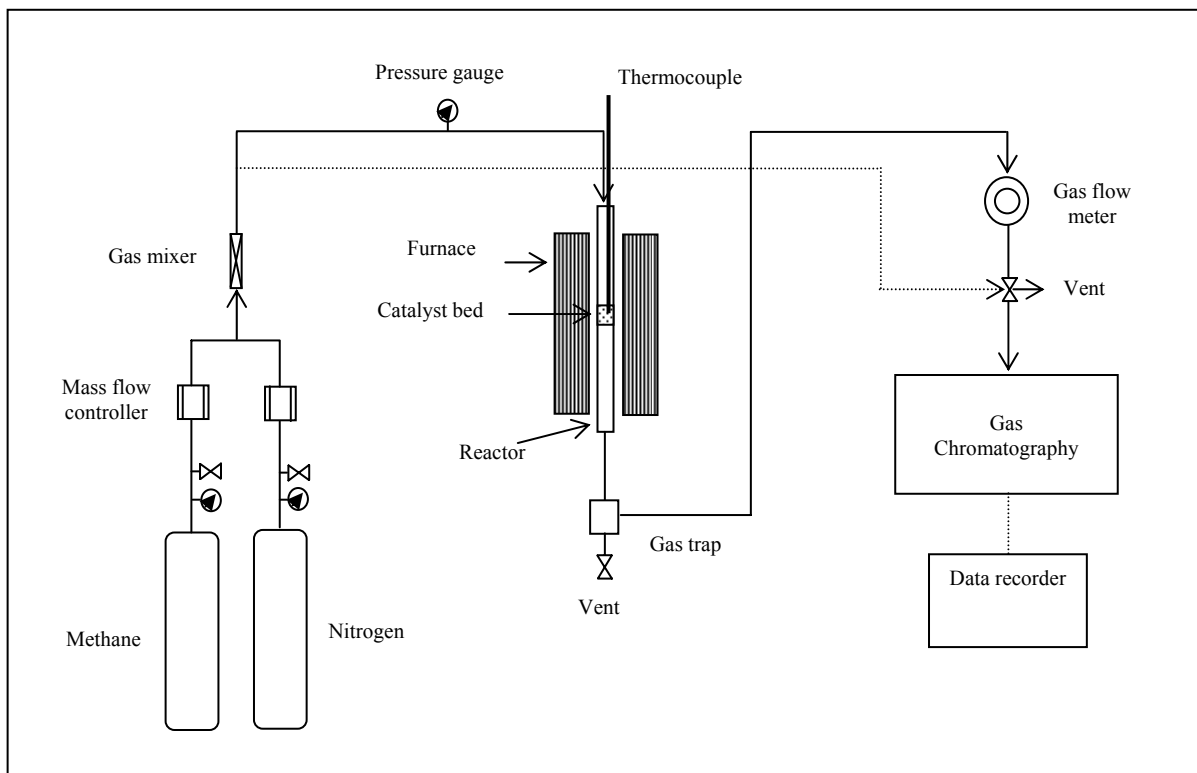

Figure 1   Schematic diagram of the experimental apparatus.

3.0   Results and Discussion

3.1   The effect of catalyst promoters

Table 1 shows the catalytic performance of NiO/SiO_2 catalyst promoted with different metal oxide species for methane decomposition at 700^oC. The promoted catalysts are denoted as NiO-M/SiO_2 in this paper (where M = AgO, CoO, CuO, FeO, MnOx and MoO). The loadings of NiO-M were adjusted to 10 wt.% with respect to the weight of catalyst and the weight ratio of NiO to M was set at 9:1. For all the catalysts, methane decomposition proceeded selectively to form hydrogen as only gaseous product. Methane conversion over NiO/SiO_2 catalyst was high during the initial reaction. The conversion decreased remarkably with time on stream, possessing conversion of below 1% after 30 min of time on stream. The addition of CoO and MoO slightly improved the catalytic lifetime of NiO/SiO_2 for the methane decomposition. In contrast, the addition of AgO, FeO, and MnOx shortened the catalytic lifetime of NiO/SiO_2. One can notice that NiO/SiO_2 promoted with CuO showed significant increase in the catalytic activity and lifetime in methane decomposition. In the

presence of CuO as promoter for NiO/SiO_2, the stability and activity of catalyst were enhanced markedly.

Fig. 2 shows the hydrogen yields over the tested catalysts for 90 min of reaction. The yields were estimated from the obtained methane conversion, assuming that methane conversion to hydrogen and carbon proceeded stoichiometrically ($CH4 \rightarrow C + 2H2$). Hydrogen yield for NiO/SiO_2 was evaluated to be 140. The hydrogen yields for 9NiO-1CoO, 9NiO-1FeO, and $9NiO-1MoO/SiO_2$ were 157, 134, 161, respectively. However, NiO/SiO_2 promoted with AgO and MnOx were less active in methane decomposition, giving the hydrogen yields of 19 and 14, respectively. According to Takenaka et al. [15], the addition of Cu into Ni/SiO_2 subjected to lower the hydrogen yield as compared to Ni/SiO_2 itself for methane decomposition at 550°C. In the present study, the results shown in Table 1 and Fig. 2 indicate that the addition of CuO into NiO/SiO_2 improves the catalytic lifetime and hydrogen yield for more than three times that of NiO/SiO_2, i.e. 494, in the methane decomposition at a reaction temperature of 700°C. It is likely that the addition of CuO stabilized the NiO/SiO_2 by forming CuO-NiO alloys, which bring about a long catalytic lifetime and a high hydrogen yield in the methane decomposition.

Table 1
Methane conversions after 90 min reaction over 9NiO-1M catalysts supported on SiO_2 at 700°C.

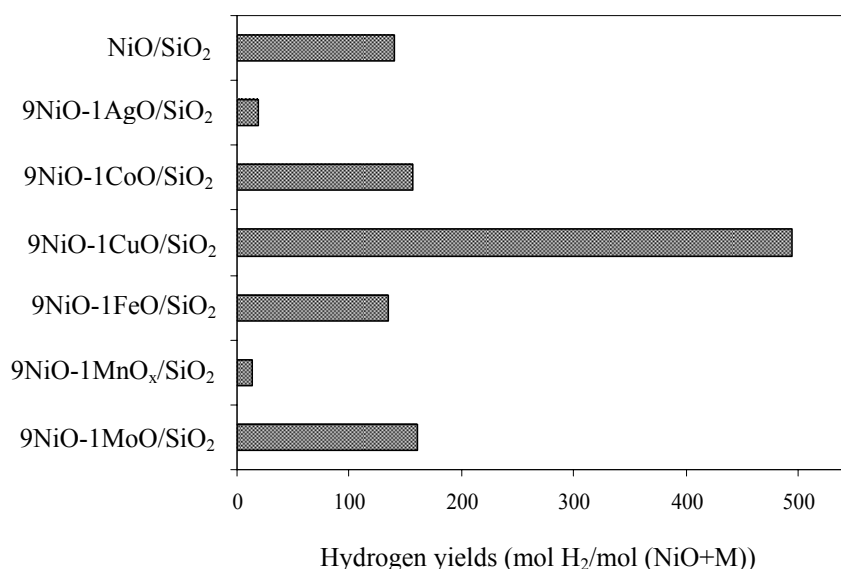| Catalyst	Methane conversion (%)			
	0 min	30 min	60 min	90 min
NiO/SiO_2	47.57	0.81	0.65	0.52
$9NiO-1AgO/SiO_2$	1.74	0.94	0.88	0.74
$9NiO-1CoO/SiO_2$	48.79	3.49	1.64	1.37
$9NiO-1CuO/SiO_2$	51.52	43.03	26.21	1.45
$9NiO-1FeO/SiO_2$	44.08	0.96	0.71	0.63
$9NiO-1MnO_x/SiO_2$	3.20	0.66	0.53	0.37
$9NiO-1MoO/SiO_2$	47.81	2.08	1.60	1.37

Figure 2   Hydrogen yields in the methane decomposition over NiO/SiO_2 and $9NiO-1M/SiO_2$ catalysts at 700 °C.

3.2   *The effect of catalyst supports for bimetallic catalysts*

Table 2 shows the catalytic performance of 9NiO-1CuO catalysts loaded on different supports. Al_2O_3, CeO_2, La_2O_3, SiO_2, and TiO_2, which are widely used as catalytic support in methane decomposition [10,12,16,17], were selected as the supports in this study. For all the catalysts, the loadings of NiO-CuO were adjusted to 10 wt.% with respect to the weight of catalyst. The initial activities of 9NiO-1CuO/La_2O_3 and 9NiO-1CuO/TiO_2 for the methane decomposition were low, possessing the methane conversions of 16.06% and 14.69%, respectively. After 30 min of reaction, 9NiO-1CuO supported on Al_2O_3, and La_2O_3 possessed methane conversions of below 1%, revealing that both catalysts are not stable in methane decomposition at this temperature. The results shown in Table 2 indicate that NiO-CuO supported on SiO_2 is the most suitable for methane decomposition, which showed higher catalytic activity and stability in the methane decomposition.

Table 2
Methane conversions after 90 min reaction over 9NiO-1CuO supported on different supports at 700 ^{o}C.

Catalyst	Methane conversion (%)			
	0 min	30 min	60 min	90 min
9NiO-1CuO/Al_2O_3	26.08	0.59	0.33	-
9NiO-1CuO/CeO_2	42.28	23.19	0.63	0.55
9NiO-1CuO/La_2O_3	16.06	0.34	-	-
9NiO-1CuO/SiO_2	51.52	43.03	26.21	1.45
9NiO-1CuO/TiO_2	14.69	5.16	1.98	0.60

The amounts of hydrogen produced over the tested catalysts after 90 min of reaction are summarized in Fig. 3. The hydrogen yield was the highest for NiO-CuO/SiO_2 catalyst among all the supported 9NiO-1CuO catalysts examined in this work. The hydrogen yields after 90 min of reaction decreased in the order of SiO_2>CeO_2>TiO_2>Al_2O_3>La_2O_3 supports with the obtained hydrogen yields of 494, 234, 77, 71, and 43, respectively.
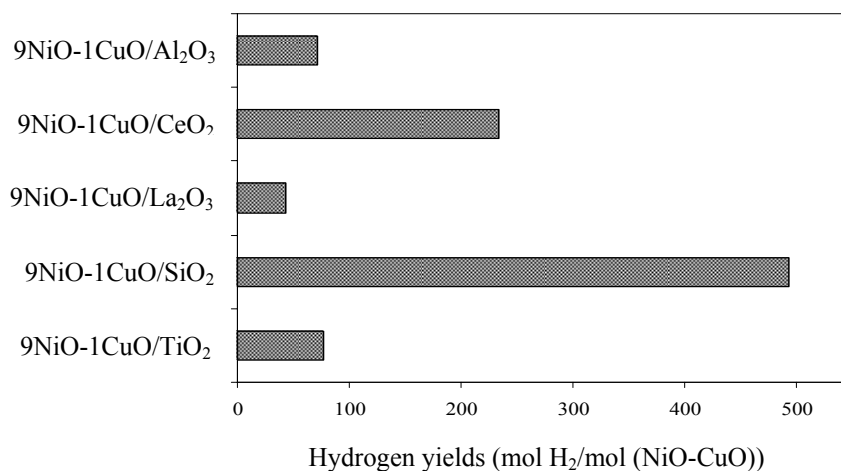

Figure 3   Hydrogen yields in the methane decomposition over different supported 9NiO-1CuO catalysts at 700 ^{o}C.

3.3   The effects of weight ratio of active metals to promoters

Fig. 4 shows the changes of methane conversion with time stream of methane over NiO-CuO/SiO$_2$ catalysts with different weight ratio of NiO to CuO. The hydrogen yields in the methane decomposition were estimated from the kinetic curves of methane conversion and are shown in Fig. 5. It was noticed that the addition of CuO into NiO/SiO$_2$ catalyst at the weight ratio of NiO:CuO from 9:1 to 5:5 prolonged the catalytic lifetime remarkably. However, the addition of excess amounts of CuO (weight ratio NiO:CuO < 4:6) decreased the catalytic lifetime for the methane decomposition. As shown in Fig. 5, the hydrogen yield increased significantly with an increase in CuO loading into NiO/SiO$_2$ catalyst and the yield attained the maximum at NiO:CuO = 8:2. The maximum hydrogen yield was 536, which was about 4 times greater than that of NiO/SiO$_2$ catalyst. The hydrogen yields obtained for the catalysts with the weight ratio NiO:CuO of 9:1, 7:3, 6:4, 5:5, and 4:6 are 494, 452, 272, 208, and 128, respectively. This shows that the increase of copper content improved the catalyst stability, but the continual increase of copper content led to a great decrease of the catalyst stability.
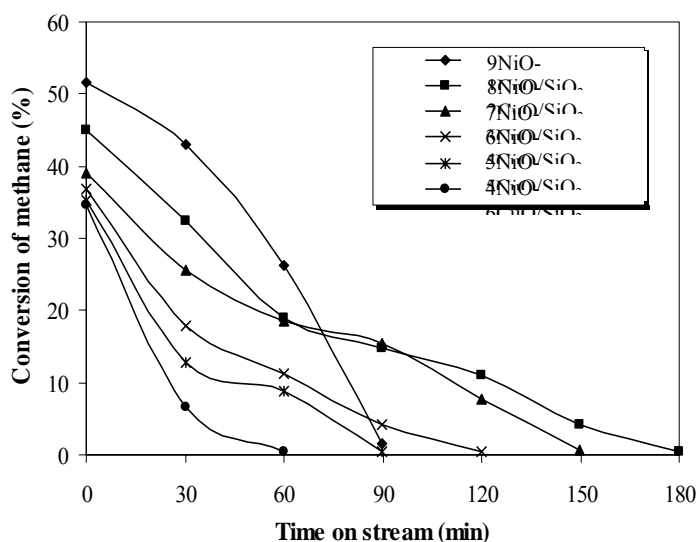

Figure 4   Kinetic curves of methane conversions as a function of time on stream over 9NiO-1CuO/SiO$_2$ catalysts with different weight ratio of NiO to CuO at 700°C..
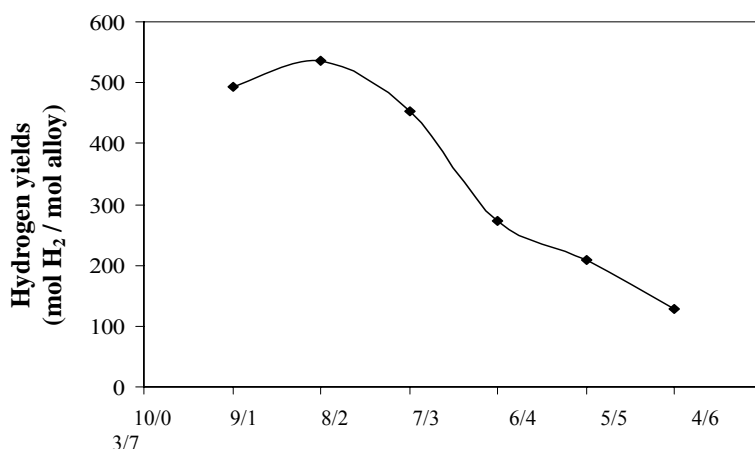

Figure 5   Hydrogen yields in the methane decomposition over NiO-CuO/SiO$_2$ catalysts with different weight ratio of NiO to CuO at 700°C.

3.4   Characterization of used catalysts

Fig. 6 shows the TEM images of carbon deposited by the methane decomposition over NiO/SiO_2 and $8NiO-2CuO/SiO_2$ catalysts. It was found that carbon nanofibers were formed on the surfaces of both catalysts. However, there are differences in the morphology of the grown carbon nanofibers. One can notice that the average diameter of the carbon nanofibers grown on $8NiO-2CuO/SiO_2$ catalyst was clearly larger than those on the NiO/SiO_2 catalyst. Furthermore, carbon nanofibers on $8NiO-2CuO/SiO_2$ catalyst seem more fragile as compared to those formed on NiO/SiO_2 catalyst. This reveals that the carbon nanofibers grown on NiO/SiO_2 catalyst have higher degree of graphitization than those on $8NiO-2CuO/SiO_2$ catalyst. Owing to the high activity and stability of $8NiO-2CuO/SiO_2$ catalyst in methane decomposition, the grown carbon nanofibers were denser, forming an interwoven coverage under TEM observation. It is of importance to note that catalyst particles were present at the tips of carbon nanofiber grown on NiO/SiO_2 catalyst, whereas no catalyst particles were observed at the tips of carbon nanotubes formed by $8NiO-2CuO/SiO_2$ catalyst. This shows that the growth model of carbon nanofibers on these two catalysts is different. We deduce that the carbon nanofiber grown by the NiO/SiO_2 catalyst followed the tips-growth model where the catalyst particles located at the tips of the carbon nanofibers were active for methane decomposition. On the other hand, based-growth model were taken place for growing carbon nanofibers on $8NiO-2CuO/SiO_2$ catalyst, where the catalyst particles attached on the SiO_2 support were active for methane decomposition.
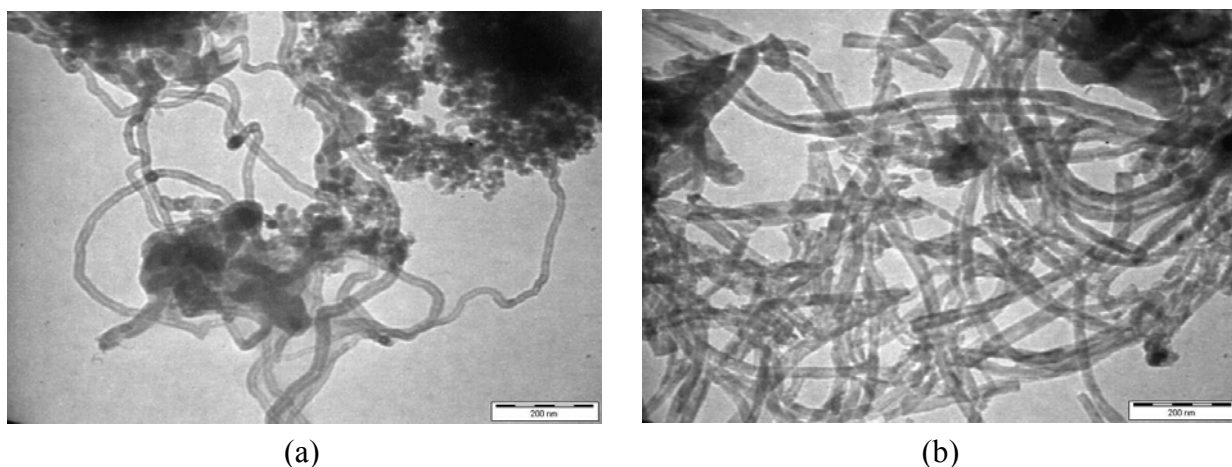

(a)   (b)

Figure 6   TEM image of carbon nanofibers produced on (a) NiO/SiO_2 and (b) $8NiO-2CuO/SiO_2$ in methane decomposition at 700^oC.

4.0   Conclusions

A comparison of catalytic properties of NiO/SiO_2 catalyst promoted with AgO, CoO, CuO, FeO, MnO_x, and MoO showed that the addition of CuO increased the hydrogen yield and prolonged the lifetime of bimetallic NiO-CuO catalysts in methane decomposition at 700^oC. The examination of catalyst supports indicated that SiO_2 is the best catalyst support tested for NiO-CuO. The highest hydrogen yield, being 536 mol H_2/mol alloy, was obtained by using this catalyst with the weight ratio NiO:CuO of 8:2 on SiO_2 support. With this weight ratio, the NiO-CuO alloys formed on SiO_2 possessed high stability in methane decomposition even though the reaction was conducted at high temperature. It is important to note that only hydrogen was detected by the GC as gaseous product. Analysis of the deposited carbons by

TEM indicated carbon nanofibers were grown on the surfaces of NiO/SiO_2 and NiO-CuO/SiO_2 catalysts. These carbon structures have great potential applications as catalyst supports and nanocomposites.

5.   Acknowledgements

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