

Hydrogen Production via Thermo Catalytic Decomposition of Methane over Bimetallic Ni-Cu/AC Catalysts: Effect of Copper Loading and Reaction Temperature

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Abstract—This study investigated on the effect of copper loading on the catalytic performance of Ni/AC catalysts at various reaction temperatures. Cu loading was varied from 0%, 5%, 10% and 15%, and the reaction temperatures tested were 600 °C, 750 °C and 900 °C. The reaction was carried out in a U-tube quartz plug flow micro-reactor, and allowed to proceed for 8 hours. The highest initial methane conversion of 29.95% was observed on the Ni/AC catalyst without Cu loading at 900 °C. However, this catalyst rapidly deactivated after only 3 hours. On the other hand, the 6.7Ni-5Cu/AC catalyst at 900 °C had an initial methane conversion of 27%, but slower catalyst deactivation was observed. This is due to the positive effect of copper on the metallic Ni particles, enhancing the ability of the catalyst to accumulate carbon, thus increasing stability at high temperatures. Statistical analysis of the experimental data using two-way ANOVA method determined that for a 95% confidence interval, only reaction temperature had a significant effect on the activity of the Ni-Cu/AC catalysts, while Cu loading was an insignificant factor. XRD results showed the formation of Ni₃C crystallite for all catalyst samples except 6.7Ni-5Cu/AC, which may have contributed to catalyst deactivation. Also, SEM images of the spent 6.7Ni-5Cu/AC catalyst, which exhibited the best catalytic performance, showed the formation of valuable filamentous carbon, which may be used extensively in many other fields of application.

Index Terms—Copper promoter, hydrogen production, ni/ac catalyst, thermocatalytic decomposition of methane

I. INTRODUCTION

Nowadays, the conventional source for energy production is the burning or combustion of fossil fuels. However, harmful carbon dioxide emissions are brought into the atmosphere as a consequence of burning fossil fuels, and this has largely contributed to the phenomenon of global warming which has received widespread attention as a huge threat to the environment. Thus, in order to minimize the combustion of fossil fuels while still being able to answer the demand for energy production, there arises a need to look for an alternative source of energy. One of the most widely recommended alternatives is the use of hydrogen energy as a source of power, because of its availability [1]. Moreover, it is considered to be an environment-friendly source of energy

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and a promising source of clean fuel [2].

One of the rapidly emerging processes involved in the production of hydrogen energy that has recently garnered the attention of many researchers is the thermocatalytic decomposition (TCD) of methane, alternatively known as the catalytic cracking of methane. The TCD of methane offers many advantages in the production of hydrogen energy. One of the main advantages of the process is that the reaction only produces solid carbon as one of its products besides H₂ gas, unlike the methane reforming processes which result in carbon monoxide gas as one of the products.

The production of CO_x-free hydrogen gas results in an easier separation of H₂ gas from the product stream, which is desired because of its application in the Polymer Electrolyte Membrane (PEM) fuel cell. After obtaining the hydrogen gas after reaction, it may then be channeled directly to the PEM fuel cell without fear of poisoning the platinum electrocatalyst inside due to the presence of CO gas. Conversely, other means of hydrogen production such as the methane reforming processes produce a stream of outlet gases containing both H₂ and CO, which has to undergo an additional water-gas shift reaction step followed by methanation in order to ensure the complete separation of the CO and H₂ gases. These additional steps only add to the complexity of the entire process and are detrimental to the economical aspect of the reaction [3].

In order for the TCD of methane to be an economical process, highly efficient and effective catalysts must be developed [4]. Nowadays, researchers have been continuously looking for new, innovative, and better catalysts for the TCD of methane which will result in high rates of methane conversion while having long catalytic lifetimes. Numerous studies have been conducted on the use of metal catalysts in the TCD of methane. These catalysts generally result in high activities and exhibit great chemical and mechanical stability over the course of the reaction [5]. Some of the common metal catalysts used are nickel, iron, copper, cobalt, platinum and palladium, among others. However, these metal catalysts are expensive; therefore, support materials such as silica, alumina, titania, magnesia, zirconia, and activated carbon are used to increase the specific surface area to be used as active sites for the catalytic reaction.

Among the supported metal catalysts used, Ni catalysts have been identified as the most effective for the TCD of methane, since they are known to provide a higher yield of H₂ per mass unit of the active component [6]. In addition, the use of Ni catalysts generally results in the formation of

filamentous carbon as the solid carbon product [7]. These carbon nanofibers possess desirable properties that may be applied extensively in other fields of research, such as in nanotechnology, optics, and material science.

Activated carbon has been suggested as a good support material for Ni catalysts in the TCD of methane primarily because it is a stable and non-toxic material which can easily be obtained from various raw materials such as coal and other renewable resources [8]. Furthermore, its major advantages include high thermal stability, high surface area, and cheap recovery of the spent metal catalyst by simple combustion [9]. It has been shown that using Ni catalysts supported on activated carbon results in good catalytic performance in the TCD of methane [8]. Nonetheless, there is still room for improvement of the catalytic activity of the Ni/AC catalysts, which displayed initial percent methane conversions of less than 25% for all reaction temperatures tested, as well as fast deactivation times.

Meanwhile, numerous studies have reported the positive effect of copper addition on the catalytic performance of various supported Ni catalysts [10]–[15]. Copper addition has been found to increase the thermal stability of supported Ni catalysts by enhancing the ability of the Ni catalyst to accumulate carbon, resulting in longer catalytic lifetimes [2]. However, though the addition of Cu is able to promote the activity of Ni catalysts, the relationship between the catalytic activity and the properties of the Ni-Cu alloy which is formed has not yet been fully understood [14].

The addition of Cu on Ni/AC catalysts for the TCD of methane has not yet been investigated by researchers. Conducting a study on the TCD of methane over Ni/AC catalysts with various copper loadings will help determine how effective the catalyst is, compared to other catalysts studied in literatures, in terms of overall catalytic performance for the TCD of methane.

This paper reports the results obtained from the activity tests conducted for the TCD of methane over Ni-Cu/AC catalysts with different percent copper loadings at various reaction temperatures. The results of the catalyst characterization using X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) are also reported, along with the observed correlations with the catalytic performance of the Ni-Cu/AC catalysts.

II. EXPERIMENTAL

A. Preparation of Catalysts

The AC support material used was obtained from the Department of Science and Technology – Industrial Technology Development Institute (DOST-ITDI). The catalysts were prepared using the dry impregnation method. Nickel (II) nitrate and copper (II) nitrate precursors were dissolved in water, and small amounts of methanol were added to facilitate better dispersion due to the hydrophobic nature of the ITDI-AC. This was followed by dropwise addition of the solution to the AC support until it was slightly wet, and it was dried overnight at 105 °C.

The impregnated catalysts were then calcined at 500 °C under inert helium flow for 2 hours, and then subjected to reduction pre-treatment at 300 °C under a stream of H₂ gas for

4 hours. Nickel loading was held constant at 6.7% (weight percentage), while copper loading was varied at 0%, 5%, 10%, and 15%.

B. TCD of Methane – Activity Testing

Activity tests for the TCD of methane were conducted in a fixed-bed continuous-flow quartz tube reactor (i.d. = 7 mm) with 300 mg of the catalysts, set inside an electric variable temperature nichrome wire furnace at atmospheric pressure. The furnace temperature was adjusted through the use of a programmable temperature controller, and rotameters were used to monitor the flowrates. The inlet stream flowrate was set at 100 mL/min (1:4 CH₄-to-He ratio), and the reaction temperature was varied at 600 °C, 750 °C, and 900 °C.

The product gas stream exiting the flow reactor system was analyzed by gas chromatography (model: Thermo Finnigan Trace GC Ultra Gas Chromatograph), using He as carrier gas. The exit stream was analyzed at intervals of 30 minutes for a total of 8 hours. For each interval, GC analysis determined the percent (v/v) composition of the exit stream, and the values for methane conversion were then calculated afterwards and plotted against time. Blank tests using only AC as the catalyst were also performed.

C. Catalyst Characterization

The prepared Ni-Cu/AC catalysts were characterized by X-ray diffraction (XRD) analysis in order to determine the bulk crystallographic structure of the catalysts, as well as to detect the presence of new crystallite patterns which may have been formed during the catalyst preparation stage. The XRD tests were performed using the Siemens Kristalloflex 760 X-Ray Generator with Philips PW 1380 vertical goniometer diffractometer with Cu-K α radiation (32 kV, 20 mA).

The catalysts were also analyzed by scanning electron microscopy (SEM) before and after activity tests were conducted in order to determine the changes in the surface morphology of the fresh and spent Ni-Cu/AC catalysts. The SEM images were taken using the JEOL JSM-5310 SEM model.

D. Statistical Analysis of Results

The catalytic activity tests consisted of two parameters: the copper loading on the Ni/AC catalysts which has four levels (0%, 5%, 10% and 15%), and the reaction temperature which has three levels (600 °C, 750 °C, 900 °C). The runs for each combination of copper loading and temperature were done in duplicate, resulting in a total number of 24 runs for the catalytic activity testing. Two-way analysis of variance (ANOVA) using the MINITAB® software was done in order to determine which of the factors examined had significant effects of the catalytic performance of Ni-Cu/AC catalysts. The response for the experimental design and statistical analysis performed was the initial methane conversion. The blank tests using AC as the catalyst were not included in the statistical analysis.

III. RESULTS AND DISCUSSION

A. Activity Testing

The results obtained for percent methane conversion over

time for each of the catalysts at different temperatures are shown in Fig. 1. It was observed that as reaction temperature increased, the catalytic activity also increased. Methane conversion values were insignificant at $T = 600\text{ }^{\circ}\text{C}$, with all values being less than 3%. This is consistent with the values obtained from other studies on the TCD of methane performed at similar temperatures [8], [16], [17].

Meanwhile, the methane conversion of the catalysts subjected to a reaction temperature of $900\text{ }^{\circ}\text{C}$ had high initial values of up to 30%. However, the catalytic activity of most of the catalysts rapidly dropped after two hours. This is consistent with the observations made in other studies, which showed that the catalyst rapidly deactivated at high temperatures even though the initial rates of hydrogen production were very high [3], [8], [10]. This behavior is most noticeable on the Ni/AC catalyst without copper loading.

Also, it should be noted that the AC catalyst without any loading performed poorly in terms of catalytic performance at all temperatures. This is significantly lower than any of the

TABLE I: SUMMARY OF INITIAL METHANE CONVERSIONS

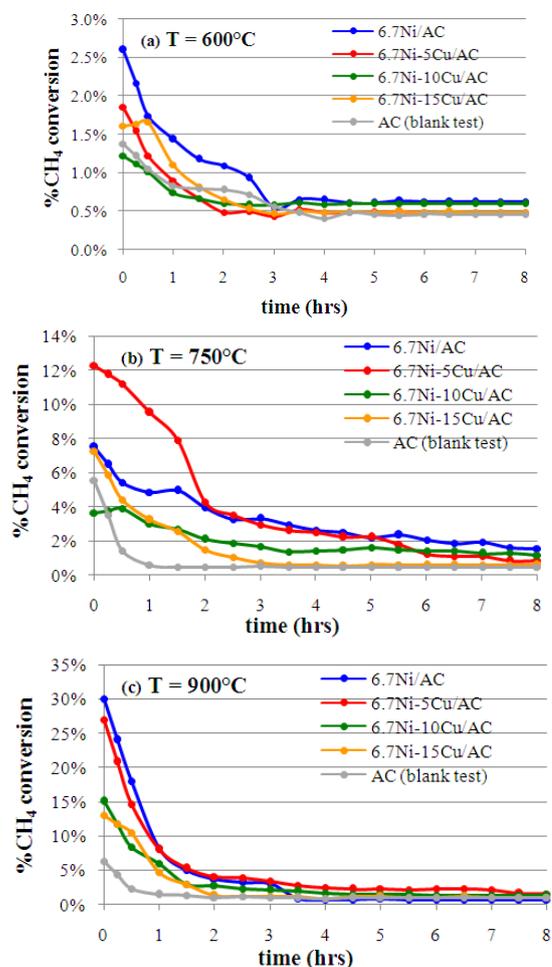
Catalyst	Temperature		
	600 °C	750 °C	900 °C
6.7Ni/AC	2.60%	7.48%	29.95%
6.7Ni-5Cu/AC	1.85%	12.27%	27.00%
6.7Ni-10Cu/AC	1.22%	7.42%	15.03%
6.7Ni-15Cu/AC	1.61%	7.27%	13.02%
AC (blank test)	1.38%	5.53%	6.34%

other catalysts tested at all temperatures, indicating that the addition of Ni and Cu particles on the AC is needed for the catalyst to yield good catalytic performance.

The initial methane conversions obtained are summarized in Table I. The combination of catalyst and temperature which resulted in the highest initial percent methane conversion was the 6.7Ni/AC catalyst at $900\text{ }^{\circ}\text{C}$, with a value of 29.95%. However, there was a sudden drop in conversion after 3 hours on stream, indicating that the catalyst had rapidly deactivated. On the other hand, the 6.7Ni-5Cu/AC catalyst had a slightly lower initial conversion of 27%, but there was no similar drop in catalytic activity. This is attributed to the presence of Cu on the catalyst surface, which increased the stability of the catalyst at higher temperatures by reducing the tendency for the catalyst to deactivate due to coking and poisoning.

However, when the copper loading was increased to 10% and 15%, the initial percent methane conversion dropped to 15.03% and 13.02%, respectively. The same trend was also observed at a temperature of $750\text{ }^{\circ}\text{C}$, and this could possibly mean that the best copper loading for 6.7Ni/AC catalysts among those tested is approximately 5%, and any value above this would result in weaker catalytic activity. One suggested reason for this may be the large amount of copper particles which blocked the active sites on the catalyst surface. Similar trends have been observed in other studies, where it was found that the catalytic activity increased until a certain value for percent metal loading was reached, after which the activity of the catalysts decreased [16], [18]. This was attributed to the presence of too much metal particles, weakening the stability of the catalyst at higher temperatures.

The presence of too much copper may have also significantly reduced the number of active sites available that would have increase the activity of the Ni-Cu/AC catalysts.


 Fig. 1. Time-course activity graphs of % CH_4 conversion against time for (a) $T = 600\text{ }^{\circ}\text{C}$, (b) $T = 750\text{ }^{\circ}\text{C}$, and (c) $T = 900\text{ }^{\circ}\text{C}$.

B. Statistical analysis of the activity test results

The confidence interval used in the statistical analysis is 95%, and thus the corresponding alpha value is equal to 0.05. As seen in Table II, The p-value calculated for temperature as a factor is less than 0.05; thus, it can be said that the temperature is a significant factor for the TCD of methane over Ni-Cu/AC catalysts. However, since the p-value for the copper loading is greater than 0.05, then it is quantitatively determined that it is not a significant factor in terms of its effect on the methane conversion.

In order to further visualize the relationship between the factors of copper loading and temperature, and the response of methane conversion, a main effects plot was generated using the MINITAB® software, as shown in Fig. 2. It should be noted in the main effects plot that for copper loading, the numbers from 1 to 4 correspond to the 6.7Ni/AC,

TABLE II: RESULTS OF TWO-WAY ANOVA STATISTICAL ANALYSIS

Source	DF	SS	MS	F	P
Copper loading	3	106.2	35.4	1.66	0.273
Temperature	2	777.9	388.9	18.25	0.003
Error	6	127.9	21.3		
Total	11	1011.9			

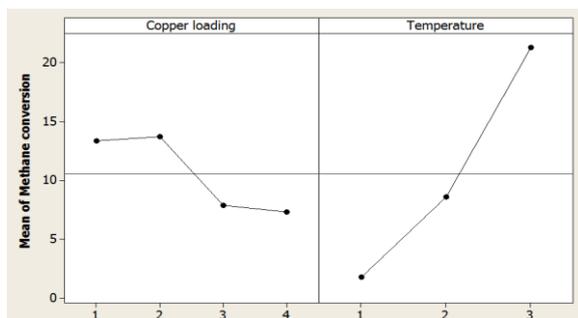


Fig. 2. Main effects plot generated from the two-way ANOVA statistical analysis for methane conversion.

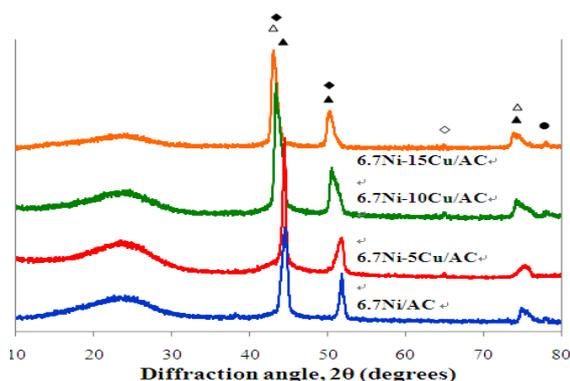


Fig. 3. XRD patterns of the fresh catalyst samples. Ni (▲), Cu (◆), NiO (△), CuO (◇), Ni₃C (●).

6.7Ni-5Cu/AC, 6.7Ni-10Cu/AC, and 6.7Ni-15Cu/AC catalysts respectively, while for temperature, the numbers from 1 to 3 correspond to 600 °C, 750 °C, and 900 °C, respectively.

It is observed that for the factor of copper loading, the 6.7Ni/AC and 6.7Ni-5Cu/AC catalysts had higher values above the mean for percent methane conversion, as compared to the 6.7Ni-10Cu/AC and 6.7Ni-15Cu/AC catalysts. This is in agreement with the findings from the time-course activity graphs, where a significant drop in activity was observed as the copper loading was increased to 10% and 15%. Meanwhile, for temperature, the values for the percent methane conversion were significantly higher as the reaction temperature was increased to 900 °C, also similar to the findings from the activity testing phase.

C. Catalyst pre-Characterization

1) Bulk crystallographic structure by X-ray diffraction (XRD) analysis

As observed from the XRD graphs presented in Fig. 4, there are three sharp peaks which are prominent for each catalyst used. These reflections, which are found at $2\theta = 44.2^\circ$, 51.7° and 76.4° , correspond to the presence of metallic Ni particles on the crystalline structure of the impregnated catalysts. However, slight shifting of some of the peak reflections towards the left is observed for the Ni peaks in the 6.7Ni-10Cu/AC and 6.7Ni-15Cu/AC catalysts, and this may be a result of the presence of the NiO phase, which corresponds to reflections at $2\theta = 43.3^\circ$ and 75.3° . Thus, the Ni phase of these two catalysts may not have been fully reduced from NiO to metallic Ni during the reduction step. Small peaks can also be found at around $2\theta = 65^\circ$ for all catalysts except for 6.7Ni/AC, and these correspond to the presence of CuO, resulting from incomplete reduction of the CuO phase to metallic Cu. The presence of these metal oxides

on the catalyst surface may have had a negative effect on the performance of the catalysts for the TCD of methane.

Furthermore, the peaks for the metallic Ni phase correspond to different surface planes. The peak reflection at

$2\theta = 44.2^\circ$ corresponds to the Ni(1 1 1) plane, which contributes to the carbon capacity of the catalyst [14], while the peaks at $2\theta = 51.7^\circ$ and $2\theta = 76.4^\circ$ correspond to the Ni(2 0 0) and Ni(2 2 0) planes, respectively. It can be observed that the relative intensity of the peak corresponding to the Ni(1 1 1) plane, compared to the two other peaks pertaining to Ni(2 0 0) and Ni(2 2 0) planes, is higher for the 6.7Ni-5Cu/AC catalyst. It has been suggested that as the relative intensity increases, there is a larger amount of Ni(1 1 1) planes, and thus the stability of the catalyst increases because of an improved ability to accumulate carbon on the catalyst surface [18]. This confirms the improved stability of the 6.7Ni-5Cu/AC catalyst compared to the other catalysts used.

Meanwhile, the presence of copper particles can be detected from peak reflections at approximately $2\theta = 43^\circ$ and 50° . It is difficult to detect for the case of the Ni-Cu/AC catalysts because it may have overlapped with the reflection of the metallic Ni phase at 44.2° and 51.7° . However, upon further inspection, the peaks that were obtained within these ranges were broader for the catalysts with Cu added as a promoter, while it was much narrower for the 6.7Ni/AC catalyst without copper. It has been suggested that this observation is a result of the overlapping of the Ni and Cu diffraction lines due to the segregation of some of the metallic Cu particles from the Ni-Cu alloy particles formed after thermal treatment [15].

There are also very small peaks which were observed on all the catalysts, except the 6.7Ni-5Cu/AC catalyst, at around $2\theta = 78^\circ$. These peaks are attributed to the formation of Ni₃C crystallites, possibly during the calcinations and reduction steps carried out at elevated temperatures. The formation of these crystallites have already been observed on Ni/AC catalysts [8], resulting from the diffusion of the carbon atoms into the metallic Ni particles. It has been suggested that the presence of this crystallite may be a possible reason for rapid catalyst deactivation, as the presence of the Ni₃C crystallites may result to coking of the catalyst.

2) Surface morphology of the fresh catalysts by scanning electron microscopy (SEM)

The morphological appearances of the surface of the catalysts after reduction pre-treatment are presented in Fig. 4.

From the SEM images presented, it can be seen that the Ni and Cu particles were successfully impregnated onto the surface of the AC support material, and the quantity of metallic particles on the catalyst surface noticeably increased as the loading was increased. Also, it can also be seen that there are more metallic particles of Ni and Cu which occupy the interior pore volume of the AC support for higher metal loadings. It is also important to note that there is not much agglomeration of particles on the surface of the prepared catalysts, which indicates that the nickel and copper loadings were well-dispersed in the dry impregnation method of catalyst preparation.

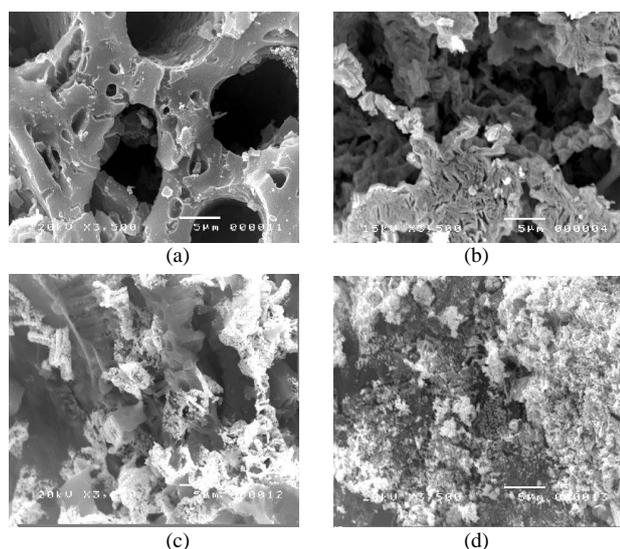


Fig. 4. SEM images (3500x magnification) of the 6.7Ni/AC catalyst with (a) no Cu loading, (b) 5% Cu loading, (c) 10% Cu loading, and (d) 15% Cu loading after reduction pre-treatment

D. Characterization of Carbon Deposits

1) Morphology from SEM images

The spent catalysts which were used in the activity tests at 900 °C were subjected to SEM analysis. As observed from the SEM images presented in Fig. 5, the formation of filamentous carbon was detected on the surface of the spent catalysts used at 900 °C. The carbon formed was fibrous in appearance for the catalysts with 5%, 10% and 15% Cu loading, indicating that carbon nanofibers were indeed formed, with diameters of less than 0.4 micrometers. This is especially seen in Fig. 6, which used a higher magnification to clearly show the filamentous carbon that was formed. However, for the 6.7Ni/AC catalyst with no copper loading, there seemed to be an agglomeration of carbon particles on the surface of the catalyst. These agglomerations were suggested to be a result of the formation of condensed encapsulating carbon, resulting in the faster deactivation of the catalyst [8]. This resulted in rapid carbon deposition on the catalyst, which is not favorable for the formation of filamentous carbon.

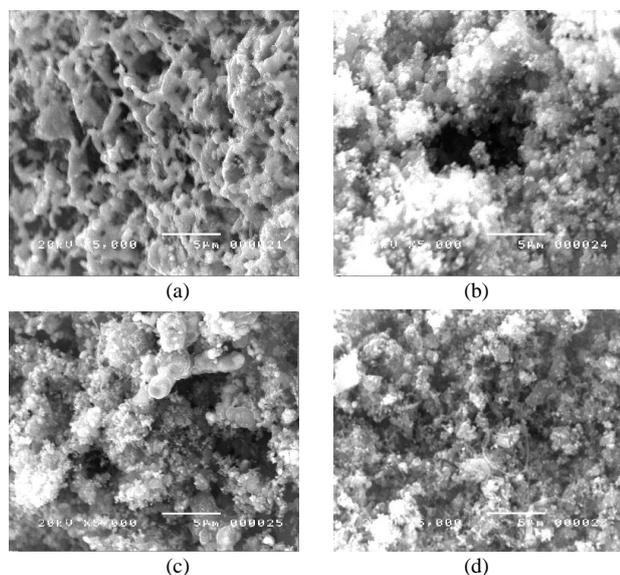


Fig. 5. SEM images (5000x magnification) of the 6.7Ni/AC catalyst with (a) no Cu, (b) 5% Cu, (c) 10% Cu, and (d) 15% Cu loading after being used at a reaction temperature of 900°C.

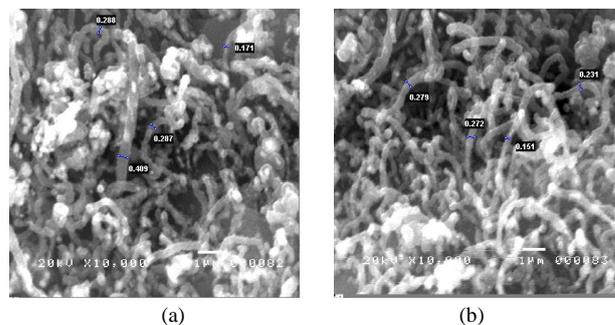


Fig. 6. SEM images (10000x magnification) of the 6.7Ni-5Cu/AC catalyst after being used at a reaction temperature of 900°C.

The ability of 6.7Ni-5Cu/AC, 6.7Ni-10Cu/AC, and 6.7Ni-15Cu/AC catalysts to withstand the high reaction temperature resulting to the formation of more filamentous carbon instead of encapsulating carbon may be attributed to the addition of Cu as a promoter. Without copper loading, encapsulating carbon was formed on the catalyst surface as a result of rapid carbon deposition and catalyst deactivation [8]. Because of the ability of copper to increase the thermal stability of the support material, the catalyst did not deactivate rapidly as shown in the time-course activity graphs. This resulted in an increase in the formation of filamentous carbon nanofibers despite the high temperature.

IV. CONCLUSIONS

The results of the study showed that the addition of copper on Ni/AC catalysts for the TCD of methane did not have a significant effect on the catalytic activity in terms of percent methane conversion, while the reaction temperature was shown to be a significant factor. However, it was observed that the presence of copper increased the stability of the Ni/AC catalysts at high temperatures. The 6.7Ni/AC catalyst without copper loading rapidly deactivated due to the formation of condensed encapsulating carbon, as observed from the SEM images of the spent catalysts.

On the other hand, the 6.7Ni-5Cu/AC catalyst was stable throughout the reaction with a slower deactivation rate. This increase in stability at high temperatures is attributed to the addition of Cu loading onto the catalyst surface. Its interaction with the metallic Ni particles resulted in an enhanced ability to accumulate carbon, thus increasing the catalytic lifetime of the catalysts by making it less susceptible to coking and rapid deactivation.

It was also observed in the study that the performance of the catalysts dropped when the Cu loading exceeded 5%. This is attributed to the larger amount of Cu particles which may block the active sites on the surface of the catalyst and weaken the stability of the catalyst as well.

XRD analysis of the impregnated catalysts revealed the presence of Ni₃C crystallites on all of the catalysts except for 6.7Ni-5Cu/AC, and this may have contributed to the deactivation of the other catalysts used in activity testing. It was also observed from the XRD patterns that the relative intensity of the peak corresponding to the Ni(1 1 1) plane is greater for the 6.7Ni-5Cu/AC catalyst, resulting in a better ability to accumulate carbon deposits on the catalyst surface. Thus, the 6.7Ni-5Cu/AC catalyst had better catalytic stability, especially at high reaction temperatures.

Post-characterization of the spent catalysts through SEM analysis showed fiber-like materials deposited on the surface of the catalysts used at 900 °C. These fibrous deposits were identified as filamentous carbon, which possesses many desirable properties beneficial to other fields of research such as in nanotechnology, optics, and material science, among others. However, condensed encapsulating carbon was observed to form on the surface of the 6.7Ni/AC catalyst without Cu loading, resulting in the rapid deactivation of the catalyst. The rapid deposition of carbon on the catalyst surface also hindered the formation of filamentous carbon at these conditions. This observation further supports the conclusion that the addition of copper as a promoter increased the stability of 6.7Ni/AC catalysts for the TCD of methane at high temperatures.

Further studies on the TCD of methane over Ni-Cu/AC catalysts may focus on the effect of different catalyst preparation methods that can be used. Other methods may be able to improve the interaction between the Ni and Cu particles, possibly further improving the stability of the catalysts. A more comprehensive characterization of the filamentous carbon formed may also be pursued, as these valuable carbon deposits have many other practical applications in other fields of research.

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