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Structural Properties of Ni/Al₂O₃ Catalyst Supported on Polymer Surface for CO₂ Reforming of Methane

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Abstract:

Synthesis dopamine methacrylamide (DMA) decorated with Ni/ γ -Al₂O₃ particles was used as catalyst for the CO₂ reforming of methane (CRM) by non-thermal plasma experiment. The Ni/ γ -Al₂O₃ catalyst is known as a high activity catalyst with excellent anti-coke properties in CO₂ reforming of methane (CRM). The structural properties of the prepared polymer combined with the Ni/ γ -Al₂O₃ catalyst was analyzed by X-ray powdered diffraction (XRD), surface area of supports and catalyst (BET), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to investigate the activity of Ni/ γ -Al₂O₃ on the polymer surface. The advantages of a polymer compound with Ni/ γ -Al₂O₃ contributed to the high dispersion of Ni particles on the surface of polymer which provided good catalyst activity space in the CRM. CH₄ and CO₂ conversion obtained as 27.2 and 38.8 % by non-thermal plasma at MW power 1500 W without using the catalyst while in the presence of Ni/ γ -Al₂O₃ polymer catalyst conversion of CH₄ and CO₂ increased to 79% and 84%. The result confirmed that using the polymer as a carrier for Ni/ γ -Al₂O₃ has significant influence on the surface characteristics of the catalyst activity site by increasing the active surface area without any effects on the Ni particle size, pore structure or crystalline diameter.

Keywords: CO₂ reforming of methane, Ni/ γ -Al₂O₃, polymer, microwave plasma

1. Introduction

The carbon dioxide reforming of methane (CRM) on catalyst not only a key step to decrease the concentration level of two major greenhouse gases in atmosphere, it also a principle method to produce syngas with H₂/CO molar ratio closer to unity in the products. The produce syngas due to CH₄+CO₂ = 2CO +2H₂ $\Delta H=247.3$ [1-3] with the low ratio of H₂/CO is suitable for production of valuable synthetic liquid fuels in Fischer-Tropsch process, and synthesis of oxygenated chemicals such as aldehydes, methyle alcohol, acetic acid and dimethyl ether [2, 4-9]. CO₂-CH₄ reforming using plasma treatment technologies such as dielectric barrier discharge (DBD), corona discharge, glow discharge and non-thermal plasma combined with catalyst materials are consider to be one potential method for efficient conversion of these gases and possibly achieve the high percent of CO and H₂.

Ni-based catalyst chosen as catalyst for CH₄-CO₂ reaction due to high initial catalyst activity, inherent availability and lower cost compare to noble metals [4, 6, 7, 10, 11]. However, the major disadvantages of nickel based catalyst is deposition of carbon produced during the CO₂ and methane decomposition process on the active sites of catalyst which significantly reduce the catalyst activity [10, 11-13] Boudouard reaction 2CO = C + CO₂ and CH₄= C + 2H₂. It is well believed that dispersion Ni catalyst particles showed better ability to suppress carbon deposition. However, control of Ni particles within nanoscale dimension size was not so easy because under the high temperature of CDR reaction, sintering of Ni particles easily took place [14, 15].

Many studies investigated the Ni-based catalyst performance in CO₂-CH₄ reforming using plasma treatment technologies. The process involves placing of about 50 to 400 mg of catalyst sample in a powder form into the quartz tube where the plasma is created by microwave generator [16, 17]. However, the major obstacle encountered in this process is the reduction of reaction surface area between syngas and catalyst materials which significantly decrease the catalyst performance. Other problem is replacement of used catalyst materials after coke formation with the new form which is requiring a removal of the powders from quartz tube after the reaction process which is not practical in industrial process. Other researches considered the effect of structured catalyst supported onto ceramic and metallic honeycomb monoliths in the reduction gases pollutant emission. The most usual way to deposit the catalyst

onto a honeycomb structure is by using the wash coating process. This method includes the dipping the monolith in the slurry prepared with catalyst material and withdraw it after a certain time [18, 19]. The major drawback of using such a honeycomb structure catalyst is the lack of interconnectivity between the channels, poor radial heat conductivity, and large residence time distribution which is unfavorable for high conversion levels when the emission mixture are complex or when the considered gases pollutants concentration oscillates from the low values to rather high concentration [19, 20]. In this research, Ni/ γ -Al₂O₃ particles prepared by wetness method were successfully loaded on the synthesis dopamine methacrylamide (DMA) surface. The obtained compound showed the high dispersion of Ni/ γ -Al₂O₃ on the surface of polymer which caused increasing the active surface area without any effects on the Ni particle size, pore structure or crystalline diameter. Then, we demonstrate the effect of prepared polymer decorated by Ni/ γ -Al₂O₃ on the catalytic performance of Ni based catalysts for CRM reaction.

2. Experimental

2.1. Experimental System and Product Analysis

The experimental setup for CO₂ and CH₄ conversion is shown schematically in Figure 1. The system consists of a water-cooled magnetron heater that launches 2.45-GHz wave powered by a 3-KW power generator, a circulator, a 3-stub tuner, a dummy load, a WR-430 waveguide and a plasma torch. The reduced size of the waveguide provides the maximum electron field for the MW field to in crosses the waveguide line device [21, 22]. The main parts of the plasma torch consist of two cylindrical steel tubes in which the quartz tubes are placed. The lower steel tube is in the microwave waveguide where the CO₂-CH₄ reactions took place, and the polymer catalyst materials placed in the upper cylindrical waveguide. The syngas produced from the plasma passed through the second quartz tube and interacted with the catalyst. After the reaction, the concentration of the resulting gases was analyzed on a gas chromatograph (GC7900) equipped with a thermal conductivity reactor (TCD) and flame ionization detector.

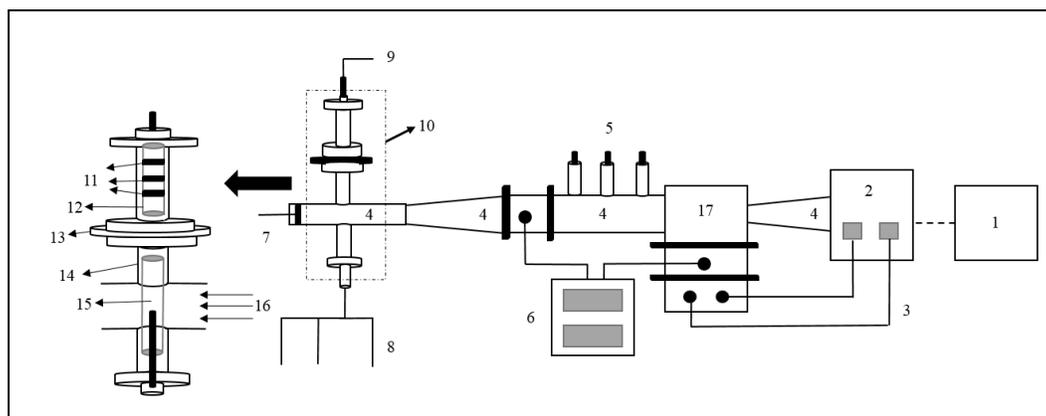


Figure 1: Input power control; 2. Magnetron; 3. Water sink; 4. Waveguide; 5. Circulator; 6. 3-stub tuner; 7. Reflected and transmitted power control; 8. Sliding short; 9. Inflow gases; 10. Output gases; 11. Catalyst; 12. Quartz tube; 13. Porous plate; 14. Quartz jacket; 15. Plasma; 16. Microwave radiation

A gas hourly space velocity (GHVS) of 40,000 mL g⁻¹ h⁻¹ was used to monitor the catalyst effectively. In this work, the conversion of CO₂, CH₄ and H₂/CO ratio are defined as the following equations:

$$\text{Conversion of CH}_4 (\%) = \frac{V_{\text{CH}_4, \text{inlet}} - V_{\text{CH}_4, \text{outlet}}}{V_{\text{CH}_4, \text{inlet}}} \times 100\%$$

$$\text{Conversion of CO}_2 (\%) = \frac{V_{\text{CO}_2, \text{inlet}} - V_{\text{CO}_2, \text{outlet}}}{V_{\text{CO}_2, \text{inlet}}} \times 100\%$$

$$\text{H}_2/\text{CO}_2 \text{ ratio} = \frac{\text{Mol of H}_2 \text{ produced}}{\text{Mol of CO produced}}$$

In this experiment high purity reactants Ar, CH₄ and CO₂ > 99.5% served as the plasma working gas. The feed gases of CH₄ and CO₂ diluted with Ar were introduced through mass flow controllers (Apex, AX-MC-5SLPM-D) into the experimental chamber and passed through the quartz tube where plasma was created by the microwave generator (Figure 1). In an order to analyze the CO₂ and CH₄ conversion using the polymer catalyst compound, the power of the generator was adjusted to 1500 W and the CH₄:CO₂: Ar ratio to 1:1:5. The experiments were done under atmospheric pressure and at a constant frequency of 2450 MHz.

2.2. Ni/ γ -Al₂O₃ Catalyst Preparation

The incipient wetness method was used to the impregnated Ni (NO₃)₂·6H₂O, Aldrich over γ -Al₂O₃ (S_{BET} = 290 M²/g, ϕ ~ 3 mm Aldrich). The γ -Al₂O₃ support was first impregnated with an aqueous solution of Ni (NO₃)₂. The quantitative loading of Ni was adjusted to Ni = 5 wt%. The prepared samples were dried at 100°C in an oven for 12 h and calcined at 500 °C for 4 h and reduced at 300°C in pure hydrogen and argon for 2 h. The total flow rate of H₂ and Ar was adjusted to 60 ml/min when the ratio of Ar:H₂ was 1.

Aluminum Oxide was supplied by Degussa AG, Frankfurt, Germany. It has an average primary particle size of 13 nm and a purity of 99.6%.

2.3. Dopamine Methacrylamide (DMA) Polymer Preparation

Details of the synthesis of dopamine methacrylamide (DMA) are described in a previous research report by [23]. Synthesis of poly (dopamine methacrylamide-co-methyl methacrylate) p(DMA-co-MMA), abbreviated as (MADO): MMA (4.75 g, 47 mmol) and 60 mg of azobisisobutyronitrile were added to a 50 mL round- bottom flask containing 30 mL of DMF. The DMA monomer (2.1mmol yielding 5mol% with respect to the MMA monomer) was then added to the flask and the solution was then bubbled with nitrogen for 30 minutes. The solution mixture was heated up to 70 °C and stirred overnight. The reaction mixture was added drop wise to 400 mL of diethyl ether under stirring to precipitate the synthesized copolymer. The obtained polymer was dissolved in methylene chloride and precipitated in diethyl ether twice to obtain a pure copolymer. The purified polymer was dried overnight in a vacuum oven at room temperature. The white solid was obtained as 72% yield. H NMR (250 MHz, DMSO): δ 8.72(s, 1H, -OH), 8.63 (s, 1H, -OH), 6.65-6.40 (m, 3H, Ar-H), 3.55 (s, 15H, -O-CH₃), 3.24 (m, 2H, Ar-CH₂- CH₂(NH)-), 2.50 (m, 2H, Ar-CH₂-CH₂(NH)-), 1.25-0.9 (m, 18H, -C-CH₃).

2.4. Preparation of Ni/ γ -Al₂O₃ polymer

In the typical experiment, prepared polymer added into the glass bottle contains aqueous solution of 5 mg Ni/ γ -Al₂O₃ and 15 mg ethanol. The Sonicator model Q500 was used to increase the interaction of the Ni/ γ -Al₂O₃ particles with polymer surface. The interaction between the polymer surface and hydrogen bonds of Ni/ γ -Al₂O₃ was observed immediately after addition of polymer into the catalyst aqueous solution.

2.5. Characterization of Ni/ γ -Al₂O₃ Loaded on (DMA) Polymer Surface

The X-ray powder diffraction (XRD) pattern of the catalyst sample was recorded by a Rigaku D/max-2500 diffractometer at a scanning speed of 4°/min over the 2 θ range of 10-90°. The diffractometer was equipped with a Ni-filtered Cu K α radiation source (λ = 1.54056 Å). The X-ray source was operated at 40 kV and 200 mA. The phase identification was made by comparison to the Joint Committee on Powder Diffraction Standards (JCPDSs). TEM and SEM analysis was performed on Tecnai G2 F20 and Jeol JXA 840A apparatus for the fresh catalyst. The specific surface area (BET) was measured by N₂ adsorption at -196°C using a Quantachrome Autosorb-1 analyzer. The Ni content of the catalyst was measured by atomic absorption spectroscopy (AAS) using a Hitachi 180-80 atomic absorption spectrometer. The experiment analysis was conducted at the Materials and Chemical Technologies Center of the Chonbuk National University.

3. Results and Discussion

3.1. Transmission Electron Microscopy (TEM) of Ni/ γ -Al₂O₃

The TEM images of fresh NiAl catalyst particles prepared by incipient wetness method are shown in Figure 2. The figures show that Ni particles were irregularly dispersed on a platelet-like Al₂O₃ support. Most of the Ni particles are smaller than 10 nm while a few large particles with a diameter more than 50 nm can also be observed. The presence of the larger Ni particles could be due to the agglomeration of the Ni crystallites during the catalyst preparation.

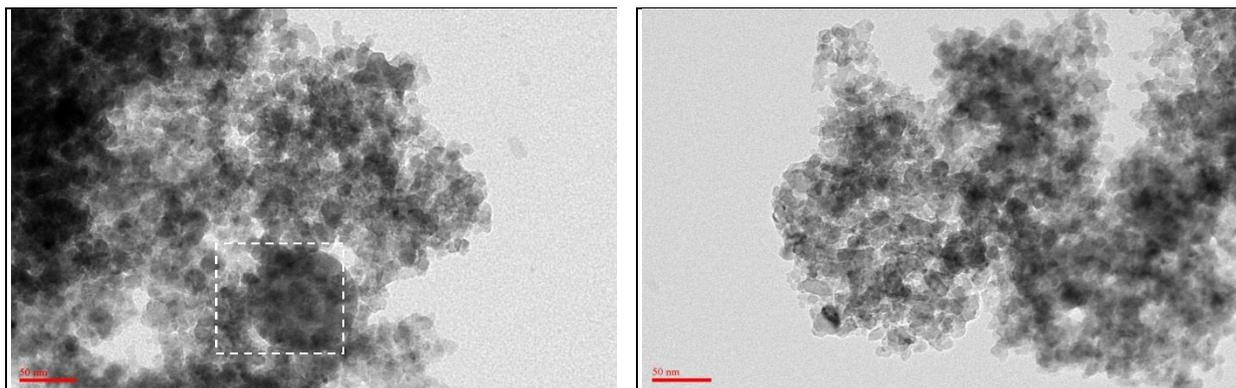


Figure 2: TEM image of Ni/Al₂O₃ catalyst prepared with incipient wetness method

3.2. Specific Surface Area (BET) of Ni/ γ -Al₂O₃

The textural properties were evaluated from nitrogen adsorption–desorption isotherms at -196°C and compiled in Table 1. It can be observed that the surface area (S_{BET}), the total pore volume (V_P) and the average pore diameter (D_P) of the catalysts are lower those of the support. However, compared to the Ni catalyst, the Ni/ γ -Al₂O₃ catalyst suffered a greater loss of S_{BET} , V_P and D_P due to the possible blockage of the mesoporous structure by Al species. The Ni contents of the catalyst measured by AAS are essentially identical, very close to the nominal Ni content (4.5 %).

	Sample		
	γ -Al ₂ O ₃	Ni	Ni/ γ -Al ₂ O ₃
Bet surface area (m ² /g)	150	133	112
V _p (cm ³ /g)	0.7	0.55	6.0
D _p (nm)	6.8	6.0	4.6
AAS Ni content (wt %)	-	-	4.5

Table 1: BET surface areas and AAS Ni contents

3.3. XRD Results of Ni/ γ -Al₂O₃ Loaded on (DMA) Polymer Surface

XRD diffractograms were used to identify the attachment of Ni/ γ -Al₂O₃ catalysts on the polymer fibers. Figure 3 presents the XRD pattern of the fresh Ni/ γ -Al₂O₃ on the polymers (5 wt% Ni). The diffraction signals at $2\theta = 47.2^\circ$ of the Ni/ γ -Al₂O₃ can be attributed to Ni/Al₂O₄. No additional signals were observed on the catalyst and polymer XRD pattern other than that of γ -Al₂O₃ at $2\theta = 67.1^\circ$. Several authors [1, 17] reported that the Ni/Al₂O₃ catalyst prepared in the incipient wetness method has an XRD peak at $2\theta = 45-48^\circ$ and $65-68^\circ$ which is due to the presence of Ni Al₂O₄ and γ -Al₂O₃ in the samples.

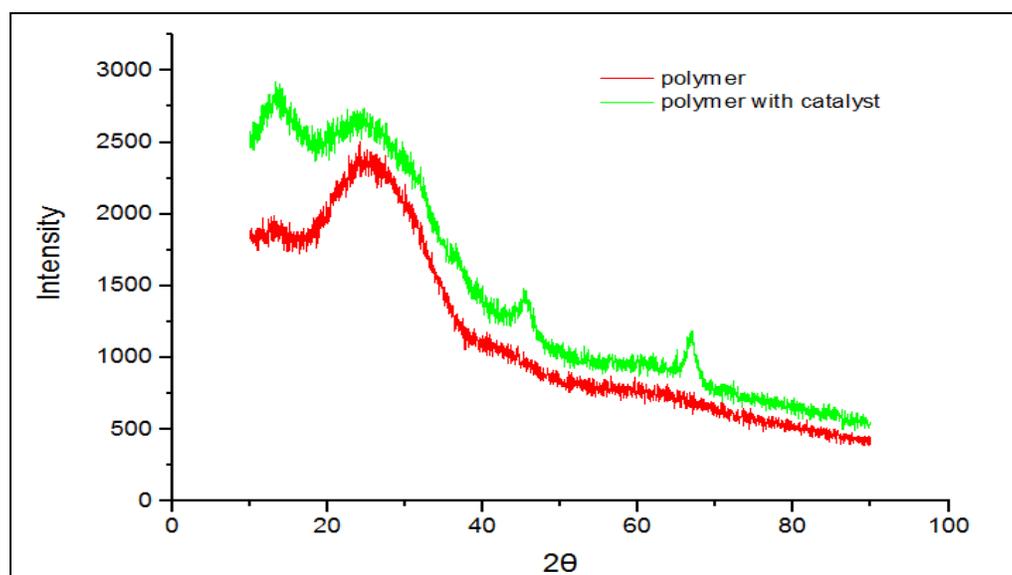


Figure 3: XRD profiles of fresh Ni/Al₂O₃ and fresh Ni/Al₂O₃ attach on polymer fiber

3.4. SEM Results of Ni/ γ -Al₂O₃ Loaded on (DMA) Polymer Surface

The SEM backscattered composition image of the Ni/ γ -Al₂O₃ catalyst particle attached to polymer fiber surfaces are given in Figure 4. The functional groups on the surface of Ni/ γ -Al₂O₃ particles interact through hydrogen bonds with the polymer. The Ni particles are almost spherical with sizes between 2-15nm. The addition of Ni/ γ -Al₂O₃ catalyst powder to the polymer fiber shows that the particles are uniformly distributed within the polymer matrix, and there is no observation of generated interconnected agglomerates supported by polymer fibers. Also, most of the particles have smooth surfaces and slight depressions, which originated during the conventional catalyst pre creation process. It should be noted that the lower amount of Ni particles (5%) was added to this system based on the polymer fibers abilities to attach to Ni.

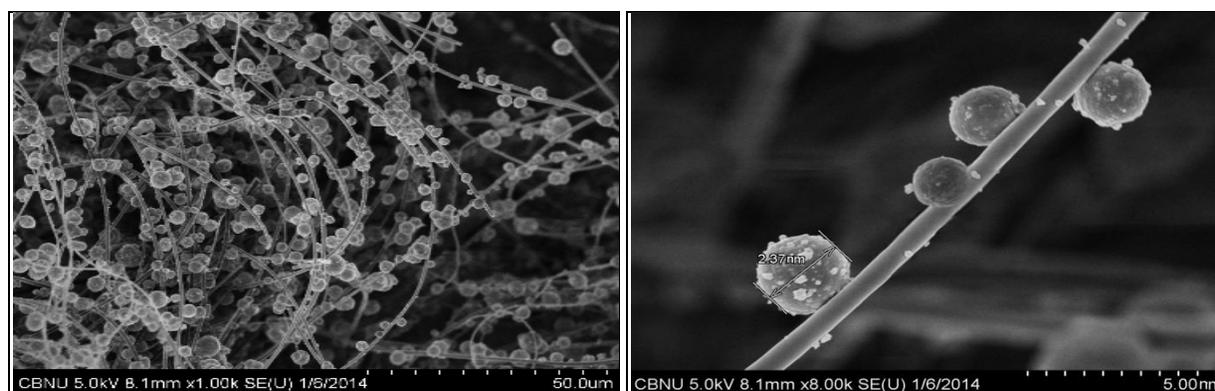


Figure 4: SEM image of Ni/Al₂O₃ particles attach on the polymer fiber.

3.5. Reactivity test

The effect of the variation of MW power from 800 to 2000 W on plasma chemistry reactions at 1 atm has been investigated by fixing the CH_4/CO_2 ratio to 1 while the Ar flow rate was 5000 sccm. Figure 5 shows the liner and gradual increase of tendency of both CH_4 and CO_2 conversion by increasing the MW power from 800 to 1500 W. With increasing the MW power from 1500 W to 2000W, slightly higher CH_4/CO_2 conversion was observed compared to when MW power change from 800 to 1500 W. At 1500W MW power CO_2 conversion increases to 38.8 % along with 27.2 % increases of CH_4 conversion.

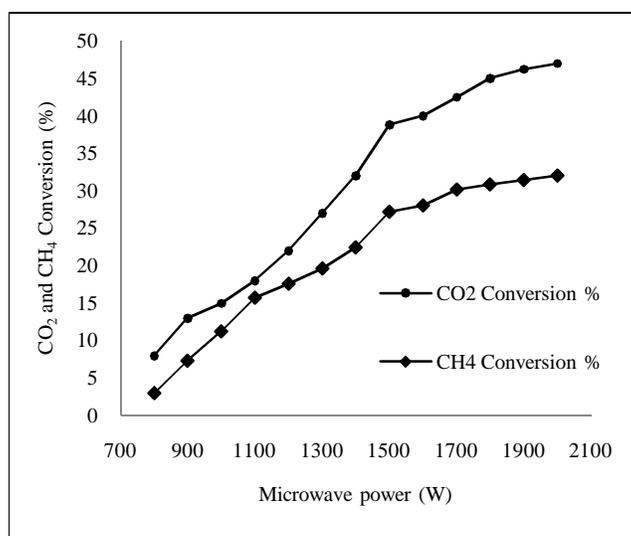


Figure 5: CH_4 and CO_2 conversion as function of MW power

The activity tests of the catalyst loaded on the polymer surface were performed as a function of reaction temperature inside the quartz tube where the catalyst was placed. Both the CO_2 and CH_4 conversion shown in Figure 6(a) increased with increasing the temperature to 300°C . The high activity of the NiAl sample is probably due to its high dispersion on the polymer surface. CH_4 and CO_2 conversion at 300°C reached to 79% and 84%. The conversion of CO_2 was higher than CH_4 because of a reverse water gas shift (RWGS) reaction. The H_2/CO increased with increasing temperature as the RWGS become less favored Figure 6(b). The Ni/Al polymer sample was tested for 10 h on the stream at 300°C and the results are shown in Figure 7. The sample showed stability for around 8 h without increasing the particle size of Ni caused by the coke formation. The conversion of CO_2 and CH_4 declined after 8 h of the stream test.

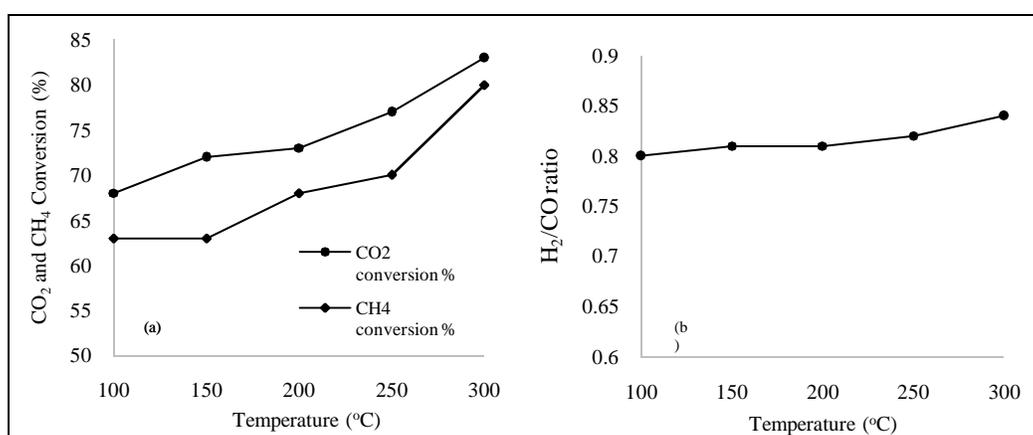


Figure 6: The Effect of Reaction Temperature on (a) CH_4 and CO_2 Conversion, MW power 1500 W and normal pressure, (B) H_2/CO Ratio of NiAl_2O_3 Catalyst on Polymer Fiber. Ration Condition: 50 mg, $\text{CH}_4:\text{CO}_2:\text{Ar} = 1:1:5$, Pressure 1 = atm, MW Power 1500 W

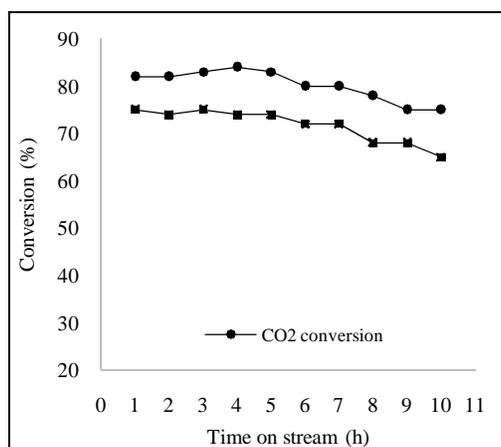


Figure 7: Stability Test of Ni/Al₂O₃ on Polymer Sample. Reaction Condition: $T = 300^{\circ}\text{C}$. 50 Mg, CH₄:CO₂:Ar = 1:1:5, Pressure 1 = atm, MW power 1500 W

4. Conclusion

In this research we studied the possibility of attachment of Ni/ γ -Al₂O₃ catalyst on the surface of polymer fibers and the activity of the obtained compound in carbon dioxide reforming of methane. The results from the XRD and SEM show the attachment of the catalyst powder on the polymer surface without changing the Ni particle size, pore structure or crystalline diameter. In addition, SEM analysis showed that the particles are uniformly distributed within the polymer matrix. The Ni/ γ -Al₂O₃ catalyst prepared by the conventional method on the polymer surface provided more active sites for the CRM reactions, load slightly higher conversions of CO₂ and CH₄. The results of catalyst stability experiments showed the catalyst activity significantly reduced after 10 hr. This can be due to the formation of coke around the Ni particle. The results from this study show that polymer fiber can be used a carrier of a catalyst in CRM reaction but the stability of the catalyst and polymer compound at higher temperatures need to be improved for further experiments.

5. Acknowledgments

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