Effect of Steam to Carbon Ratio (S:C) on Steam Methane Reforming's yield over Coated Nickel Aluminide (Ni$_3$Al) Catalyst in Micro Reactor

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ABSTRACT

This work looks into the effect of Steam to Carbon ratio (S:C) on methane (CH$_4$) conversion and hydrogen (H$_2$) yield over coated Nickel Aluminide (Ni$_3$Al) catalyst in micro reactor. The Ni$_3$Al is an intermetallic alloy which known to have good catalytic activity and selectivity. The Ni$_3$Al catalyst precursor was prepared through dip coating technique at 10wt% on top of substrate plate and characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX), Temperature Programming Reduction (TPR), activated by H$_2$ reduction, and catalytic activity test in steam methane reforming (SMR) reaction in micro reactor at S:C 2, S:C 3 and S:C 4 with 650°C reaction temperature and 300 minutes reaction time. The characterization showed the presence of Ni$_3$Al on top of the coating surface and successfully been activated at 500°C and 46 minutes. The CH$_4$ conversion and H$_2$ yield in the product of the reaction were quantified using the Gas Chromatograph technique. From the series of experiments, it was found that S:C 4 produced the highest methane conversion of 65.56% and S:C 3 produced the highest hydrogen yield of 41.34%. The S:C 2, showed faster and smoother stability trend conversion as early as 180 minutes from the start of the reaction. However, S:C 3 showed the most optimum methane conversion and hydrogen yield and achieved stability trend conversion within the defined reaction time range of 300 minutes. It is inferred that the S:C 3 is the best steam to carbon ratio for the developed catalyst in these settings.

Keywords: Steam to carbon ratio; methane conversion; micro reactor

INTRODUCTION

Hydrogen had been widely accepted as a potential alternative energy source and energy carrier to meet the increasing demand of the world's energy consumption. It is unanimously known that hydrogen (H$_2$) is the cleanest, efficient and pollution- free energy sources. Currently, hydrogen is mainly produced from chemical reaction processes of catalytic hydrocarbon reforming especially methane, such as partial oxidation, auto thermal and steam reforming. Among these, the steam methane reforming (SMR) had promised a few advantages such low reaction temperature and high hydrogen content in the reforming products (Azizi et al. 2019; Bej et al. 2013; Madon et al. 2015 & 2018 and Matsumura et al. 2004).

The catalytic SMR functionally reacts with existing of metal-based catalysts such as nickel, with known properties of good stability and high activity performance that is well suited for gas conversion reaction. The catalyst works by reducing the activation energy of methane cracking and straightly enhance the reaction rate. Besides that, some researchers had turned towards micro-scale reactors, which are capable of improvement, SMR's performance in terms of energy consumption. It is known that, the main reaction involves in SMR as Equation (1) and (2) which convert methane (CH$_4$) and steam (H$_2$O) into a mixture of hydrogen (H$_2$), carbon monoxide (CO) and carbon dioxide (CO$_2$) (Isha & Williams 2012; Izquierdo et al. 2012; Liu et al. 2012; Mansor et al. 2018 and Zhai et al. 2011).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$
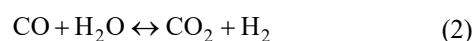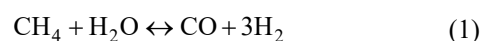
During catalyst preparation, nickel which finely dispersed over support carrier helps to produce large

catalytically active surface area and huge quantities of H_2 adsorption which acts as the key characteristics of the reaction efficiency (Madon et al. 2016; Maluf & Assaf 2009 and Sarwani et al. 2016). It was found that some intermetallic elements such as aluminide can be used as a support carrier for nickel catalyst. The nickel aluminide (Ni_3Al) is a high temperature structural materials and corrosion resistance and thus it has become a potential catalyst for the SMR process. The preparation of mixture between nickel and aluminide through aluminum leaching had some problems such as low effectiveness and the Ni_3Al formation process has very limited studies. Introducing dip coating as a deposition technique is believed to improve the Ni_3Al formation thus providing an alternative method of producing Ni_3Al effectively (Amri et al. 2012; Fang et al. 2008; Saadi et al. 2011; Xu et al. 2005 and Zangouei et al. 2010). In general, the nickel content used in the SMR catalyst does not exceed 12wt% to avoid severe aggregation or sintering of nickel particles during the reaction. Sarwani, 2017, prove that 10wt% of nickel as the most optimum catalyst impregnation on substrate plat via dip coating method to secure from severe aggregation causal.

SMR is an endothermic reaction and requires external heat input. Besides heat properties, the SMR reaction process output is also reflected by the steam to carbon ratio (S:C). It is very important to ensure the optimum S:C which being introduced to avoid carbon coking at S:C below 3 and reduce high energy consumption especially during S:C is about 3 or more (Bej et al. 2013; Charisiou et al. 2016; Maluf & Assaf 2009 and Zhai et al. 2011). Meanwhile the 300 minutes reaction time is at most operating time for new catalyst characterization properties (Pudukudy et al. 2015).

The use of a unique catalyst in this works, leads to the desired optimum operating condition. Therefore, the purpose of this study is to define the effect of steam to carbon ratio of methane conversion and hydrogen yield over a coated nickel aluminide catalyst in micro reactor. By comparing these works finding to the literature, it is expected to define critical information regarding steam to carbon ratio effect for further optimization from a practical viewpoint.

MATERIALS AND METHODS

CATALYST PRECURSOR PREPARATION AND ACTIVATION

The Nickel aluminide catalyst was prepared by using the sol-gel and dip coating method. The sol-gel was prepared by dissolving 22g Aluminum isopropoxide in 90ml ethanol. Then, 5ml Nitric acid and 5ml distilled water were added into the solution. The solution was stirred for one hour at 60°C. Next, 10g of Nickel (II) nitrate hexahydrate was added slowly and continuously into the solution and kept stirred at 60° C until homogeneous for another one hour. As the solution finished stirring, the sol-gel was obtained and ready for dip coating process.

The dip coating schematic diagram is shown as Figure 1. The PTL-MM01 Dip Coater with dipping and a withdrawal speed range of 1-200 mm/min was used for this work. For the dip coating sector, the dipping and withdrawal speed used were 160 mm/min. The 304 stainless steel plates were used as a substrate, and had been immersed into the solution and an uncoated area was kept on the top of the plate. The plate was withdrawn from the bath at a prescribed withdrawal velocity. The coated sample is pursued evaporation process for 30 minutes and followed by heat treatment of isothermal annealing by using Carbolite RHF 14/3 box furnace at an operating temperature of 500°C for 90 minutes.

For the catalyst activation, the coated plate was undergone temperature programming reduction (TPR) to define the temperature and activation time. Prior to the TPR reaction tests, the coated catalysts were reduced in Hydrogen with a condition of 300ml/min at 700 °C for 90 minutes. The catalyst is further characterized for X-ray pattern diffraction by using XRD Bruker D8 at 2 Theta between 20° till 90°.

CATALYTIC REACTION ACTIVITY

The experimental setup is shown as in Figure 2 and the coated catalyst was loaded in a few slots inside a micro reactor with a channel depth of 200 μm and placed in a box furnace for the endothermic reaction process as in Figure 3. The SMR catalytic reaction was conducted at steam to carbon ration of S:C 2, S:C 3 and S:C 4, 650°C reaction temperature, 300 minutes reaction time, using 10wt% loading of nickel aluminide (Ni_3Al) and the synthesis gas produced was collected at 60 minutes time interval.

The product gases were collected by using Tedlar sampling bags and analyzed with gas chromatography equipment (Perkin Elmer Clarus 500) fitted with a TCD detector. By assuming that SMR reactions occurred, the conversion expressed on a dry basis was calculated as in Equation 3 and Equation 4. Where $F°CH_4$ molar flow of CH_4 in feed, F_{CH4} molar flow of CH_4 in the output of the chromatograph, X_{CH4} is CH_4 conversion in products, X_{H2} is the H_2 formation from CH_4, nH_2 mole flow rate of hydrogen into the reactor, Equation 1 and Equation 2 extended mole flow rate reaction.

$$X_{CH4} = \left[\frac{CH_4 \text{ moles reacted}}{CH_4 \text{ moles fed}} \right] = \frac{F^0_{CH_4} - F_{CH_4}}{F^0_{CH_4}} \qquad (3)$$

$$X_{H2} = nH_2 + 3(\text{Equation} 1) + 1(\text{Equation} 2) \qquad (4)$$

RESULT AND DISCUSSION

NICKEL ALUMINIDE CATALYST ANALYSIS

The coated nickel aluminide (Ni_3Al) was activated by a continuous flow of H_2 passing through the coated Ni_3Al surface in the micro reactor. The reducibility of coated
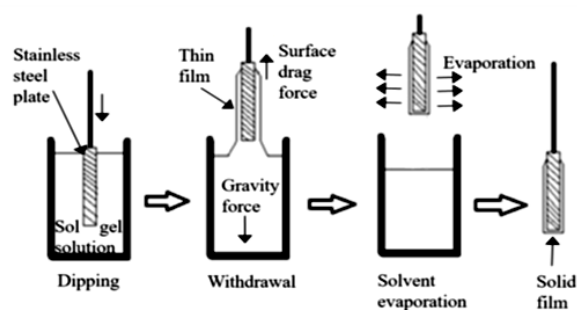
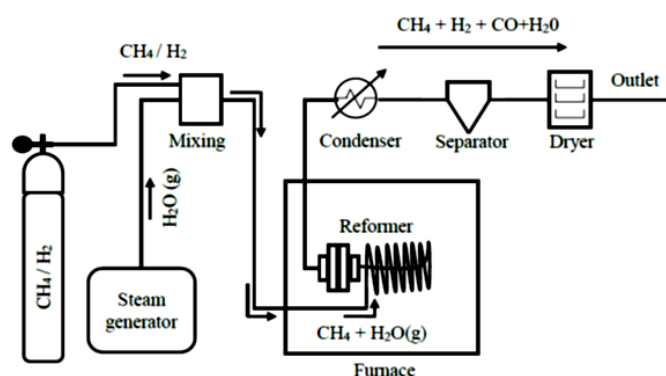FIGURE 1. Schematic diagram of dip coating process

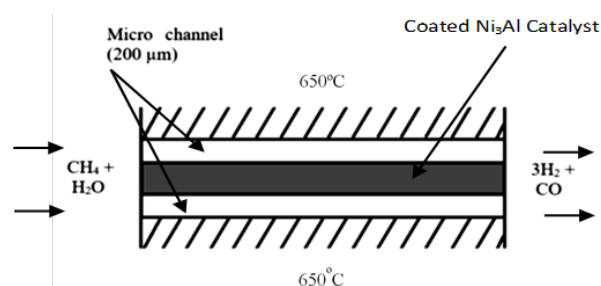FIGURE 2. Schematic diagram of SMR experimental setup

FIGURE 3. Schematic diagram of micro reactor with insert coated plate catalyst

nickel aluminide (Ni_3Al) was defined by performing temperature programming reduction (TPR). Figure 4 showed that the peak and the area under graph representing H_2 consumption. The highest peak indicating that optimum temperature and time for the activation process. It is distinctly shown that 500°C and 46 minutes is the best operating condition to secure high active surface area of the catalyst.

The coated nickel aluminide (Ni_3Al) catalyst has undergone X-Ray Diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX) analysis. Figure 5 and Figure 6, showed that the presence of Ni_3Al element and Ni / Al component on the coated substrate surface respectively to the XRD and SEM-EDX. The oxidized element is reacted with the activation agent H_2 become H_2O during the activation stage. Hence, the coated Ni_3Al catalyst is successfully activated and ready for methane conversion. These results also had

been reported by Madon et al. 2018 and been used as the supporting results in this manuscript. This study is expected to define critical information regarding steam to carbon ratio effect on methane conversion and hydrogen yield for further optimization in a practical viewpoint, compare to the Madon et al. 2018 which is focusing more on the effect of reaction temperature.

EFFECT OF STEAM TO CARBON RATIO (S:C) ON METHANE CONVERSION

In order to study the influence of steam to carbon ratio (S:C) effect on SMR catalytic behavior, the experiment was carried out accordingly to the operating condition. The catalytic activity in methane conversion was shown as in Figure 7. It is distinctly established that methane conversion is proportional to the steam to carbon ratio. The S:C 4 gives a maximum conversion of 65.56%, as
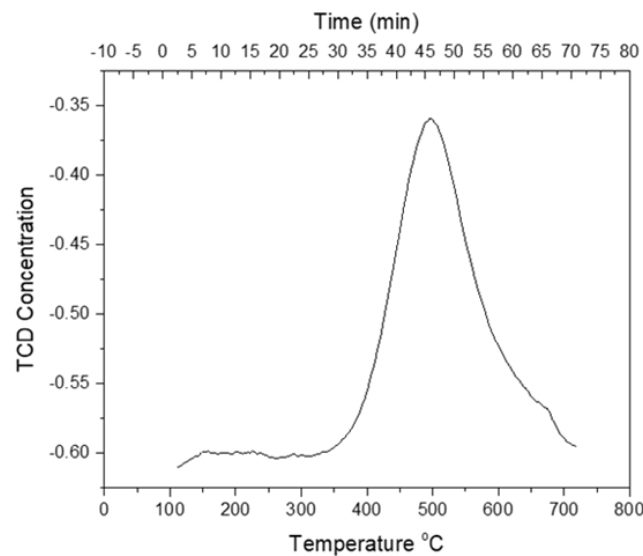
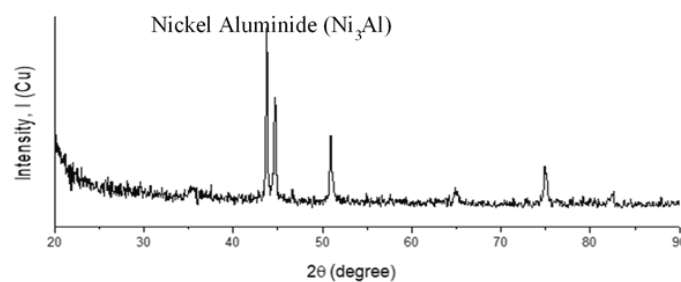FIGURE 4. TPR analysis of coated nickel aluminide catalyst

FIGURE 5. XRD analysis for nickel aluminide catalyst (Ni_3Al: JCPDS 09-0097)

compared to the minimum 30.14%, obtained in S:C 2. This is obeying the principle of steam methane reforming reaction at multiple steam to carbon ratio, whereby the methane conversion increases as the steam to carbon ratio increases. This phase took place due to the excess steam at reactant stream, which reacts and straightly enhances the methane cracking reaction to increase yield at the product stream. This finding is similar to the work done by Maluf et al. 2009 and Bej et al. 2013. For the SMR reaction, methane is the limiting reactant, whereby it is finished first, then with enough or excess steam, the methane conversion rate can be increased.

The Figure 7, showed only S:C 2 and S:C 3, exhibit trends of heterogeneous catalytic traits between 0 and 300 minutes, which are lag (pre-conversion), logarithm (rapidly increasing conversion) and stationary stage (stable remained unchanged of the conversion). Meanwhile, for the S:C 4, even though methane conversion is high and towards stability, it already exceeds the defined reaction time range of 300 minutes. The S:C 2 has a faster and smoother trend line of stability, which start the stationary stage as early 180 minutes. However, the S:C 3 yields the highest methane conversion compared with S:C 2. It is inferred that S:C 3 had become optimum steam to carbon ratio for the developed catalyst.

EFFECT OF STEAM TO CARBON RATIO (S:C) ON HYDROGEN YIELD

Figure 8, the maximum hydrogen yield is achieved at S:C 3 with a value of 41.34% and the minimum 33.29% is obtained by S:C 2. As reported by Simsek et al. 2011, according to Le Chatelier's principle, excess steam in the product direction converts the generated carbon monoxide by SMR into hydrogen and carbon dioxide, which leads to the highest H_2 ratios as observed at S:C 3 in this work. Even though the S:C 4 yielded the maximum value of methane conversion, simply due to water gas shift (WGS) reaction dominantly laid on the S:C 3, the hydrogen formation of S:C 3 slightly became greater as compared to the S:C 4. For S:C 4, only 20% methane was supplied to react with excess steam as compared to S:C 3 which obtained 25% of methane. It straightly increased the hydrogen formation at the outlet stream. On the other hands, carbon monoxide was limiting reactant in WGS; thus, it is unable to win over 100% even if the conversion reaches unity.

CONCLUSION

The coated Ni_3Al catalyst via dip coating has been successfully trialed run in a micro reactor with a few findings.
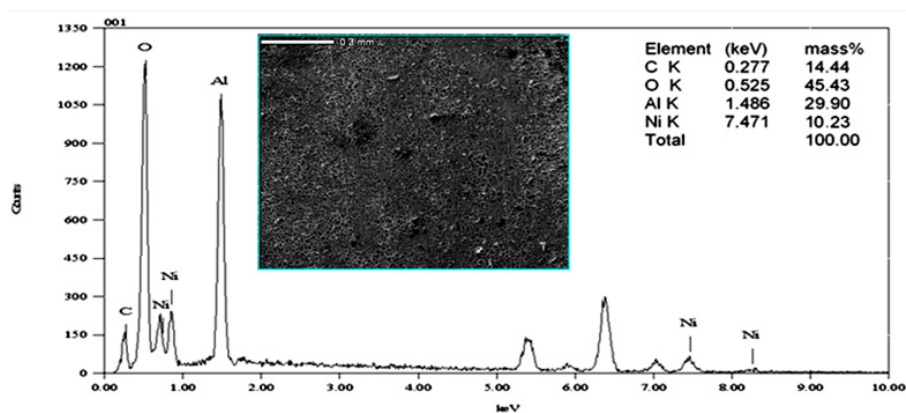
FIGURE 6. Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)
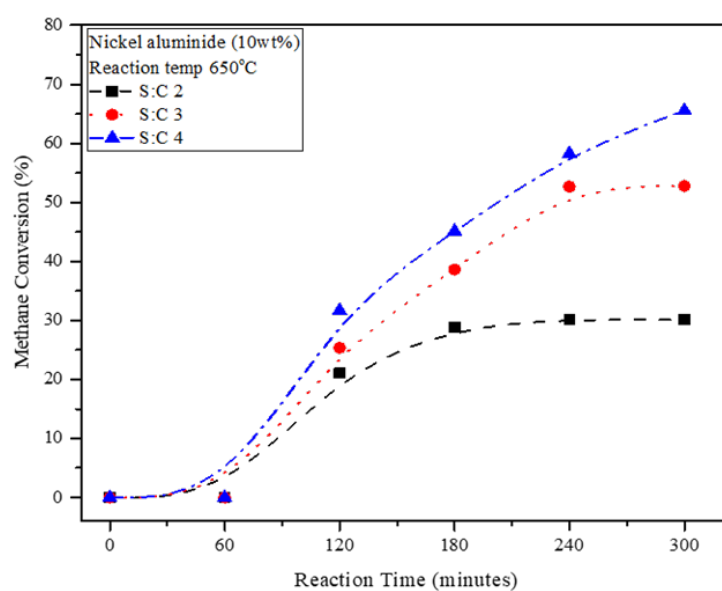

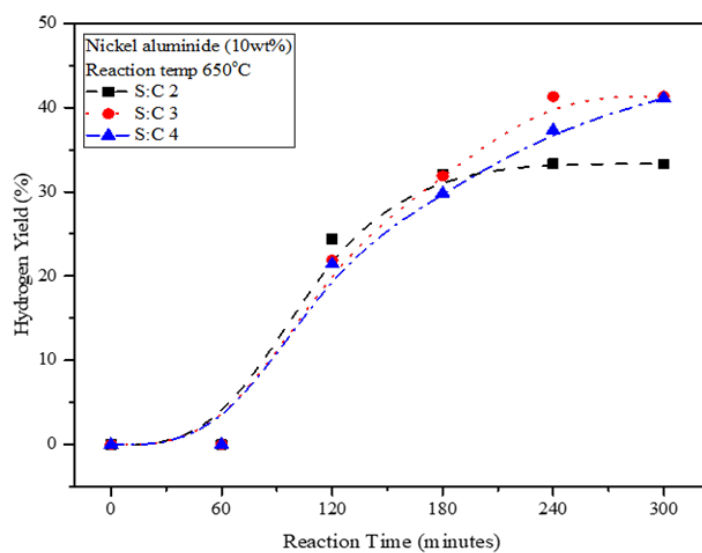FIGURE 7. Methane conversion against reaction time

FIGURE 8. Hydrogen yields against reaction time

The S:C 4 produced the highest methane conversion of 65.56% and S:C 3 produced the highest hydrogen yield of 41.34%. The S:C 2, showed faster and smoother stability trend conversion as early as 180 minutes from the start of the reaction. However, S:C 3 showed the most optimum methane conversion and hydrogen yield and achieved stability trend conversion within the defined reaction time range of 300 minutes. It is inferred that the S:C 3 is the best steam to carbon ratio for the developed catalyst in this setting. For future work, the steam to carbon ratio reaction interval should be decreased to a smaller scale to establish the most effective reaction settings.

DECLARATION OF COMPETING INTEREST

None.

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