



## Effect of Reaction Temperature on Steam Methane Reforming's yield over Coated Nickel Aluminide ( $\text{Ni}_3\text{Al}$ ) Catalyst in Micro Reactor

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### ARTICLE INFO

#### Article history:

Received 25 May 2018

Received in revised form 2 July 2018

Accepted 7 July 2018

Available online 12 October 2018

#### Keywords:

Dip coating, micro reactor, Methane conversion, Hydrogen yield, reaction temperature

### ABSTRACT

This work investigates the effect of reaction temperature on methane conversion and hydrogen yield over coated Nickel Aluminide ( $\text{Ni}_3\text{Al}$ ) as an intermetallic alloy catalyst in micro reactor. The  $\text{Ni}_3\text{Al}$  was impregnated at micro scale using dip coating technique. The coating impregnation process, consist of a few stages which are substrates and sol-gel preparation, dip coating, calcination and reduction of oxide molecule. The coated  $\text{Ni}_3\text{Al}$  were characterized by X-Ray Diffraction (XRD) and Temperature Programming Reduction (TPR) then activated using  $\text{H}_2$ . The XRD and TPR results showed present of  $\text{Ni}_3\text{Al}$  on the coated surface and was successfully activated at  $500^\circ\text{C}$  and 46 minutes. Meanwhile, the steam methane reforming with the catalytic reaction took place at temperature from  $500^\circ\text{C}$  to  $700^\circ\text{C}$ , steam to carbon ratio of 3:1 and 5 hours reaction time. The reaction temperature of  $600^\circ\text{C}$  obtained the highest methane conversion of 43% and hydrogen yield of 29%. The limitation point of reaction activity either as zero reaction or deactivation point was found at  $500^\circ\text{C}$  and  $700^\circ\text{C}$ . The coated  $\text{Ni}_3\text{Al}$  showed catalytic activity for each reaction temperature and work accordingly on the heterogenous catalyst principal theory of lag, exponential, stationary and deactivation stage.

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## 1. Introduction

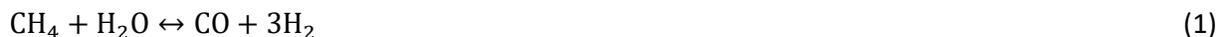
According to the world energy outlook, the world's energy sources will be threatened to meet the increasing demand of energy consumption. Hydrogen as a potential alternative energy source and energy carries had been explored to address such needs. This is due to the fact that hydrogen is widely accepted as the cleanest, efficient and pollution free energy. The production of hydrogen from various hydrocarbons, especially methane mainly comes from chemical reaction process of catalytic

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reforming technologies such as steam reforming, partial oxidation, and auto thermal reforming. Among these, steam methane reforming (SMR) has the advantage of relatively low reaction temperature and high hydrogen content in the reforming products [1-3].

Even though the SMR reaction is endothermic, the reaction temperature is widely studied in order to minimize possible temperature range. Researcher had switched to pay attention at micro scale reactors due to its applicability of process intensification on basic temperature transport phenomena, which lead to the improvement of SMR performance in terms of energy consumption. It is known that, below are the main reaction involve [1-8].



The catalytic SMR functionally acts with the existing of metal such as nickel, due to its properties which been widely accepted as a catalyst for gas conversion. This catalyst was used to lead faster reaction at certain operating temperature condition by reducing the amount of activation energy for methane cracking [8-10].

In the catalyst preparation, nickel is typically metal which finely dispersed over support of porous alumina or silica-based carrier. These value-added features result in large catalytically active surface area and huge quantities of hydrogen adsorption which act as the key characteristic of the reactions efficiency [9-11].

Some intermetallic element is known to have a good catalytic activity such as Ni<sub>3</sub>Al. Basically the mixture of Ni<sub>3</sub>Al act as an alloy precursor whereby produced by aluminum leaching. Unfortunately, the low effectiveness of aluminum leaching had become major constraint for Ni<sub>3</sub>Al formation. The Ni<sub>3</sub>Al has very limited studies. This catalyst was found to be of potential high temperature structural materials and corrosion resistance and thus most of the studies have been focused on it is mechanical and microstructure properties. Introducing dip coating as deposition method, helps to improvise the Ni<sub>3</sub>Al formation thus providing an alternative method of producing Ni<sub>3</sub>Al [12-18].

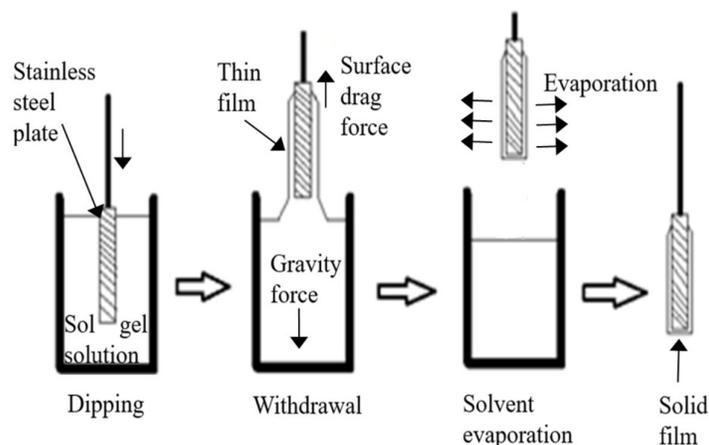
The purpose of this study is to observe the effect of reaction temperature on methane conversion and hydrogen yield over a coated nickel aluminide catalyst in micro reactor. Moreover, by comparing the results obtained in the literatures, it is expected to yield the critical information regarding reaction temperature effects for further optimization from a practical viewpoint [2-3,7-8].

## 2. Methodology

### 2.1 Catalyst Preparation

Nickel aluminide sol-gel was prepared by dissolving 22g Aluminum isopropoxide in 90ml ethanol. Subsequently, 5ml Nitric acid and 5ml distill water were further added into the solution. Then the solution was stirred at the 60 °C until homogeneous for one hour. Then, 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 finish stirring, the sol-gel was obtained and ready for dip coating process.

The dip coating schematic diagram is shown as Figure 1. The equipment used for dip coating process was PTL-MM01 Dip Coater with dipping and a withdrawal speed range of 1-200 mm/min. For dip coating sector, the dipping and withdrawal speed used were, 160 mm/min.



**Fig. 1.** Schematics diagram of dip coating process

The 304 stainless steel plates were immersed into the solution and an uncoated area was kept on the top of the plate. The plate was then withdrawn from the bath at a prescribed withdrawal velocity. The coated sample is pursued evaporation process for 30 minutes. Then, followed by heat treatment of isothermal annealing by using Carbolite RHF 14/3 box furnace at operating temperature of 500°C for 90 minutes.

## 2.2 Coated Catalyst Activation

Hereby the coated catalyst is pursued for reduction process. Where the oxidized element is reduced become non-oxidized element. This is very important to ensure the coated catalyst is free from oxidized element which can become blockage of methane and steam cracking phase. This stage is conducted by using TPR to define the temperature and time pitch point of reduction. Prior to reaction tests, the catalysts were reduced in Hydrogen with the condition of 300ml/min at 700 °C for 90 minutes.

## 2.3 Catalytic Reaction

The experimental setup is shown in Figure 2. SMR reaction was carried out in a micro reactor whereby the coated substrate plate is inserted into a few slots inside a micro reactor with a channel depth of 200  $\mu\text{m}$  at atmospheric pressure as in Figure 3. The reaction temperature was measured by a K-type thermocouple inserted directly at the output stream of micro reactor. Saturated steam was produced by steam generator and injected into the mixer with high pressure pump. The mixing composition of saturated steam and methane directly flows into micro reactor. The catalytic reactions were conducted at 500, 600 and 700 °C with steam to carbon ratio (S:C) of 3:1 for 5 hours.

Typically, the S:C 3:1 is chosen to avoid carbon coking build up at lower S:C and at higher S:C to minimize impact of low Hydrogen separation [2-5]. Meanwhile 5 hours is at most operating reaction time for new catalyst characterization properties. The effluents from the micro reactor were collected by using Tedlar sampling bag and been analyzed with a gas chromatograph of Perkin Elmer Clarus 500 and equipped with a TCD detector. By assuming that SMR reactions occurred, the conversion expressed on a dry basis were calculate as in Equation (3) and (4).

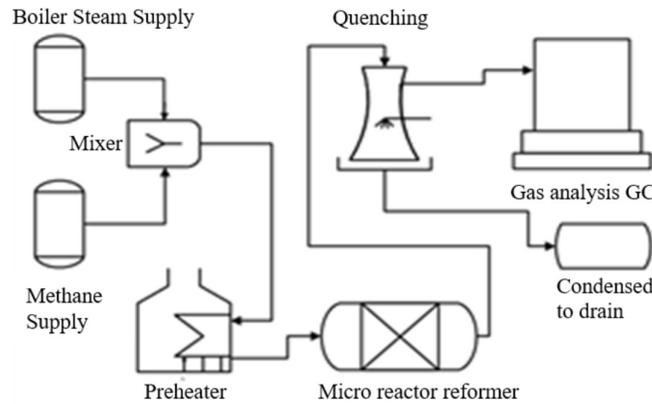


Fig. 2. Process flow diagram for steam methane reforming

$$X_{\text{CH}_4} = \left[ \frac{\text{CH}_4 \text{ moles reacted}}{\text{CH}_4 \text{ moles fed}} \right] = \frac{F_{\text{CH}_4}^0 - F_{\text{CH}_4}}{F_{\text{CH}_4}^0} \quad (3)$$

$$X_{\text{H}_2} = \left[ \frac{\text{CH}_4 \text{ moles reacted}}{\text{CH}_4 \text{ moles fed}} \right] \times \frac{2}{3} = \frac{F_{\text{CH}_4}^0 - F_{\text{CH}_4}}{F_{\text{CH}_4}^0} \times \frac{2}{3} \quad (4)$$

Where,  $F_{\text{CH}_4}^0$  = molar flow of  $\text{CH}_4$  in feed,  $F_{\text{CH}_4}$  = molar flow of  $\text{CH}_4$  in the output of the chromatograph,  $X_{\text{CH}_4}$  =  $\text{CH}_4$  conversion in products,  $X_{\text{H}_2}$  =  $\text{H}_2$  formation from  $\text{CH}_4$ .

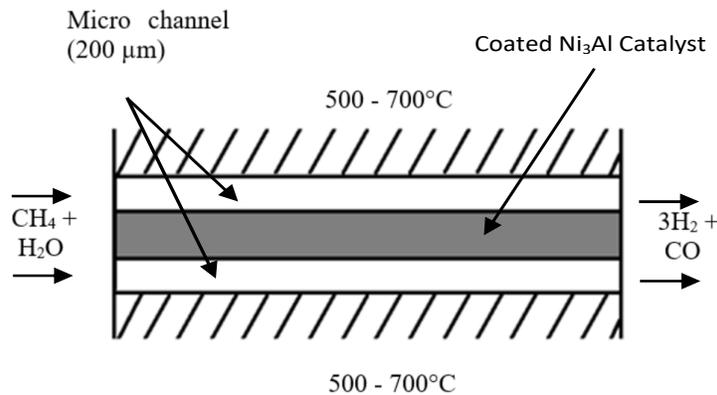


Fig. 3. Micro reactor with insert substrate slot

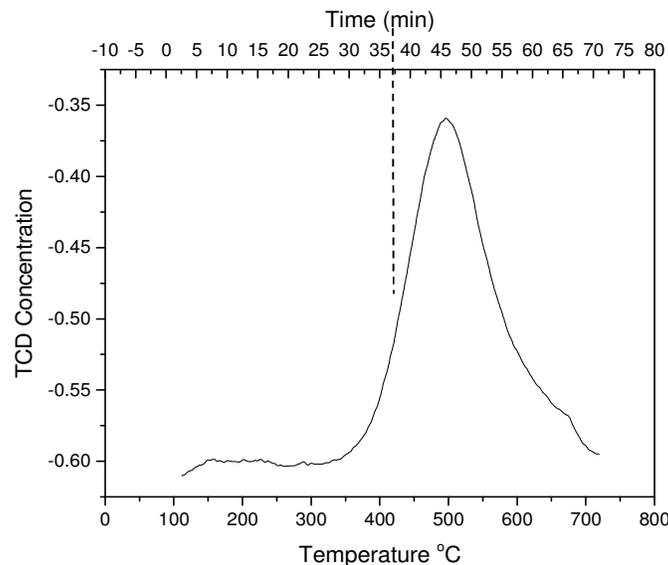
### 3. Results and Discussion

#### 3.1 Nickel Aluminide Catalyst Activations

By activating the catalyst through reduction process, the active metal catalyst was able to form. The catalyst was activated by flowing  $\text{H}_2$  gas through the coated catalyst layer in the microreactor. The reducibility of the coated catalyst was determined by performing Temperature Programming Reduction (TPR).

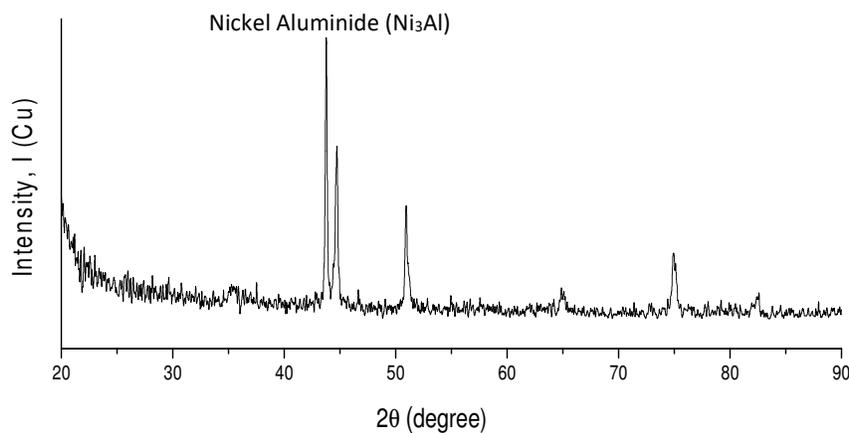
The results in Figure 4 were obtained from the sample 10% Nickel loading calcination at  $500^\circ\text{C}$  which used in SMR. The peaks and area shown in the results indicating  $\text{H}_2$  consumption. Thermal Conductivity Detector (TCD) concentration of the TPR depending on the Nickel weight percent. The highest peak indicating the most suitable temperature and time for reducing process to become

active metal catalyst. Referring to Figure 4 the highest peak located at 500 °C and timed at 46 minutes.



**Fig. 4.** TPR result for Nickel Aluminide Calcined at 500°C

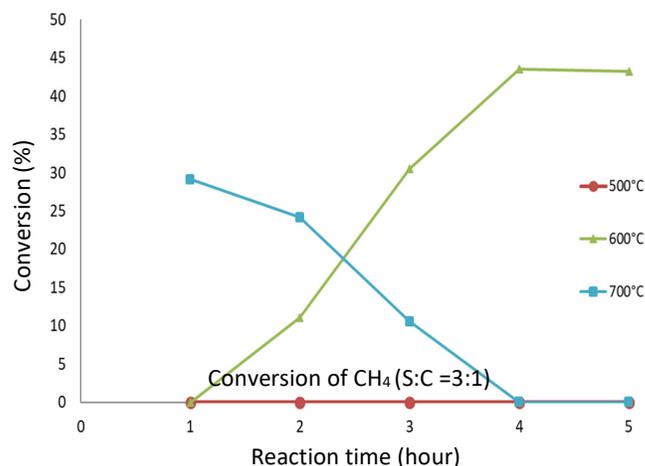
Meanwhile from the XRD characterization as in Figure 5, showed that the present of  $\text{Ni}_3\text{Al}$  on coated substrate surface. Whereby the oxidized element is reacted with the activation agent  $\text{H}_2$  become  $\text{H}_2\text{O}$ . Therefore, the deposited catalyst is successfully activated and ready for methane conversion process.



**Fig. 5.** XRD result for Nickel Aluminide activation

### 3.2 Effect of Reaction Temperature on Methane Conversion

In order to study the influence of reaction temperature on catalytic behavior, the experiment we carried out at three different temperatures, 500°C, 600°C and 700°C. The catalytic activity for the reaction temperature on methane conversion is plotted as in Figure 6.



**Fig. 6.** Methane conversion against reaction time

The methane conversion increases proportionally to the temperature and highest conversion (43%) lies at 600°C. Also from the same figure, the conversion slightly decreases with further increase in temperature above 600°C.

It was also observed, that 500°C point is zero reaction activity. This condition is may be due to the energy supply for methane and steam cracking which is not enough compare to the desired endothermic energy. We can say that point 500°C is the lower limit in our study. Meanwhile for the 600°C, conversion start at point after first hour reaction. Since there is no reaction activity from zero to first hours, we can say that it is a lag phase of catalyst activity before it is begun conversion. From the first to the fourth hours, the conversion is proportional to the reaction time. This phase showed an inclined with exponential tendency. Hereby, indicate that the catalyst is absorbing enough energy supply for methane and steam cracking. After the fourth to the fifth hours, we can observe that the conversion starts to become constant and this phase is known as stationary whereby catalyst is achieving optimum cracking activity with average 43%. Meanwhile for 700°C, the conversion is inverse proportional to the reaction time. Even though, the conversion is already occurred such early from zero hour, from plotted graph, it is believed that at this point, the catalyst activity is moving towards deactivation stage. This might be due to formation of carbon by decomposition of methane at higher temperature. The higher temperature straightly decreases catalyst activity and consequently effect in dropping methane conversion. Therefore point 700°C is upper limit in this particular experiment setup.

### 3.3 Hydrogen Yield

The results for hydrogen yield in relation with the reaction temperature is plotted as in Figure 7. This graph is based on equation 4. Since from methane conversion Figure 6, there is zero activity at point 500°C, therefore as hydrogen yield also follow the lead. Same goes to the point of 600°C, the graph tendency is similar to the methane conversion with average hydrogen yield at stationary phase is 29%. More over for point 700°C, the hydrogen yields also having the same tendency compare to the methane conversion, whereby at this point the catalyst is towards deactivation.

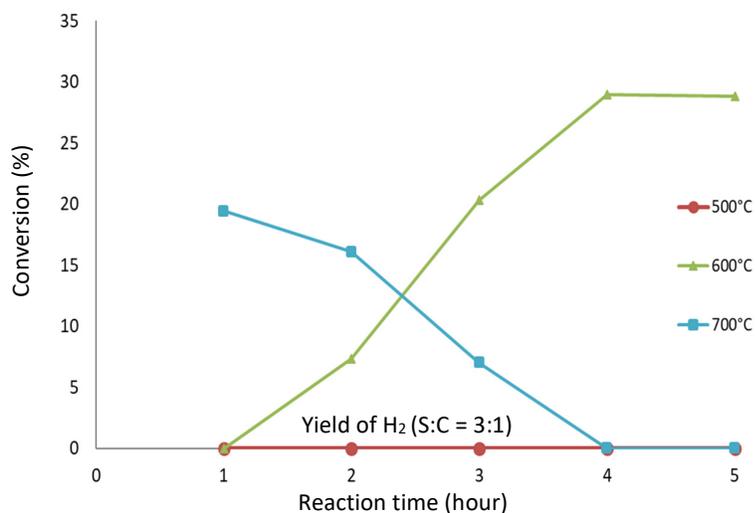


Fig. 7. Yields of hydrogen against reaction time

#### 4. Conclusion

The coated Ni<sub>3</sub>Al catalyst via dip coating has been successfully trial run in a micro reactor with a few findings. Boundary line of operating capability condition for methane conversion using Nickel Aluminate had been discovered at 500°C and 700°C. Constant stage operating condition for methane conversion and hydrogen yield start at 4 hours upwards. Therefore, this constant stage is the optimal operating capability condition with 600°C reaction temperature yield the maximum output. For future work, the reaction interval should be decreased to a smaller scale in order to establish the most effective reaction settings.

#### Acknowledgement

The author would like to thank the Ministry of Education for supporting this research under the Fundamental Research Grant Scheme (FRGS) Vot 1421, Universiti Tun Hussein Onn Malaysia (UTHM) for the facilities support and also this paper was partly sponsored by the Centre for Graduate Studies UTHM.

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