

Investigation of Coke Formation in Dry Methane Reforming over Nickel-based Monolithic Catalysts

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Abstract

Coking accumulations via dry methane reforming (DMR) over 10NAM monolithic catalyst and pelletized catalyst was investigated. 10NAM catalyst was synthesized and coated on a wall of monolithic reactor. Pelletized catalyst of 10NAM was also prepared for the comparison. Consequently, catalyst was characterized by BET, H₂-TPR and H₂-TPD. The catalytic reaction was undergone at 600°C under atmospheric pressure and CH₄ to CO₂ reactant ratio of 1:2. The coking formation over spent catalyst was then carried out in the hydrogen flow using temperature programmed technique (TPH). According to the results, DMR over 10NAM monolithic catalyst exhibits a minimized coking formation comparing to the use of pelletized catalyst. This could be attributed to a prominent heat transfer efficiency of the monolithic catalyst.

Keywords: Dry methane reforming, Ni based monolithic catalyst, TPH

1. Introduction

Recently, the process development of synthetic liquid fuels from natural gas by a technology called GTL (Gas-To-Liquids) is drawn attention, especially in country which has natural gas resource. Two main processes involve in: reforming process and Fischer Tropsch synthesis (FTS). The reforming of natural to produce a synthesis gas, which are composed mainly of hydrogen (H₂) and carbon monoxide (CO). The synthesis gas will be used as a precursor in the manufacturing process of synthetic liquid fuels by the Fischer-Tropsch synthesis. The synthetic liquid fuel products are long chain hydrocarbons in the range of gasoline, kerosene, diesel and wax. The source of natural gas available in the country is rather dry gas, which

is composed mainly of methane and carbon dioxide. The conversion of natural gas to synthesis gas through the dry methane reforming process (DMR) is selected as a appropriate method. This DMR process also reduces the greenhouse warming caused by methane and carbon dioxide [1].

Reforming reactions is an endothermic reaction operating over supported metal catalysts at high temperatures. Traditionally, nickel has been industrially attractive as a catalyst for methane steam reforming because of its relatively high activity and low cost [2-4]. Although nickel catalysts are much more economical than precious metal catalysts, nickel catalysts are more prone to carbon deposition than precious metal catalysts.

Coke obtained from the reaction can have different crystalline structures, morphologies and reactivities depending on the reaction conditions. According to the literature, it has been reviewed that there are three different types of coke that might be produced in the reforming of hydrocarbons on supported metal catalysts: polymeric, filamentous and graphitic coke [5]. Polymeric coke is derived from gas-phase decomposition of hydrocarbons or fouling, while the filamentous and graphitic coke are formed on the metallic sites of catalyst. In addition, coke can also be categorized based on its reactivity. For example, soft coke can be hydrotreated at relatively mild conditions and does not accumulate on the active sites. Hard coke is typically graphitic, which is unreactive with hydrogen treatment. This type of coke causes the blockage of active site.

Pelletized Ni catalyst is a well-known as a reforming reaction catalyst but it has bad reputation in term of heat-transfer limitations. Heat-transfer improvement in catalyst bed and fixed bed reactor for endothermic reaction system is a popular issue for research and development [6]. Moreover, conventional fixed bed reactor always confronts a pressure drop problem. Compact reactors with a high throughput or employing catalysts with a certain shape should minimize a pressure drop in the system. Monolithic reactor coated with catalyst is an interesting option to improve both heat and mass transfer rates by one to two orders of magnitude compared to the conventional fixed bed reactor. In addition, monoliths made of metal can improve radial heat-transfer characteristics because their cellular structure has a high thermal conductivity [7].

In this work, nickel-based catalysts were prepared and coated on a wall of monolithic reactor. Pelletized catalyst was also prepared for comparison of catalytic activity and selectivity. In addition, the effect of monolith and coke formation in DMR reaction over nickel-based monolithic catalyst and pelletized catalyst were investigated and performed.

2. Experimental

2.1 Catalyst preparation

Pelletized nickel-based catalyst (NAMP) was prepared by sol-gel method. The nickel loading was approximately 10 wt%. The catalyst was dried overnight at 60 °C and calcined at 450 °C and 650 °C for 4 h in air. Ni catalyst was crushed into particle size between 355 to 710 μm. The synthesized catalyst is referred to 10NAMP450 and 10NAMP650.

The cordierite monolith cylinders were cut about a width of 1 cm, a length of 1 cm and a height of 4 cm, then the monoliths were soaked in glacial acetic. After that each monoliths were dried overnight at 60 °C and calcined at 650 °C.

The cordierite monoliths were directly dipped in 10NAM solution, and then they were dried overnight at 60 °C and calcined at 450 °C and 650 °C for 4 h. The synthesized catalyst is referred to 10NAMM450 and 10NAMM650.

2.2 Catalyst characterization

The samples were characterized by N₂ adsorption (BET), stereo microscope (SM), hydrogen temperature-programmed desorption (H₂-TPD) and temperature-programmed reduction with hydrogen (H₂-TPR).

N₂ adsorption was carried out in physisorption analyzers (BELSORP-mini, BEL) at -196 °C. Total surface area, pore size distribution and mean pore diameter of catalyst samples were obtained from BET measurement. Before the operation, the samples were degassed at 350 °C for 4 h.

H₂-TPR profiles were carried out with BELCAT basic (BEL JAPAN, INC). 0.05 g catalyst was loaded in a U-type quartz tube reactor and ramped from 40 °C to 900 °C in 5% H₂/Ar gas at flow rate of 50 mL/min. The heating rate was maintained at 10 °C/min.

H₂-TPD profiles were carried out with BELCAT basic. The sample was reduced with pure H₂ (30 mL/min) at a temperature of 120 °C for 2 h. The catalyst was subsequently flushed at the same temperature with inert gas. After reduction, the sample was cooled to room temperature, and then H₂ flow was continued for 30 min at 120 °C. After adsorption, the system was purged with inert gas to remove physisorbed H₂. The H₂-TPD profile was monitored using TCD while the temperature was increased from room temperature to 900 °C at a heating rate of 10 °C/min.

H₂-TPH profiles were analyzed by gas chromatography. The sample was pretreated with inert gas. After pretreatment, the sample was cooled to room temperature, and ramped from 40 °C to 900 °C in H₂ gas at flow rate of 30 mL/min. Carbon on surface catalyst was removed. The CH₄ product was analyzed by GC with a FID detector.

2.3 Catalytic reaction test

0.05 g of nickel-based monolithic catalyst was packed into the fixed-bed reactor and reduced in situ in pure hydrogen with the flow rate of 30 mL/min at 600 °C at a heating rate of 5 °C for 10 h prior to the reaction. After the reduction, the total flow rate of reactant gas at 60 mL/min was allowed to the reactor (CH₄ 15 mL/min, CO₂ 25 mL/min and balance N₂ 20 mL/min). The flow rates of the gas components were maintained with a mass-flow controller (Brooks, Thailand; model SLA5850 and Kofloc, Thailand). The DMR reaction was carried out at 600 °C and atmospheric pressure. The products were on-line analyzed by gas chromatograph with a TCD detector.

3. Results and discussion

3.1 Catalyst characterization

Surface area, total pore volume and mean pore diameter of the catalysts are summarized in Table 1. It can be seen that the surface area of the 10NMM catalyst is less than 10NAMP catalyst because the fresh monolith used as substrate is ceramic, which has a very low surface area, low pore volume and high mean pore diameter. Comparison of surface area, pore volume and mean pore diameter of 10NAMP450 and 10NAMP650 are not different. This indicates that calcination temperature does not affect on the surface area, pore volume and mean pore diameter of a catalysts.

Table 1. BET surface area of nickel-based catalysts.

Catalyst	Surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)
Monolith	0.06	0.0032	187.41
10NMM450	2.42	0.0071	11.73
10NMM650	2.45	0.0104	16.97
10NAMP450	202	0.2969	5.87
10NAMP650	221	0.2330	4.21

The reducibility of synthesized catalyst was characterized by H₂-TPR technique. TPR profiles obtained from all of catalysts are shown in Figure 1. It can be seen that all nickel-based catalysts has two reduction peaks, one major peak around 240-590°C could be assigned to large particles and small particles of NiO. The two peaks at above 590°C could be attributed to a strong interaction between Ni²⁺ and Al₂O₃-MgO support. It indicated that the area of these reduction peaks depends on amount nickel-based catalyst.

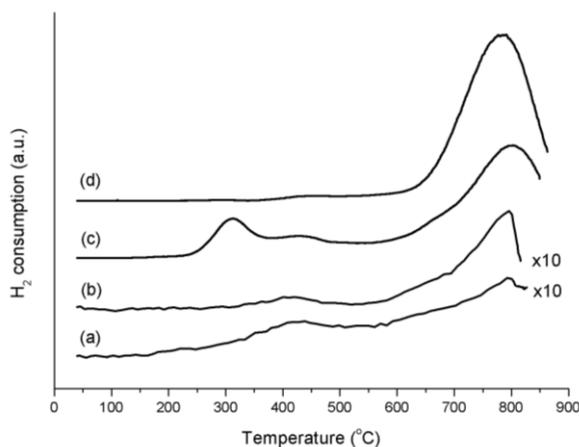


Figure 1. H₂-TPR profiles of (a) 10NAMM450, (b) 10NAMM650, (c) 10NAMP450 and (d) 10NAMP650 catalyst.

Figure 2 shows TPD profiles after adsorption of hydrogen on all nickel-based catalysts. The desorption of hydrogen from 10NAMP450 and 10NAMP650 catalyst exhibit a similar profiles, which two temperature regions of desorption were observed. Broad peak in lower temperature range locates at 130°C and in the higher temperature range peaks at 670°C. These profiles show a shoulder peak at 230°C. This result might indicate that at least two different active species presenting on the catalyst surface. The profile obtained from 10NAMM450 and 10NAMM650 catalyst present the same shape as observed from the 10NAMP450 and 10NAMP650 catalyst but less intensity was obtained because of less catalyst coated on the wall of monolithic substrate. Temperature maximum of monolithic catalyst shifts to lower temperature indicating that the interaction between hydrogen and active site might be weaker than that obtained from a pelletized catalyst.

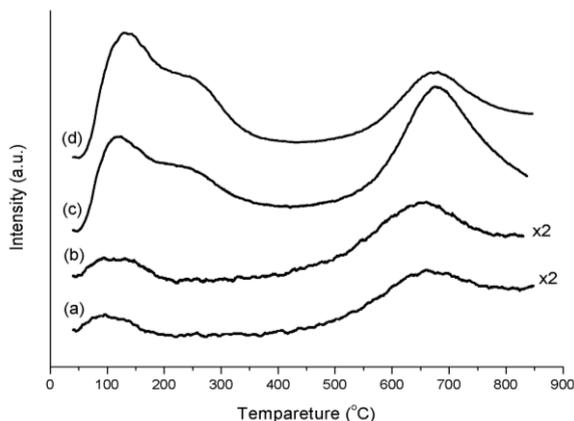


Figure 2. H₂-TPD profiles of (a) 10NAMM450, (b) 10NAMM650, (c) 10NAMP450 and (d) 10NAMP650 catalyst.

3.1 Performance of dry methane reforming reaction

CH₄ conversion of 10NAMP650 catalyst presented in Figure 3 shows a higher activity comparing to 10NAMM650 catalyst. The catalytic activity of 10NAMP650 catalyst tends to gradually reduce over the reaction time, whereas the activity of 10NAMM650 catalyst steeply decreases. The CH₄ conversion of 10NAMM450 catalyst is more than 10NAMP450 catalyst at the beginning of the reaction time, but activity of 10NAMM450 catalyst dramatically declines at the beginning of reaction. The cause may be ascribed by the sintering of nickel particles at high temperature reaction condition (600°C). Moreover, coke formation on the catalyst surface leads to a decrease in CH₄ conversion. From the results, it can be concluded that the calcination temperature has a major effect on the activity of catalyst. The high calcination temperature might promote the strong metal support interaction between metallic Ni particle and support. This effect suppresses the agglomeration of Ni catalyst. Besides, high temperature treatment during calcinations might assist the strong interaction between the catalyst and the monolithic substrate, resulting in the strong adhesive of catalyst on the substrate surface.

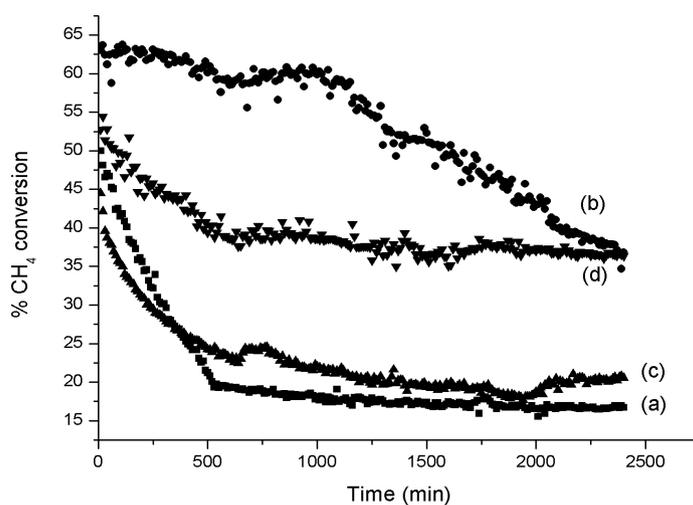


Figure 3. CH₄ conversion of (a) 10NAMM450, (b) 10NAMM650, (c) 10NAMP450 and (d) 10NAMP650 catalyst.

Figure 4 shows H₂ selectivity of nickel-based catalysts for all catalyst investigated. It was found that the catalyst calcined at 450°C, 10NAMM450 and 10NAMP450 catalyst, has the highest H₂ selectivity compared to the catalyst calcined at high temperature. H₂ selectivity received from monolithic catalyst is higher than that from pelletized catalyst. The 10NAMP650 and 10NAMM650 catalyst have less H₂ selectivity compared to the catalyst calcined at 450°C. It has to be noticed that H₂ selectivity of 10NAMM650 catalyst increase gradually during 1,000 min of reaction time, then it tend to steeper increase. Overall result can be concluded that calcinations temperature has more influence than catalyst forming effect. This result could be combined with the discussion of CH₄ conversion. The higher the activity of CH₄ conversion the lower the H₂ selectivity. The high H₂ selectivity might be due to the CH₄ decomposition, which is a side reaction at high temperature. During 1,000 minute of reaction time, monolithic catalyst presents quite stable trend and it tends to increase obviously. This means that when the reaction proceeds longer, the decomposition of methane might easily occur.

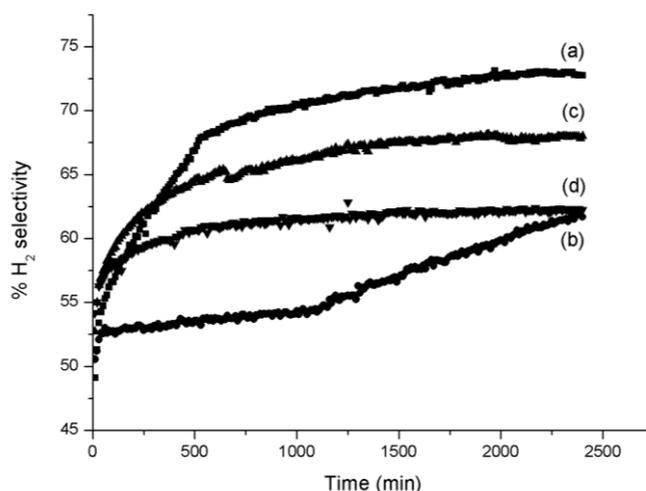


Figure 4. H₂ selectivity of (a) 10NAMM450, (b) 10NAMM650, (c) 10NAMP450 and (d) 10NAMP650 catalyst.

Figure 5 shows H₂/CO ratio of nickel-based catalysts. It was observed that the result shows a similar picture of H₂ selectivity results. During 1,000 min, H₂/CO ratio of 10NAMM650 catalyst approximates 1.1, while other catalysts present H₂/CO ratio of 1.5, 2.0 and 2.4. The reaction after 1,000 min depicts an increase trend of H₂/CO. This result agrees with the H₂ selectivity result.

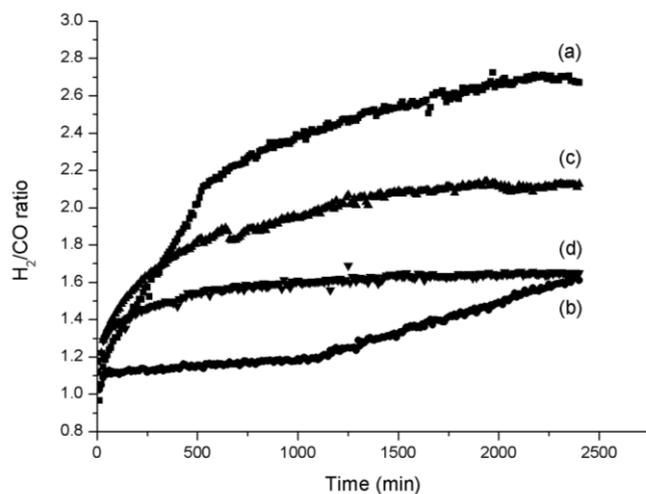


Figure 5. H₂/CO ratio of (a) 10NAMM450, (b) 10NAMM650, (c) 10NAMP450 and (d) 10NAMP650 catalyst.

In order to investigate the accumulation of coke laid down on the surface, H₂-TPH technique was applied. Figure 6 shows H₂-TPH profiles of nickel-based catalyst. It was found that carbon was removed from the catalyst by hydrogenation, which CH₄ is a main product. TPH profile illustrates two temperatures region of methane desorption. The 10NAMM650 catalyst presents sharp peaks with the highest intensity, indicating high amount of coke on the catalyst. Coke formation on the catalyst is directly proportional to CH₄ conversion. Reaction involved is according to equations (1) and (2)



In comparison, TPH profile observed from 10NAMP450 and 10NAMM450 catalyst shows a similar result. Less intensity of broad overlapping peak presents less coke formation. This is also agreed with the CH₄ conversion result. The comparison of the effect of monolith substrate was found that peak of 10NAMM shifts toward high temperature than 10NAMP. This could be attributed to less active of coke formed over monolithic catalyst.

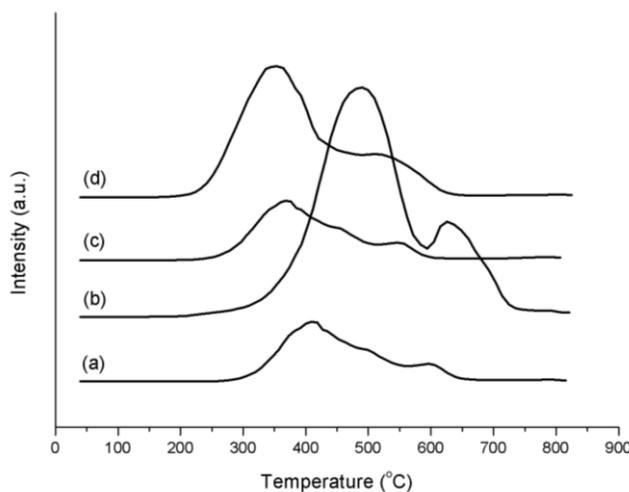


Figure 6. H₂-TPH profiles of (a) 10NAMM450, (b) 10NAMM650, (c) 10NAMP450 and (d) 10NAMP650 catalysts.

4. Conclusions

The 10NAMM650 and 10NAMP650 catalyst exhibit a good catalytic performance for dry methane reforming reaction at 600°C, in which the CH₄ conversion is higher than that obtained from 10NAMM450 and 10NAMP450 catalyst. The monolith substrate and calcinations temperature have an effect on CH₄ conversion of catalyst. The 10NAMM650 catalyst is the best catalyst compared to others for this research work. Although, CH₄ conversion and coke formation are high but H₂ selectivity and H₂/CO ratio remains quite stable with the value that appropriate to be used as synthesis gas for Fischer-Tropsch reaction.

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