

Developing Carbon Tolerance Catalyst for Dry Methane Reforming

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The overall goal of this work is to develop carbon tolerance catalyst for dry methane reforming using homogeneous method. Therefore, three different catalysts, named as NA, NM, and NAM, were synthesized, characterized, and tested. Their reducibility and basic site strength were carried out by temperature programmed reduction (TPR) and CO₂- temperature programmed desorption (CO₂-TPD), respectively. Activities for dry methane reforming of all prepared catalyst were also investigated. The TPR profiles show that the reduction temperature should be equal to or greater than 450 °C to reach a complete reduction. According to CO₂-TPD results, NAM presents the greatest number of basic sites. To evaluate the activity of dry methane reforming, catalyst samples were tested at temperatures of 600 °C and 700 °C using CH₄:CO₂ of 15 (mL/min):25 (mL/min) for 6h. As expected, methane conversion increases when operating temperature increases. For operating temperature of 700 °C, NM and NAM show similar methane conversions, around 94 %, with high CO yield. In contrast, NA presents lower activity (methane conversion of 50 %) and lower CO/H₂ in the product. The dry methane reforming was also performed over synthesized catalysts at 600 °C using CH₄:CO₂ of 25 (mL/min):15 (mL/min). Using CH₄:CO₂ of 25 (mL/min):15 (mL/min), carbon can deposit on the catalyst easier than the previous condition because of the critical amount of CO₂. NAM provides the higher CO/H₂ than NM. It indicates that NAM is the most carbon tolerance catalyst because of the basicity of this catalyst.

1. Introduction

Currently, hydrogen is considered as a future fuel and synthesis gas (the mixture of carbon monoxide and hydrogen) is an interesting reactant of the alternative fuel synthesis (Kechagiopoulos et al., 2006). The available resource for hydrogen and synthesis gas production within Thailand is pretreated natural gas using catalytic reforming. Because the natural gas in Thailand is dry and also contains an abundance of carbon dioxide, the suitable reforming reaction for this natural gas composition is dry methane reforming process (DMR), Eq(1), which methane (CH₄) reacts with carbon dioxide (CO₂) on the active surface of solid catalyst to form equimolar synthesis gas.



This reaction typically takes place over Ni-based catalysts at the temperatures from 550 °C-1000 °C. According to the high operating temperature and hydrocarbon reactant, two major problems should be

mentioned here: sintering of crystallite Ni and carbon deposition (Rostrup-Nielsen et al., 2002). The sintering of metal active particle leads to the loss of active site causing catalyst deactivation. For carbon deposition, regarding to the thermodynamic properties, the carbon can polymerize on the catalyst surface along methane decomposition and CO disproportionation expressed in Eq (2) and Eq (3), respectively. This carbon type not only deactivates a catalyst deactivation, but also plugs the gas flow channel. The rate of carbon growth was found to depend on crystallite size, metal dispersion metal-support interaction and acidity-basicity of the catalyst.



In this work, three different solid catalysts, named as NA, NM, and NAM, were developed in a form of homogeneous solid mixture to improve the metal-support interaction. This strong interaction is supposed to increase carbon tolerance. Their physical and chemical properties were analysed by nitrogen physisorption measurement, temperature programmed reduction (TPR) and CO₂-temperature programmed desorption (CO₂-TPD) techniques. The reforming activities were also compared among different catalysts and different operating temperatures and different methane to carbon dioxide ratios (CH₄:CO₂) in this paper.

2. Methodology

2.1 Catalyst preparation

The preparation of the mixed metal oxides support and active metal was begun with the pre-cursor solutions in the appropriate amount and finish with slurry product. Then, the product was dried at 48 °C for 48 h (Figure 1a) calcined in air at 500 °C for 48 h (Figure 1b).

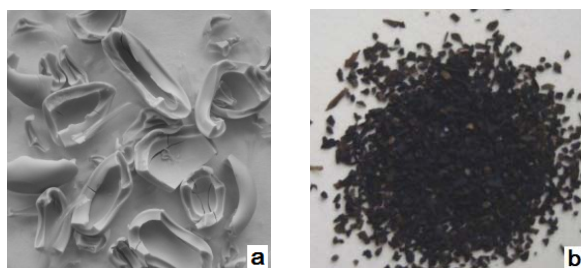


Figure 1: Synthesized catalyst a) after dried at 48 °C ; b) after calcined at 500 °C

2.2 Catalyst characterization

The prepared catalysts were characterized the surface area (S_{BET}), pore volume (V_p) and pore diameter (D_p) by nitrogen physisorption measurement via Belsorp system (Belsorp Mini-II, Belsorp Japan). Temperature-programmed reduction (H₂-TPR) was applied in order to reveal their reducibility. A catalyst sample packed in a down-flow reactor was pretreated with pure argon at 150 °C for 40 min, following by cooling down to room temperature. Then, the reactor was heated up at 10 °C/min from the room temperature to 800 °C in 5 %H₂/Ar. The output gas was detected by TCD detector and reported as TPR profile. Similarly, for TPR technique, the sample was firstly packed and pretreated by Ar at 400 °C for 30 min. The reactor was cooled down to 50 °C and the adsorption of CO₂ was carried out for 60 min. After that, a flow of N₂ was allowed to flush the system before the temperature was programmed from 50 °C to 850 °C at a heating rate of 10 °C/min. The amount of CO₂ desorption was detected by TCD detector and presented as CO₂-TPD profile.

2.3 Catalytic activity

Catalyst 0.2 g was packed in a fixed bed reactor and reduced in-situ at 600 °C under hydrogen flow for overnight. Then, the activity of catalyst in dry methane reforming was performed at temperatures of 600 °C and 700 °C in the mixed feed of CH₄:CO₂ (15 (mL/min):25 (mL/min)) for 6 h. To study the effect of CH₄:CO₂ ratio on the carbon deposition, CH₄:CO₂ of 25 (mL/min):15 (mL/min) was also used as feed for

the reaction at 600 °C. During the dry methane reforming, the output gases were analyzed online by a gas chromatograph (GC)(Agilent 7890) using TCD detector.

3. Results and discussions

3.1 Physical and chemical properties

Total surface area, total pore volume and mean pore diameter of all synthesized catalyst were summarized in Table 1. NA catalyst presents the highest value. Total surface area and total pore volume of NM catalyst shows the lowest value. The surface area and total pore volume of catalyst seems to decrease with the composition of M. However, mean pore diameter of all catalyst is approximately 2 nm indicating the microporous structure.

Table 1: Textural properties of prepared catalysts

Catalyst	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter (nm)
NA	192	0.101	2.11
NM	92	0.005	2.02
NAM	178	0.009	2.00

TPR profiles of all catalyst investigated illustrate in Figure 2. The reduction temperature of NAM catalyst was observed in three temperature regions indicating at least three types of metal oxide species exist in the catalyst. The lower reduction temperature between (100 - 300 °C) was presented for the metal oxides which are easily reduced. The profile shows the defined maximum peak (at 400 °C) of H₂ reduction between 300 - 550 °C, indicating that most of metal oxides are reduced at this temperature region. The profile also depicts the reducibility of metal oxide at higher temperature more than 600 °C and the curve of profile was monitored to soar. This could be due to the reduction of stable metal oxide species which has the strong metal-support interaction. The reduction profile of NM catalyst is similar to the profile observed from NA catalyst but the reducibility is less than that observed from NAM catalyst. Most of metal oxides are reduced in the temperature range of 300 - 600 °C and the reducibility of catalyst at higher temperature region was also presented. TPR profile of NA catalyst demonstrates the different behavior in which the reduction of metal oxide begins at 600 °C and peak maximum was observed at around 750 °C. The curve of profile declines before the final temperature of TPR study.

The high reducibility of NAM catalyst could be due to the high amount of transition metal oxide exposed to surface. This catalyst is composed of two types of mixed oxide support and active transition metal component. The interaction of two mixed oxide supports themselves leading to the stable phase could assist transition metal oxide exposed to surface, which are readily reduced to active metal component. The hydrogen consumption for the reduction of NAM catalyst is high. On the other hand, NA and NM catalyst have only one metal oxide support resulting in the interaction of metal oxide support occurs with active transition metal component. This leads to the less amount of hydrogen consumed for the reduction of transition metal oxide to active metal component.

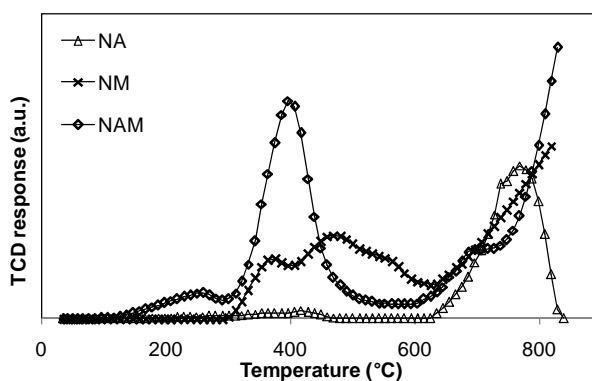


Figure 2: H₂-TPR profile of NA, NM and NAM catalysts.

CO₂-TPD technique was used to determine the basicity of catalyst surface. TPD profiles obtained from temperature programmed desorption of CO₂ for all catalyst are demonstrated in Figure 3. TPD profiles of

NA and NAM catalyst show a similar result. The profile of NAM catalyst shows a shoulder peak between 250-400 °C with the peak maximum around 450 °C (Coleman et al., 2009 has reported the similar desorption temperature), while a single temperature peak of NA catalyst is around 500 °C. Two desorption temperature regions indicate two different basic sites appearing on the surface of NAM catalyst. The lower temperature curve is due to the desorption of CO₂ from weak basic sites, while the desorption of CO₂ in higher temperature region is attributed to the strong basic site. In contrast, the TPD profile observed from NM catalyst presents a different result. A small hump of CO₂ desorption is around 180 °C - 400 °C and the desorption profile slightly increases until 800 °C and drop after that. The amount of CO₂ desorption is less than that observed from other catalysts. The results from all catalysts could be concluded that NAM catalyst has the highest number of strong basic site compared to NA and NM catalyst. This is in agree with TPR result that the highest number of strong basic site observed from NAM catalyst might be due to the basicity of stable phase occurring from the strong support interaction of two mixed oxide support.

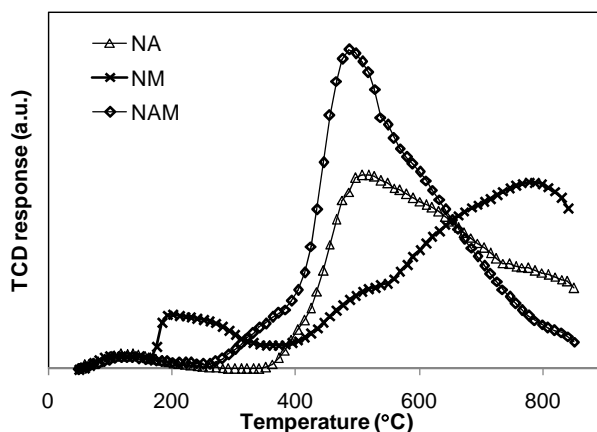


Figure 3: CO₂-TPD profile of NA, NM and NAM catalysts.

3.2 Effect of catalyst composition on reforming activity

The results of dry methane reforming (CH₄:CO₂ = 15:25 mL/min) over NA, NM and NAM catalyst at 700 °C for 6 h are summarized in Figure 4.

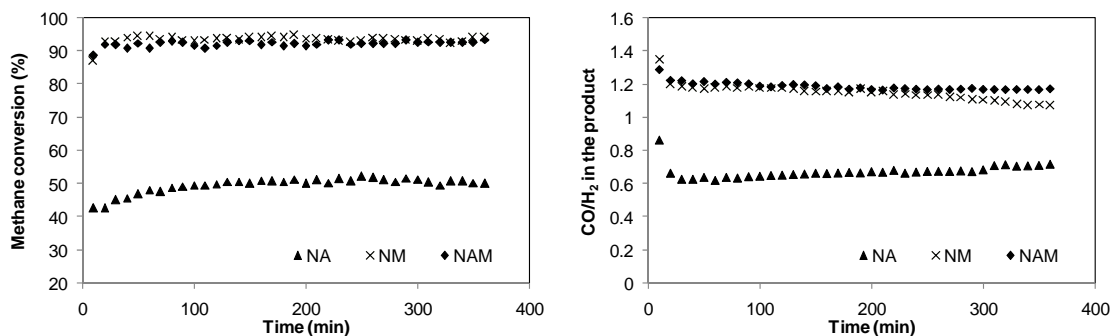


Figure 4: Methane conversion and CO/H₂ in product over NA, NM and NAM catalyst at 700 °C and CH₄:CO₂ of 15 (mL/min):25 (mL/min)

Methane conversions of NM and NAM catalyst are approximately 94 %, while NA catalyst gives 50 % methane conversion. This could be confirmed by H₂-TPR, which shows that NM and NAM catalysts show high reducibility compared to NA catalyst. Products obtained from the reaction are H₂ and CO. The ratio of CO to H₂ (CO/H₂) in the product presents that NM and NAM catalysts give CO/H₂ more than one. This could be indicating that less carbon depositing on the catalyst surface. The excess CO₂ in the reaction could oxidise carbon deposited on the catalyst surface resulting in CO formation. The results are confirmed by CO₂-TPD results that NAM catalyst presents the high number of strong basic sites on the catalyst surface. For NA catalyst, it was observed that the CO/H₂ is approximately 0.65 because of hydrogen formation from CH₄ decomposition. According to the results, it could be concluded that catalyst composition has an effect on the activity of dry methane reforming. This could be due to the interaction

between two types of mixed metal oxide support. As a result, metal active component has less interaction with metal oxide support and it is more exposed to the surface. The basicity of catalyst is also an important property for the resistance to carbon deposition.

3.3 Effect of CH₄:CO₂ ratio in the feed on reforming activity

The influence of CH₄:CO₂ ratio on methane conversion and CO/H₂ was investigated over NAM and NM at 600 °C using the ratios of 15 (mL/min):25 (mL/min) and 25 (mL/min):15 (mL/min). Figure 5 shows that methane conversion decreases as CH₄:CO₂ ratio increases as well as the CO/H₂ ratio. Considering NAM catalyst, for the ratio of 15:25, CH₄ is the limiting reagent. Without the limitation of CO₂, higher proportional methane can be reacted with CO₂ over the catalyst surface. In addition, CO/H₂ for this ratio is almost equal to the theoretical value (CO/H₂=1) because this condition has abundant oxide resulting in less amount of carbon depositing on the catalyst. Once the CH₄:CO₂ ratio is more than unity, CO₂ becomes the limiting reagent. Consequently, the methane conversion depends on how much CO₂ is reacted and also excess methane will not be converted. Moreover, CO/H₂ in the product is approximately 0.7. It means that the product has less carbon monoxide than an aspect indicating the considerable carbon deposition due to the lack of oxide reactant (CO₂). The NM catalyst was also tested in this condition to be compared with NAM catalyst. Although higher conversion is observed after 200 min, CO/H₂ decreases to 0.4. This lower CO/H₂ in the product is an evidence of larger amount of carbon deposition. The reason can refer to CO₂-TPD results. It showed that NAM provides higher number of basic sites on surface than NM catalyst. Similar composition of NAM catalyst synthesized by different method was also confirmed by Guo et al. (2004) that the metal-support interaction in this type of catalyst causes a high activity with low acidity. Its properties lead to coking tolerance.

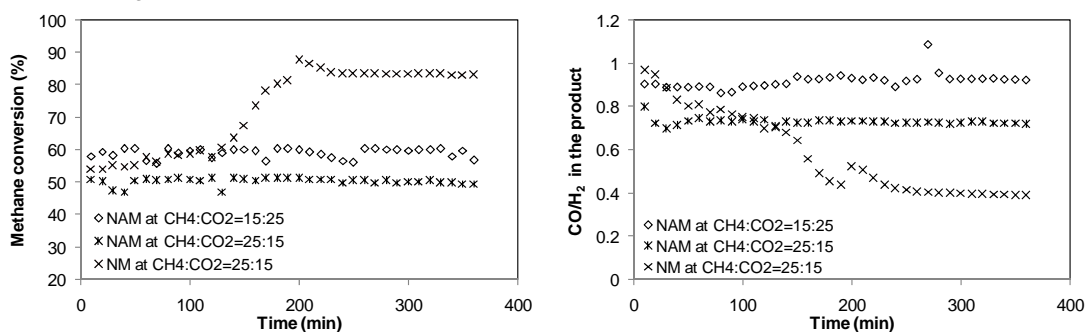


Figure 5: Methane conversion and CO/H₂ in product over NAM and NM catalyst at 700 °C using CH₄:CO₂ of 15 (mL/min):25 (mL/min) and CH₄:CO₂ of 25 (mL/min):15 (mL/min)

3.4 Effect of operating temperature on reforming activity

Figure 6 represents the results of DMR over NAM catalyst at 700 °C and 600 °C employing a feed CH₄:CO₂ ratio of 15 (mL/min):25 (mL/min). As expected, the conversion increases when the temperature increases. The CO/H₂ ratio at 600 °C is about 0.9 which is slightly below one indicating an apparent of carbonaceous formation on the catalyst surface. However, it may be negligible as long as the conversion still maintains. In the case of 700 °C, the methane conversions and H₂/CO ratios in the product remain stable at 700 °C along the operating time.

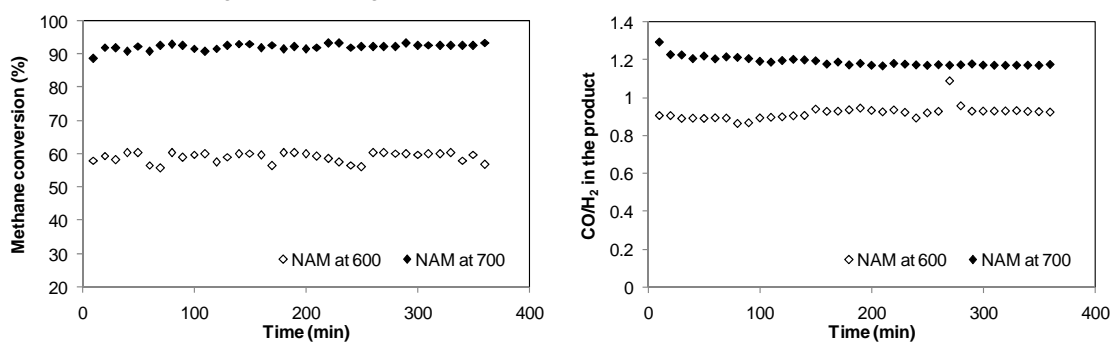


Figure 6: Methane conversion and CO/H₂ in product over NAM catalyst using CH₄:CO₂ of 15 (mL/min):25 (mL/min) at 700 °C and 600 °C

4. Conclusions

The catalysts prepared in a homogeneous solid form: NA, NM and NAM, provide high surface area with microporous structure. The TPR profiles represent that NAM possesses the best reducibility and the suitable range of temperature starts from 300 °C to 600 °C. It should be noted that it also has higher reducing temperature range that can be due to strong metal-support interaction. According to the CO₂-TPD results, NM has the strong basic site strength; whereas, NAM shows the greatest number of basic sites. From the DMR activity tests, at 700 °C, not only the methane conversion as high as 94 % but also the satisfied CO/H₂ ratio in the product was obtained when using NAM and NM. However, NM catalyst is not recommended for the case of CH₄:CO₂ in the feed below one. In all these tests, the deactivation of NAM has not been found. NAM has achieved remarkable activity and stability because of high reducibility and basicity, respectively. Thus, NAM can be considered as a candidate catalyst for dry methane reforming.

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