

## **CH<sub>4</sub>/CO<sub>2</sub> Reforming over Ni-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Catalyst for Synthesis Gas Production**

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**Abstract:** In this work the improvement of stability of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by ZrO<sub>2</sub> addition for synthesis gas production from CH<sub>4</sub>/CO<sub>2</sub> reforming reaction was investigated. Effect of Ni content was firstly conducted followed by effect of operating temperature in the range of 500-700°C, and effect of ZrO<sub>2</sub> loading at CH<sub>4</sub>:CO<sub>2</sub> of 1:1 in feed. The experimental results showed that 15%Ni was the minimum nickel loading on alumina giving high feed conversion of 67.26% for CH<sub>4</sub> and 61.38% for CO<sub>2</sub> and high H<sub>2</sub> yield of 59.46% and CO yield of 62.23% while maintaining the ratio of H<sub>2</sub>:CO close to 1. The suitable reaction temperature of 700 °C provided the highest CH<sub>4</sub> and CO<sub>2</sub> conversion and H<sub>2</sub> yield. The containing ZrO<sub>2</sub> catalysts (15%Ni-x%ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; x=5, 10 and 15%ZrO<sub>2</sub>) showed much higher stability than the ZrO<sub>2</sub>-free/Ni/Al<sub>2</sub>O<sub>3</sub> catalyst due to reduction of coke formation by ZrO<sub>2</sub> probably by suppressing methane dissociation step and facilitating CO<sub>2</sub> dissociation on the Ni active sites indicated by the decrease of CH<sub>4</sub> conversion and H<sub>2</sub> yield.

**Keywords:** CH<sub>4</sub> / CO<sub>2</sub> Reforming, Synthesis Gas, Ni-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

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## Introduction

The reforming of methane by carbon dioxide over heterogeneous catalysts has been received a revival of interest as it can generate synthesis gas having a  $H_2/CO$  ratio around 1, suitable for specific synthesis processes such as the production of alcohols and dimethylether. This reaction also has important environmental implications as two greenhouse gases are converted into valuable feedstocks. This reaction is also considered for energy transformation or chemical heat-pipe applications, in which a power source (e.g. solar or nuclear) drives the endothermic reforming reaction, and the product gases are transported to consumers at remote areas, where the reverse exothermic methanation reaction can be performed [1].

It is well known that the supported group VIII metals are good catalysts for this reforming reaction giving high yield of synthesis gas. However, one serious problem is the catalyst deactivation by carbon deposition on the active surface. It has been well established that noble metals (Rh, Ru, Pt) do not suffer the carbon deposition while Co, Ni and Pd are very sensitive to deactivation by coking. The expensive prices of noble metals render their industrial application quite questionable. Thus, this leads to the investigation of supported catalysts consisting of non-noble metal and promoters, in order to obtain a catalyst having a high catalytic activity without suffering the coke deactivation.

$ZrO_2$  was frequently reported to be a unique support for a number of catalyst systems in various catalytic reactions [2,3]. It was shown recently by Lercher et al. [4] that  $ZrO_2$  was a crucial component for platinum catalyst to minimize coke deposition under the  $CO_2/CH_4$  reforming conditions. Many authors proposed that  $ZrO_2$  facilitates the  $CO_2$  dissociation, which when takes place near the metal particle, aids in the removal of carbon formed on the metal from the dissociation of  $CH_4$  [5,6].

In this work, an inexpensive catalyst, Ni supported over  $Al_2O_3$ , was modified with  $ZrO_2$  promoter for improving catalyst stability in  $CH_4/CO_2$  reaction. The catalysts were prepared by wet impregnation method and both fresh and spent catalysts were characterized to gain coke formation results and to explain the effect of  $ZrO_2$  addition on Ni/ $Al_2O_3$  catalyst stability and activity.

## Experimental

### Catalyst preparation

A series of Ni/ $Al_2O_3$  and Ni/ $ZrO_2/Al_2O_3$  catalysts were prepared by impregnating the support  $Al_2O_3$  powder (JRC ALO 6, product of Japan Chemical company) with a solution containing a given concentration of metal nitrate salts,  $Ni(NO_3)_2 \cdot 6H_2O$  and  $ZrO(NO_3)_2 \cdot xH_2O$ . Different amount of metal salts yielded different metal and/or oxide loading wt%. After drying at  $110^\circ C$  overnight the catalysts were calcined at  $500^\circ C$  in air for 3 h. Two groups of catalysts were prepared according to the detailed studies as follows: 1) Impregnation of  $Ni(NO_3)_2 \cdot 6H_2O$  into the  $Al_2O_3$  powder to prepare x%Ni/ $Al_2O_3$  and the optimum Ni loading was selected to use in the next part. 2) Co-impregnation of  $Ni(NO_3)_2 \cdot 6H_2O$  and  $ZrO(NO_3)_2 \cdot xH_2O$  solution into the support  $Al_2O_3$  powder and Ni- $ZrO_2/Al_2O_3$  catalysts were obtained.

### CH<sub>4</sub>-CO<sub>2</sub> reforming

The CH<sub>4</sub>/CO<sub>2</sub> reforming reaction was conducted in a fixed bed reactor of a 316-stainless steel tube with inner diameter of 1.27 cm at atmospheric pressure. The bed was packed with 1.18 - 1.70 mm catalyst pellets. The reactor tube was placed in a vertical tube furnace and connected to a stream of the reaction gas mixture. A thermocouple was located outside the reactor tube wall at the position corresponding to the middle of the catalyst bed.

The reactant gas, CH<sub>4</sub> (99.99%)/CO<sub>2</sub> (99.999%) mole ratio of 1, passed over the catalyst bed at a GHSV of 18,000 cm<sup>3</sup>/g-h. Before catalytic reaction took place, the catalyst was reduced at 500°C with a flow of H<sub>2</sub> at a rate of 30 cm<sup>3</sup>/min in He for about 3 h. Afterwards, the reforming reaction at the selected operating condition was conducted. The reaction gas products were analyzed using a Hewlett Packard 6890 gas chromatography equipped with thermal conductivity detector (TCD) and Carbosieve SII column for H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> gas composition analysis. The reaction was carried out for 5 hr and results were presented in terms of reactant conversion and product yield as the average values. H<sub>2</sub> and CO yield reported in this work were calculated based on inlet feed.

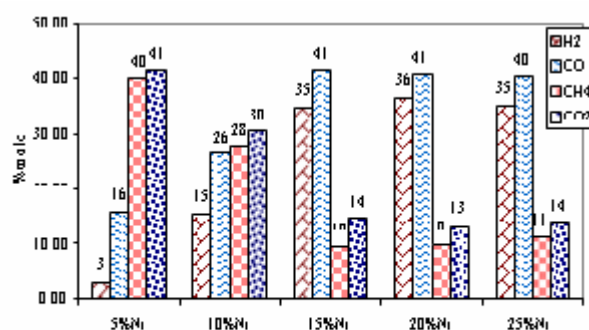
### Catalyst characterization

X-ray diffraction technique was used to identify the internal structure, bulk phase, and composition of catalysts. Spent catalysts were examined for coke deposition amount by thermogravimetric analysis (TGA) under the flow of air at 20 cm<sup>3</sup>/min in temperature range of 30-900°C and heating rate of 10°C/min.

## Results and Discussion

### Effect of Ni loading

In this step effect of %Ni loading on CH<sub>4</sub>/CO<sub>2</sub> reforming product at 700°C was conducted. Five Ni loadings, 5%, 10%, 15%, 20% and 25%, on Al<sub>2</sub>O<sub>3</sub> were the range of interest.



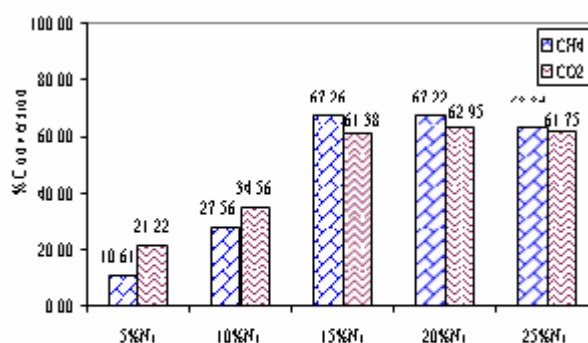
**Fig. 1** Effect of Ni loading on product gas composition during CH<sub>4</sub>/CO<sub>2</sub> reforming at 700°C and CH<sub>4</sub>:CO<sub>2</sub> ratio of 1.

Fig.1 shows the gas composition obtained from CH<sub>4</sub>/CO<sub>2</sub> reforming over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts prepared at various nickel loadings. As it can be seen that main products of CH<sub>4</sub>/CO<sub>2</sub> reforming are syngas (CO+H<sub>2</sub>) following the equation:

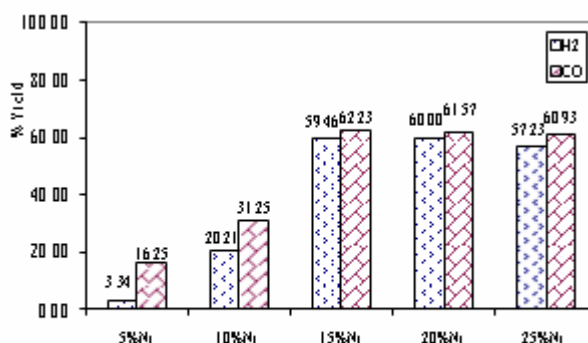


Amount of syngas produced were increased when Ni loading in catalyst was increased from 5% to 15% and almost constant when increasing to 20% and 25%. It can be described that when Ni loading was more than 15%, number of Ni active sites was not sensitively increased since excess amount of Ni was added and multilayer of Ni active sites was formed on alumina support surface resulting in an ineffectiveness of catalyst at higher Ni loading.

The tendency of CH<sub>4</sub> and CO<sub>2</sub> conversion and the gas product yields (H<sub>2</sub> yield and CO yield) were similar to the H<sub>2</sub> composition obtained as shown in Fig. 2 and 3. This is because the dissociation of CH<sub>4</sub> greatly depends on the number of Ni active sites. From these results 15%Ni was the minimum loading that was selected to use in further study of the effect of reaction temperature.



**Fig. 2** Effect of Ni loading on CH<sub>4</sub> and CO<sub>2</sub> conversion during CH<sub>4</sub>/CO<sub>2</sub> reforming at 700°C and CH<sub>4</sub>:CO<sub>2</sub> ratio of 1.

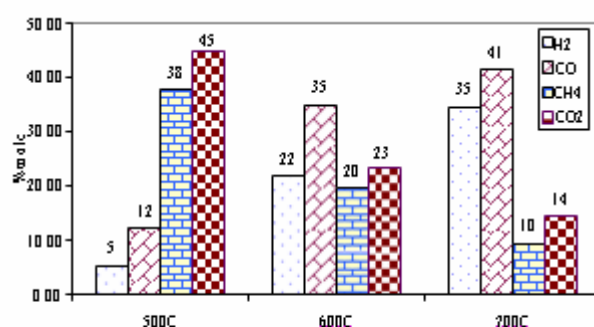


**Fig. 3** Effect of Ni loading on product yields during CH<sub>4</sub>/CO<sub>2</sub> reforming at 700°C and CH<sub>4</sub>:CO<sub>2</sub> ratio of 1.

The trend of H<sub>2</sub>/CO ratios obtained also follows the H<sub>2</sub> gas composition and approach 0.9 as Ni loading was increased up to 15%.

### ***Effect of reaction temperature***

Results of the study of reaction temperature (500°C, 600°C and 700°C) effect on product gas composition and yield in CH<sub>4</sub>/CO<sub>2</sub> reforming over 15%Ni/Al<sub>2</sub>O<sub>3</sub> are displayed in Figs. 4-6.

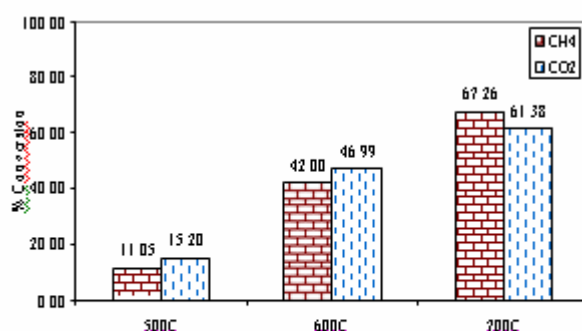


**Fig. 4** Effect of reaction temperature on product gas composition during  $\text{CH}_4/\text{CO}_2$  reforming over 15%Ni/ $\text{Al}_2\text{O}_3$  and at  $\text{CH}_4:\text{CO}_2$  ratio of 1.

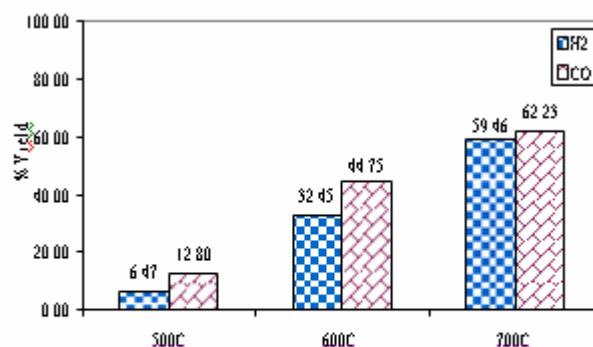
Fig.4 shows that reaction temperature of 700°C gives the highest  $\text{H}_2$  and  $\text{CO}$  composition since  $\text{CH}_4/\text{CO}_2$  reforming reaction is an endothermic reaction in which the extent of reaction increases with reaction temperature. In other words the degree of  $\text{CH}_4$  dissociation is strongly favorable high reaction temperature.

As illustrated in Fig. 5, the low reaction temperature at 500°C gives the least feed conversion approximately 10% but at 600°C and 700°C give the feed conversion four and six times higher than at 500°C, about 44% and 64%, respectively.

Similarly,  $\text{CH}_4/\text{CO}_2$  reforming performed at higher temperature gave higher  $\text{H}_2$  and  $\text{CO}$  yield as well as the  $\text{H}_2:\text{CO}$  ratio closer to 1. Hence 700°C was the most suitable temperature for this reaction in the range of study and it was chosen to use in the next study



**Fig. 5** Effect of reaction temperature on  $\text{CH}_4$  and  $\text{CO}_2$  conversion during  $\text{CH}_4/\text{CO}_2$  reforming over 15%Ni/ $\text{Al}_2\text{O}_3$  and at  $\text{CH}_4:\text{CO}_2$  ratio of 1.

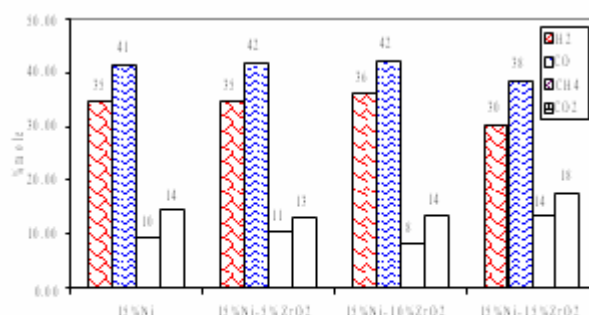


**Fig. 6** Effect of reaction temperature on product yields during  $\text{CH}_4/\text{CO}_2$  reforming over 15%Ni/ $\text{Al}_2\text{O}_3$  and at  $\text{CH}_4/\text{CO}_2$  ratio of 1.

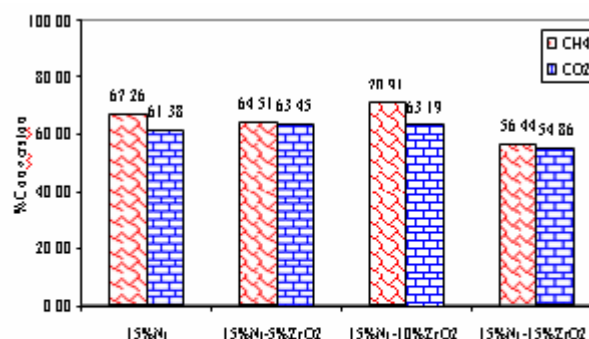
### Effect of $\text{ZrO}_2$ loading

In this part the effect of  $\text{ZrO}_2$  promoter loading, 5, 10 and 15% $\text{ZrO}_2$  in Ni/ $\text{Al}_2\text{O}_3$  catalyst on  $\text{CH}_4/\text{CO}_2$  reforming was investigated. The results are shown in Figs. 7-9.

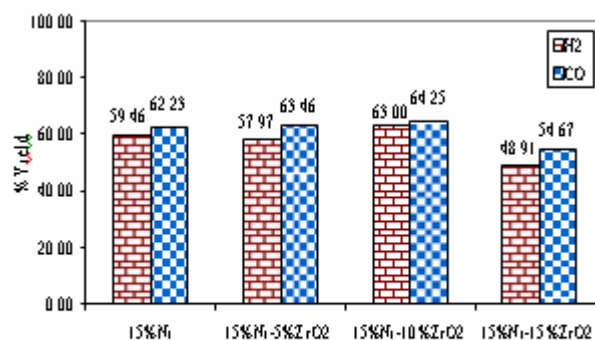
From Figs.7-9, influence of addition of zirconia on gas composition, feed conversion and product yield during the reaction period of 5 hrs could not be observed. The reaction time might not be long enough to see such effect. Catalyst containing 15%  $\text{ZrO}_2$ , however, slightly decreases the gas composition when comparing with  $\text{ZrO}_2$ -free catalyst. This might be due to the reduction in surface area of catalyst when more  $\text{ZrO}_2$  promoter is added.



**Fig. 7** Effect of  $\text{ZrO}_2$  loading in Ni/ $\text{Al}_2\text{O}_3$  on gas composition during  $\text{CH}_4/\text{CO}_2$  reforming at 700°C and  $\text{CH}_4/\text{CO}_2$  of 1.



**Fig. 8** Effect of  $\text{ZrO}_2$  loading in Ni/ $\text{Al}_2\text{O}_3$  on  $\text{CH}_4$  and  $\text{CO}_2$  composition during  $\text{CH}_4/\text{CO}_2$  reforming at 700°C and  $\text{CH}_4/\text{CO}_2$  of 1.

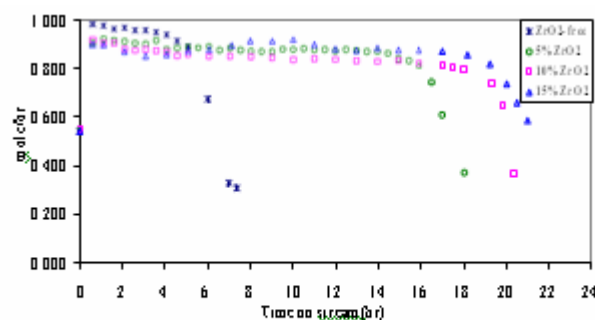


**Fig. 9** Effect of ZrO<sub>2</sub> loading in Ni/Al<sub>2</sub>O<sub>3</sub> on gas product yield during CH<sub>4</sub>/CO<sub>2</sub> reforming at 700°C and CH<sub>4</sub>:CO<sub>2</sub> of 1.

### Stability of catalysts

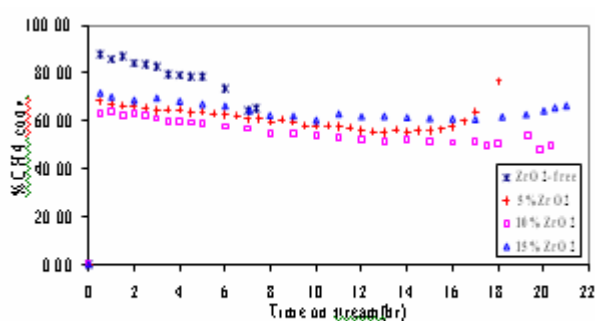
Due to an ambiguity of results in previous section, four catalysts containing different ZrO<sub>2</sub> loadings, 15%Ni/Al<sub>2</sub>O<sub>3</sub>, 15%Ni-5%ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 15%Ni-10%ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 15%Ni-15%ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> were again tested until deactivation was observed to study the effect of ZrO<sub>2</sub> addition on lifetime of catalyst.

Fig.10 compares the dry gas production rate obtained when different ZrO<sub>2</sub> loading was added into the catalysts. It shows that 15%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (without ZrO<sub>2</sub>) rapidly deactivates by coke deposition at reaction time of 6 hr while the catalysts containing ZrO<sub>2</sub> have higher stability at reaction time in the range of 17-21 hr. The 15%Ni-15%ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> shows the least deactivation.

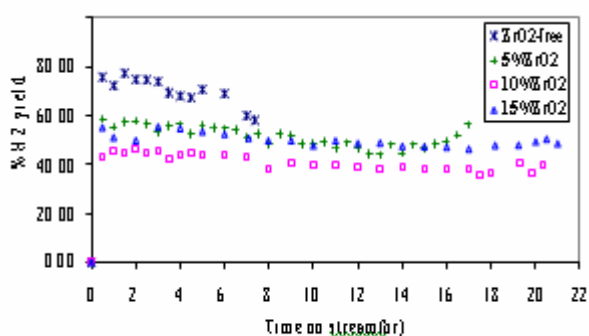


**Fig.10** Dry gas production rate in CH<sub>4</sub>/CO<sub>2</sub> reforming over Ni/Al<sub>2</sub>O<sub>3</sub> Containing various ZrO<sub>2</sub> Loadings at 700°C, and CH<sub>4</sub>: CO<sub>2</sub> of 1.

The results of CH<sub>4</sub> conversion and H<sub>2</sub> yield shown in Fig. 11 and 12 also support the stability information obtained; since function of ZrO<sub>2</sub> was to suppress CH<sub>4</sub> dissociation.



**Fig. 11** CH<sub>4</sub> conversion in CH<sub>4</sub>/CO<sub>2</sub> reforming over Ni/Al<sub>2</sub>O<sub>3</sub> Containing various ZrO<sub>2</sub> loadings at 700°C and CH<sub>4</sub>:CO<sub>2</sub> of 1.



**Fig.12** H<sub>2</sub> yield in CH<sub>4</sub>/CO<sub>2</sub> reforming over Ni/Al<sub>2</sub>O<sub>3</sub> Containing various ZrO<sub>2</sub> loadings at 700°C and CH<sub>4</sub>: CO<sub>2</sub> of 1.

## Conclusion

From the experimental results, the minimum Ni loading on Al<sub>2</sub>O<sub>3</sub> provided high feed conversion and syngas products was 15%. Reaction temperature of 700 °C was the best among 500°C - 700°C that gives the highest reactant conversion and yield. Stability of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst can be improved by addition of ZrO<sub>2</sub> promoter since ZrO<sub>2</sub> suppresses CH<sub>4</sub> dissociation and facilitates CO<sub>2</sub> dissociation which is useful for cleaning the carbon deposited on active metal.

## Acknowledgements

The authors gratefully acknowledge the Energy Planning and Policy Office (EPPO) of Thailand for the financial support for this research.

## References

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