Role of Promoters in Hoisting the Catalytic Performance for Enhanced CO Methanation

Hussain, I.[1], Jalil, A. A.[1, 2, 3*], Mamat, C. R.[1], Siang, T. J.[2], Azami, M. S.[1], Hambali, H. U.[2]

[1]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

[2]School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

[3]Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

Corresponding author: aishahaj@utm.my

Abstract

The increasing demand of natural gas and its rising cost have urged some countries to take initiatives to fulfil their energy needs. The production of substituted natural gas (SNG) by syngas ($CO + H_2$) from coal or biomass is one of the most effective methods. As a promising source of energy, SNG has attracted much attention on research and applications due to the high demand for environmental protection. It is regarded as a clean energy source and an effective method for the application of coal resources, particularly in the regions with abundant coal resources but scarce natural gas such as in China [1-3]. SNG has attracted increasing attention due to its lower emission of sulphur and particulate matter. SNG is expected to be one of the main energy sources of the 21st century. It is environmentally friendly and less costly, has high calorific value, complete combustion, and smoke free compared to other energy sources. It has significant importance for the industrial level and transportation sectors.

Keywords: Role of promoters; enhanced CO methanation; catalytic performance; CO methanation
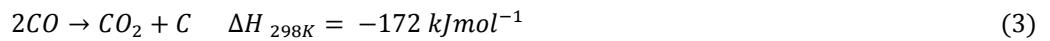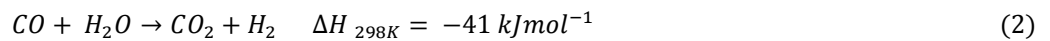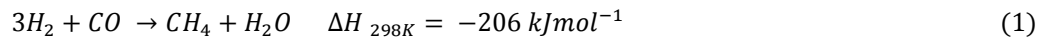
1.0 INTRODUCTION

The increasing demand of natural gas and its rising cost have urged some countries to take initiatives to fulfil their energy needs. The production of substituted natural gas (SNG) by syngas ($CO + H_2$) from coal or biomass is one of the most effective methods. As a promising source of energy, SNG has attracted much attention on research and applications due to the high demand for environmental protection. It is regarded as a clean energy source and an effective method for the application of coal resources, particularly in the regions with abundant coal resources but scarce natural gas such as in China [1-3]. SNG has attracted increasing attention due to its lower emission of sulphur and particulate matter. SNG is expected to be one of the main energy sources of the 21st century. It is environmentally friendly and less costly, has high calorific value, complete combustion, and smoke free compared to other energy sources. It has significant importance for the industrial level and transportation sectors. Conversion of coal to SNG consists of many elementary steps (Figure 1) including coal gasification, methanation of syngas, and separation of products. Methanation of CO is an important step to convert syngas (mixture of CO + H_2) into SNG [1, 5].

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn. Authors should discuss the results and how they can be interpreted in perspective of previous studies and of the working hypotheses. The findings and their implications should be discussed in the broadest context possible. Future research directions may also be highlighted.

Figure 1 Basic elementary steps involved in the production of SNG.

In addition, CO methanation reaction is extensively used to remove CO content from reformate gases to an extremely lower level (less than 50 ppm) as required for fuel cell technology. It is also used in removing traces of CO from H_2 and ammonia production plants [6-7]. The main CO methanation reaction is represented by Equation 1, which is also known as the Sabatier reaction, whereas other main side reactions during CO methanation are represented by Equations 2–4, which are water gas shift reaction, Boudouard reaction, and CH_4 dissociation, respectively [8].

$$3H_2 + CO \rightarrow CH_4 + H_2O \quad \Delta H_{298K} = -206 \, kJmol^{-1} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41 \, kJmol^{-1} \tag{2}$$

$$2CO \rightarrow CO_2 + C \quad \Delta H_{298K} = -172 \, kJmol^{-1} \tag{3}$$

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298K} = -74 \, kJmol^{-1} \tag{4}$$

CO methanation is highly exothermic in nature. It is very difficult to transfer heat of reaction from fixed bed reactors during CO methanation. Carbon black can be easily produced on the surface of catalysts at higher temperature as mentioned in Equations 3 and 4, which can deactivate catalysts. Furthermore, at higher temperature, sintering can also happen on active metals in catalysts. To avoid these issues, it is uneconomical for industries to carry out the process at lower temperature because it could decrease the efficiency of the reaction and affect the actual yield of the products [2]. Furthermore, durability and excellent catalytic activity at higher temperature are very important factors during the application of a catalyst. Technically, the catalytic properties of nickel-based catalysts can be improved by several techniques, such as by increasing the dispersion of nickel particles or reducing nickel particles by improving the preparation methods, increasing nickel loading on supports, or adding a proper amount of promoters or additives to catalysts. The addition of promoters or increasing nickel loadings have been used extensively to enhance the catalytic activity in CO methanation [13]. A good understanding of the properties of promoters, which are recently used in CO methanation, is very important to design new catalysts. This review will be useful a guide to synthesise and achieve the desired characteristics such as higher catalytic activity, stability, and selectivity for CO methanation.

2.0 PROMOTERS/ADDITIVES

It was reported that Ni/SiC catalyst showed improved catalytic performance and high stability during CO methanation upon addition of cerium (Ce) as a promoter, which might be due to improved interactions between SiC support and Ni particles, and this improved the dispersion of Ni active species [2]. Figure 2 describes the role of Ce as a promoter in the catalytic activity of Ce-Ni/SiC catalyst. The addition of a small amount of lanthanum (La), zirconium (Zr), cobalt (Co), Ce, and magnesium (Mg) on Ni-Al$_2$O$_3$ improved the stability and catalytic activity of the catalysts for CO methanation [9]. Therefore, it is easy to remove OH species in terms of H_2O molecules, which generates enough vacant space of active sites for a continuous CO methanation reaction [10]. For further improvement in the stability and catalytic performance of Ni-based catalysts in CO methanation, many studies have been conducted with the addition of second metals such as molybdenum (Mo), Ce, Co, La, iron (Fe), and copper (Cu) to improve the stability and catalytic activity of nickel catalysts [11]. Ni-supported ɤAl$_2$O$_3$ catalyst is considered as a preferable selection for large-scale production of SNG due to its low cost. However, it shows lower stability at high temperature and causes sintering of Ni particles present in catalyst. It is well known that La metal as an additive/promoter can inhibit phase transformation of ɤAl$_2$O$_3$ and sintering of metal [12]. Furthermore, in another study, Ni/SiO$_2$ catalyst was synthesised with trace amount of Ru promoter by either polyethylene glycol (PEG)-free impregnation or PEG-assisted method for CO methanation. PEG molecules form bimetallic Ni-Ru particles with better anti-sintering property, smaller size, and low-temperature reducibility on SiO$_2$ support compared to conventional PEG-free derived Ni-Ru/SiO$_2$ catalyst [3]. A comparative study of different promoter-based catalysts is summarised in Table 1.

Table 1 Comparative study of the results for some recent CO methanation catalysts.

Catalysts	Promoter	Temp. (C)	Xco (%)	S_{CH4} (%)	Y_{CH4} (%)	Stability (h)	References
Ni-MCM-41	-	350	69	65	44.85	-	[14]
Mo-Ni-MCM-41	**Mo**	**350**	**100**	**93**	**92**	100	
Ni/KIT-6		300	93.7	81.4	76.27		[15]
Mo-Ni/KIT-6	**Mo**	**300**	**99.9**	**86.4**	**86.31**	-	
Ni/MgO-Al$_2$O$_3$	-	240	8.2	22	2	-	[18]
Ni/MgO–Al$_2$O$_3$	**CeO$_2$**	**240**	**99.5**	**95**	**94.5**	60	
Ni-V/KIT-6	-	350	29	87	33	-	[19]
Ni-V/KIT-6	**V**	**350**	**100**	**85**	**85**	60	
NiO / Al$_2$O$_3$	-	400	80	72	**57.6**		[21]
NiO–Sm$_2$O$_3$/Al$_2$O$_3$	**Sm$_2$O$_3$**	**400**	**94**	**76**	**71.44**		
Ni/SiO$_2$	-	210	8	100	8	-	[8]
Ni/SiO$_2$	**La, Ce**	**210**	**100**	**85**	**85**	200	
Ce-Ni/SiC	-	600	92	80	73.6		[2]
Ce-Ni/SiC	**Ce**	**600**	**95**	**85**	**80.75**	100	
MCM-41	-	400	86	92	79.12		[22]
La-MCM-41	**La**	**400**	**92**	**97**	**89.24**	100	

2.1 Molybdenum

Mo promoter-based Ni/MCM-41 catalyst was used for CO methanation and the results demonstrated excellent catalytic performance. CO conversion and selectivity of CH$_4$ were enhanced up to 100% and 93%, respectively. It was found that the addition of Mo with Ni-supported MCM-41 catalyst improved the interaction between support oxide and nickel metal by the formation of Ni-Mo alloy. The results confirmed that Mo could promote the metal nickel particles refinement to a certain extent, which was conducive to improve the catalytic activity of the catalyst and it was consistent with the catalytic results. Therefore, Mo addition makes it hard for Ni particles to migrate and inhibit sintering of metal particles. The results are consistent with a previous study [14]. In another study, it was found that promoter-based Mo-KIT-6 catalyst for CO methanation could increase CO conversion and CH$_4$ selectivity to 99.9% and 86.4%, respectively. It was suggested that Mo improved the interaction between Ni and support by the formation of Ni-Mo alloy, which increased thermal stability and performance of the catalyst in CO methanation to a significant extent [15].

2.2 Zirconium

Haidong Li *et al*. [7] used Zr as a promoter in the synthesis of Zr/SBA-15 catalyst for CO methanation. In comparison to 10Ni/SBA-15 catalyst, the catalytic performance of promoter-based catalyst was significantly enhanced. It was suggested that Zr species contributed to the formation of oxygen vacancies during reduction and calcination. Consequently, it enhanced the ability of CO to adsorb or dissociate. CO adsorbed on oxygen vacancies and reacted with H$_2$ to produce CH$_4$. In another study, the use of ZrO$_2$ as a promoter in the synthesis of Ni/SiO$_2$ catalyst significantly improved the catalytic performance for CO methanation in CH$_4$ formation [25]. In addition, ZrO$_2$ was used in the modification of Al$_2$O$_3$ support for CO$_2$ methanation. It was claimed that highly dispersed ZrO$_2$ on the surface of γ-Al$_2$O$_3$ inhibited the formation phase changes in γ-Al$_2$O$_3$, which led to easier reduction of NiO species and improved better dispersion of NiO species, and subsequently enhanced catalytic performance of the corresponding catalyst [26].

2.3 Cerium

Shu-Sen Liu *et al*. [2] synthesised Ce-Ni/SiC catalyst and performed CO methanation at high temperature. The results in terms of CO conversion and CH$_4$ selectivity were 95% and 85%, respectively. It was suggested that Ce improved the interaction between SiC and Ni particles, where Ce might significantly influence Ni^{2+} reducibility due to special capacity of valence fluctuation, oxygen vacancies, and Ni particle size that might effectively promote the resistance to carbon deposition and anti-sintering of Ni particles. It could make a strong interaction between catalyst support and metal particles, and the addition of Ce on Ni/SiC catalyst inhibited the formation of graphite carbon. In addition, Ni/Al$_2$O$_3$ was modified with Ce as a promoter. The catalytic performance results illustrated that Ce-Ni/Al$_2$O$_3$ catalyst synthesised by co-impregnation method demonstrated smaller Ni particle size, higher Ni species dispersion, lower reduction temperature, and higher catalytic activity for CO

methanation (Figure 2). CO conversion of 95.4% and CH_4 selectivity of 90.7% were recorded [16]. Another study revealed that highly active, coking- and sintering-resistant CeO_2-decorated Ni/ɤ-Al_2O_3 catalyst synthesised by impregnation method showed enhanced catalytic performance for CO methanation. CeO_2 nanoparticles act as a physical barrier to inhibit the growth of Ni particles during the catalytic reaction at high temperatures and the addition of CeO_2 can retard the growth of carbon by increasing the supply of active oxygen species on Ni surface during the reaction [17].
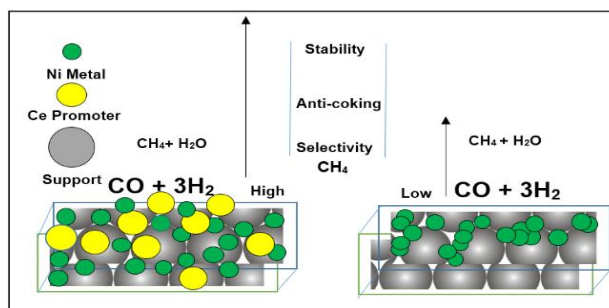

Figure 2. The role of Ce as a promoter in catalytic activity during CO methanation.

2.4 Lanthanum

Yang Han *et al*. [22] synthesised a catalyst by adding La as a promoter to study CO methanation. The results revealed that La-MCM-41 catalyst greatly improved catalytic activity and achieved 92% and 97% of CO conversion and selectivity, respectively, with 100 h stability during CO methanation. FTIR study confirmed that La metal atoms entered into the framework of MCM-41. La was used to restrain the growth of NiO particles, which could increase the dispersion of Ni particles on the catalyst support. The results showed that La enhanced catalytic activity and boosted the stability against sintering of metal particles and coking during CO methanation. In another study, La-Ni/SiO_2-supported catalyst showed good anti-carbon deposition and anti-sintering properties, and consequently enhanced the catalyst's reaction stability significantly. They claimed that the effect of La as a promoter for the dispersion of NiO particles was more significant compared to other promoters [23-24].

2.5 Vanadium

Ni-V/KIT-6 catalyst was synthesised to investigate CO methanation. The results showed excellent performance with the conversion of CO around 100% and CH_4 yield of approximately 85%, whereas the conversion of CO and CH_4 yield over Ni/KIT-6 (non-promoter) were 33% and 29%, respectively. It was claimed that the formation of Si-O-V linkage and confinement effect of 3D mesopores by the addition of V species were favourable to generate small-sized Ni nanoparticles and further prevented the aggregation of Ni nanoparticles during high-temperature reduction and CO methanation [21]. In another study, a highly active and coking-resistant Ni-V_2O_3/Al_2O_3 catalyst was prepared for CO and CO_2 methanation. Ni-V_2O_3/Al_2O_3 catalyst demonstrated a significant improvement in catalytic activity, resistance to coke formation, and thermal stability. For V_2O_3, the formation of smaller Ni particle size led to higher Ni dispersion, as well as the increase of oxygen vacancies, which enhanced the dissociation of CO_2 and generated surface oxygen intermediates [20].

3.0 CONCLUSION

CO methanation is an important step in the production of SNG. There is a big challenge to synthesise the catalyst due to its higher exothermic nature. Deactivation of catalysts and coke formation are the main consequences during CO methanation. More research efforts are necessary to design suitable methanation catalysts by adding promoters or additives in CO methanation in order to enhance catalytic performance with high stability. Many encouraging results have been obtained from previous studies, which provide useful information and findings to design suitable catalysts in CO methanation for the production of SNG.

References

[1]   Ren, J., H. Li, Y. Jin, J. Zhu, S. Liu, J. Lin, and Z. L- Key. 2017. Silica/titania Composite-Supported Ni Catalysts For CO Methanation: Effects Of Ti Species On The Activity, Anti-Sintering, And Anti-Coking. *Applied Catalysis B: Environmental.* 201: 561-572.

[2]   Liu, S. S., Y. Yong Jin, Y. Han, J. Zhao, J. Ren. 2018. Highly Stable And Coking Resistant Ce Promoted Ni/Sic Catalyst Towards High Temperature CO Methanation. *Fuel Processing Technology.* 177: 266-274.

[3]   Wang, J., C. Yuan, N. Yao, and X. Li. 2018. Effect of the Nanostructure And The Surface Composition Of Bimetallic Ni-Ru Nanoparticles On The Performance Of CO Methanation. *Applied Surface Science..* 441: 816-823.

[4]   Li, S., H. Tang, D. Gong, Z. Ma, Y. Liu. 2017. Loading Ni/La$_2$O$_3$ on SiO$_2$ for CO Methanation From Syngas. *Catalysis Today.* 297: 298-307.

[5]   Kamata, H., Z. Q. Tian, Y. Izumi, C.K.S. Choong, J. Chang, M. Schreyer, L. Chen, A. Borgna. 2018. Dispersed and High Loading Ni Catalyst Stabilized In Porous Sio$_2$ Matrix For Substituted Natural Gas Production. *Catalysis Today.* 299: 193-200.

[6]   Teh, L. P., S. Triwahyono, A. A. Jalil, R. Mamat, S. M. Sidik, N. A. A. Fatah, R. R. Muktie, T. Shishido. 2015. Nickel-Promoted Mesoporous ZSM5 For Carbon Monoxide Methanation. *RSC Advances 5*: 64651-64660.

[7]   Li, H., J. Ren, X. Qin, Z. Qin, J. Lin, Z. Li. 2015. Ni/SBA-15 Catalysts For CO Methanation: Effects Of V, Ce, And Zr Promoters. *RSC Advances* 5: 96504-96517.

[8]   Gong, D., S. Li, S. Guo, H. Tang, H. Wang, Y. Liu. 2018. Lanthanum and Cerium Co-Modified Ni/Sio$_2$ Catalyst For CO Methanation From Syngas. *Applied Surface Science.* 434: 351-364.

[9]   X, He,. Wang, R. Liu, S. Gao, T. Xiao. 2015. Effect of Reaction Variables On CO Methanation Process Over Nio– La$_2$O$_3$-Mgo/Al$_2$O$_3$ Catalyst For Coal To Synthetic Natural Gas. *Applied Petrochemical Research*. 5: 413-417.

[10]   Zhang, C., B. Liu, Y. Wang, L. Zhao, J. Zhang, Q. Zong, J. Gao and C. Xu. 2017. The Effect Of Cobalt Promoter On The CO Methanation Reaction Over Mos$_2$ Catalyst: A Density Functional Study. *RSC Advances* 7: 11862-11871.

[11]   Hwang, S., J. Lee, U. G. Hong, J. C. Jung , D. J. Koh, H. Lim, C. Byun, I. K. Song. 2012. Hydrogenation of Carbon Monoxide To Methane Over Mesoporous Nickel-M-Alumina (M = Fe, Ni, Co, Ce, And La) Xerogel Catalysts. *Journal of Industrial and Engineering Chemistry.* 18: 243-248.

[12]   H. Song, K., X. Yan, D. J. Koh, T. Kim, J. S. Chung. 2017. La Effect On The Long-Term Durability Of Ni-Mg-Al$_2$O$_3$ Catalysts For Syngas Methanation. *Applied Catalysis A: General.* 530: 184-192.

[13]   Liu, Q., Z. Zhong, F. Gu, X. Wang, X. Lu, H. Li, G. Xu, F. Su. 2016. CO Methanation On Ordered Mesoporous Ni–Cr–Al Catalysts: Effects Of The Catalyst Structure And Cr Promoter On The Catalytic Properties. *Journal of Catalysis.* 337: 221-232.

[14]   Zhang, J., Z. Xin, X. Meng, Y. Lv, M. Tao. 2014. Effect of MoO$_3$ On The Heat Resistant Performances Of Nickel Based MCM-41 Methanation Catalysts. *Fuel.* 116 :25-33.

[15]   Lv, Y., Z. Xin, X. Meng, M. Tao, Z. Bian, J. Gu, W. Gao. 2017. Effect of La, Mg and Mo Additives On Dispersion And Thermostability Of Ni Species On KIT-6 For CO Methanation. *Applied catalysis A: General* 543: 125-132.

[16]   Meng, F., Z. Li, J. Liu, X. Cui, H. Zheng. 2015. Effect of promoter Ce On The Structure And Catalytic Performance Of Ni/Al$_2$O$_3$ Catalyst For CO Methanation In Slurry-Bed Reactor. *Journal of Natural Gas Science and Engineering.* 23: 250-258.

[17]   Liu, Q., J. Gao, M. Zhang, H. Li, F. Gu, G. Xu, Z. Zhong, F. Su. 2017. Highly Active And Stable Ni/G-Al$_2$O$_3$ Catalysts Selectively Deposited With Ceo$_2$ For CO Methanation. *RSC Advances*. 4: 16094-16103.

[18]   Zhang, L. , D. X. Gu1, Y. liu, Y. Zhang. 2017. Highly Active And Stable Ni/G-Al$_2$O$_3$ Catalysts Selectively Deposited With Ceo$_2$ For CO Methanation. *Catalysis letters* 147: 1172-1180.

[19]   X. Cao, H., J. Zhang, C. L. Guo, J. G. Chen, X. K. Ren. 2017. Modifying Surface Properties Of KIT-6 Zeolite With Ni And V For Enhancing Catalytic CO Methanation. *Applied Surface Science*. 426: 40-49.

[20]   Liu, Q., F. Gu, X. Lu, Y. Liu. H. Li, Z. Zhong, G. Xu, F. Su. 2014. Enhanced Catalytic Performances Of Ni/Al$_2$O$_3$catalyst Via Addition Ofv$_2$o$_3$for CO Methanation. *Applied Catalysis A: General.* 488: 37-47.

[21]   Liu, Q., H. Yang, H. Dong, W. Zhang, B. Bian, Q. He, J. Yang, X. Meng, Z. Tian, G. Zhao. 2018. Effects of Preparation Method And Sm$_2$O$_3$ Promoter On CO Methanation By A Mesoporous NiO–Sm$_2$O$_3$/Al$_2$O$_3$ catalyst. *New Journal of chemistry* 42: 13096-13106.

[22]   Han, Y., B. Wen, M. Zhu, B. Dai. 2018. Lanthanum Incorporated In MCM-41 And Its Application As A Support For A Stable Ni-Based Methanation Catalyst. *Journal of Rare Earths.* 36: 367-373.

[23]   Zhu, J., X. Peng, L. Yao, J. Shen , D. Tong , C. Hu. 2011. The Promoting Effect Of La, Mg, Co And Zn On The Activity And Stability Of Ni/Sio$_2$ Catalyst For CO$_2$ Reforming Of Methane. International Journal Of Hydrogen Energy. 36: 7094-7104.

[24]   Mo, L., X. Zheng, Q. Jing, H. Lou, and J. Fei. 2005. Combined Carbon Dioxide Reforming and Partial Oxidation of Methane to Syngas over Ni-La_2O_3/SiO_2 Catalysts in a Fluidized-Bed Reactor. *Energy & Fuels*. 19: 49-53.

[25]   Wang, Y., R. Wu and Y. Zhao. 2010. Effect of ZrO_2 Promoter On Structure And Catalytic Activity Of The Ni/Sio_2 Catalyst For CO Methanation In Hydrogen-Rich Gases. *Catalysis Today*. 158: 470-474.

[26]   Cai, M., J. Wen, W. Chu, X. Cheng and Z. Li. 2011. Methanation of Carbon Dioxide On Ni/Zro_2-Al_2O_3 Catalysts: Effects Of Zro_2 Promoter And Preparation Method Of Novel Zro_2-Al_2O_3 Carrier. *Journal of Natural Gas Chemistry*. 20: 318-324.