

CO₂ Methanation over Mesoporous Silica Based Catalyst: A Comprehensive Study

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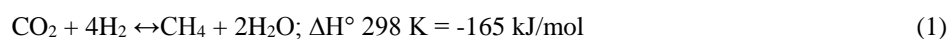
Abstract

The abundance presence of CO₂ released into the atmosphere has gained numerous consideration for an effective method to mitigate the CO₂ build up and recycling the carbon resource. Among the catalytic reactions, the methanation of CO₂ has been an indispensable reaction to transform toxic CO₂ into methane which can be use as energy carrier or valuable chemical. The application of heterogeneous catalyst in CO₂ methanation plays a significant role due to its effectiveness and stability which led to lower costs for large scale production. This article discussed the recent developments of silica based catalyst for CO₂ methanation with emphasized on its physicochemical properties and catalytic performance. In summary, the nature of silica support material such as morphology, textural properties and nature of basicity has a great influence on its catalytic performance towards CO₂ methanation.

Keywords: carbon dioxide; methanation; mesoporous; silica; basicity

1.0 INTRODUCTION

There is a growing awareness that anthropogenic CO₂ emissions should be reduced as CO₂ is a major greenhouse gas in the atmosphere. It is estimated that human activities emit about 5.5 Gt of CO₂ per year and the amount of CO₂ in the atmosphere is estimated to kept continuously increasing up to 380 ppm from 270 ppm since the pre-industrial era [1]. Hence, the CO₂ consumption for the production of fuels may provide a useful option to the manufacturing of syngas or methanol from conventional routes with better efficiency. Besides, utilizing the carbon source from CO₂ as for production of fuels and chemicals should be reflected as a more sustainable application of the resources which definitely lead to decrease carbon-based fossil resources consumption without generating more CO₂ from the complete process [2][3]. The catalytic methanation of CO₂, which also called as Sabatier reaction has become a promising method to utilize CO₂ and to produce fuel at the same time (Equation 1). Thermodynamically, the process is the most profitable reaction since it is significantly faster than other reactions which form alcohols or hydrocarbons.



Besides, the reaction is also considered as a key route which able to assist the future manned space missions by the recycling of CO₂ originates from wasted H₂ electrolysis or from water breathing on the International Space Station [4].

Even though the methanation process are thermodynamically favourable, catalyst is essential to reach an appropriate rate. The efficiency of the materials used as catalyst supports is primarily attributed from their microstructures characteristic, which provide good dispersion of active catalytic sites on the outsized internal pores and surfaces, which consequently enhance the catalytic activity [5]. Nevertheless, limited access to the active sites inside the pores occasionally decreased their uses since significant mass transport is necessary in catalytic reaction. Thus, highly accessible silica supports with high surface areas offer a great solution for afore mentioned limitation. Previously, numerous researches have been conducted on the hydrogenation of CO₂ to methane over mesoporous silica supported catalyst. The application of mesoporous silica as support material in the CO₂ methanation was based on its benefits such as high surface area and tuneable pore size. However, there is no review regarding the application of mesoporous silica has been reported. In this present review, we comprehensively report the latest developments of mesoporous silica material which acts as catalysts support in CO₂ methanation. Besides, the origins of active sites in the silica support and its correlation with their catalytic performance was also emphasize.

2.0 POTENTIAL SILICA SUPPORT FOR CO₂ METHANATION

Since the catalyst support has an important effect on the morphology of the active phase and catalytic performances, supported catalysts with high dispersion of metal has been the focus of significant study. Previously, numerous studies have reported the application of mesoporous silica materials such as MCM-41, mesostructured silica nanoparticles (MSN) and KCC-1 for catalytic CO₂ methanation, which attributed to their high surface area which provides good metal dispersion and high stability [6][7][8].

2.1 MCM-41 and SBA-15

MCM-41 mesoporous silica has been extensively used as catalyst support in CO₂ methanation attribute to its characteristics such as high surface area (1024 m²/g) and ordered hexagonal structure [2]. Table 1 shows the summary of the various metal supported MCM-41 for CO₂ methanation. Previously, Yang et al. has reported a physically stable Ni-MCM-41 prepared by isomorphous substitution into the silica framework for CO₂ methanation [2]. The catalyst gave a 12.4% CO₂ conversion with 69.4% CH₄ selectivity at 573 K reaction temperature.

Meanwhile, Du et al. reported that a proper hydrogen treatment of 3wt% Ni-MCM-41 at reaction temperature of 973 K resulted in thermally stable and highly disperse of metallic Ni catalyst. At reaction temperature of 673 K, the catalyst gave 16.8% of CO₂ conversion with 96% selectivity towards CH₄ [3]. Aziz et al. also has reported 5wt% Ni supported on MCM-41 prepared via impregnation method which highly selective towards CH₄ (98.3%). The performance was attributed to the high surface area of MCM-41 support which preventing Ni metal sintering as well as providing good thermal stability [4].

Table 1 Catalytic performance of metal supported MCM-41 and SBA-15 for CO₂ methanation.

Catalyst	Catalytic performance [%]		Reaction temperature [K]	Reference
	CO ₂ conversion	CH ₄ selectivity		
2wt%Ni-MCM-41	12.4	69.4	573	[2]
3wt% Ni-MCM-41	16.8	96	673	[3]
5wt% Ni-MCM-41	63	98.3	573	[4]
15wt%NiO/SBA-15	82	96	723	[5]
70 wt.% NiO/SBA-15	99.2	100	773	[11]

SBA-15 is an interesting mesoporous silica with uniform hexagonal pores with a narrow pore size distribution between 5 to 15 nm [6]. It possesses thickness of framework walls of 3.1 to 6.4 nm, contributing to the high mechanical and thermal stability. Besides that, the high surface area of SBA-15 which is in average of 400-900 m²/g make it as a suitable material as support in catalytic CO₂ methanation. Previously, Liu et al. has reported that NiO supported on SBA-15 prepared by one-pot hydrothermal procedure exhibit a highly disperse Ni with high surface area and big pore volume which led to high activity

and stability for CO₂ methanation [5]. The catalyst exhibits 82% conversion of CO₂ with 96% selectivity towards CH₄ at reaction temperature of 723 K. Meanwhile, Lu et al. has reported a high loading of 70% NiO on SBA-15 which gave up to 99.2% CO₂ with 100% selectivity towards CH₄ [7]. It was claimed that the prepared catalyst by heat treatment gave a very high thermal stability under methanation.

Based on Table 1, the performance of Ni supported MCM-1 catalyst showed lower CO₂ conversion and yield of CH₄ compared to the Ni supported on SBA-15 catalysts. This results were plausibly due to the high loading of Ni on SBA, providing more active sites for the adsorption and dissociation of H₂ and CO₂. Moreover, the reaction temperature of the reported Ni supported SBA-15 was higher compared to the Ni supported MCM-41.

2.2 Mesostructured silica nanoparticles (MSN)

The development of highly ordered mesostructured silica nanoparticles (MSN) with high surface area (1080 m²/g) and tunable pore size (3.77 nm) has attracted a lot of interest in heterogenous catalysis field [8][9]. The high amount of basic sites concentration in MSN which originated from the presence of intra and inter-particle porosity and its high surface area suggest that the material is a great potential support for CO₂ methanation. Previous study by Aziz et al. found the Ni supported MSN acts as dissociation sites for hydrogen in the CO₂ methanation to form atomic hydrogen. On the other hand, the production of surface carbon species in the reaction was greatly attributed to the defect sites or oxygen vacancies which available in MSN. Consequently, the methane was produced as the product from the interaction between the atomic hydrogen with surface carbon species [4].

Besides, a plausible CO₂ methanation mechanism over metal supported MSN has been proposed by conducting an in-situ FTIR adsorbed CO₂ and H₂ as depicted in Figure 1 [10]. Based on the FTIR result, the adsorbed CO₂ and H₂ on the catalyst system was dissociated on metal sites to produce atomic CO, O and H, which consequently migrate onto the surface of MSN. Then, the linear carbonyl and bridged carbonyl were formed from the interaction between the dissociated CO with oxide surfaces presence in MSN. At the same time, bidentate formate was formed by the facilitation of the presence H atom. It was proposed that the bidentate formate species could be the main route to formation of methane. Significantly, the MSN support exhibit a significant part in the mechanism by assisting the formation of carbonyl species which plays as active intermediate in methane production.

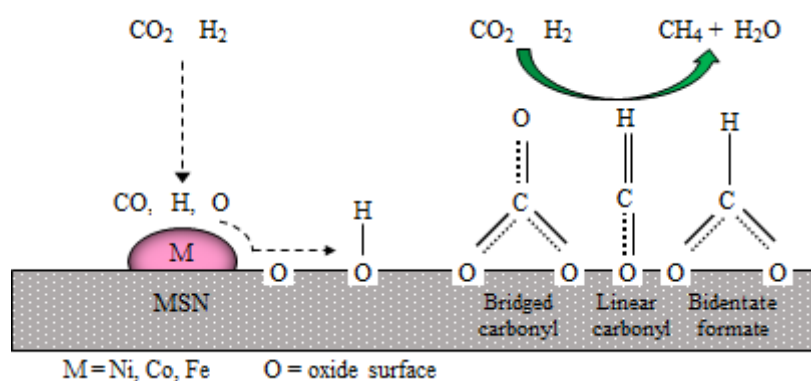


Figure 1 Propose mechanism of CO₂ methanation on metal supported MSN [10].

2.3 Bicontinuous Lamellar Silica (KCC-1)

The demand of silica support with easily accessible high surface area has led to the development of bicontinuous lamellar silica KCC-1 [11][12]. According to Moon and Lee, the small size and large surface-to-volume ratio of the bicontinuous lamellar silica allows the better metal dispersion on the surface which led to improved accessibility to their functional site [13]. The formation of fibrous morphology involves microemulsion formation from surfactant. The morphology of this material is influenced by the equilibrium between hydrophilic and hydrophobic interaction among the surfactant, precursor, hydrolyzing agent, and solvent. The fundamental to the formation of fibrous morphology is in the balance in microemulsion system. In microemulsion, there are three main elements that control its behavior, surfactant, oil phase, and aqueous phase. Surfactant such as cetylpyridinium and cetyltrimethylammonium has been successfully used in silica-based fibrous material. The fibrous morphology was lost when utilize of double hydrocarbon chain surfactant such as benzalkonium chloride as the

surfactant. This is due to the difference in packing parameters and steric hindrance between surfactant molecules in micelle formation [14]. Addition of co-surfactant such as short-chain alcohol has been proved to increase the possibility for formation of fibrous morphology [13].

In previous study, the distinctive morphology of bicontinuous lamellar silica KCC-1 has shown superior activity and ability in certain type of catalytic reaction such as drug delivery [15], alkane isomerization [16] and CO₂ capture [17]. Several recent study of CO₂ methanation over KCC-1 catalyst showed that the high catalytic performance of KCC-1 was attributed to its high number of basicity and oxygen vacancy [18].

3.0 CONCLUSION AND FUTURE PROSPECTS

Carbon dioxide has been known as a main culprit which responsible for the greenhouse effect as the accumulating amounts of CO₂ in the atmosphere has contribute to the climate changes on a global scale. Thus, CO₂ methanation over heterogeneous catalyst is an urgent necessity in reduction of CO₂ content in the atmosphere. The extensive application of silica materials as catalyst support plays a significant contribution towards the enhancement of catalytic performance in CO₂ methanation. In summary, the nature of silica support material such as morphology, textural properties and nature of basicity has a great influence on its catalytic performance towards CO₂ methanation. On the other hand, the preparation method also plays a significant role in determining the catalyst activity. Besides, further study to improve the properties of silica support such as KCC-1 can be developing during the synthesis procedure. A details study regarding the fibrous formation or the effect of different microemulsion system can be done that may require various changes in synthesis parameters and precursors.

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References

- [1] Fatah, N. A. A., A. A. Jalil, N. F. M. Salleh, M. Y. S. Hamid, Z. H. Hassan and M. G. M. Nawawi. 2019. Elucidation of Cobalt Disturbance On Ni/Al₂O₃ In Dissociating Hydrogen Towards Improved CO₂ Methanation And Optimization By Response Surface Methodology (RSM). *International Journal of Hydrogen Energy*. In press. <https://doi.org/10.1016/j.ijhydene.2019.04.119>
- [2] Yang, Y., S. Lim, G. Du, Y. Chen, D. Ciuparu and G. L. Haller. 2005. Synthesis and Characterization of Highly Ordered Ni-MCM-41 Mesoporous Molecular Sieves. *Journal of Physical Chemistry B*. 109: 13237–13246.
- [3] Du, G., S. Lim, Y. Yang, C. Wang, L. Pfefferle and G. L. Haller. 2007. Methanation of Carbon Dioxide On Ni-Incorporated MCM-41 Catalysts: The Influence Of Catalyst Pretreatment And Study Of Steady-State Reaction. *Journal of Catalysis*. 249: 370–379..
- [4] Aziz, M. A. A., A. A. Jalil, S. Triwahyono, R. R. Mukti, Y. H. Taufiq-Yap and M. R. Sazegar. 2014. Highly Active Ni-Promoted Mesostructured Silica Nanoparticles For CO₂ Methanation. *Applied Catalysis B Environmental*. 147: 359–368.
- [5] Liu, Q., and Y. Tian. 2017. One-Pot Synthesis Of NiO/SBA-15 Monolith Catalyst With A Three-Dimensional Framework For CO₂ Methanation. *International Journal of Hydrogen Energy*. 42: 12295–12300.
- [6] Zhao, D., J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky. 1998. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science*. 80: 548– 552.
- [7] Lu, B., and K. Kawamoto. 2012. Direct synthesis Of Highly Loaded And Well-Dispersed NiO/SBA-15 For Producer Gas Conversion. *RSC Advances*. 2: 6800.
- [8] Fatah, N. A. A., S. Triwahyono, A. A. Jalil, A. Ahmad and T. A. T. Abdullah. 2016. *n*-Heptane Isomerization Over Mesostructured Silica Nanoparticles (MSN): Dissociative-Adsorption Of Molecular Hydrogen On Pt And Mo Sites. *Applied Catalysis A General*. 516: 135–143.
- [9] N.A.A., F., J. A.A. and T. S. 2018. Platinum and Molybdenum Oxide Supported on Mesostructured Silica Nanoparticles for *n*-Pentane and Cyclohexane Isomerization. *Journal of Energy & Safety Technology*. 1: 24–30.
- [10] Aziz, M. A. A., A. A. Jalil, S. Triwahyono and S. M. Sidik. 2014. Methanation of carbon Dioxide On Metal-Promoted Mesostructured Silica Nanoparticles. *Applied Catalysis A General*. 486: 115–122.
- [11] Febriyanti, E., V. Suendo, R. R. Mukti, A. Prasetyo, A. F. Arifin, M. A. Akbar, S. Triwahyono, I. N. Marsih and Ismunandar. 2016. Further Insight into the Definite Morphology and Formation Mechanism of Mesoporous Silica KCC-1. *Langmuir*. 32: 5802–5811.
- [12] Polshettiwar, V., D. Cha, X. Zhang and J. M. Basset. 2010. High-surface-area silica nanospheres (KCC-1) with a fibrous Morphology. *Angewandte*

Chemie International Edition. 49: 9652–9656.

- [13] Moon, D. S., and J. K. Lee. 2012. Tunable Synthesis of Hierarchical Mesoporous Silica Nanoparticles with Radial Wrinkle Structure. *Langmuir*. 28:12341–12347.
- [14] Bayal, N., B. Singh, R. Singh and V. Polshettiwar. 2016. Size and Fiber Density Controlled Synthesis of Fibrous Nanosilica Spheres (KCC-1). *Scientific Report*. 6: 1–11.
- [15] Yang, P., S. Gai and J. Lin. 2012. Functionalized Mesoporous Silica Materials For Controlled Drug Delivery. *Chemical Society Reviews*. 41: 3679–3698.
- [16] Fatah, N. A. A., S. Triwahyono, A. A. Jalil, N. Salamun, C. R. Mamat and Z. A. Majid. 2017. *n*-Heptane Isomerization Over Molybdenum Supported On Bicontinuous Concentric Lamellar Silica KCC-1: Influence Of Phosphorus And Optimization Using Response Surface Methodology (RSM). *Chemical Engineering Journal*. 314: 650–659.
- [17] Patil, U., A. Fihri, A.-H. Emwas and V. Polshettiwar. 2012. Silicon Oxynitrides Of KCC-1, SBA-15 And MCM-41 For CO₂ Capture With Excellent Stability And Regenerability. *Chemical Science*. 3: 2224.
- [18] Hamid, M. Y. S., M. L. Firmansyah, S. Triwahyono, A. A. Jalil, R. R. Mukti, E. Febriyanti, V. Suendo, H. D. Setiabudi, M. Mohamed and W. Nabgan. 2017. Oxygen vacancy-Rich Mesoporous Silica KCC-1 for CO₂ methanation. *Applied Catalysis A General*. 532: 86–94.