

A short review on mesoporous silica-supported catalysts for methane dry reforming

Sharanjit Singh, Osaze Omoregbe, Tan Ji Siang, Fahim Fayaz, Dai-Viet N. Vo*
Faculty of Chemical and Natural Resource Engineering
Universiti Malaysia Pahang (UMP)
Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia
*Corresponding author. Tel.: +609 549 2874; fax: +609 549 2889
E-mail address: vietvo@ump.edu.my (D.-V. N. Vo).

Abstract— The aim of this review is to gain a better insight in to the recent developments made in mesoporous silica molecular sieves, such as MCM-41, SBA-15, and SBA-16, as supports for dry reforming of methane. It further explored how different constraints such as the synthesis method for the mesoporous materials and techniques for metal loading on the mesoporous materials influence the dry reforming reactions and products yields. The high surface area and 2D hexagonal arrays of MCM-41 and SBA-15, 3D cage like structure of SBA-16 allow for good dispersion of metals inside their channels, which in turn, facilitates high catalytic activity and less catalyst deactivation. In this review, attention will be given to different strategies for enhancing catalytic activities, and the effect of metal dispersion on mesoporous silica supports.

Keywords— methane dry reforming; mesoporous materials; metal dispersion.

1. INTRODUCTION

Methane is a key constituent of natural gas and cheap source of energy (4.4USD/giga joule), which can be obtained through fermentation and decay of organic materials. Although there are large deposits of natural gas globally, most of them are located in remote areas. Consequently, the transportation of the natural gas to its markets becomes a problem because of the large distance that need to be covered. Moreover, the high diffusibility of methane also makes it problematic in transporting it to the point of utilization. These limitations have led to series of research on how methane can be converted into more useful and easily transportable chemicals. However, properties of methane such as similar electronegativity, high bond dissociation energy of CH₃-H bond (439.3 kJ/mol) and low polarity values of carbon and hydrogen, make its conversion at the point of exploration more challenging [1]. Researchers explored different ways by which methane can be converted to easy transportable products.

Methane dry reforming (MDR) is an eco-friendly approach [2], which involves the reaction between two abundantly available greenhouse gases (CH₄ and CO₂) to produce syngas [3]. The syngas produced in MDR is industrially important because the product ratio (H₂/CO ratio) which is close to unity, makes it suitable for production of aldehyde and long chain hydrocarbons by Oxo-synthesis [4] and Fischer-Tropsch (F-T) reaction [5]. Although, other techniques, such as partial oxidation, steam reforming, autothermal reforming, and oxidative dry reforming have been practiced by researchers to produce syngas, the obtained syngas is however, not suitable for F-T synthesis. Steam reforming of methane is currently the most significant method to produce hydrogen [6]. But high H₂/CO \geq 3 (unsuitable for downstream processing such as Fischer-Tropsch reaction), steam corrosion and cost to handle excess of steam are major drawbacks in steam reforming of methane [7]. In literature, CO₂ is represented as oxidizing agent in the process of MDR, whereas, CH₄ serves as a source of H₂. Moreover, there is proportional consumption of one mole of CO₂ per mole of CH₄ being introduced. Therefore, the reduction of carbon footprint can be achieved by the effective utilization of methane via MDR.

One of the main bottlenecks for production of syngas by MDR is the need for catalyst with anti-sintering property and high stability and resistance against coke formation characteristics. Any catalyst which can overcome these impediments is considered as suitable and good catalyst for MDR. Unfortunately, MDR technology has not yet been established to industrial scale due to the absence of highly stable and active catalyst [8, 9]. Group VIII (noble metals: Ru, Pd, Pt, Rh), transition metals (Ni and Co) are the most commonly used metals for this reaction. The noble metals containing catalyst give promising results against deactivation and coke formation. But their high cost and low availability make these metals uneconomical in comparison to transition metals. Non precious transition metal nickel, has been recommended as the best candidates for methane reforming technologies. Ni metal has excellent capability to rupture C-H and C-C in methane and carbon dioxide to produce syngas [10,

11]. However, Ni metal deactivates fast at harsh conditions as compare to noble metals. Fortunately, studies have shown that carbon deposition can be suppressed by the use of supports [12] and basic promoters [13].

Nickel metal has been impregnated on different supports, such as Al_2O_3 , La_2O_3 , CeO_2 , MgO , SiO_2 , ZrO_2 , perovskite, and mesoporous materials (MCM-41, MCM-48, SBA-15, SBA-16 and Zeolites), as catalysts for MDR. The introduction of a metal with small particle size on high surface area support is recommended for better dispersion, and strong metal-support interactions [14, 15]. The use of mesoporous materials as metal supports has been recommended because of the open framework and tunable metal porosities provided by these materials [16].

This review highlights the recent work and achievements on the use of mesoporous materials as supports, and the effect of different metal combinations used with the various mesoporous supports for the production of syngas by methane dry forming. In this review, attention will be given to different strategies for the enhancement of the catalytic activity and effect of subsequent metal deposition on the mesoporous support for dry reforming technology. Several literatures were cited, and there results are compared to provide the better understanding of the effect of different constraints in the mesoporous materials for MDR.

2. EFFECT OF SYNTHESIS TECHNIQUE FOR METAL INCORPORATION IN FRAMEWORK

The efficacy of these materials are exhibited in their mesoporous structures. The mesopores allow the metals to enter inside the channels that enhances catalytic activity [17]. Mobil scientist prepared ordered MCM-41 hexagonal molecular sieves by using cationic cetyl-trimethylammoniumbromide (CTAB) surfactant [18]. The materials are synthesized under conditions where silica surfactant self-assembly and condensation of inorganic species occurs simultaneously [19]. These materials are extensively explored by many researchers for MDR. Zhao et.al reported the use of biodegradable, low cost commercially available non-ionic amphiphilic block copolymer as structure directing agent for the production of well-ordered mesoporous silica (SBA-15). The transition metals in combination with basic promoters is extensively used for almost all reforming technologies. The table below summarizes the performance of different mesoporous materials used for the methane dry reforming and technique of preparation.

A Alberazi et al. [20] used three different type of methods to synthesize ceria-zirconia doped Ni/SBA-15 and investigated its effect on catalytic activity for MDR, where they concluded that the synthesis route has significant effect on the physicochemical features and activity of the catalyst. The co-precipitation method for loading of ceria and zirconia (Cz) and Ni on SBA-15 is effective because it facilitates strong metal-support interactions, which is favourable for high catalytic activity, stability and resistance towards deactivation. Wang, Ning, et. al. [21] incorporated different concentration of cerium promoter inside the framework of SBA-15 by one pot synthesis and then impregnated with nickel and concluded that incorporation of cerium inside framework of SBA-15 promoted the formation of small nickel metallic particles, which eventually suppressed the formation of carbon. Ceria promoted Ni/SBA-15 synthesized by simple impregnation technique for ethanol steam reforming have been explored by the Li, Di, et.al, [22] and they reported that CeO_2 could effectively control the particle size of Ni by strong metal support interaction and exhibited superior activity. The captivity provided by SBA-15 support restricted the nickel particle growth under harsh reaction conditions. Similar kind of strategies have also been applied to the MCM-41 by introducing nickel in the framework, and then impregnating with Ru and Mg for MDR [23]. However, the catalyst was deactivated over a long time-on-stream. This problem of early catalyst deactivation was resolved by introducing Zr^{4+} as promoter, which activated the CO_2 and resulted in high catalytic activity and long term stability [24]. The promotion of nickel-supported SBA-16 by ceria was reported to showed higher durability in MDR reaction when compared to the unpromoted Ni/SBA-16 [25]. The remarkable stability of ceria promoted Ni/SBA-16 was attributed to the cage-like structure of the support, which kept the catalyst framework from collapse.

3. ROLE OF SURFACE AREA AND DISPERSION

The mesoporous materials (SBA-15 and SBA-16) can be synthesized by hydrothermal and non-hydrothermal technique by using different surfactant materials. The silicate mesoporous structures have uniform parallel pores and high surface area, which provides high permeation of metal and low resistance to mass transfer. High pore volume give longer contact time for interaction between active metals and reactants [7]. As earlier mentioned, metal-support interactions play a vital role in catalysts stability. Metal particle growth also helps in enhancing the catalyst stability and activity. Indirectly it enhances the dispersion of metal particles on the silica support. Many strategies have been employed such as insitu self-assembled core shell precursor route to increase the dispersion of nickel and lanthanum on the surface of SBA-15 and this results as high metal support interaction and high catalytic activity and stability [8, 26]. The basic promoters also played crucial role to increase the dispersion of metal on the catalytic support in framework and outside by impregnation and one pot synthesis technique. The wide angle XRD analysis studies clarified that the incorporation of cerium inside framework of SBA-15 promoted dispersion, which results in better dispersion and strong interaction between small nickel metallic particles and support [21]. The strong metal-support interactions by introducing oleic acid precursor route and basic promoter in the catalyst showed excellent catalytic activity and stability for long duration for syngas production by MDR.

Table.1 Summary of performance by mesoporous silica materials used for methane dry reforming

Mesoporous material and surface area	Template	Structure	Technique used for metal loading	X _{CH₄} and X _{CO₂} @T	Ref
Ce-Ni/SBA-16	Pluronic F127	Cage like structure & tubular channels	Incipient wetness impregnation	X _{CH₄} = 72%, X _{CO₂} = 77% @973K	(25)
La-Ni-SBA-15	Tri-block polymer P123	Hexagonal mesoporous structure	Core-shell precursor and Incipient wetness impregnation	X _{CH₄} = 82%, X _{CO₂} = 85% @ 973K	(26)
Ni-CZ-SBA-15	Tri-block polymer P123	Mesoporous structure	Two sequential incipient wetness impregnation	X _{CH₄} = 49%, X _{CO₂} = 56% @ 873K	(20)
LaNiO ₃ -SBA-15	TCP(E ₂₀ -PO ₇₀ -E ₂₀)	Mesoporous structure	Incipient wetness impregnation and vacuum drying	X _{CH₄} = 88%, X _{CO₂} = 91% @ 973K	(27)
Ni-MCM-41	C ₁₆ H ₃₃ (CH ₃)NBr	Mesoporous structure	One-pot hydrothermal procedure	X _{CH₄} = 26%, X _{CO₂} = 47% @ 873K	(28)
Pt-Ni-Co-MCM-14	CTAB	Hexagonal mesoporous structure	Wet impregnation method	X _{CH₄} = 66%, X _{CO₂} = - % @ 1023K	(29)
Ni-grafted SBA-15	Non-ionic surfactant P123	Mesoporous material	Atomic layer deposition	X _{CH₄} = 75%, X _{CO₂} = - % @ 1023K	(30)
Rh-Ce-SBA-15	P123	Mesoporous framework	Wet impregnation method	X _{CH₄} = -%, X _{CO₂} = - % @ 1023K	(31)
Ni-Mg-SBA-15	Pluronic P123	2D hexagonal framework	One-pot synthesis method	X _{CH₄} = 78%, X _{CO₂} = 96% @ 1073K	(32)
La-Ni-SBA-15	Pluronic P123	P6mm hexagonal symmetry	Wetness impregnation technique	X _{CH₄} = 73%, X _{CO₂} = 80% @ 1073K	(33)
Ru-Co/SBA-15	P123	Mesoporous silica	Two solvent method	X _{CH₄} = 82%, X _{CO₂} = 71% @ 1063K	(34)
Y doped-Ni-SBA-15	P123	Two dimensional hexagonal with cylindrical pores	Impregnation method	X _{CH₄} = 36 %, X _{CO₂} = 50 % @ 1073K	(35)
Ni/Ce-SBA-15	Pluronic P123	Mesoporous structure with cylindrical channels	One pot and Incipient impregnation	X _{CH₄} = 95%, X _{CO₂} = 92% @ 1073K	(21)
Ni/MgO-SBA-15	P123	Mesoporous structure	One pot and incipient impregnation	X _{CH₄} = 74%, X _{CO₂} = 76% @ 1073K	(36)
Ru-Mg/Ni-MCM-41	C ₁₆ H ₃₃ (CH ₃)NBr	Mesoporous Structure	One pot and Incipient wetness impregnation	X _{CH₄} = 35%, X _{CO₂} = 38% @ 873K	(23)
Ce-Ni- SBA-15	P123	Hexagonal porous structure	Two solvent technique	X _{CH₄} = 97%, X _{CO₂} = 85% @ 923K	(37)

4. CONCLUSION AND FUTURE OUTLOOK

Mesoporous materials show remarkable textural properties which make them attractive as support for MDR catalysts. Catalysts synthesis routes, however, have significant effects on the catalytic performance. In this review, we tried to draw a correlation between the constraints involved in the preparation of mesoporous supports and the catalysts for MDR with catalytic performance by citing various work reported in literature. Properties such as strong metal-support interaction (SMSI) and dispersion can be achieved by different synthesis techniques. Metal dispersion is significant in CH₄ activation step because it is the most important and slowest step during the MDR reactions, and this occurs mainly on the metallic site. High surface and better dispersion provided by mesoporous structure facilitates a better metal to dispersion, which will results in improved catalytic activity. The support played crucial role for activation of carbon dioxide and stability of catalyst by increasing oxygen mobility in the catalytic reaction occurring during MDR.

5. ACKNOWLEDGEMENT

This work was funded by the University Malaysia Pahang- Postgraduate Research grant scheme 160314 and Doctoral scholarship scheme.

6. REFERENCES

- [1] A. Caballero, and P. J. Perez, "Methane as raw material in synthetic chemistry: the final frontier," *Chem. Soc. Rev.* 2013, vol. 42, pp. 8809-8820, March 2013.
- [2] J. M. Lavoie, "Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation," *Front. Chem.*, vol. 2, 2014.
- [3] P. Ferreira-Aparicio, C. Marquez-Alvared, I. Rodriguez-Ramis, Y. Schuurman, A. Guerrero-Ruiz, and C. Mirodatos, "A transient kinetic study of the carbon dioxide reforming of methane over supported Ru catalysts," *Journal of Catalysis*, vol. 184, pp. 202-212, May 1999.
- [4] E. Drent and P. Budzelaar, "The oxo-synthesis catalyzed by cationic palladium complexes, selectivity control by neutral ligand and anion", *Journal of Organometallic Chemistry*, vol. 593-594, pp. 211-225, January 2000.
- [5] D. Vo, V. Arcotumapathy, B. Abdullah and A. Adesina, "Evaluation of Ba-promoted Mo carbide catalyst for Fischer-Tropsch synthesis", *J. Chem. Technol. Biotechnol.*, vol. 88, pp. 1358-1363, July 2012.
- [6] D.P. Serrano, J.M. Coronado, A. Víctor, P. Pizarro, and J.Á. Botas, "Advances in the design of ordered mesoporous materials for low-carbon catalytic hydrogen production," *J. Mater. Chem. A*, vol. 1, pp. 12016-12027, July 2013.
- [7] D. Pakhare, and J. Spivey, "A review of dry (CO₂) reforming of methane over noble metal catalysts," *Chem. Soc. Rev.*, vol. 43, pp. 7813-7837, November 2013.
- [8] L. Mo, K. K. M. Leong, and S. Kawi, "A highly dispersed and anti-cooking Ni-La₂O₃/SiO₂ catalyst for syngas production from dry carbon dioxide reforming of methane," *Catal. Sci. Technol.*, vol. 4, pp. 2107-2114, March 2014.
- [9] D. Liu, R. Lau, A. Borgna, and Y. Yang, "Carbon dioxide reforming of methane to synthesis gas over Ni-MCM-41 catalyst," *Appl. Catal. A*, vol. 358, pp. 110-118, February 2009.
- [10] A. Albarazi, P. Beaunier and P. Da Costa, "Hydrogen and syngas production by methane dry reforming on SBA-15 supported nickel catalysts: On the effect of promotion by Ce_{0.75}Zr_{0.25}O₂ mixed oxide", *International Journal of Hydrogen Energy*, vol. 38, pp. 127-139, January 2013.
- [11] V. Arcotumapathy, F. Alenazey, R. Al-Otaibi, D. Vo, F. Alotaibi and A. Adesina, "Mechanistic investigation of methane steam reforming over Ce-promoted Ni/SBA-15 catalyst", *Appl Petrochem Res*, vol. 5, pp. 393-404, December 2015.
- [12] I. Luisetto, S. Tuti, C. Battocchio, S. Lo Mastro, and A. Sodo, "Ni/CeO₂-Al₂O₃ catalyst for the dry reforming of methane: the effect of CeAlO₃ content and nickel crystallite size on catalytic activity and coke resistance," *Appl. Catal. A*, vol. 500, pp. 12-22, May 2015.
- [13] R. Martínez, E. Romero, C. Guimon, and R. Bilbao, "CO₂ reforming of methane over coprecipitated Ni-Al catalysts modified with lanthanum," *Appl. Catal. A*, vol 274, pp. 139-149, July 2004.
- [14] X Xie, T Otremba, P Littlewood, R Schomäcker, A Thomas, "One-Pot Synthesis of Supported, Nanocrystalline Nickel Manganese Oxide for Dry Reforming of Methane," *ACS Catal.*, vol 3, pp. 224-229, December 2012.
- [15] J. L. Ewbank, L. Kovarik, C. C. Kenvin, and C. Sievers, "Effect of preparation methods on the performance of Co/Al₂O₃ catalysts for dry reforming of methane," *Green Chem.*, vol 16, pp. 885-896, January 2014.
- [16] Y Wan, D Zhao, "On the controllable soft-templating approach to mesoporous silicates," *Chem. Rev.*, vol 107, pp. 2821-2860, June 2007.
- [17] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, "A new family of mesoporous molecular sieves prepared with liquid crystal templates," *J. Am. Chem. Soc.*, vol 114, pp.10834-10843, June 1992.
- [18] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, "Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism," *Nature*, vol 359, pp. 710-712, October 1992.
- [19] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, "Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores," *Sciences*, vol. 279, pp. 548-552, January 1998.

- [20] A. Albarazi, M.E. Gálvez, and P. Da Costa, "Synthesis strategies of ceria-zirconia doped Ni/SBA-15 catalysts for methane dry reforming," *Catal. Commun.*, vol. 59, pp. 108-112, January 2015.
- [21] N. Wang, W. Chu, T. Zhang, and X. S. Zhao, "Synthesis, characterization and catalytic performances of Ce-SBA-15 supported nickel catalysts for methane dry reforming to hydrogen and syngas," *Int. J. of Hydrogen Energy*, vol. 37, pp. 19-30, January 2012.
- [22] D. Li, L. Zeng, X. Li, X. Wang, H. Ma, S. Assabumrungrat, and J. Gong, "Ceria-promoted Ni/SBA-15 catalysts for ethanol steam reforming with enhanced activity and resistance to deactivation," *Appl. Catal. B*, vol. 176, pp. 532-541, October 2015.
- [23] S. Yasyerli, S. Filizgok, H. Arbag, N. Yasyerli, and G. Dogu, "Ru incorporated Ni-MCM-41 mesoporous catalysts for dry reforming of methane: Effects of Mg addition, feed composition and temperature," *Int. J. Hydrogen Energy*, vol. 36, pp. 4863-4874, April 2011.
- [24] D. Liu, X. Y. Quek, W. N. E. Cheo, R. Lau, A. Borgna, and Y. Yang, "MCM-41 supported nickel-based bimetallic catalysts with superior stability during carbon dioxide reforming of methane: Effect of strong metal-support interaction," *J. Catal.*, vol. 266, pp. 380-390, September 2009.
- [25] S. Zhang, S. Muratsugu, N. Ishiguro, and M. Tada, "Ceria-doped Ni/SBA-16 catalysts for dry reforming of methane," *ACS Catal.*, vol. 3, pp. 1855-1864, July 2013.
- [26] U. Oemar, Y. Kathiraser, L. Mo, X.K. Ho, and S. Kawi, "CO₂ reforming of methane over highly active La-promoted Ni supported on SBA-15 catalysts: mechanism and kinetic modelling," *Catal. Sci. Technol.*, vol. 6, pp. 1173-1186, 2016.
- [27] I. Rivas, J. Alvarez, E. Pietri, M. J. Pérez-Zurita, M. R. Goldwasser, "Perovskite-type oxides in methane dry reforming: Effect of their incorporation into a mesoporous SBA-15 silica-host," *Catal. Today*, vol 149, pp. 388-393, January 2010.
- [28] H. Arbag, S. Yasyerli, N. Yasyerli, and G. Dogu, "Activity and stability enhancement of Ni-MCM-41 catalysts by Rh incorporation for hydrogen from dry reforming of methane," *Int. J. Hydrogen Energy*, vol 35, pp. 2296-2304, March 2010.
- [29] D. Liu, W. N. E. Cheo, Y. W. Y. Lim, A. Borgna, R. Lau, and Y. Yang, "A comparative study on catalyst deactivation of nickel and cobalt incorporated MCM-41 catalysts modified by platinum in methane reforming with carbon dioxide," *Catal. Today*, vol 154, pp. 229-236, September 2010.
- [30] D. Liu, X.-Y. Quek, H. H. A. Wah, G. Zeng, Y. Li, and Y. Yang, "Carbon dioxide reforming of methane over nickel-grafted SBA-15 and MCM-41 catalysts," *Catal. Today*, vol. 148, pp. 243-250 November 2009.
- [31] X. Wu, and S. Kawi, "Rh/Ce-SBA-15: Active and stable catalyst for CO₂ reforming of ethanol to hydrogen," *Catal. Today*, vol 148, pp. 251-259, November 2009.
- [32] H. Zhang, M. Li, P. Xiao, D. Liu, C. J. Zou, "Structure and catalytic performance of Mg-SBA-15-supported nickel catalysts for CO₂ reforming of methane to syngas," *Chem. Eng. Technol.*, vol 36, pp. 1701-1707, October 2013.
- [33] L. Qian, Z. Ma, Y. Ren, H. Shi, B. Yue, S. Feng, J. Shen, and S. Xie, "Investigation of La promotion mechanism on Ni/SBA-15 catalysts in CH₄ reforming with CO₂," *Fuel*, vol 122, pp. 47-53, April 2014.
- [34] K. Jabbour, N. El Hassan, S. Casale, J. Estephane, and H. El Zakhem, "Promotional effect of Ru on the activity and stability of Co/SBA-15 catalysts in dry reforming of methane," *Int. J. Hydrogen Energy*, vol 39, pp. 7780-7787, May 2014.
- [35] B. Li, and S. Zhang, "Methane reforming with CO₂ using nickel catalysts supported on yttria-doped SBA-15 mesoporous materials via sol-gel process," *Int. J. Hydrogen Energy*, vol 38, pp. 14250-14260, November 2013.
- [36] N. Wang, X. Yu, K. Shen, W. Chu, and W. Qian, "Synthesis, characterization and catalytic performance of MgO-coated Ni/SBA-15 catalysts for methane dry reforming to syngas and hydrogen" *Int. J. Hydrogen Energy*, vol 38, pp. 9718-9731, August 2013.
- [37] M.N. Kaydouh, N. El Hassan, A. Davidson, S. Casale, H. El Zakhem, and P. Massiani, "Highly active and stable Ni/SBA-15 catalysts prepared by a "two solvents" method for dry reforming of methane," *Microporous and Mesoporous Mater.*, vol 220, pp. 99-109, January 2016.