# Catalytic Conversion of Methane at Low Temperatures: A Critical Review

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# Catalytic Conversion of Methane at Low Temperatures - A Critical Review

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## Abstract

The current study reviews the recent development in the direct conversion of methane into syngas, methanol, light olefins, and aromatic compounds. For syngas production, nickel-based catalysts are considered as a good choice. Methane conversion (84%) is achieved with nearly no coke formation when the 7% Ni-1%Au/$Al_2O_3$ catalyst is used in the steam reforming of methane (SRM), whereas for dry reforming of methane (DRM), a methane conversion of 17.9% and $CO_2$ conversion of 23.1% are found for 10%Ni/ZrOxMnOx/$SiO_2$ operated at 500$^oC$. The progress of direct conversion of methane to methanol is also summarized with an insight into its selectivity and/or conversion, which shows that in liquid-phase heterogeneous systems, high selectivity (>80%) can be achieved at 50$^oC$, but the conversion is low. The latest development of nonoxidative coupling of methane (NOCM) and oxidative coupling of methane (OCM) for the production of olefins is also reviewed. The $Mn_2O_3$–$TiO_2$–$Na_2WO_4$/$SiO_2$ catalyst is reported to show the high $C_2$ yield

(22%) and a high selectivity toward $C_2$ (62%) during the OCM at 650°C. For NOCM, 98% selectivity of ethane can be achieved when a tantalum hydride catalyst supported on silica is used. In addition, the Mo-based catalysts are the most suitable for the preparation of aromatic compounds from methane.

Keywords: Methane; catalytic conversion, low temperature, catalysis, direct-methane-to-methanol

## 1. Introduction

Methane is the main component of natural gas with a typical volumetric fraction of about 70-90% [1, 2]. To date, a significant amount of work has been conducted to convert methane into useful chemicals, for instance, syngas, methanol, light olefins, aromatic compounds, etc. Syngas is made of $H_2$ and CO, which plays an important role in chemical industry because it is the feedstock for the manufacture of a wide range of chemicals, such as ammonia, acetic acid, MTBE, methanol, olefins, gasoline, phosgene, oxo-alcohols and synthetic liquid fuels [3]. Although it can be generated using raw materials such as coal, biomass, petroleum coke and natural gas, its production using natural gas as the feedstock is the most cost-effective option [4]. However, due to the highly stable bonds between the C atom and the four H atoms, the steam reforming of methane has to be conducted at high temperatures and high steam to carbon ratios (S/C) [5-7], while the dry reforming of methane (DRM) still faces technical problems such as severe coke formation [8-10]. Therefore, the conversion of methane into syngas at low temperatures is still full of challenges [5, 11].

Methane can also be used as a feedstock for the synthesis of methanol, a type of bulk chemicals [10]. Currently, the indirect synthesis of methanol using methane is employed by industries, which requires the conversion of methane firstly into syngas. However, the production of clean syngas requires 60 to 70% of the capital investment of a methanol manufacture unit [12]. This makes the indirect methane-based production of methanol production an energy-intensive and cost-ineffective option. Therefore, direct conversion of methane to methanol (DMTM) through the oxidation of methane is highly desirable due to its better process economics and greater environmental benefits as compared with indirect methane-based methanol production. However, this route is of significant challenges, such as low selectivity and low conversion efficiency [13].

Other value-added products, such as olefin and aromatic compounds, are of great interests and can be produced using methane as the feedstock. Currently, there are two options for the direct conversion of methane into olefins, i.e., oxidative coupling of methane and non-oxidative coupling of methane [14]. Recently, the production of methane-based aromatics via the non-oxidative coupling route has received growing attention [15, 16].

In this article, the low temperature conversion of methane into syngas is reviewed with a focus on the catalysts that had been developed for the steam reforming of methane (SRM) and the dry reforming of methane (DRM) together with the measures that had been proposed for the mitigation of coke formation during these two processes. In addition, the latest development of methane-based direct and indirect synthesis of methanol was reviewed. Lastly, the challenges and opportunities in the conversion of methane into olefins via OCM and NOCM at low temperatures are reviewed. The progress of the development of catalysts for this purpose is summarized with a special focus on the Mo-based catalysts for aromatic compounds production at low temperatures.

## 2. Methane to Syngas

To date, there are seven reforming technologies for the generation of syngas using methane as the feedstock, i.e., steam reforming of methane, dry reforming of methane, auto-thermal reforming (ATR), partial oxidation (POX), reforming with a membrane, combined reforming of methane (CRM) and tri-reforming of methane (TRM). In this article, the most widely studied two reforming processes under relatively low temperature, i.e., SRM and DRM, are reviewed.

## 2.1 Steam Reforming of Methane

The SRM process is the commonly adopted route for $H_2$ production [11], which involves two major reactions:

$CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $\Delta H^o_{298}$= 206.1 kJ/mol (R1)

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H^o_{298}$= -41.2 kJ/mol (R2)

Due to the high endothermicity of R1, the industrial SRM process is conducted at high temperatures (800-1100 ºC) in the presence of metal-based catalysts [6, 7, 17], which makes the process energy-intensive. The other problems associated with the high operating temperature include metal sintering, coke formation due to thermal cracking of methane, etc., which subsequently deteriorate activity of the catalysts.

Operating under low-temperature conditions offers many advantages including lower energy consumption. However, it also leads to a low $CH_4$ conversion owing to the thermodynamic limitations. The thermodynamic equilibrium study on the influence of S/C ratio and pressure in the temperature range of 400 to 700 ºC showed that both $CH_4$ conversion and $H_2$ yield increase when S/C ratio increases [18]. When the temperature was 550 ºC, the $CH_4$ conversion and $H_2$ content reached 60% and 70%, respectively when the S/C ratio was kept at 3. The $CH_4$ conversion reached 97.1% at 700 ºC and S/C=3. Besides, it is found that high pressure suppressed steam reforming of methane [18]. All these findings were validated by Roh et al. [19], which showed that SRM at low temperatures is thermodynamically feasible. However, these calculations did not consider carbon formation and how it affects the SRM at low temperatures. To promote $H_2$ yield, studies were carried out on the use of a Pd membrane to separate $H_2$ from the product stream. It is demonstrated that the equilibrium conversion of methane of such an innovative design was improved, which demonstrates a practical approach to address the low methane conversion efficiency for the low-temperature SRM[2].

Normally, catalysts play critical roles in determining methane conversion, hydrogen production and coke formation. Catalysts that are of high methane conversion, good stability and high coke resistivity under relatively low temperatures (<550 ºC) are highly desirable [11].

Generally, the Group VIII metals can be used to catalyse most of the SRM reactions [20]. Among these metals, nickel is usually regarded as the most suitable active component to be used in SRM catalyst, while the other metals have their specific problems. For instance, iron can be quickly oxidized; catalytic performance of cobalt cannot be sustained when steam exists in the gas phase; noble metals (Pt, Rh, Ir, Ru and Pd) are too expensive for commercial applications [20]. However, the formation of coke is the major technical issue when the Ni-based catalyst is employed in SRM, which leads to the deactivation of catalyst and subsequently a short catalyst lifespan [11]. In some research, noble metals (such as Ag and Au) were added to mitigate coke formation [21, 22]. Materials such as α-alumina, magnesia, calcium aluminate and magnesium aluminate are commonly used as the support of catalysts [8, 23-28].

### 2.1.1 Nickel-Based Catalyst

The comparison between theoretical and experimental data using a modified Ni-based catalyst ($Ni/Ce\text{-}ZrO_2/\theta\text{-}Al_2O_3$) is shown in Figure 1 (S/C=2.98, GHSV=5010 ml $CH_4/(g_{cat}$ h), pressure = 1 atm) [18]. Such a Ni-based catalyst is of high catalytic performance at low temperatures. It is reported that the increase in reaction temperature resulted in the formation of more CO but a lower $H_2/CO$ ratio. It agrees with the fact that water gas shift reaction (WGSR) is exothermic and is therefore unfavored at high temperatures. Furthermore, it is found that the catalyst exhibited an excellent stability for 200 h, during which the $CH_4$ conversion, CO selectivity and $H_2$ yield had very little change.

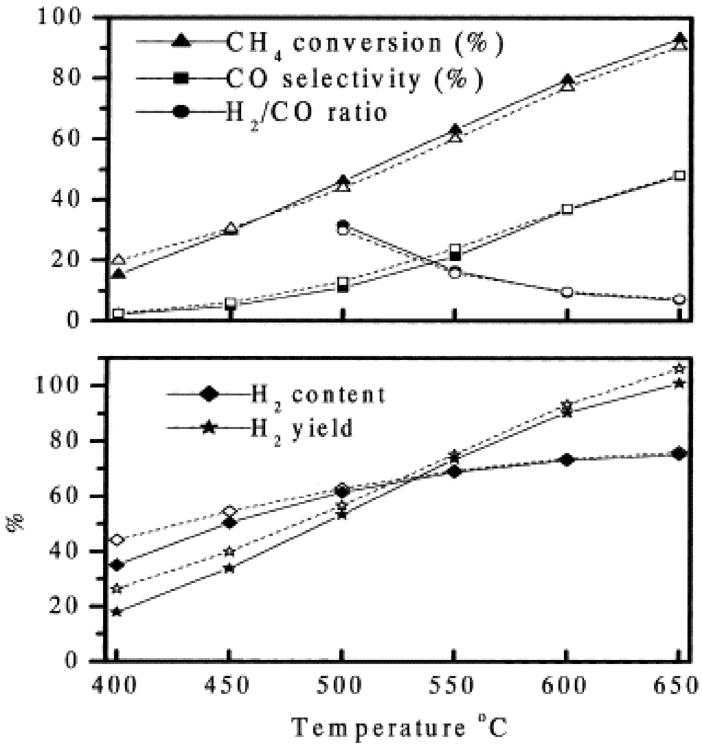


**Figure 1 Impact of temperature on catalytic performance. Dash line: thermodynamic data. Solid line: experimental data. Copyright 2002, Journal of Power Sources [18].**

Generally, nickel is less active compared with noble metals and is more easily to deactivate due to the formation of coke [29]. However, promoters and support also play important roles and affect catalytic performance of the catalyst at low temperatures. It was reported that for low-temperature SRM, some supports improve the stability of the catalyst and indirectly enhance the activity of the catalysts via the improved metal dispersion on the support [6, 18, 30]. Table 1 summarizes Ni-based catalysts for SRM at low temperatures (<550ºC). However, it should be noted that the conversion values of Reference 30 [30] cannot be compared to the others because the methane conversions were calculated based on methane concentration variation, whereas the others listed in the table were based on methane flows.

To date, the influence of support (such as $ZrO_2$, $SiO_2$, $Al_2O_3$, $ZnAl_2O_4$ and $MgAl_2O_4$) on the catalytic performance of Ni-based catalysts has been investigated by many researchers

[6, 31]. Table 1 shows the methane conversion of $Ni/ZrO_2$, $Ni/Al_2O_3$ and $Ni/SiO_2$ at 0.5 h on the stream [6]. The catalytic performance of the 20 wt.% $Ni/SiO_2$ was the highest among these three catalysts initially but decreased gradually and completely deactivated at 4 h on the stream. The mass spectrometer detection for hydrogen showed it decreased after 2 h on the stream and almost became zero at 4 h on the stream. The deactivation of $Ni/SiO_2$ was ascribed to the phenomenon that nickel particles were gradually oxidized by steam. The initial activity of $Ni/Al_2O_3$ was observed to decrease, which was induced probably by the formation of spinel $NiAl_2O_4$, which reduces the active sites on the surface. The $Ni/ZrO_2$ was found to be stable in the test with little coke formed on the catalyst. At 4h on the stream, the methane conversion over the $Ni/ZrO_2$ increased to 25.5%, which was the highest value among the three supports studied. Furthermore, the investigation on the influence of different nickel loadings demonstrated that the catalytic performance increased with nickel content. The 5 wt.% of nickel on $ZrO_2$ support showed a higher activity than the 20 wt.% of nickel on $Al_2O_3$, which also demonstrated the impacts of support on the catalytic performance. Besides, the order of catalytic performance at steady state was found to be $Ni/MgAl_2O_4 \approx Ni/ZnAl_2O_4 > Ni/Al_2O_3 > Ni/SiO_2$ [31]. The $Ni/SiO_2$ lost its activity after about 10 mins on the stream, while $Ni/ZnAl_2O_4$ showed the least coke formation (1.5 wt.%) after 2 h on the stream.

To mitigate the formation of coke on the Ni-based catalysts, other species such as Ce [32-34], La [30, 35], Mn [36, 37], Co [36, 38] have been used as promoters. Generally, $CeO_2$ is a good option since it possesses required properties, such as good mechanical resistance, excellent thermal stability and sufficient oxygen storage capacity. The high oxygen storage capacity is vital in the consumption of coke once it is formed at the active sites [34]. It is found that the presence of more oxygen vacant sites in $CeO_2$ promotes the mobility of atomic oxygen from steam and/or $CO_2$, which facilitates the oxidation of coke deposited on the surface of the catalyst [32-34]. It was reported [30] that the addition of 6 wt.% ceria to the $Ni/Al_2O_3$ catalyst contributed to a 10 wt.% increase in $CH_4$ conversion at 550 ºC, while no significant change in conversion was observed when 6 wt.% of $La_2O_3$ were added ( as shown in Table 1). Graphitic carbon formed after $Ni/Al_2O_3$ and $Ni/La_2O_3$-$Al_2O_3$ catalysts had been 48 h on the stream, which subsequently resulted in partial deactivation of the catalysts. In addition, porous amorphous carbon was formed on the surface of the $Ni/CeO_2-Al_2O_3$ but activity of the catalyst was not influenced after 48 h on the stream.

**Table 1 SRM at low temperatures over nickel-based catalysts at atmospheric pressure in the fixed bed continuous flow reactor**

| Catalyst | T (ºC) | S/C ratio | WHSV ($mL/g_{cat}h$) | Methane conversion/ conversion rate | Coke formation (%) | Ref. |
|---|---|---|---|---|---|---|
| 20%$Ni/Al_2O_3$ | 500 | 2.00 | 15000 | 15.0 % | N/A | 6 |
| 20%$Ni/SiO_2$ | 500 | 2.00 | 15000 | 21.8 % | N/A | 6 |
| 20%$Ni/ZrO_2$ | 500 | 2.00 | 15000 | 14.1 % | N/A | 6 |
| 8.4%$Ni/SiO_2$ | 500 | 2.00 | 18000 | 0.02 mol $g_{Ni}^{-1}h^{-1}$ | 0.5 | 31 |
| 8%Ni/ $-Al_2O_3$ | 500 | 2.00 | 18000 | 1.10 mol $g_{Ni}^{-1}h^{-1}$ | 0.1 | 31 |
| 7%$Ni/ZnAl_2O_4$ | 500 | 2.00 | 18000 | 2.88 mol $g_{Ni}^{-1}h^{-1}$ | 1.5 | 31 |
| 8.6%$Ni/MgAl_2O_4$ | 500 | 2.00 | 18000 | 0.69 mol $g_{Ni}^{-1}h^{-1}$ | 3.2 | 31 |
| 7%$Ni/Al_2O_3$ | 550 | 4.00 | 3000 | 75.0 % | 3.16 | 30 |
| 7%Ni-6%$CeO_2/Al_2O_3$ | 550 | 4.00 | 3000 | 82.0 % | 13.81 | 30 |
| 7%Ni-6%$La_2O_3/Al_2O_3$ | 550 | 4.00 | 3000 | 74.2 % | 16.41 | 30 |
| 10%$Ni/Ce_{0.15}Zr_{0.85}O_2$ | 500 | 2.00 | 54000 | 10.0 % | N/A | 39 |
| 12%$Ni/Ce-ZrO_2/\theta-Al_2O_3$ | 500 | 2.98 | 20000 | 45.0 % | N/A | 18 |

In addition, apart from the promoters and the supports that influence the performance of Ni-based catalysts, the size of Ni clusters also significantly affects the coke resistance even at a temperature as high as 700 ºC [40]. It is reported that smaller particle size leads to less severe of coke formation [41-45]. Recently, experimental and theoretical studies of the effects of Ni cluster size (8.3 - 12 nm) on catalytic activity at low temperatures (500-575ºC) showed that the activity improved with the decrease of particle size. It is concluded that reducing Ni particles (<6 nm) could be a promising method to improve SRM efficiency [46].

Although all the SRM catalysts were tested under different experimental conditions in terms of space velocity, S/C ratios, metal loading, it is generally the case that the use of $ZrO_2$ and $CeO_2$ as promotors improved the performance of Ni-based catalysts in the low-temperature SRM through the mitigation of coke formation and the increase of the catalytic activity.

### 2.1.2 Bimetallic Catalysts

Although noble metals are expensive, there are still extensive studies being carried out owing to their high performance and good resistivity to coke formation. To date, many bimetallic catalysts that coupling nickel with noble metals have been developed, aiming at reducing the cost and improving the catalytic performance [11].

The doping of Rh in Ni/ $\gamma$-$Al_2O_3$ was found to improve the catalytic activity by the enhanced dispersion of metal on the support and therefore raised the quantity of active sites on the surface [47]. According to their research, at 525ºC, the bimetallic catalyst with the addition of 0.2 wt.% of Rh reached nearly 26% increase in conversion than the primary catalyst (as shown in Table 2). The addition of Au to the Ni/$MgAl_2O_4$ catalyst was found preventing the formation of coke in the steam reforming of n-butane at 550 ºC [48]. In this research, a superficial alloy was observed in the Ni-Au binary system, which blocks the high energy steps and the edge sites mitigated coke formation [48]. It is also found that the incorporation of Au suppresses the coke formation on the catalyst, while the doping of Au in Ni/$Al_2O_3$ led to a 10% improvement and the significant mitigation of carbon formation as compared with the non-incorporated catalyst at 550 ºC [30]. The doping of 0.01-1.0 wt.% of Pt on the 15% Ni/$MgAl_2O_4$ catalyst showed that a synergetic effect only occurred with a lower loading of Pt at 600 ºC and 1 bar [49]. The optimum Pt loading level was reported as 0.1 wt.%, which enhances catalytic performance and dispersion of metal. The higher Pt addition led to the agglomeration of the active metals, which subsequently result in the loss of the catalyst stability as well as activity.

Generally, most studies indicated that the reduced coke formation could be achieved by the interaction of the noble metals, such as Rh, Au and Pt, with Ni due to a higher barrier being created for Ni sintering [50]. The better catalytic performance of noble metal doped Ni-based catalyst at low temperatures (<550 ºC) is attributed to the increased number of active sites and the improved metal dispersion on the surface [11]. However, the high cost of noble metal can be compensated by the low loading level of these noble metals as promoters. It can be concluded that in order to apply this type of bimetallic catalyst in commercial scale, a trade-off among the improved catalyst activity, reduced coke deposition and increased cost is necessary.

**Table 2 Bimetallic catalysts for methane to syngas reaction under ambient pressure in the fixed bed flow reactor**

| Catalyst | Reaction Temperature (ºC) | WHSV (mL/gcath) | S/C ratio | $CH_4$ conversion (%) | Coke formation (%) | Ref. |
|---|---|---|---|---|---|---|
| **7% Ni/$Al_2O_3$** | 550 | 3000 | 2 | 75 | 3.16 | 30 |
| **7% Ni-1% Au/$Al_2O_3$** | 550 | 3000 | 2 | 84 | 0 | 30 |
| **10.2% Ni/$Al_2O_3$** | 525 | N/A | 3 | 17.8 | N/A | 47 |
| **10.2%Ni-0.05% Rh/$Al_2O_3$** | 525 | N/A | 3 | 21.8 | N/A | 47 |
| **10.2%Ni-0.2% Ru/$Al_2O_3$** | 525 | N/A | 3 | 30.1 | N/A | 47 |
| **8.8% Ni/$MgAl_2O_4$** | 550 | 3300000 | 1 | 9 | 121.1* | 48 |
| **8.8%Ni-0.1%Au/$MgAl_2O_4$** | 550 | 3300000 | 1 | 6.5 | 108.2* | 48 |

*: Cumulative amount of coke deposition after 500 min SRM.

## 2.2 Dry Reforming of Methane

DRM uses $CO_2$ as one of the reactants and is the route with significant potential in generating syngas using $CO_2$, a greenhouse gas that is abundant and cheap, as a feedstock. This approach is therefore an environmentally friendly option and has attracted significant attention [51, 52]. The process can be described by following reaction,

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^o 298 = 248 \text{ kJ/mol} \qquad \text{(R3)}$$

For DRM, the CO to $H_2$ molar ratio is usually around 1. The gas product can be further applied in the F-T synthesis to produce long-chain hydrocarbons or oxygenate chemicals [53, 54]. Despite the obvious economic and environmental benefits, the DRM process is still not fully commercialized due to various challenges, which include the coke formation and the rapid sintering of the catalyst leading to the rapid deactivation of catalytic performance [9, 55, 56].

Generally, the DRM reaction is slightly more endothermic than SRM reaction and the coke formation is more easily to occur during the DRM than the SRM. Therefore, the DRM is often performed under at a temperature higher than >800 ºC [10, 57-60], and very little research on the DRM has been conducted at low temperatures (<550 ºC). However, the high-temperature DRM not only has the drawback of high cost but also problems such as catalyst sintering and coke formation [61-65], it is therefore highly desirable to develop novel catalysts to enable the DRM process to occur at low temperature conditions.

Thermodynamic modelling demonstrated that theoretically $H_2$ could be produced at about 100 ºC and CO at about 300 ºC by the low-temperature activation of $CH_4$ and $CO_2$[66], which requires highly efficient novel catalysts. To date, much research has been conducted to show the effects of noble metal-based catalysts, such as Pt [67, 68], Rh [69-71] and Ir [72], at low temperatures (around 450 ºC) owing to their better propensity in coke resistivity and catalytic performance. However, the commercialization of these precious metal-based catalysts is hindered by the high cost associated with these noble metals. Many researchers shifted their study to focus on nickel-based catalysts by choosing different support and doping different promoters to enhance its catalytic performance [67, 73-76]. Table 3 summarizes the recently reported Ni-based catalysts at temperatures below 500 ºC. It can be seen that the lowest operating temperature was 400 ºC, but poorer $CH_4$ and $CO_2$ conversions were achieved compared to those experiments carried out at high temperatures, under which both $CH_4$ and $CO_2$ conversion were greater than 80% [77].

**Table 3 Performance of Ni-based catalysts in the DRM under ambient pressure in the fixed bed flow reactor**

| Catalysts | GHSV $h^{-1}$ | T (ºC) | Conversion (%) | | Yield(%) | | $H_2/CO$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | $CH_4$ | $CO_2$ | $H_2$ | CO | | |
| 1%Ni-$SiO_2$ | 180,000 | 500 | 7 | 13 | N/A | N/A | 0.4-0.15 | 73 |
| 10%Ni/$ZrO_x$ $MnO_x/SiO_2$ | 24,000 | 500 | 17.9 | 23.1 | 9.2 | 14.5 | 0.64 | 74 |
| 10%Ni/ZrOx/ $MnO_x/SiO_2$ | 24,000 | 400 | 2.2 | 4.9 | 1.4 | 2.3 | 0.56 | 74 |
| 5%Ni-CaO/$La_2O_3$-$ZrO_2$ | 5882 | 450 | 9.8 | 12.9 | 5.8 | 9.9 | 0.58 | 74, 75 |
| 10%Ni-Zr/$SiO_2$ | 24,000 | 400 | 2 | 2 | 0.8 | 1.2 | 0.67 | 76 |
| 10%Ni-Zr/$SiO_2$ | 24,000 | 450 | 6.5 | 9.1 | 0.2 | 0.3 | 0.61 | 76 |
| 0.5Pt/8%Ni/Mg/Ce0.6Zr0.4$O_2$ | 68000 | 454 | 10 | 10 | N/A | N/A | 0.23 | 67 |
| 5%Ni/ɣ-$Al_2O_3$ | 18000 | 500 | 12 | 15 | N/A | N/A | N/A | 78 |
| 11%Ni-2.9%Sc/$Al_2O_3$ | N/A | 450 | 10 | 12 | N/A | N/A | N/A | 79 |
| 1.2%Ni/$TiO_2$ | N/A | 450 | 3.2 | 5.9 | N/A | N/A | N/A | 80 |

$Al_2O_3$ is the most extensively studied support for a DRM catalyst, which has been commercially used in a wide range of applications [81]. It is demonstrated that $Al_2O_3$ support prepared via a novel templated synthesis method [82] presented a higher $CH_4$ conversion due to the higher basicity and surface area than the commercial one. Although the DRM tests were conducted at 800 ºC, it can be concluded that the performance of a catalyst could be altered by adjusting properties of the support with a novel preparation method.

Many researchers have studied the interactions between nickel and other supports, such as MgO, $TiO_2$ and $SiO_2$, and showed that the active components interact with the support and influence metal dispersion, electronic effects and nickel particle size [80, 83], which subsequently affect in the catalytic performance of the catalysts. It is showed that there are strong interactions existing between Ni particles and the $TiO_2$, which increased the electron density of the metal crystallites and efficiently activated the C-H bond in $CH_4$ at 450°C [80]. It is also suggested that a solid solution of NiO-MgO was formed in the Ni/MgO catalyst, the Ni-O bond directly enhanced the stability of Ni-Ni bonds because of the exceptional strength of the strong electron donor. Thus, the higher surface stability prevents nickel surface reconstruction, prohibiting carbon diffusion and reducing carbon formation. Their stability results showed that this catalyst could be stable up to 44 h on stream. On the contrary, the activity of Ni/MgO is the lowest among these three supports. When Ni/$SiO_2$ was used, some filamentous carbon was formed as a result of the weaker interaction between the metal and the support than the other two supports [80].

Investigation of the impacts of morphological properties of $La_2O_3$-$ZrO_2$ on the stability of catalysts showed that mesoporous Ni/$La_2O_3$-$ZrO_2$ possessed the higher stability than microporous and macroporous structures because of confinement effect of the pores [84]. Generally speaking, the addition of promoters (i.e. La, Ce and $Ce_{0.75}Zr_{0.25}O_2$) [83] can enhance the performance of the Ni-based catalysts by improving the reduction of nickel oxide and the basic site [85-87].

The above studies indicated that the nickel-support interactions influence the activity of the catalyst in the DRM process. Generally, the strong interactions between the metal and the support can enhance catalytic activity and resistivity to coke formation. Besides, the mesoporous structure of the support generally leads to an enhancement in the catalyst stability at low-temperature DRM.

## 3. Direct Methane to Methanol

Theoretically, the DMTM reaction is spontaneous at room temperature [88]. Nonetheless, the stability of methanol is lower than the other oxidation products. Also, because of the stronger C-H bond in methane, its reactivity is lower than methanol (the dissociation energy of C-H bond is 440 KJ $mol^{-1}$ for methane and 393 kJ $mol^{-1}$ for methanol). Table 4 shows how temperature affects the direct oxidation of methane to different products [88]. The Gibbs free energy value shows that methanol production from methane is favoured at lower temperatures. However, more stable products such as CO and $CO_2$ are easier to be produced, which results in the difficulty in achieving a high methanol selectivity in the one-step process [13].

**Table 4 Gibbs free energy of the oxidation of methane via different routes [88].**

| Reaction | $\Delta\mathbf{G}$ values | | | |
|---|---|---|---|---|
| | 298K | 650K | 800K | 1000K |
| $CH_4 + 0.5O_2 \rightarrow CH_3OH$ | -111 | -93 | -86 | -76 |
| $CH_4 + O_2 \rightarrow HCHO + H_2O$ | -288 | -294 | -295 | -298 |
| $CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$ | -544 | -573 | -582 | -603 |
| $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ | -801 | -800 | -799 | -798 |

Note: more negative value is energetically more favourable in reaction.

Theoretically, the highest conversion that can be achieved at 25 ºC is near 33%, which corresponds to a maximum selectivity of around 5%, much lower than that of the conventional indirect process, which is ca. 70 to 75% [89].

To date, worldwide researchers have developed catalyst-free, solid-catalysed and aqueous catalyzed oxidation processes for the direct methanol production over the past century. In this review, the focus is on the catalytic processes at relatively low temperatures, i.e., below 550 ºC. There are numerous articles on transition metal oxides-based catalysts for the direct oxidation of methane. Among these, molybdenum, copper-zinc and iron compounds-based catalysts are among the ones being most extensively studied [10, 13].

### 3.1 Molybdenum-based Catalysts

One of the earliest and the most impressive reports about molybdenum-based catalyst in the DMTM application was published in 1971 by Dowden and Walker [90]. A series of molybdenum catalysts with and without a support at 50 bar was investigated in a temperature range between 439 and 493 ºC. It is found that the most active catalyst was $Fe_2O_3$ ($MoO_3$), resulting in the formation of 869 g methanol/(kg cat h) [90]. The selectivity of methanol was 65%, whereas methane conversion was as low as 2.1%. However, it is also found that the methanol selectivity could be raised efficiently by adding steam to the feed gas [91].

The study on the $ZrO_2$ and La-Co-O supported $MoO_3$ catalysts using oxygen as an oxidant at 400 and 420 ºC, respectively, showed that only a trace amount of methanol was found when $MoO_3/ZrO_2$ catalyst was used [92]. Different amounts of $MoO_3$ were tried on the La-Co-O support and showed that the best catalytic performance was achieved when 7 wt.% $MoO_3$/La-Co-O was used, which showed a methanol selectivity of 60% and a methane conversion of 11.2%.

However, gaseous hydroxide species form when water exists in the reaction system because of the high volatility of molybdenum. Hence, it is difficult to apply this type of catalyst into commercial applications [93]. Therefore, very limited studies on molybdenum catalyst for DMTM have been reported in recent years.

### 3.2 Iron and Copper-based Catalyst

In the late 20th century and early 21st century,  there is increasing attention being paid to study iron and copper-based catalysts, which is to replace molybdenum-based catalyst in the DMTM [1]. This change was originated from the discovery of zeolites (e.g. mordenite and ZSM-5), stabilize binuclear iron [94, 95] as well as the methane monooxygenase (MMO) enzymes that exist in methanotrophic bacteria. The catalytic activity of Fe/Cu-based catalysts for the DMTM is listed in Table 5.

**Table 5 Comparison of Fe/Cu-based catalysts in the partial oxidation of methane to methanol.**

| Catalyst | Reaction temperature (ºC) | Pressure (bar) | $CH_4$ conversion (%) | $CH_3OH$ selectivity (%) | Ref. |
|---|---|---|---|---|---|
| Fe-HZSM-5 | 630 | 1 | 11.22 | 16.51 | [96] |
| Fe-NaZSM-5 | 390 | 1 | 0.06 | 74.37 | [96] |
| Cu-ZSM-5 | 50 | 30.5 | 0.3 | 83 | [97] |
| Cu-Fe/ZSM-5 | 50 | 30.5 | 0.7 | 85 | [97] |
| Fe-MFI[a] | 50 | 30 | N/A | 85 | [98] |
| Cu-MOR[b] | 400 | 7 | N/A | 97 | [99] |
| Cu-MOR[b] | 200 | 1 | N/A | 80[c] | [82] |
| Cu-NU-1000 | 150 | 1 | N/A | 45-61[c] | [100] |

a: heterogeneous liquid phase system

b: Cu-MOR: Mordenite structured copper-exchanged zeolites

c: sum of methanol and dimethyl ether

Normally, the DMTM route via gas-solid phase heterogeneous catalytic process requires a high temperature (>473 K) due to the strong chemical stability of methane, and $CO_2$ is likely to be generated. The Fe-ZSM-5 together with Fe-NaZSM-5 was used for the conversion of methane at ambient pressure and at a temperature below 650 ºC. It is showed that the catalytic performance of these catalysts increased with the increase in iron loading level [96]. However, the over oxidation to form $CO_2$ was unavoidable, hence reducing the methanol selectivity. For instance, the highest methanol selectivity (74.37%) was obtained at 390 ºC by using Fe-NaZSM-5 with a Si/Fe ratio of 45, whereas the conversion is only 0.06%. On the contrary, the higher conversion was achieved with Fe-HZSM-5 catalyst, while the corresponding methanol selectivity was lower than 16.51%.

In the liquid-phase homogeneous catalytic process, a high methane conversion together with a high methanol selectivity were achieved, but highly concentrated acids have to be employed [98]. The liquid system with heterogeneous catalyst often used environmentally friendly oxidants, such as $H_2O_2$ and $O_2$ [98]. Study on a series of iron and copper-based catalysts in an aqueous system with hydrogen peroxide as the oxidizing agent under mild conditions (50-70 ºC, 30.5 bar) showed that a low-energy pathway for methane oxidation could be realized by the interaction between the catalyst and hydrogen peroxide, whereas hydrogen peroxide as a terminal oxidant inhibited over-oxidation to formic acid and $CO_2$[97]. The optimal methanol selectivity was found to be 96% with a conversion of 10% by adopting appropriate reaction conditions. The low methane conversion was believed to be associated with the low solubility of methane in the aqueous system [98]. Most recently, research on an organic solvent sulfolane, a stable polar solvent, showed that the increase in the methane solubility in $H_2O_2$ aqueous system in the presence of the Fe-MFI zeolite catalyst resulted in the methane selectivity being raised to a maximum of 85% and led to a high methane conversion [98].

It is also stated that there are two types of MMO present in bacteria, i.e., particulate MMO (pMMO) and soluble MMO (sMMO), which can transform methane selectively into methanol at ambient temperature [101]. It is generally accepted that the diiron sites (Figure 2) in the sMMO enzyme are the active sites for the methane oxidation into methanol [102, 103]. A dinuclear $Fe^{IV}$ cluster is discovered in the intermediates of the reaction process, which was a bis-µ-oxo diamond core structure [104]. Conversely, such precise evidence is still missing about the structure of and mechanism of pMMO. Most researchers have considered that its catalytic site is trinuclear copper cluster [105-107], which effectively catalyzes the oxygen insertion into the C-H bond at a high rate of 1 $s^{-1}$ turnover frequency [108].

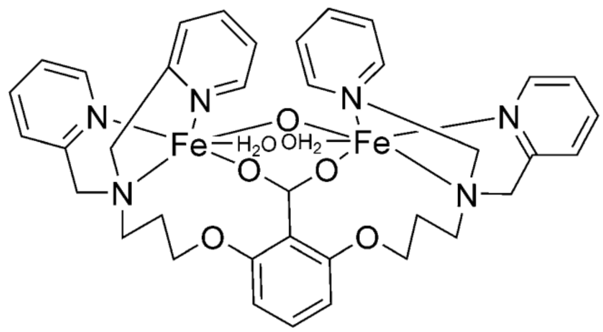


Figure 2 Proposed diiron center in sMMO [1]. Copyright 2017, Angewandte Chemie International Edition.

Subsequently, a number of biomimetic catalysts inspired by MMO enzymes emerged. Some tricopper cluster complexes by mimicking pMMO have also been developed and studied [105], which can effectively oxidate hydrocarbons (activate C-H bond) under ambient temperature and pressure. These researchers reported a tricopper complex $[Cu^{I}Cu^{I}Cu^{I}(7\text{-}N\text{-}Etppz)]^{1+}$ where (7-N-Etppz) refers to the ligand 3,3'-(1,4-diazepane-1,4- diyl)bis[1-(4-ethylpiperazine-1-yl)propan-2-ol] to successfully convert methane to methanol in acetonitrile. They also pointed out that the spent catalyst was recovered by the addition of an appropriate amount of hydrogen peroxide after the oxygen atom was transferred to methane. Compared to a lot of the previous methane catalytic oxidation systems [109-111], the biomimetic tricopper complex takes the advantage of low temperature required.

In addition, research has also been carried out on biomimic area and showed that the selective transformation of methane into methanol can be achieved on the single-site trinuclear copper-oxygen cluster in mordenite [82], in which the mordenite microporours structure stabilizes the trinuclear copper-oxo clusters [82].

Although the solid-based catalysts have been widely investigated by many researchers, it is still challenging to simultaneously achieve high methanol selectivity and high methane conversion. For instance, the high selectivity of methanol (~74%) was achieved with a very low methane conversion 0.06%, while a higher conversion (~32%) corresponds to a poor methanol selectivity (~11%). It is concluded that the liquid-phase heterogeneous catalysts system is promising for the low-temperature DMTM process. Besides, developing catalysts mimicking pMMO enzymes is an effective strategy to enhance methanol selectivity.

## 4. Direct Conversion of Methane to Light Olefins

Although the activation of methane at low temperatures faces various challenges, it is still necessary to develop processes that enable the yield of methane-derived value-added chemicals using methane as the feeds, for instance, hydrocarbon-based chemicals, via the direct conversion of methane [112]. Generally, there are two major routes for the direct conversion of methane to light olefins, i.e., OCM and NOCM.

### 4.1 oxidative coupling of methane

The OCM is an exothermic reaction when the oxidant is added to overcome the thermodynamic restrictions and make the reaction exothermic. The general reaction is expressed as $CH_4 + ½ O_2$   $1/2\ C_2H_4 + H_2O$. $\Delta H^o_{298}$= -175 kJ/mol. Nevertheless, a high temperature is still required to activate the high bond energy of C-H in methane. Usually, a relatively high temperature (700 - 850 ºC) is necessary for the OCM, while no $C_2$ hydrocarbon can be detected below the temperature of 550-600 ºC [113]. Apart from that, the separation of by-product should be carried out under low temperature (below 100 ºC). Therefore, the energy consumption of value-added $C_2$ hydrocarbon collection should be considered and be reduced. In the whole process of producing $C_2$, the catalysts become the main factor to influence methane conversion rate and $C_2$ selectivity. Consensually, over 30% of $C_2$ yield could meet the industrial requirement and development. Table 6 summarized various catalysts studied by many other researchers.

**Table 6 Catalytic performance for OCM**

| **Catalyst** | | **Temp. (℃)** | **Pressure** | **Space velocity** | **$X_{CH4}$ (%)** | **$S_{C2}$ (%)** | **$Y_{C2}$ (%)** | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| **Active metal** | Supporting materials | | Mpa | mL/(g.h) | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **2%Mn-$Na_2WO_4$** | n-$SiO_2$ | 800 | 0.1 | N/A | 28.5 | 73.3 | 18.5 | 114 |
| | | | 0.1 | 36000 | 36.8 | 64.9 | 23.0 | 115 |
| | | 800 (Chemical looping) | 0.1 | N/A | 18.0 | 89.0 | 17.0 | 116 |
| **1%Mn-8%Na-3.1%W** | $SiO_2$ | 800 | NA | N/A | 30.2 | 63.4 | 19.1 | 117 |
| **Li- $TbO_x$** | n-MgO | 700 | 0.1 | N/A | 24.9 | 63.6 | 14.5 | 118 |
| **Li- $PrO_y$** | n-MgO | 700 | 0.1 | N/A | 25.6 | 60.6 | 12.9 | |
| **Na- $Sm_2O_3$** | n-MgO | 700 | 0.1 | N/A | 25.5 | 57.8 | 13.7 | |
| **Na** | Cs/Mg/Cl | 880 | 0.1 | N/A | 30.0 | 82.0 | 20.0 | 119 |
| **Fe** | $SiO_2$ | 1090 | 0.1 | 21400 | 48.1 | 20.0 | 9.0 | 120 |
| **Pt** | $CeO_2$ | 702 | 0.1 | 6000 | 14.4 | 74.6 | N/A | 121 |

$X_{CH4}$: Conversion of methane

$S_{C2}$: $C_2$ selectivity

$Y_{C2}$: $C_2$ yield

The study of the OCM into $C_2$ hydrocarbon can be dated back to 1980s[122, 123]. Since then, extensive efforts have been made in this area, resulting in the development of a series of catalysts for the OCM, which include Mn-$Na_2WO_4$/$SiO_2$, $ABO_3$ type perovskite oxide, Li/MgO, and $Re_xO_y$ (Re: Rare earth). Among these catalysts, the Mn-$Na_2WO_4$/$SiO_2$ demonstrated a $C_2$ yield of 18–25% under ambient reaction conditions and showed excellent stability for an extended period (>450 h) [114], while the Li/MgO showed a selectivity of $C_2$ around 20% and a yield reached the highest at relatively high temperatures (780 ºC) [124]. However, under a high-temperature condition, the active sites are unstable and can be damaged leading to the loss of lithium.

Another series of promising catalysts for OCM is rare earth metal oxides. It is reported that the RexOy displayed a much-improved reaction performance at low-temperature region (<750 ºC) and with a $C_2$ yield of around 15%. Lately, a number of $Re_xO_y$ catalysts (Re=Sm, Tb, Pr and Ce) modified by adding Li, Na, Mg and/or Ca metals have been tried for the OCM [118]. The doping of alkali and alkaline earth metal alters basicity property of the catalysts to influence the stability of the catalysts, the $C_2$ selectivity and the catalytic activity. It was reported that catalysts with more basic sites tend to become more selective towards $C_2$ formation [119]. It is also stated that Li-TbOx/n-MgO was superior to all the others in catalytic activity and $C_2$ selectivity at temperatures above 600°C. Despite this, the low OCM performance of the Li-TbOx/n-MgO below 600°C can be attributed to the problems associated with the regeneration of active oxygen sites on the bare MgO under low temperature [118]. In contrast, at lower temperatures, Ca-$CeO_2$/n-MgO, Ca-$Sm_2O_3$/n-MgO, and the undoped $Sm_2O_3$/n-MgO catalysts obtained more $C_2$ yields than the Li- and Na-doped catalysts, because the activity sites of latter catalyst are not fully activated at low temperature [118].

Most recently, it is found that $MnTiO_3$ showed high activity at low-temperature OCM, which resulted in a methane conversion of 20% and a $C_2$ selectivity of 70%[125]. As for the enhanced catalytic performance, it was found that during the OCM reaction, $Mn_2O_3$ and $TiO_2$ were converted to $MnTiO_3$ (achieved during the initial OCM reaction at 800°C), which subsequently led to an enhanced OCM performance (CH4 conversion is 22%, $C_2$ selectivity is 62%) at 650°C.[126]

In summary, as a promising process for methane conversion, the OCM still faces the challenge of low selectivity (<50 %) toward value-added chemicals (ethane/ethylene), which leads to the reduced process economics and therefore hinders its industrial applications [14]. Thus, there is a need for the development of novel catalysts/processes to achieve simultaneously high carbon selectivity and high conversion to yield $C_2$ hydrocarbons from methane in non-oxidative conditions.

### 4.2 Nonoxidative coupling of methane

Since the 1990s, numerous efforts have been made to produce hydrocarbons through the NOCM, the aim of which is to enhance carbon atom economy [127, 128]. It has been elucidated that hydrogen and $C_2H_6$ can be immediately yielded when $CH_4$ was fed continuously to a 6wt% Pt/$SiO_2$ catalyst at 250°C [129]. However, these two products disappeared when time-on-stream exceeds 8 min, which is caused by the accumulation of surface carbonaceous residue. This shows that the activation temperature of methane in NOCM can be lower than the temperature commonly adopted at OCM processes (>700°C). It is also reported [130] that a selectivity of 98% ethane was achieved at temperatures below 500°C over tantalum hydride supported by silica although the methane conversion was lower than 0.5%. It is stated that 48% methane conversion over a Fe/SiO2 catalyst was achieved via the NOCM at 950°C leading to the production of ethylene, naphthalene and benzene with a selectivity of 53 %, 25% and 22%, respectively [131]. Similar products over a Pt-Sn catalyst at 700°C were produced, whereas the methane conversion was lower than 0.3% [132]. These demonstrate that a higher temperature favours a higher methane conversion during the NOCM.

## 5. Direct Aromatization of Methane

Direct aromatization of methane is direct, a non-oxidative pathway to produce higher hydrocarbons. It is considered as an endothermic reaction with a quite high reaction temperature (800-1000$^o$C) required in most reports [139,140]. This is an energy-intensive process and as far as our knowledge, the lowest temperature used in this reaction is around 650$^o$C. Here in this section, catalytic reactions performed under relatively low temperatures are reviewed.

Thermodynamically, the conversion of methane into aromatics is more favourable than into olefins. The dehydroaromatization of methane (DAM) was firstly conducted in a fixed-bed reactor and lead to the yield of benzene and $H_2$ over a Mo/HZSM-5 zeolite supported catalyst [133], which outperformed some other catalysts in the selective formation of benzene under similar conditions. The main reason can be attributed to the framework of zeolite, whose pore and channel containing many active sites, and intrinsic properties of pores (size and shape) [134]. It is a common approach to improve catalytic performance, selectivity and stability of the catalyst via modifying the structure of the zeolite supports and adjusting metal species and acidity. Extensive studies [135] on the production of methane-derived aromatics showed that those novel catalysts demonstrated better performance and suppressed the excessive formation of coke during the reaction. Aiming at achieving high conversion and low coke formation, a few studies [127, 136-138] were carried out to demonstrate the effect of catalytic support, the nature of the transition metal on the support (Mo, Mn and W would be most active metal to achieve better results), and the introduction of the second metallic promoter (Pt remains exceedingly controversial), as shown in Table 7. It is evident that HZSM-5 is still considered as a potential support.

**Table 7 Catalyst performance for methane aromatization reaction**

| Catalyst | Temp. °C | Pressure (MPa) | Space velocity (mL/(g.h)) | Methane conversion (%) | Aromatic conversion (%) | Ref. |
|---|---|---|---|---|---|---|
| **3%Mo/HZSM-5** | 700 | 0.1 | 1600 | 5.9 | 91.3 | [139] |
| **10%Mo/HZSM-5 (MA)** | 1500 | 0.1 | 973 | 11.8 | 87.1 | [140] |
| **4% Mo-1% ZnHZSM-5** | 750 | 0.1 | 15.8 | 7.4 | 99 | [141] |
| **3%Mo/$SiO_2$** | 700 | 0.1 | 1520 | 5.3 | 9.37 | [142] |
| **2%Mo/MCM-22** | 700 | 0.1 | 1500 | 5.7 | 75.7 | [143] |
| **Zn/HZSM-5** | 700 | 0.1 | 1500 | 1 | 79.1 | [141] |
| **2%W/HZSM-5** | 750 | 0.1 | 1500 | 5.7 | 99 | [141] |
| **4%Mn/HZSM-5** | 700 | 0.1 | 1600 | 2.1 | 91.5 | [144] |
| **2%Ni/HZSM-5** | 700 | 0.1 | 1500 | 0.01 | N/A | [145] |
| **1%Pt-2%Mo/HZSM-5** | 700 | 0.1 | 1400 | 6.4 | 82.2 | [139] |
| **1%La-2%Mo/HZSM-5** | 650 | 0.1 | 1440 | 3.3 | 93.9 | [146] |

| | | | | | | |
|---|---|---|---|---|---|---|
| **1%V-2%Mo/HZSM-5** | 650 | 0.1 | 1440 | 2.7 | 88.9 | 146 |
| **1.2%Pt-6%Mo/HZSM-5** | 750 | 0.3 | 2700 | 7.2 | 93.3 | 147 |

Recently, it is reported that the Mo/HZSM-5 catalyst, which is of a novel capsule structure, is superior to conventional solid catalysts, which showed significantly enhanced conversion, increased rate of formation for benzene, and mitigated formation of coke that is attributed to the hollow structure-accelerated mass-transfer rate [148]. The ZSM-5 zeolite based on the template of activated carbon was synthesized via hydrothermal crystallization, and the catalysis system showed significantly improved benzene formation performance and stability. For the synthesis of meso-/microporous zeolite catalysts, the impregnation of Mo into multilamellar support material (i.e. MWW) was attempted and led to the formation of a Mo/lamellar MWW catalysts, which showed a greater conversion, the formation of more naphthalene, and the yield of less benzene and toluene, as compared with those of Mo-loaded microporous MWW [149]. This can be attributed to the accessible active sites in the mesopores of MWW.

Furthermore, the other metal promoters were also tested, for example, eight different metal species have been used as dopants to promote the performance of Mo/HZSM-5 through a co-impregnation approach [150]. The results demonstrated that only the doping of Fe showed enhanced catalytic performance. In further investigations, a series of characterization and testing techniques were attempted to reveal the mechanism of the iron addition on the enhanced catalytic performance [151]. It was speculated that the generation of carbon nanotubes inhibited the formation of coke on iron species, and therefore promoted the catalytic activity.

In addition, a mechanistic study has also been conducted with several possible DAM mechanisms over a number of Mo-based zeolite catalysts [152], which indicated that the reaction pathways are very complicated and involves around 54 reactions.

## 6. Conclusions and Perspective

This article reviews the latest research on the four routes for the direct conversion of methane to high-value chemicals at low-temperatures, typically below 550°C. Although an enormous amount of effort has been made in this field, there are still many challenges, which also indicate opportunities for future research.

The SRM and DRM are the two most widely studied syngas production process from methane. However, the coke formation on catalyst remains the biggest challenge, which leads to the deactivation of the catalyst. Nickel is considered the most suitable metal for both SRM and DRM catalysts but supports as well as promoters also affects its catalytic performance. $ZrO_2$ and $Al_2O_3$ are found to be good support for nickel-based catalysts with good stability and high activity, whereas $CeO_2$ is the good option as a promoter to increase catalytic activity and reduce coke formation. In addition, it is found that the smaller nickel cluster size, the stronger interactions between the metal and the support, and appropriate surface properties of the support facilitate better catalytic activity and enhance the resistivity to coke formation. Therefore, to develop catalysts with well-dispersed small metal particles, for example, metal organic framework-confined nanoclusters is a promising direction for future research in the methane-based syngas production.

For the DMTM, the main challenge is either the low selectivity of methanol or the low conversion of methane. The liquid heterogeneous system using environmentally friendly oxidants ($H_2O_2$) is considered as the most promising area for research in which the C—H bond can be activated at low temperatures (50–70°C). In addition, the catalyst mimicking the pMMO enzymes is a promising choice to enhance the selectivity of DMTM at low temperatures.

For the OCM, the $Na_2WO_4$–Mn/$SiO_2$ has shown the potential for industrial-scale use, which demonstrates a long-term stability, especially after some challenges are resolved, such as the overoxidization under oxidative conditions resulting in the selectivity toward $CO/CO_2$. The recently discovered $MnTiO_3$ for lowtemperature OCM greatly stimulates the hope of further improvements in the OCM process. Generally, the NOCM can improve the selectivity of $C_2$ production, but there is a need to study how methane conversion can be enhanced while $C_2$ selectivity can be maintained high.

Mo-based catalyst is of great potential in the direct aromatization of methane; however, the formation of coke and polyaromatics is still a challenge that requires further research. Moreover, the removal of hydrogen from the reaction system is found to be a promising strategy to lower the temperature for the efficient direct aromatization of methane.

# 7. References

1. Ravi, M.; Ranocchiari, M.; van Bokhoven, J. A., The direct catalytic oxidation of methane to methanol—A critical assessment. *Angewandte Chemie International Edition* **2017,** *56*, (52), 16464-16483.

2. Bottino, A.; Comite, A.; Capannelli, G.; Di Felice, R.; Pinacci, P., Steam reforming of methane in equilibrium membrane reactors for integration in power cycles. *Catalysis Today* **2006,** *118*, (1-2), 214-222.

3. Ghoneim, S. A.; El-Salamony, R. A.; El-Temtamy, S. A., Review on innovative catalytic reforming of natural gas to syngas. *World J. Eng. Technol* **2016,** *4*, (1), 116.

4. Spath, P. L.; Dayton, D. C. *Preliminary screening--technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas*; National Renewable Energy Lab., Golden, CO.(US): 2003.

5. Experimental and Numerical Study of Low Temperature Methane Steam Reforming for Hydrogen Production. *Catalysts* **2017,** *8*, (1).

6. Matsumura, Y.; Nakamori, T., Steam reforming of methane over nickel catalysts at low reaction temperature. *Applied Catalysis A: General* **2004,** *258*, (1), 107-114.

7. Ayabe, S.; Omoto, H.; Utaka, T.; Kikuchi, R.; Sasaki, K.; Teraoka, Y.; Eguchi, K., Catalytic autothermal reforming of methane and propane over supported metal catalysts. *Applied Catalysis A: General* **2003,** *241*, (1-2), 261-269.

8. Son, I. H.; Lee, S. J.; Soon, A.; Roh, H.-S.; Lee, H., Steam treatment on Ni/γ-Al2O3 for enhanced carbon resistance in combined steam and carbon dioxide reforming of methane. *Applied Catalysis B: Environmental* **2013,** *134*, 103-109.

9. Muraza, O.; Galadima, A., A review on coke management during dry reforming of methane. *International Journal of Energy Research* **2015,** *39*, (9), 1196-1216.

10. Al-Fatesh, A.; Amin, A.; Ibrahim, A.; Khan, W.; Soliman, M.; AL-Otaibi, R.; Fakeeha, A., Effect of Ce and Co addition to Fe/Al2O3 for catalytic methane decomposition. *Catalysts* **2016,** *6*, (3), 40.

11. Angeli, S. D.; Monteleone, G.; Giaconia, A.; Lemonidou, A. A., State-of-the-art catalysts for CH4 steam reforming at low temperature. *International Journal of Hydrogen Energy* **2014,** *39*, (5), 1979-1997.

12. Haggin, J., Direct conversion of methane to fuels, chemicals still intensely sought. *Chem. Eng. News* **1992,** *70*, (17), 33-35.

13. da Silva, M. J., Synthesis of methanol from methane: Challenges and advances on the multi-step (syngas) and one-step routes (DMTM). *Fuel Processing Technology* **2016,** *145*, 42-61.

14. Karakaya, C.; Kee, R. J., Progress in the direct catalytic conversion of methane to fuels and chemicals. *Progress in Energy and Combustion Science* **2016,** *55*, 60-97.

15. Hamid, S. B. D. A., Anderson, J.R., Schmidt, I., Bouchy, C., Jacobsen, C.J., Derouane, E.G., Effect of the activation procedure on the performance of Mo/H-MFI catalysts for the non-oxidative conversion of methane to aromatics. *Catalysis Today* **2000,** *63*, (2-4), 461-469.

16. Zhao, T.; Wang, H., Methane dehydro-aromatization over Mo/HZSM-5 catalysts in the absence of oxygen: Effect of steam-treatment on catalyst stability. *Journal of Natural Gas Chemistry* **2011,** *20*, (5), 547-552.

17. Rostrup-Nielsen, J. R.; Sehested, J.; Nørskov, J. K., Hydrogen and synthesis gas by steam- and C02 reforming. **2002**.

18. Liu, Z.-W.; Jun, K.-W.; Roh, H.-S.; Park, S.-E., Hydrogen production for fuel cells through methane reforming at low temperatures. *Journal of power sources* **2002,** *111*, (2), 283-287.

19. Roh, H.-S.; Jun, K.-W., Low temperature methane steam reforming for hydrogen production for fuel cells. *Bulletin of the Korean Chemical Society* **2009,** *30*, (1), 153-156.

20. Lee, S., *Methane and its Derivatives*. Crc Press: 1996; Vol. 70.

21. Chin, Y.-H. C.; King, D. L.; Roh, H.-S.; Wang, Y.; Heald, S. M., Structure and reactivity investigations on supported bimetallic AuNi catalysts used for hydrocarbon steam reforming. *Journal of Catalysis* **2006,** *244*, (2), 153-162.

22. Parizotto, N.; Rocha, K.; Damyanova, S.; Passos, F.; Zanchet, D.; Marques, C.; Bueno, J., Alumina-supported Ni catalysts modified with silver for the steam reforming of methane: effect of Ag on the control of coke formation. *Applied Catalysis A: General* **2007,** *330*, 12-22.

23. Arpornwichanop, A.; Wasuleewan, M.; Patcharavorachot, Y.; Assabumrungrat, S., Investigation of a dual-bed autothermal reforming of methane for hydrogen production. *Chemical Engineering Transactions* **2011,** *25*, 929-934.

24. Baek, S.-C.; Bae, J.-W.; Cheon, J. Y.; Jun, K.-W.; Lee, K.-Y., Combined steam and carbon dioxide reforming of methane on Ni/MgAl 2 O 4: Effect of CeO 2 promoter to catalytic performance. *Catalysis letters* **2011,** *141*, (2), 224-234.

25. de Miguel, N.; Manzanedo, J.; Arias, P. L., Active and Stable Ni ‐ MgO Catalyst Coated on a Metal Monolith for Methane Steam Reforming under Low Steam ‐ to ‐ Carbon Ratios. *Chemical Engineering & Technology* **2012,** *35*, (12), 2195-2203.

26. Jung, Y.-S.; Yoon, W.-L.; Rhee, Y.-W.; Seo, Y.-S., The surfactant-assisted Ni–Al2O3 catalyst prepared by a homogeneous precipitation method for CH4 steam reforming. *International Journal of Hydrogen Energy* **2012,** *37*, (11), 9340-9350.

27. Seo, Y.-S.; Jung, Y.-S.; Yoon, W.-L.; Jang, I.-G.; Lee, T.-W., The effect of Ni content on a highly active Ni–Al2O3 catalyst prepared by the homogeneous precipitation method. *International Journal of Hydrogen Energy* **2011,** *36*, (1), 94-102.

28. ZHAO, Y.-l.; Yong-kang, L.; CHANG, L.-p.; BAO, W.-r., Effects of MgO and CaO on properties of Ni/γ-Al_2O_3 catalyst for the reforming of methane and steam [J]. *Journal of Fuel Chemistry and Technology* **2010,** *2*.

29. Rostrup-Nielsen, J. R., Production of synthesis gas. *Catalysis today* **1993,** *18*, (4), 305-324.

30. Dan, M.; Mihet, M.; Biris, A. R.; Marginean, P.; Almasan, V.; Borodi, G.; Watanabe, F.; Biris, A. S.; Lazar, M. D., Supported nickel catalysts for low temperature methane steam reforming: comparison between metal additives and support modification. *Reaction Kinetics, Mechanisms and Catalysis* **2012,** *105*, (1), 173-193.

31. Nieva, M. A.; Villaverde, M. M.; Monzón, A.; Garetto, T. F.; Marchi, A. J., Steam-methane reforming at low temperature on nickel-based catalysts. *Chemical Engineering Journal* **2014,** *235*, 158-166.

32. Laosiripojana, N.; Assabumrungrat, S., Methane steam reforming over Ni/Ce–ZrO2 catalyst: Influences of Ce–ZrO2 support on reactivity, resistance toward carbon formation, and intrinsic reaction kinetics. *Applied Catalysis A: General* **2005,** *290*, (1-2), 200-211.

33. Koo, K. Y.; Roh, H.-S.; Seo, Y. T.; Seo, D. J.; Yoon, W. L.; Park, S. B., Coke study on MgO-promoted Ni/Al2O3 catalyst in combined H2O and CO2 reforming of methane for gas to liquid (GTL) process. *Applied Catalysis A: General* **2008,** *340*, (2), 183-190.

34. Vagia, E. C.; Lemonidou, A. A., Investigations on the properties of ceria–zirconia-supported Ni and Rh catalysts and their performance in acetic acid steam reforming. *Journal of Catalysis* **2010,** *269*, (2), 388-396.

35. Yu, X.; Wang, N.; Chu, W.; Liu, M., Carbon dioxide reforming of methane for syngas production over La-promoted NiMgAl catalysts derived from hydrotalcites. *Chemical engineering journal* **2012,** *209*, 623-632.

36. Yu, X.; Zhang, F.; Chu, W., Effect of a second metal (Co, Cu, Mn or Zr) on nickel catalysts derived from hydrotalcites for the carbon dioxide reforming of methane. *RSC Advances* **2016,** *6*, (74), 70537-70546.

37. Nandini, A.; Pant, K.; Dhingra, S., K-, CeO2-, and Mn-promoted Ni/Al2O3 catalysts for stable CO2 reforming of methane. *Applied Catalysis A: General* **2005,** *290*, (1-2), 166-174.

38. Takanabe, K.; Nagaoka, K.; Nariai, K.; Aika, K.-i., Titania-supported cobalt and nickel bimetallic catalysts for carbon dioxide reforming of methane. *Journal of Catalysis* **2005,** *232*, (2), 268-275.

39. Kusakabe, K.; Sotowa, K.-I.; Eda, T.; Iwamoto, Y., Methane steam reforming over Ce–ZrO2-supported noble metal catalysts at low temperature. *Fuel Processing Technology* **2004,** *86*, (3), 319-326.

40. Liu, C. j.; Ye, J.; Jiang, J.; Pan, Y., Progresses in the preparation of coke resistant Ni ‐ based catalyst for steam and CO2 reforming of methane. In *ChemCatChem*, 2011; Vol. 3, pp 529-541.

41. Bengaard, H. S.; Nørskov, J. K.; Sehested, J.; Clausen, B.; Nielsen, L.; Molenbroek, A.; Rostrup-Nielsen, J., Steam reforming and graphite formation on Ni catalysts. *Journal of Catalysis* **2002,** *209*, (2), 365-384.

42. Chen, D.; Christensen, K. O.; Ochoa-Fernández, E.; Yu, Z.; Tøtdal, B.; Latorre, N.; Monzón, A.; Holmen, A., Synthesis of carbon nanofibers: effects of Ni crystal size during methane decomposition. *Journal of Catalysis* **2005,** *229*, (1), 82-96.

43. Wei, J.; Iglesia, E., Structural and mechanistic requirements for methane activation and chemical conversion on supported iridium clusters. *Angewandte Chemie International Edition* **2004,** *43*, (28), 3685-3688.

44. Jones, G.; Jakobsen, J. G.; Shim, S. S.; Kleis, J.; Andersson, M. P.; Rossmeisl, J.; Abild-Pedersen, F.; Bligaard, T.; Helveg, S.; Hinnemann, B., First principles calculations and experimental insight into methane steam reforming over transition metal catalysts. *Journal of Catalysis* **2008,** *259*, (1), 147-160.

45. Ligthart, D.; Van Santen, R.; Hensen, E., Influence of particle size on the activity and stability in steam methane reforming of supported Rh nanoparticles. *Journal of catalysis* **2011,** *280*, (2), 206-220.

46. Wang, Y.; Wang, H.; Dam, A. H.; Xiao, L.; Qi, Y.; Niu, J.; Yang, J.; Zhu, Y.-A.; Holmen, A.; Chen, D., Understanding effects of Ni particle size on steam methane reforming activity by combined experimental and theoretical analysis. *Catalysis Today* **2019**.

47. Luna, E. C.; Becerra, A.; Dimitrijewits, M., Methane steam reforming over rhodium promoted Ni/Al 2 O 3 catalysts. *Reaction Kinetics and Catalysis Letters* **1999,** *67*, (2), 247-252.

48. Chin, Y.; King, D.; Roh, H.; Wang, Y.; Heald, S., Structure and reactivity investigations on supported bimetallic AuNi catalysts used for hydrocarbon steam reforming. *Journal of Catalysis* **2006,** *244*, (2), 153-162.

49. Jaiswar, V. K.; Katheria, S.; Deo, G.; Kunzru, D., Effect of Pt doping on activity and stability of Ni/MgAl2O4 catalyst for steam reforming of methane at ambient and high pressure condition. *International Journal of Hydrogen Energy* **2017,** *42*, (30), 18968-18976.

50. Budiman, A. W.; Song, S.-H.; Chang, T.-S.; Shin, C.-H.; Choi, M.-J., Dry Reforming of Methane Over Cobalt Catalysts: A Literature Review of Catalyst Development. *Catalysis Surveys from Asia* **2012,** *16*, (4), 183-197.

51. Yu, M.; Zhu, K.; Liu, Z.; Xiao, H.; Deng, W.; Zhou, X., Carbon dioxide reforming of methane over promoted NixMg1− xO (1 1 1) platelet catalyst derived from solvothermal synthesis. *Applied Catalysis B: Environmental* **2014,** *148*, 177-190.

52. Yu, M.; Zhu, Y.-A.; Lu, Y.; Tong, G.; Zhu, K.; Zhou, X., The promoting role of Ag in Ni-CeO2 catalyzed CH4-CO2 dry reforming reaction. *Applied Catalysis B: Environmental* **2015,** *165*, 43-56.

53. Gould, T. D.; Izar, A.; Weimer, A. W.; Falconer, J. L.; Medlin, J. W., Stabilizing Ni catalysts by molecular layer deposition for harsh, dry reforming conditions. *Acs Catalysis* **2014,** *4*, (8), 2714-2717.

54. Xie, X.; Otremba, T.; Littlewood, P.; Schomäcker, R.; Thomas, A., One-pot synthesis of supported, nanocrystalline nickel manganese oxide for dry reforming of methane. *ACS Catalysis* **2013,** *3*, (2), 224-229.

55. Arora, S.; Prasad, R., An overview on dry reforming of methane: strategies to reduce carbonaceous deactivation of catalysts. *RSC Advances* **2016,** *6*, (110), 108668-108688.

56. Jang, W.-J.; Shim, J.-O.; Kim, H.-M.; Yoo, S.-Y.; Roh, H.-S., A review on dry reforming of methane in aspect of catalytic properties. *Catalysis Today* **2018**.

57. Mette, K.; Kühl, S.; Tarasov, A.; Düdder, H.; Kähler, K.; Muhler, M.; Schlögl, R.; Behrens, M., Redox dynamics of Ni catalysts in CO2 reforming of methane. *Catalysis Today* **2015,** *242*, 101-110.

58. Angeli, S. D.; Turchetti, L.; Monteleone, G.; Lemonidou, A. A., Catalyst development for steam reforming of methane and model biogas at low temperature. *Applied Catalysis B: Environmental* **2016,** *181*, 34-46.

59. Cao, C.; Bourane, A.; Schlup, J. R.; Hohn, K. L., In situ IR investigation of activation and catalytic ignition of methane over Rh/Al2O3 catalysts. *Applied Catalysis A: General* **2008,** *344*, (1-2), 78-87.

60. Bian, Z.; Kawi, S., Highly carbon-resistant Ni–Co/SiO2 catalysts derived from phyllosilicates for dry reforming of methane. *Journal of CO2 Utilization* **2017,** *18*, 345-352.

61. Kathiraser, Y.; Thitsartarn, W.; Sutthiumporn, K.; Kawi, S., Inverse NiAl2O4 on LaAlO3–Al2O3: unique catalytic structure for stable CO2 reforming of methane. *The Journal of Physical Chemistry C* **2013,** *117*, (16), 8120-8130.

62. Gao, X.; Tan, Z.; Hidajat, K.; Kawi, S., Highly reactive Ni-Co/SiO2 bimetallic catalyst via complexation with oleylamine/oleic acid organic pair for dry reforming of methane. *Catalysis Today* **2017,** *281*, 250-258.

63. Li, Z.; Mo, L.; Kathiraser, Y.; Kawi, S., Yolk–satellite–shell structured Ni–Yolk@ Ni@ SiO2 nanocomposite: superb catalyst toward methane CO2 reforming reaction. *Acs Catalysis* **2014,** *4*, (5), 1526-1536.

64. Sutthiumporn, K.; Kawi, S., Promotional effect of alkaline earth over Ni–La2O3 catalyst for CO2 reforming of CH4: role of surface oxygen species on H2 production and carbon suppression. *International Journal of Hydrogen Energy* **2011,** *36*, (22), 14435-14446.

65. Gao, X.; Hidajat, K.; Kawi, S., Facile synthesis of Ni/SiO2 catalyst by sequential hydrogen/air treatment: A superior anti-coking catalyst for dry reforming of methane. *Journal of CO2 Utilization* **2016,** *15*, 146-153.

66. Dębek, R.; Motak, M.; Grzybek, T.; Galvez, M.; Da Costa, P., A short review on the catalytic activity of hydrotalcite-derived materials for dry reforming of methane. *Catalysts* **2017,** *7*, (1), 32.

67. Elsayed, N. H.; Roberts, N. R.; Joseph, B.; Kuhn, J. N., Low temperature dry reforming of methane over Pt–Ni–Mg/ceria–zirconia catalysts. *Applied Catalysis B: Environmental* **2015,** *179*, 213-219.

68. Wei, J.; Iglesia, E., Mechanism and site requirements for activation and chemical conversion of methane on supported Pt clusters and turnover rate comparisons among noble metals. *The Journal of Physical Chemistry B* **2004,** *108*, (13), 4094-4103.

69. Bradford, M. C.; Vannice, M. A., The role of metal–support interactions in CO2 reforming of CH4. *Catalysis today* **1999,** *50*, (1), 87-96.

70. El Hassan, N.; Kaydouh, M.; Geagea, H.; El Zein, H.; Jabbour, K.; Casale, S.; El Zakhem, H.; Massiani, P., Low temperature dry reforming of methane on rhodium and cobalt based catalysts: active phase stabilization by confinement in mesoporous SBA-15. *Applied Catalysis A: General* **2016,** *520*, 114-121.

71. Nakamura, J.; Aikawa, K.; Sato, K.; Uchijima, T., Role of support in reforming of CH 4 with CO 2 over Rh catalysts. *Catalysis letters* **1994,** *25*, (3-4), 265-270.

72. Erdőhelyi, A.; Fodor, K.; Solymosi, F., Reaction of CH4 with CO2 and H2O over supported Ir catalyst. In *Studies in Surface Science and Catalysis*, Elsevier: 1997; Vol. 107, pp 525-530.

73. Baudouin, D.; Rodemerck, U.; Krumeich, F.; de Mallmann, A.; Szeto, K. C.; Ménard, H.; Veyre, L.; Candy, J.-P.; Webb, P. B.; Thieuleux, C., Particle size effect in the low temperature reforming of methane by carbon dioxide on silica-supported Ni nanoparticles. *Journal of catalysis* **2013,** *297*, 27-34.

74. Yao, L.; Wang, Y.; Shi, J.; Xu, H.; Shen, W.; Hu, C., The influence of reduction temperature on the performance of ZrOx/Ni-MnOx/SiO2 catalyst for low-temperature CO2 reforming of methane. *Catalysis Today* **2017,** *281*, 259-267.

75. Bachiller-Baeza, B.; Mateos-Pedrero, C.; Soria, M.; Guerrero-Ruiz, A.; Rodemerck, U.; Rodríguez-Ramos, I., Transient studies of low-temperature dry reforming of methane over Ni-CaO/ZrO2-La2O3. *Applied Catalysis B: Environmental* **2013,** *129*, 450-459.

76. Yao, L.; Shi, J.; Xu, H.; Shen, W.; Hu, C., Low-temperature CO2 reforming of methane on Zr-promoted Ni/SiO2 catalyst. *Fuel Processing Technology* **2016,** *144*, 1-7.

77. Abdullah, B.; Abd Ghani, N. A.; Vo, D.-V. N., Recent advances in dry reforming of methane over Ni-based catalysts. *Journal of Cleaner Production* **2017,** *162*, 170-185.

78. Wang, S.; Lu*, G., A comprehensive study on carbon dioxide reforming of methane over Ni/γ-Al2O3 catalysts. *Industrial & engineering chemistry research* **1999,** *38*, (7), 2615-2625.

79. Zhao, X.; Cao, Y.; Li, H.; Zhang, J.; Shi, L.; Zhang, D., Sc promoted and aerogel confined Ni catalysts for coking-resistant dry reforming of methane. *RSC Advances* **2017,** *7*, (8), 4735-4745.

80. Bradford, M. C.; Vannice, M. A., Catalytic reforming of methane with carbon dioxide over nickel catalysts I. Catalyst characterization and activity. *Applied Catalysis A: General* **1996,** *142*, (1), 73-96.

81. Mohamedali, M.; Henni, A.; Ibrahim, H., Recent Advances in Supported Metal Catalysts for Syngas Production from Methane. *ChemEngineering* **2018,** *2*, (1), 9.

82. Grundner, S.; Markovits, M. A.; Li, G.; Tromp, M.; Pidko, E. A.; Hensen, E. J.; Jentys, A.; Sanchez-Sanchez, M.; Lercher, J. A., Single-site trinuclear copper oxygen clusters in mordenite for selective conversion of methane to methanol. *Nature communications* **2015,** *6*, 7546.

83. Wang, Y.; Yao, L.; Wang, S.; Mao, D.; Hu, C., Low-temperature catalytic CO2 dry reforming of methane on Ni-based catalysts: a review. *Fuel Processing Technology* **2018,** *169*, 199-206.

84. Sokolov, S.; Kondratenko, E. V.; Pohl, M.-M.; Barkschat, A.; Rodemerck, U., Stable low-temperature dry reforming of methane over mesoporous La2O3-ZrO2 supported Ni catalyst. *Applied Catalysis B: Environmental* **2012,** *113*, 19-30.

85. Liu, H.; Wierzbicki, D.; Debek, R.; Motak, M.; Grzybek, T.; Da Costa, P.; Gálvez, M. E., La-promoted Ni-hydrotalcite-derived catalysts for dry reforming of methane at low temperatures. *Fuel* **2016,** *182*, 8-16.

86. Dębek, R.; Radlik, M.; Motak, M.; Galvez, M. E.; Turek, W.; Da Costa, P.; Grzybek, T., Ni-containing Ce-promoted hydrotalcite derived materials as catalysts for methane reforming with carbon dioxide at low temperature–on the effect of basicity. *Catalysis Today* **2015,** *257*, 59-65.

87. Albarazi, A.; Beaunier, P.; Da Costa, P., Hydrogen and syngas production by methane dry reforming on SBA-15 supported nickel catalysts: On the effect of promotion by Ce0. 75Zr0. 25O2 mixed oxide. *international journal of hydrogen energy* **2013,** *38*, (1), 127-139.

88. Zhang, Q.; He, D.; Zhu, Q., Recent progress in direct partial oxidation of methane to methanol. *Journal of Natural Gas Chemistry* **2003,** *12*, (2), 81-89.

89. Baliban, R. C.; Elia, J. A.; Floudas, C. A., Novel natural gas to liquids processes: process synthesis and global optimization strategies. *AIChE Journal* **2013,** *59*, (2), 505-531.

90. Dowden, D.; Walker, G., Oxygenated hydrocarbons production. *Brit. Pat* **1971,** *1*.

91. Liu, H.; Liu, R.; Liew, K. Y.; Johnson, R.; Lunsford, J., Partial oxidation of methane by nitrous oxide over molybdenum on silica. *Journal of the American Chemical Society* **1984,** *106*, (15), 4117-4121.

92. Zhang, X.; He, D.; Zhang, Q.; Xu, B.; Zhu, Q., Comparative studies on direct conversion of methane to methanol/formaldehyde over La–Co–O and ZrO 2 supported molybdenum oxide catalysts. *Topics in catalysis* **2005,** *32*, (3-4), 215-223.

93. Millner, T.; Neugebauer, J., Volatility of the oxides of tungsten and molybdenum in the presence of water vapour. *Nature* **1949,** *163*, (4146), 601.

94. Marturano, P.; Drozdová, L.; Kogelbauer, A.; Prins, R., Fe/ZSM-5 prepared by sublimation of FeCl3: the structure of the Fe species as determined by IR, 27Al MAS NMR, and EXAFS spectroscopy. *Journal of Catalysis* **2000,** *192*, (1), 236-247.

95. Battiston, A.; Bitter, J.; De Groot, F.; Overweg, A.; Stephan, O.; van Bokhoven, J. A.; Kooyman, P.; Van Der Spek, C.; Vanko, G.; Koningsberger, D., Evolution of Fe species during the synthesis of over-exchanged Fe/ZSM5 obtained by chemical vapor deposition of FeCl3. *Journal of catalysis* **2003,** *213*, (2), 251-271.

96. Michalkiewicz, B., Partial oxidation of methane to formaldehyde and methanol using molecular oxygen over Fe-ZSM-5. *Applied Catalysis A: General* **2004,** *277*, (1-2), 147-153.

97. Hammond, C.; Forde, M. M.; Ab Rahim, M. H.; Thetford, A.; He, Q.; Jenkins, R. L.; Dimitratos, N.; Lopez ‐ Sanchez, J. A.; Dummer, N. F.; Murphy, D. M., Direct catalytic conversion of methane to methanol in an aqueous medium by using copper ‐ promoted Fe ‐ ZSM ‐ 5. *Angewandte Chemie International Edition* **2012,** *51*, (21), 5129-5133.

98. Xiao, P.; Wang, Y.; Nishitoba, T.; Kondo, J. N.; Yokoi, T., Selective oxidation of methane to methanol with H 2 O 2 over an Fe-MFI zeolite catalyst using sulfolane solvent. *Chemical Communications* **2019,** *55*, (20), 2896-2899.

99. Sushkevich, V. L.; Palagin, D.; Ranocchiari, M.; van Bokhoven, J. A., Selective anaerobic oxidation of methane enables direct synthesis of methanol. *Science* **2017,** *356*, (6337), 523-527.

100. Ikuno, T.; Zheng, J.; Vjunov, A.; Sanchez-Sanchez, M.; Ortuno, M. A.; Pahls, D. R.; Fulton, J. L.; Camaioni, D. M.; Li, Z.; Ray, D.; Mehdi, B. L.; Browning, N. D.; Farha, O. K.; Hupp, J. T.; Cramer,

C. J.; Gagliardi, L.; Lercher, J. A., Methane Oxidation to Methanol Catalyzed by Cu-Oxo Clusters Stabilized in NU-1000 Metal-Organic Framework. *J Am Chem Soc* **2017,** *139*, (30), 10294-10301.

101. Rosenzweig, A. C.; Frederick, C. A.; Lippard, S. J., Crystal structure of a bacterial non-haem iron hydroxylase that catalyses the biological oxidation of methane. *Nature* **1993,** *366*, (6455), 537.

102. Friedle, S.; Reisner, E.; Lippard, S. J., Current challenges of modeling diiron enzyme active sites for dioxygen activation by biomimetic synthetic complexes. *Chemical Society Reviews* **2010,** *39*, (8), 2768-2779.

103. Tinberg, C. E.; Lippard, S. J., Dioxygen activation in soluble methane monooxygenase. *Accounts of chemical research* **2011,** *44*, (4), 280-288.

104. Banerjee, R.; Proshlyakov, Y.; Lipscomb, J. D.; Proshlyakov, D. A., Structure of the key species in the enzymatic oxidation of methane to methanol. *Nature* **2015,** *518*, (7539), 431.

105. Chan, S. I.; Chien, C. Y.-C.; Yu, C. S.-C.; Nagababu, P.; Maji, S.; Chen, P. P.-Y., Efficient catalytic oxidation of hydrocarbons mediated by tricopper clusters under mild conditions. *Journal of catalysis* **2012,** *293*, 186-194.

106. Nagababu, P.; Maji, S.; Kumar, M. P.; Chen, P. P. Y.; Yu, S. S. F.; Chan, S. I., Efficient Room‐Temperature Oxidation of Hydrocarbons Mediated by Tricopper Cluster Complexes with Different Ligands. *Advanced Synthesis & Catalysis* **2012,** *354*, (17), 3275-3282.

107. Chan, S. I.; Lu, Y. J.; Nagababu, P.; Maji, S.; Hung, M. C.; Lee, M. M.; Hsu, I. J.; Minh, P. D.; Lai, J. C. H.; Ng, K. Y., Efficient oxidation of methane to methanol by dioxygen mediated by tricopper clusters. *Angewandte Chemie International Edition* **2013,** *52*, (13), 3731-3735.

108. Bordeaux, M.; Galarneau, A.; Drone, J., Catalytic, mild, and selective oxyfunctionalization of linear alkanes: current challenges. *Angewandte Chemie International Edition* **2012,** *51*, (43), 10712-10723.

109. Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H., Platinum catalysts for the high-yield oxidation of methane to a methanol derivative. *Science* **1998,** *280*, (5363), 560-564.

110. Dietl, N.; Schlangen, M.; Schwarz, H., Thermal hydrogen‐atom transfer from methane: the role of radicals and spin states in oxo‐cluster chemistry. *Angewandte Chemie International Edition* **2012,** *51*, (23), 5544-5555.

111. Periana, R. A.; Taube, D. J.; Evitt, E. R.; Löffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T., A mercury-catalyzed, high-yield system for the oxidation of methane to methanol. *Science* **1993,** *259*, (5093), 340-343.

112. Alvarez-Galvan, M. C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R. M.; Fierro, J. L. G., Direct methane conversion routes to chemicals and fuels. *Catalysis Today* **2011,** *171*, (1), 15-23.

113. Schwach, P.; Pan, X.; Bao, X., Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem Rev* **2017,** *117*, (13), 8497-8520.

114. Elkins, T. W.; Hagelin-Weaver, H. E., Characterization of Mn–Na2WO4/SiO2 and Mn–Na2WO4/MgO catalysts for the oxidative coupling of methane. *Applied Catalysis A: General* **2015,** *497*, 96-106.

115. Xueping, F., Shuben, L., Jingzhi, L., Yanlai, C., Oxidative Coupling of methane on W-Mn Catalysts. *Journal OF Molecular Catalysis* **1992,** *6*.

116. Fleischer, V.; Littlewood, P.; Parishan, S.; Schomäcker, R., Chemical looping as reactor concept for the oxidative coupling of methane over a Na 2 WO 4 /Mn/SiO 2 catalyst. *Chemical Engineering Journal* **2016,** *306*, 646-654.

117. Ji, S. F., Xiao, T.C., Li, S.B., Xu, C.Z., Hou, R.L., Coleman, K.S., Green, M.L., The Relationship between the Structure and the Performance of Na-W-Mn/SiO2 Catalysts for the Oxidative Coupling of Methane. *Applied Catalysis A: General* **2002,** *225*, (1-2), 271-284.

118. Elkins, T. W.; Roberts, S. J.; Hagelin-Weaver, H. E., Effects of alkali and alkaline-earth metal dopants on magnesium oxide supported rare-earth oxide catalysts in the oxidative coupling of methane. *Applied Catalysis A: General* **2016,** *528*, 175-190.

119. Zavyalova, U.; Holena, M.; Schlögl, R.; Baerns, M., Statistical Analysis of Past Catalytic Data on Oxidative Methane Coupling for New Insights into the Composition of High-Performance Catalysts. *ChemCatChem* **2011,** *3*, (12), 1935-1947.

120. Xiaoguang Guo, G. F., Gang Li, Hao Ma, Hongjun Fan, Liang Yu, Chao Ma, Xing Wu, Dehui Deng, Mingming Wei, Dali Tan, Rui Si, Shuo Zhang, Jianqi Li, Litao Sun, Zichao Tang, Xiulian Pan, Xinhe Bao, Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen. *Science* **2014,** *344*, (6184), 616-619.

121. Xie, P.; Pu, T.; Nie, A.; Hwang, S.; Purdy, S. C.; Yu, W.; Su, D.; Miller, J. T.; Wang, C., Nanoceria-supported single-atom platinum catalysts for direct methane conversion. *ACS Catalysis* **2018,** *8*, (5), 4044-4048.

122. Wolf, E. E., *Methane coversion by oxidative processes: fundamental and engineering aspects*. Springer: 1992; Vol. 85.

123. Keller, G. E., Bhasin, M.M., Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *Journal of Catalysis* **1982,** *73*, (1), 9-19.

124. Ross, S. J. K. A. R. R. H., The Development of Doped Li/MgO Catalyst Systems for the Low-Temperature Oxidative Coupling of Methane. *Springer* **1992**, 168-199.

125. Wang, P.; Zhao, G.; Liu, Y.; Lu, Y., TiO 2 -doped Mn 2 O 3 -Na 2 WO 4 /SiO 2 catalyst for oxidative coupling of methane: Solution combustion synthesis and MnTiO 3 -dependent low-temperature activity improvement. *Applied Catalysis A: General* **2017,** *544*, 77-83.

126. Wang, P.; Zhao, G.; Wang, Y.; Lu, Y. J. S. a., MnTiO3-driven low-temperature oxidative coupling of methane over TiO2-doped Mn2O3-Na2WO4/SiO2 catalyst. **2017,** *3*, (6), e1603180.

127. Majhi, S.; Mohanty, P.; Wang, H.; Pant, K., Direct conversion of natural gas to higher hydrocarbons: A review. *Journal of Energy Chemistry* **2013,** *22*, (4), 543-554.

128. Xiao, Y.; Varma, A., Highly Selective Nonoxidative Coupling of Methane over Pt-Bi Bimetallic Catalysts. *ACS Catalysis* **2018,** *8*, (4), 2735-2740.

129. M. Belgued, P. P., A. Amariglio, H. Amariglio Conversion of methane into higher hydrocarbons on platinum. *Nature* **1991,** *352*, 789–790.

130. Soulivong, D.; Norsic, S.; Taoufik, M.; Coperet, C.; Thivolle-Cazat, J.; Chakka, S.; Basset, J. M., Non-oxidative coupling reaction of methane to ethane and hydrogen catalyzed by the silica-supported tantalum hydride: ([triple bond]SiO)2Ta-H. *J Am Chem Soc* **2008,** *130*, (15), 5044-5.

131. By Xiaoguang Guo, G. F., Gang Li, Hao Ma, Hongjun Fan, Liang Yu, Chao Ma, Xing Wu, Dehui Deng, Mingming Wei, Dali Tan, Rui Si, Shuo Zhang, Jianqi Li, Litao Sun, Zichao Tang, Xiulian Pan, Xinhe Bao, Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen. *Science* **2014,** *344*, (6184), 616-619

132. Gerceker, D.; Motagamwala, A. H.; Rivera-Dones, K. R.; Miller, J. B.; Huber, G. W.; Mavrikakis, M.; Dumesic, J. A., Methane Conversion to Ethylene and Aromatics on PtSn Catalysts. *ACS Catalysis* **2017,** *7*, (3), 2088-2100.

133. Linsheng Wang, L. T., Maosong Xie, Guifen XuJia, sheng Huang, Yide Xu, Dehydrogenation and aromatization of methane under non-oxidizing conditions. *Catalysis Letter* **1993,** *21*, (1-2), 35-41.

134. Chun-Lei Zhang, S. L., Yi Yuan, Wen-Xiang Zhang, Tong-Hao Wu, Li-Wu LIn, Aromatization of methane in the absence of oxygen over Mo-based catalysts supported on different types of zeolites. *Catalysis Letters* **1998,** *56*, (4), 207-213.

135. Anggoro, D. D.; Amin, N. A. S., Methane to Liquid Hydrocarbons over Tungsten-ZSM-5 and Tungsten Loaded Cu/ZSM-5 Catalysts. *Journal of Natural Gas Chemistry* **2006,** *15*, (4), 340-347.

136. Ding, W.; Meitzner, G. D.; Iglesia, E., The Effects of Silanation of External Acid Sites on the Structure and Catalytic Behavior of Mo/H–ZSM5. *Journal of Catalysis* **2002,** *206*, (1), 14-22.

137. Wu, P.; Kan, Q.; Wang, X.; Wang, D.; Xing, H.; Yang, P.; Wu, T., Acidity and catalytic properties for methane conversion of Mo/HZSM-5 catalyst modified by reacting with organometallic complex. *Applied Catalysis A: General* **2005,** *282*, (1-2), 39-44.

138. Liu, H.; Li, Y.; Shen, W.; Bao, X.; Xu, Y., Methane dehydroaromatization over Mo/HZSM-5 catalysts in the absence of oxygen: effects of silanation in HZSM-5 zeolite. *Catalysis Today* **2004,** *93-95*, 65-73.

139. Chen, L.; Lin, L.; Xu, Z.; Zhang, T.; Li, X., Promotional effect of Pt on non-oxidative methane transformation over Mo-HZSM-5 catalyst. *Catalysis Letters* **1996,** *39*, (3-4), 169-172.

140. Tan, P., Ammonia-basified 10 wt% Mo/HZSM-5 material with enhanced dispersion of Mo and performance for catalytic aromatization of methane. *Applied Catalysis A: General* **2019,** *580*, 111-120.

141. Zeng, J. L., Xiong, Z.T., Zhang, H.B., Lin, G.D., Tsai, K.R., Nonoxidative dehydrogenation and aromatization of methane over W/HZSM-5-based catalysts. *Catalysis Letters* **1998,** *53*, (3-4), 119-124.

142. Liu, S.; Wang, L.; Ohnishi, R.; Ichikawa, M., Bifunctional catalysis of Mo/HZSM-5 in the dehydroaromatization of methane to benzene and naphthalene XAFS/TG/DTA/MASS/FTIR characterization and supporting effects. *Journal of Catalysis* **1999,** *181*, (2), 175-188.

143. Shu, Y., Ma, D., Xu, L., Xu, Y., Bao, X., Methane dehydro-aromatization over Mo/MCM-22 catalysts: A highly selective catalyst for the formation of benzene. *Catalysis Letters* **2000,** *70*, (1-4), 67-73.

144. Tan, P. L., Au, C.T., Lai, S.Y., Methane dehydrogenation and aromatization over 4 wt% Mn/HZSM-5 in the absence of an oxidant. *Catalysis Letters* **2006,** *112*, (3-4), 239-245.

145. Liu, J. F.; Liu, Y.; Peng, L. F., Aromatization of methane by using propane as co-reactant over cobalt and zinc-impregnated HZSM-5 catalysts. *Journal of Molecular Catalysis A: Chemical* **2008,** *280*, (1-2), 7-15.

146. Szöke, A., Solymosi, F., Selective oxidation of methane to benzene over K2MoO4/ZSM-5 catalysts. *Applied Catalysis A: General* **1996,** *142*, (2), 361-374.

147. Kojima, R., Kikuchi, S., Ma, H., Bai, J., Ichikawa, M., Promotion effects of Pt and Rh on catalytic performances of Mo/HZSM-5 and Mo/HMCM-22 in selective methane-to-benzene reaction. *Catalysis Letters* **2006,** *110*, (1-2), 15-21.

148. Zhu, P.; Yang, G.; Sun, J.; Fan, R.; Zhang, P.; Yoneyama, Y.; Tsubaki, N., A hollow Mo/HZSM-5 zeolite capsule catalyst: preparation and enhanced catalytic properties in methane dehydroaromatization. *Journal of Materials Chemistry A* **2017,** *5*, (18), 8599-8607.

149. Wu, Y.; Emdadi, L.; Wang, Z.; Fan, W.; Liu, D., Textural and catalytic properties of Mo loaded hierarchical meso-/microporous lamellar MFI and MWW zeolites for direct methane conversion. *Applied Catalysis A: General* **2014,** *470*, 344-354.

150. Xu, Y.; Wang, J.; Suzuki, Y.; Zhang, Z.-G., Improving effect of Fe additive on the catalytic stability of Mo/HZSM-5 in the methane dehydroaromatization. *Catalysis Today* **2012,** *185*, (1), 41-46.

151. Xu, Y.; Wang, J.; Suzuki, Y.; Zhang, Z.-G., Effect of transition metal additives on the catalytic stability of Mo/HZSM-5 in the methane dehydroaromatization under periodic CH4–H2 switch operation at 1073K. *Applied Catalysis A: General* **2011,** *409-410*, 181-193.

152. Karakaya, C.; Morejudo, S. H.; Zhu, H.; Kee, R. J., Catalytic Chemistry for Methane Dehydroaromatization (MDA) on a Bifunctional Mo/HZSM-5 Catalyst in a Packed Bed. *Industrial & Engineering Chemistry Research* **2016,** *55*, (37), 9895-9906.