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**Catalytic hydrogen production from methane partial oxidation: mechanism
and kinetic study mini-review**

Ahmed I. Osman ^{a*}

^a School of Chemistry and Chemical Engineering, Queen's University Belfast,
Belfast BT9 5AG, Northern Ireland, UK

Corresponding Authors: Dr. Ahmed I. Osman

Email: aosmanahmed01@qub.ac.uk

Address: School of Chemistry and Chemical Engineering, Queen's University Belfast,
David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, United Kingdom

Fax: +44 2890 97 4687

Tel.: +44 2890 97 4412

Abstract

Herein, this mini review investigates the multifunctional potential of a transition and noble metal catalyst supported on either a single support or combined oxide support in the catalytic partial oxidation of methane (CPOM). Also highlighted is the close interaction and interfacial area between the metal, reducible oxide and acidic support, which are crucial for the low-temperature CPOM reaction. The effect of the catalyst component and its preparation methods were considered herein. Their impact on the catalytic performance and stability on the CPOM reaction was evaluated. The two main mechanisms of CPOM; direct partial oxidation (DPO) and the combustion and reforming reaction (CRR) mechanism was also covered along with the most recent kinetic studies. Finally, the deactivation of the CPOM catalysts was studied in term of coke and carbon deposition along with the CO poisoning.

Keywords: Methane, Partial oxidation, Zeolite support, Oxygen carrier, Nickel, Hydrogen production.

1. Introduction

Methane is the simplest, most symmetrical occurring hydrocarbon and is the main component of natural gas (>88 vol.%) [1]. It is also generated from renewable resources such as biogas (50-70 vol.%), which is a valuable resource for energy generation and chemical feedstock supply [1, 2]. Combustion, in general, is an exothermic redox chemical reaction between a fuel and an oxidant, which is triggered by activation energy in the form of heat or a flame. Methane total combustion with excessive O₂ to CO₂ and H₂O generates a large amount of energy (802.3 kJ.mol⁻¹); with lower greenhouse gas emissions (GHG) compared to that of other hydrocarbon fuels [3] (Eq. 1). While its partial combustion using a stoichiometric ratio of 2:1 (CH₄ : O₂) produces synthesis gas (syngas); a mixture of CO and H₂ as shown in Eq. 2. Hydrogen can be produced after the removal of CO using the water gas shift reaction (WGSR).

Catalytic partial oxidation of methane (CPOM) requires high-temperature (>800 °C) which produces alongside CO and H₂ as main products: carbon as soot or ash, CO₂ and H₂O as by-products [1]. This means that coke formation is thermodynamically favoured at relatively high temperature, thus reducing the yield of syngas [4-6]. To overcome the catalyst deactivation by coke formation, additional catalyst is needed to maintain production throughout regeneration cycles. Others general byproducts of the combustion process are nitrogen oxide (NO_x), sulfur oxide (SO_x) and others particulates. Usually, fuel combustion reactions at high temperatures under air atmosphere (78 vol.% N₂) generates NO_x, since N₂ combustion is thermodynamically favourable at high temperature, but not at low temperatures. The release of such emissions is positively correlated to adverse health and environmental effects [7]. Hence, the production of syngas at low-temperature range offers significant financial and environmental advantages,

including lower energy requirements, materials costs as well as reduced formation of NO_x emissions.

Syngas is generally formed from the large scale steam reforming of hydrocarbons and is used for a variety of applications including the manufacture of fuels and feedstocks and the production of hydrogen [8, 9]. However, with increasing utilisation of stranded and small scale sources of methane such as farms and AD plants in remote areas as well as decreasing acceptance of flaring at source, development of a catalyst to allow CPOM to syngas on a smaller scale is desired [4].

2. Why partial oxidation is the most suitable reforming reaction for liquid fuels

There are three main reforming routes to produce syngas from methane which are dry reforming, steam reforming and oxy reforming (partial oxidation). The first two reforming routes are highly endothermic processes (Eq. 3-4), along with the fact they are both prone to coke formation and eventually catalyst deactivation. However, partial oxidation is a mildly exothermic reaction as shown in Eq. 2.

More importantly, for the production of liquid fuel such as methanol and consequently, the biofuel dimethyl ether (DME) as shown in Eq. 5, a H₂ : CO ratio of 2 in the produced syngas is required [10]. Interestingly, partial oxidation offers that ratio requirement, whereas steam and dry reforming produce syngas with a ratio of 3 and 1, respectively. Thus, steam reforming is more appropriate for hydrogen production, combining with WGSR to remove the CO produced [11]. While dry reforming with a ratio of 1 is appropriate for dimethyl ether production in one single step at high pressure as shown in Eq. 6.

Partial oxidation of methane is also the most appropriate reforming process for the Fischer-Tropsch process, where a $\text{H}_2 : \text{CO}$ ratio of 2 in the produced syngas is also required [4, 12, 13].

3. Types of metal catalysts

There are mainly two types of metal catalysts in CPOM reaction which are transition or noble metals catalysts as shown below.

3.1 Transition metal catalysts

Among the transition metal catalysts, nickel is recognised as one of the cheapest and most active catalysts. However, it is prone to carbon deposition which poisons and consequently, deactivates the catalyst [13]. Thus, numerous work in the literature is devoted to using Ni-based catalysts with reduced carbon deposition [14]. One example of suppressing the carbon deposition is to use reducible oxide support such as CeO_2 or ZrO_2 as single support or CeO_2 - ZrO_2 as combined oxide support. Other oxygen supports that were also used were TiO_2 and La_2O_3 , where the lattice oxygen within the oxide support oxidise any carbon deposited on the surface of the catalyst during CPOM reaction [15-21]. The typical temperature range for Ni-based catalysts in CPOM reaction is 550-850 °C. The three biggest challenges with Ni catalysts in CPOM reaction are the high temperature required for high syngas yield (>850 °C), high selectivity of CO_2 and the coke formation. For instance, Ni supported on a single support such as Ni/ CeO_2 catalyst showed a temperature at 50% conversion ($T_{50\%}$) of 720 °C. While on combined oxide support such as Ni/ CeO_2 / La_2O_3 catalyst, $T_{50\%}$ was at 675 °C using a gas hourly space velocity (GHSV) of 60,000 $\text{mL.g}^{-1}.\text{h}^{-1}$. Recently, Ni/ CeO_2 - ZrO_2 /ZSM-5 (80) catalyst showed enhanced catalytic activity, where $T_{50\%}$ was at 400 °C using WHSV of 63,000 $\text{mL.g}^{-1}.\text{h}^{-1}$ [13]. That catalyst showed also good stability over 25 hours reaction stream at reaction temperatures of both 400 and 700 °C,

respectively. Wang et al. improved the coking resistance of Ni-based catalyst along with synthesising small Ni particles by doping Praseodymium oxide [22] in the autothermal reforming of CH₄ reaction. Furthermore, the Pr loading improved the catalytic activity along with the H₂:CO molar ratio.

3.2 Noble metal catalysts

Several noble catalysts have been used in CPOM reaction, especially group VIII-X (8-10) metals. For instance: rhodium (Rh), ruthenium (Ru), palladium (Pd), Lanthanum (La) and platinum (Pt) [1, 4-6, 17, 23-31], where rhodium showed good activity [17, 23-26]. It was reported that Rh is more selective to syngas production (CO and H₂) than that of Pt in CPOM reaction in the corresponding catalysts of Rh/ α -Al₂O₃ and Pt/ α -Al₂O₃, respectively [26]. However, a high reaction temperature was still required (1000 °C) for Rh/ α -Al₂O₃ catalyst to achieve 37% methane conversion at 6 vol.% CH₄ in the reaction feed. On the other hand, Rh/CeZrO₂ catalyst showed 95% conversion at a reaction temperature of 750 °C (3.3% CH₄ in the feed). Lately, Rogozhnikov et al.[32] prepared Rh/ θ -Al₂O₃/FeCr alloy in the form of a wire mesh composite catalyst for CPOM reaction. They reported that the catalyst showed good performance with equilibrium product distribution and syngas productivity of 56.7 m³.L.cat⁻¹.h⁻¹ (s.c.) at 800 °C at 23.5 vol.% CH₄ in the reaction feed (GHSV of 80000 h⁻¹) [32]. In a recent study, Alvarez-Galvan et al.[33] studied the impact of doping Rh on Ni-based catalyst in CPOM reaction. It is not surprising that unmodified Ni-based catalyst suffered from fast deactivation. However, they found out that Rh favours Ni reduction, which led to an improvement in the conversion and yield alongside 80% conversion at 750 °C (29.5% CH₄ in the feed) [33]. Boukha et al.[34] studied the role of the Rh particle size in hydroxyapatite catalysts for CPOM reaction where Rh(x)/HAP catalysts showed high coke-resistance from a stability test which lasted for 30 hours at 700 °C.

They found the interaction between the Rh and the TCP support had a negative impact on the performance of the catalyst during CPOM reaction.

Ru metal was included in a combination of Co-Ni-Ru catalyst for CPOM reaction and showed 98% conversion along with high CO selectivity (94%) [35] at 10000 h^{-1} . La metal is usually used to promote methane total oxidation (MTO) into CO_2 and H_2O , where Ni is added as a promoter to convert those products into syngas [29]. Thus, Ni and La were used as a bimetallic catalyst in CPOM reaction. For instance, Pantaleo et al. [5] used 5%Ni/ CeO_2 - La_2O_3 catalyst in CPOM reaction with $T_{50\%}$ found to be at $675\text{ }^\circ\text{C}$ at GHSV of $60000\text{ mL.g}^{-1}.\text{h}^{-1}$. Re metal is also used to promote the Ni-based catalyst. For instance, Cheephat et al. [36] studied the promotion effect of Rh or Re on Ni/ Al_2O_3 catalyst. They found out that Re-Ni/ Al_2O_3 showed high stability with slight deactivation in H_2 yield after 18 hours of operation.

4. Effect of catalyst components

As discussed above, the most common active noble metal is rhodium, whilst for transition metals it is nickel. Accompanied by the metal content, acidic catalyst supports such as Al_2O_3 , ZSM-5 and oxygen support materials (TiO_2 , CeO_2 - ZrO_2) play a crucial role in CPOM reaction. Ni-based catalysts were prepared on different supports: acidic (Al_2O_3), oxygen storage (CeO_2) and basic (MgO); where Ni- Al_2O_3 and Ni- CeO_2 catalysts showed better activity and stability than that of Ni- MgO [33]. This was explained due to the higher surface area of Ni nanoparticles on the alumina support and the existence of oxygen vacancies in the ceria oxide lattice, which act as oxygen storage during the CPOM reaction. On the other hand, Ni- MgO catalyst suffered from the fast deactivation due to the formation of NiO/ MgO solid solution, which is hardly reduced under the CPOM reaction conditions [33]. Thus, acidic supports are better than basic supports in CPOM reaction and in general, zeolite support performs better than alumina due to their higher

acidity, along with surface area. Osman et al. [13] prepared Ni on η -Al₂O₃ and ZSM-5(80) on the addition of CeO₂-ZrO₂ as oxygen storage, where Ni/ CeO₂-ZrO₂/ZSM-5(80) showed higher methane conversion than that of Ni/ CeO₂-ZrO₂/ η -Al₂O₃ catalyst with T_{50%} of 392 and 415 °C, respectively. This was explained due to three reasons; the larger surface area, surface acidity and increased interaction and interfacial area between the Ni and ZSM-5(80) compared to the η -Al₂O₃ catalyst. Firstly, the larger S_{BET} and pore structure of the ZSM-5 (80) resulted in higher dispersion in the catalyst pores (Ni/ CeO₂-ZrO₂/ZSM-5(80)) and a correspondingly larger number of smaller Ni nanoparticles within the catalyst. Secondly, it is well known that zeolite type catalysts offer strong Bronsted acidic sites, compared to the weak and medium Lewis acidic sites in alumina type catalysts. Thus, ZSM-5(80) increased the electrophilicity of the Ni metal and consequently enhanced the re-oxidation step in the catalytic cycle during the CPOM reaction, accordingly, increasing the rate of the reaction. Thirdly, the increased acidity led to strong interaction and increased the interfacial area between the Ni and the ZSM-5(80) support which boosted the oxygen transfer from the oxygen storage (CeO₂-ZrO₂) and ZSM-5(80) support onto the Ni metal for its re-oxidation and also the oxidation of any carbon atom deposited on the surface of the catalyst into CO or CO₂, thus removal of the coke [13]. 5%Ni/Ce_{0.25}-Zr_{0.75}O₂ catalyst was used in CPOM reaction with a T_{50%} of 550 °C and CO selectivity of 90% at 750 °C (GHSV of 106,000 ml.g⁻¹.h⁻¹) [37]. However, most oxygen storage materials such as CeO₂, ZrO₂ or a mixture of both intrinsically offer low surface area along with a high associated cost. Therefore, they are not preferred to be used as a single support. Consequently, to overcome this, many studies added alumina as dual support along with the oxygen storage due to their high surface area and their low cost [20, 38]. For instance, a substantial increase in the catalytic activity was found for the Ni/CeO₂-ZrO₂-Al₂O₃ catalyst with S_{BET} of 165.3 m².g⁻¹, compared to that without Al₂O₃ which had S_{BET} of 25.8 m².g⁻¹ with T_{90%} at a temperature of 720 °C and >800 °C, respectively (GHSV of 200,000 mL.g⁻¹.h⁻¹) [20]. The CO selectivity was also slightly

increased from 93% to 95% at reaction temperature 700 °C for Ni/CeO₂-ZrO₂ and Ni/CeO₂-ZrO₂-Al₂O₃, respectively. Xiulan Cai et al.[38] examined Ni loaded on Al₂O₃, ZrO₂-Al₂O₃, CeO₂-Al₂O₃ and CeO₂-ZrO₂-Al₂O₃ for methane auto-thermal reforming. The catalyst supports were prepared using coprecipitation method while the 10 wt.% Ni was loaded using wetness impregnation method. The results showed that the catalytic performance and stability of Ni/CeO₂-ZrO₂-Al₂O₃ was the best in this particular work. The 10 wt.% Ni/Al₂O₃ catalyst showed methane conversion of 73%, while Ni/CeO₂-ZrO₂-Al₂O₃ catalyst showed 93%.

5. Effect of preparation methods:

The close interaction and interfacial area between the metal, reducible oxide and acidic support are crucial during the CPOM reaction, which leads to improving the catalytic performance along with the catalyst stability. The close interaction is required to allow better interaction between the metal and the oxygen vacancies on the support, which not only improves the redox behaviour of the metal during the COPM reaction cycle, but also supplies oxygen to facilitate the oxidation and removal of any coke deposited. This can be achieved by preparing catalysts with very small particle sizes or by using a co-precipitation method to prepare the CPOM catalysts. For example, 10% Ni/CeO₂ catalyst was prepared using co-precipitation method which significantly improved the interaction between the CPOM catalyst components and hence, enhanced the catalytic performance with a T_{50%} at 525 °C, compared with 630 °C for the catalyst prepared by impregnation (GHSV of 10,400 mL.g⁻¹.h⁻¹) [21]. Cai et al. [38] used the co-precipitation method to prepare Ni-based catalyst on different supports (Al₂O₃, ZrO₂-Al₂O₃, CeO₂-Al₂O₃ and CeO₂-ZrO₂-Al₂O₃) and used these for the methane auto-thermal reforming reaction. They found out that Ni/CeO₂-ZrO₂-Al₂O₃ catalyst showed good dispersion of NiO allowing improved oxygen transfer, but also decreased the formation of nickel aluminate which has no catalytic activity during combustion reactions. Recently, the co-precipitation method was used to prepare higher

S_{BET} CPOM catalyst than the equivalent catalysts prepared with a wet-impregnation method for both alumina and ZSM-5 (80) support [13]. The CO-chemisorption test also revealed that the co-precipitation method offered higher Ni dispersion than that of the wet-impregnation method. The catalytic activity of zeolite catalysts, 10% Ni/ CeO₂-ZrO₂/ZSM-5 (80) using co-precipitation and wet-impregnation methods showed T_{50%} at 392 and 415 °C, respectively. Ozdemir et al.[39] studied the effect of the calcination temperature along with the time of the calcination on Ni/MgAl₂O₄ catalyst for CPOM reaction. They reported that the calcination temperature (500-1000 °C for 3hrs) improved the metal oxide support interaction, but calcination time only caused the catalyst sintering (1000 °C for 10 hrs). Moreover, the higher ratio of basicity to acidity increased with increasing the calcination temperature and inhibited the amount of coke deposition on the catalyst due to the enhanced CO₂ chemisorption. They also found that coke deposition increased with increasing the Ni particle size [39].

6. Reaction mechanism

There are mainly two mechanisms for CPOM reaction where there are several factors affecting the reaction mechanisms such as the catalyst components, reaction conditions and the interaction between the metals and support within the catalyst [26, 30, 40-45]. The first mechanism is the direct partial oxidation (DPO) which involves the dissociation of CH₄ followed by oxidation of surface carbon to CO and subsequent desorption of CO and H₂ gases as shown in Figure 1 (a). The combustion and reforming reaction (CRR) mechanism involves the complete combustion of CH₄ into combustion products (CO₂ and H₂O), which are then converted through dry or steam reforming to CO and H₂ as shown in Figure 1 (b).

Figure 1: shows the two reaction mechanisms involved in the catalytic partial oxidation of methane (a, b).

In TMO reaction mechanism, CH_4 is dissociatively adsorbed on the metal and the methyl species are then fully oxidised by PdO present on the surface. The resulting reduced metal species is then oxidised by the lattice oxygen from the oxygen storage such as (TiO_2 and $\text{CeO}_2\text{-ZrO}_2$) or from the gas phase oxygen in the reaction stream [46]. Thus, the total methane oxidation mechanism is similar to the DPO mechanism. Lanza et al. [30] studied the CPOM reaction mechanism over Pt-Ru catalyst using alumina, ceria and zirconia as catalyst supports in the temperature range of 300-800 °C and GHSV of 25000-100000 h^{-1} . They reported that Pt-Ru catalysts support the indirect route which is the CRR mechanism where combustion occurred followed by reforming reactions. However, by increasing the O_2 in the reaction feed over the stoichiometric ratio of

CPOM reaction, the combustion products were increased at low reaction temperature, thus increased the CO₂ selectivity over the CO selectivity [30]. Tavazzi et al. also proposed the CRR mechanism on Rh/ α -Al₂O₃ catalyst [47]. On the other hand, recently, Osman et al. [13] reported a DPO mechanism on Ni-based catalyst for CPOM reaction.

7. Kinetic studies

The theoretical thermodynamic equilibrium calculations of different % CH₄ in the reaction are shown in Figure 2, where the low CH₄ concentration was composed of 10% CH₄, 5% O₂, 5% Ne and 80% Ar (feed A). While the high CH₄ concentration was 20% CH₄, 10% O₂, 5% Ne and 65% Ar (feed B). By taking in consideration of the formation of coke during the reaction, the selectivity of the coke decreased with increasing the reaction temperature as shown in Figure 2 (a, d) and Table 1, regardless of the methane concentration in the reaction feed. The coke selectivities in feed A, at reaction temperatures of 250, 515, 705 and 800 °C were 77, 57, 10.5 and 2%, respectively, as shown in Table 1. In general, the coke formation slightly increased by increasing the methane concentration from 10 CH₄% (feed A) into 20 CH₄% (feed B) with a dramatic increase at high reaction temperatures. For instance, the coke selectivity in feed B, at reaction temperatures of 250, 515, 705 and 800 °C were 77, 62, 21 and 8%, respectively, as shown in Table 1. The CO₂ selectivity for both feeds (A and B) showed a slight increase in the reaction temperature range of 250-500 °C, followed by a dramatic decrease in the temperature range of 550-800 °C where feed B had higher CO₂ selectivity in general as shown in Figure 2 (a, d) and Table 1. The CO₂ selectivities in feed A, at reaction temperatures of 250, 515, 705 and 800 °C were 22.9, 27.2, 5.7 and 1.2%, respectively. While at same reaction temperatures for feed B were 22.9, 27.5, 9.1 and 2.4%, respectively. On the other hand, the CO selectivity decreased with increasing the reaction temperature, with a rapid decrease in the temperature range of 477-800 °C, regardless of the methane concentration in the reaction feed where feed A had higher

selectivity in general as shown in Figure 2 (a, d). The CO selectivities in feed A, at reaction temperatures of 250, 515, 705 and 800 °C were 0.02, 15.7, 83.7 and 96.6%, respectively. While at same reaction temperatures for feed B were 0.02, 10.5, 70.3 and 89.7%, respectively, as shown in Table 1. The molar fraction of the reaction products are shown in Figure 2 (b, e) and Table 1. Firstly, Ne inert gas was used as an internal standard, thus its concentration remains constant, while the oxygen concentration in partial oxidation reaction is totally used in the reaction, thus its molar fraction in the products is zero. The molar fractions of CO and H₂ increased with increasing the reaction temperature while the opposite is occurring for H₂O and CH₄, as shown in Figure 2 (b, e) and Table 1. Figure 2 (c, f) shows the methane and oxygen conversions for feed A and B. It is not surprising that the O₂ conversion is always 100% in the reaction temperature range of 250-800 °C. Furthermore, by increasing the methane concentration in the reaction feed from 10 CH₄% (feed A) into 20 CH₄% (feed B), the CH₄ conversion decreased. The CH₄ conversion in feed A, at reaction temperatures of 250, 515, 705 and 800 °C were 43.6, 79.8, 96.5 and 98.6%, respectively, while at the same reaction temperatures for feed B were 42.0, 73.1, 94.3 and 97.6 %, respectively as shown in Figure 2 (c, f).

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299 **Table 1:** The theoretical thermodynamic equilibrium selectivity and product mole fraction of
 300 different methane concentrations in the reaction feed.

Reaction Temp.	%CH ₄ in feed	% selectivity			Products mole fraction					
		CO	CO ₂	Coke	CO	H ₂	CO ₂	H ₂ O	CH ₄	Ar
250 °C	10% CH ₄ *	0.02	22.93	77.05	0.0	0.01	0.01	0.08	0.06	0.81
	20% CH ₄ **	0.02	22.94	77.04	0.00	0.01	0.02	0.17	0.11	0.66
515 °C	10% CH ₄ *	15.7	27.2	57.1	0.01	0.11	0.02	0.04	0.02	0.76
	20% CH ₄ **	10.52	27.5	61.96	0.02	0.17	0.04	0.09	0.05	0.60
705 °C	10% CH ₄ *	83.75	5.76	10.49	0.07	0.16	0.00	0.01	0.00	0.71
	20% CH ₄ **	70.31	9.07	20.62	0.11	0.28	0.01	0.02	0.01	0.53
800 °C	10% CH ₄ *	96.58	1.25	2.17	0.08	0.17	0.00	0.00	0.00	0.71
	20% CH ₄ **	89.71	2.39	7.90	0.14	0.30	0.00	0.01	0.00	0.51

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302 *Feed A is the reaction feed composition of (10% CH₄ + 5% O₂ + 5% Ne + 80% Ar)

303 ** Feed B is the reaction feed composition of (20% CH₄ + 10% O₂ + 5% Ne + 65% Ar)

Figure 2: Theoretical thermodynamic equilibrium calculations of different % CH₄ in the feed (10% CH₄ (left) and 20% CH₄ (right): selectivity (a, d), fraction yield (b, e) and conversion (c, f).

8. Deactivation of CPOM catalysts

As shown in Figure 2 that the coke selectivity is higher at lower reaction temperatures which is one of the main reason for catalyst deactivation in CPOM reaction. It is well known that the produced CO adsorbs strongly over the surface of the catalyst at the lower reaction temperature, leading to reversibility deactivate the catalyst. In previous work, CO was added to the reaction stream as shown in Figure 3, where the extent of CO poisoning increased with decreasing the reaction temperature. For instance, at a reaction temperature of 600 °C, the % methane conversion decreased from 83 to 79%. While at a reaction temperature of 400 °C, there was a significant decrease of 10% in the methane conversion from approximately 52 to 42% as shown in Figure 3. Thus having oxygen storage such as reducible oxide support helps to re-oxidise and clean the surface of the catalyst. On the other hand, molybdenum phosphide is being used in methane dry and oxy-reforming (partial oxidation) where MoP is the dominant active site and it deactivates due to the bulk oxidation [48]. The MoP catalyst deactivates gradually when it converted into the less active phase molybdenum carbide (Mo_2C) then a rapid deactivation due to the bulk oxidation into the non-active phase of MoO_2 . Cui et al. also reported that due to the higher H_2 yield in CPOM reaction compared to dry reforming which maintains the redox cycle of the MoP catalyst, thus showed higher catalytic stability [48]. Recently, Karaismailoglu et al.[49] studied the effect of doping yttria oxide (Y_2O_3) doped nickel-based catalyst on methane decomposition. They found out the pure Ni-based catalyst suffers from rapid deactivation due to coke formation while loading yttria oxide helps to improve the catalytic activity and reduce the carbon deposition. One of the main factors of deactivating nickel-based catalyst is the formation of nickel aluminate.

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335 **Figure 3:** The inhibition effect of CO added to the CPOM reaction feed. Reaction conditions:
 336 temperature, 400-700 °C with WHSV, 63000 mL.g⁻¹ h⁻¹ [13].

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9. Conclusion

Nickel is recognised as one of the cheapest and most active transition metal catalysts and rhodium as a noble metal. However, Ni is more prone to carbon deposition which poisons and consequently deactivates the catalyst. However, recent studies showed that nickel loaded on dual supports including a reducible metal oxide such as TiO_2 or $\text{CeO}_2\text{-ZrO}_2$, which act as oxygen storage and re-oxidise any coke deposition, thus clean-up the catalyst and enhance its stability. The acidity in zeolite or alumina supports enhances the reoxidation of the metal catalyst, thus enhancing the redox cycle during the CPOM reaction. Therefore, the three main components; the metal, reducible mixed oxide and acidic catalyst support are crucial in CPOM reaction along with the close interaction and interfacial area between the catalyst components for the catalyst activity and stability. However, this is not the case for molybdenum phosphide catalysts in the reforming reactions, where MoP is the dominant active site and it deactivates due to the bulk oxidation. Given the fact of the close interaction, the co-precipitation offered better and close interaction between the active components than the wet-impregnation method. The extent of the reversible CO poisoning increased with decreasing the reaction temperature during the CPOM reaction. Bimetallic catalysts showed better stability than a single metal catalyst such as Pt stabilises the Pd metal in total methane oxidation or Y_2O_3 stabilises Ni-based catalysts in CPOM reaction.

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Symbols and abbreviations

Abbreviation and nomenclature			
Catalytic partial oxidation of methane	<i>CPOM</i>	Methane total oxidation	<i>MTO</i>
Combustion and reforming reaction	<i>CRR</i>	Molybdenum carbide	Mo_2C
Dimethyl ether	<i>DME</i>	Nitrogen oxide	NO_x
Direct partial oxidation	<i>DPO</i>	Sulfur oxide	SO_x
Gas hourly space velocity	<i>GHSV</i>	Water gas shift reaction	<i>WGSR</i>
Greenhouse gas	<i>GHG</i>	Yttria oxide	Y_2O_3

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Figure and Table legends:

Figure 1: shows the two reaction mechanisms involved in the catalytic partial oxidation of methane (a, b).

Figure 2: Theoretical thermodynamic equilibrium calculations of different % CH₄ in the feed 10% CH₄ (left) and 20% CH₄ (right): selectivity (a, d), fraction yield (b, e) and conversion (c, f).

Figure 3: The inhibition effect of CO added to the CPOM reaction feed. Reaction conditions: temperature, 400-700 °C with WHSV, 63000 mL.g⁻¹ h⁻¹ [13].

Table 1: The theoretical thermodynamic equilibrium selectivity and product mole fraction of different methane concentrations in the reaction feed.

Short text for the table of contents section

Herein, the mini-review investigates the multifunctional potential of a transition and noble metal catalyst supported on either single support or combined oxide support in the catalytic partial oxidation of methane. The factors that influence the oxidation reaction along with the mechanism and the kinetic studies were also reported. The main reasons for catalyst deactivation were also explored.