

## Review Article

# Catalysts and Reactors for Synthesis Gas Production via Dry Reforming of Methane: A Review assisted with DWSIM Simulation

Amol Narendra Joshi<sup>1</sup>, Sreedevi Upadhyayula<sup>2\*</sup>

<sup>1</sup>Department of Chemical Engineering, Vishwakarma Institute of Technology, Bibvewadi, Pune, Maharashtra, India

<sup>2</sup>Department of Chemical Engineering, Indian Institute of Technology-Delhi, Hauz Khas, New Delhi, India

\***Corresponding author:** Sreedevi Upadhyayula, Department of Chemical Engineering, Indian Institute of Technology-Delhi, Hauz Khas, New Delhi, 110016, India

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## Abstract

Dry reforming of methane (DRM) produces synthesis gas which is comprised of hydrogen (H<sub>2</sub>) and carbon monoxide (CO). The enthalpy of the reaction is 247 kJ/mol suggesting that the reaction is highly endothermic and hence enormous temperature is required for the reaction to proceed. A major drawback of this reaction is the deactivation of catalysts due to coke formation and sintering. Plenty of research work has been done to develop various catalysts – bimetallic, supported, nano-catalysts to name a few. However, there exists some lacuna in the exhaustive literature of catalysts for dry reforming of methane. Different reactors have proved to be best suited for dry reforming of methane – membrane reactor, fixed bed reactor, plasma reactor, and microreactor. So, an attempt has been made in the present review paper to compile all the data available and analyze the catalysts which reduce coke formation, sintering; analyze various advancements in the synthesis methods of these catalysts and their structure along with the reaction mechanism. The experimental analysis is simulated in DWSIM software to check for the effect of variations in pressure and mole fractions on the reactant conversion.

**Keywords:** Catalysts; Coke; Dry reforming; Endothermic; Methane

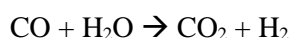
## Introduction

Carbon dioxide and methane are major greenhouse gases arising from anthropogenic activities and they must be reduced to decrease global warming and climate change. CH<sub>4</sub> is 21 times more potent than CO<sub>2</sub> to increase atmospheric temperature [1]. Dry Reforming of Methane (DRM) has gained attention by researchers in present years due to its environmental benefit and effective utilization of CO<sub>2</sub> and CH<sub>4</sub> for the production of producer gas, also known as synthesis gas which mainly consists of Carbon monoxide (CO) and Hydrogen (H<sub>2</sub>). This synthesis gas can be utilized for oil production using Fischer-Tropsch synthesis, oxygenated chemicals like methanol, and other value-added products [2,3]. Dry reforming of Methane is a cheaper process to obtain synthesis gas as there is no need of separating the products [4].

The DRM reaction equation is as follows:



The value of  $\Delta H$  is positive, suggests that the reaction is highly endothermic and hence the reaction requires a very high temperature to proceed forward. The instability of catalyst at the reaction conditions is one of the reasons for DRM not being used on an industrial scale [6]. The other reason being catalyst deactivation due to coke formation [7] and sintering. At the reaction conditions, a series of side reactions also take place, most important being the water gas shift reaction (WGS) [8]:



Also, Boudouard reaction is one of the side reaction which forms carbon.



$\text{CO}_2$  utilization could be the bridging gap for the deployment and geographical constraints of capture technologies based on boosting legislative schemes [10]. Thus,  $\text{CO}_2$  reutilization is important to curb its green-house effects.

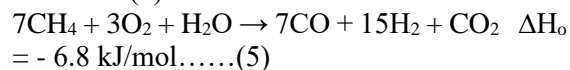
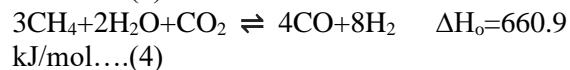
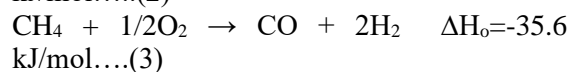
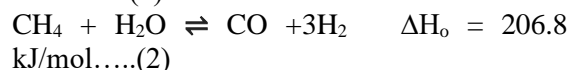
The catalysts used for DRM are comprised of two main types of metals – noble metals and non-noble metals. The noble metals have high stability and considerably high catalytic activity. But these noble metals are expensive and availability is limited so this causes limitations in commercial use. Hence non-noble metals are widely used for DRM. Various approaches have been studied by researchers to minimize coke formation, synthesize stable catalysts, optimize reaction time and temperature to increase conversion of methane and carbon dioxide, and increase the yield of carbon monoxide and hydrogen in the ratio 1:1. Few research articles depict the use of different types of reactors like membrane reactor, fixed bed reactor, plasma reactor, microreactor, etc. for DRM. Gregor D. Wehinger, et al. performed studies on packed bed reactor using CFD packed bed being majorly used for DRM [11]. Major work has been done in synthesizing various catalysts using Ni, zeolites, minerals, actinides, bimetallic catalysts, nano-catalysts and to name a few with enhanced activities, stability, and better performance. But still, there is some sort of gap in the literature review solely devoted to different catalysts, synthesizing methods of catalysts. The

conversion of  $\text{CH}_4$  and  $\text{CO}_2$  to syngas using low-cost nickel catalysts has attracted considerable interest in the clean energy and environment field. Ni single-atom catalysts exhibit excellent resistance to carbon deposition and high atom efficiency with a high reaction rate [12]. Therefore, an attempt is made to review all possible catalysts for the process of dry reforming of methane.

### Comparison of different reforming processes

#### Reactions

$\text{CH}_4$  can undergo various reforming processes like dry reforming, steam reforming, combination of both [13], partial oxidation of methane [14]. The reactions are given as below:  
 $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad \Delta H_o = 247 \text{ kJ/mol} \dots(1)$

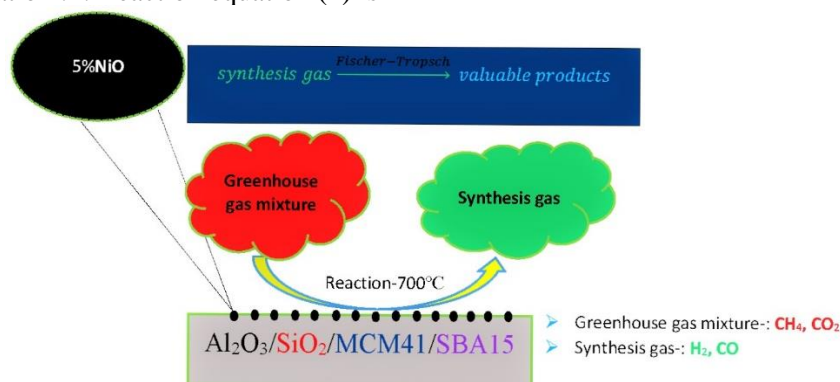


#### Comparison

Steam reforming of methane as shown in reaction (2), requires a large heat supply, and the products formed are in the ratio  $\text{CO}:\text{H}_2 = 1:3$  which is not useful for Fischer Tropsch synthesis. Deactivation of the catalyst by coke formation is a major issue here. The partial oxidation of methane – reaction (3) is an exothermic process, is economical than steam reforming, can work without catalyst, and give  $\text{CO}:\text{H}_2 = 1:2$  which is then utilized for downstream Fischer Tropsch synthesis but partial oxidation requires pure  $\text{O}_2$  and high purity separation air separation plant is required and reaction equipments to handle high temperatures up to 1200K [15]. Reaction equation (5) is autothermal reforming of methane [15]. This process is slightly exothermic and is economical than steam reforming but here extensive control systems

are required for proper fuel combustion which is a major challenge. Dry reforming of methane as depicted in reaction equation (1) gives CO:H<sub>2</sub> in the ratio 1:1. Reaction equation (4) is

combined dry and steam reforming, is endothermic and requires high energy to sustain the reaction.



**Figure 1:** General Scheme of Dry Reforming of Methane [16].

### Catalysts used in DRM

Metals used in catalysts are divided into two parts- base metals and noble metals. Generally, Ni is used as active species for DRM catalysts due to its high activity and low cost. Some other metals as Co or noble metals are added to examine bimetallic effects on the catalysts. Noble metals (Ru, Rh, Pd, and Pt) have high activity and low sensitivity for carbon deposition/coke formation.

The industrial choice of metal catalysts is Ni because of ease of availability, low cost but this Ni tends to get deactivated by carbon deposition. So various advancements have been to increase the stability of catalysts, minimize carbon deposition and develop recyclable catalysts.

### Role of Promoters

Julian R.H. Ross, Bhari Mallanna Nagaraja, Dmitri A. Bulushev have developed potassium doped Ni-MgO-ZrO<sub>2</sub> catalyst [17]. MgO, TiO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> interact with Ni to significantly inhibit carbon deposition. Alkali metal like potassium (K) acts as a promoter in small amounts (0.2-0.5 % by weight). Potassium acetate and Ni in the ratio 0.125 pose strong resistance to carbon deposition.

Ye Wang Lu, et al. synthesized ZrO<sub>2</sub> supported Ni catalyst with Si as a promoter. The catalyst was synthesized by the impregnation method with a Ni nanoparticle size of 6-9 nm. The reaction was carried out at two temperatures 400°C and 450°C. Coke deposits were observed at both temperatures but at 450°C, the coke formed could not be removed because the CO<sub>2</sub> preferred to react with H species and not with carbon [18].

Yu. M, et.al synthesized catalysts with Sn, Ce, Mn, Co as promoters on Ni<sub>x</sub>Mg-xO [19]. Bottom-up approach was used for synthesis. Here Sn and Co get evenly distributed whereas Mn and Ce remain segregated. Hence Sn and Co have greater resistance to coke formation and inhibit β-Carbon deposit.

Guo xia Zhang, et al. added Gd as a promoter on Ni/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst. The precursor used was Gd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O. One-pot Pechini method was used for catalyst synthesis [20]. Along with catalyst (200 mg), some sand particles were put to eliminate the bed temperature gradient. Weight percent of Gd was 0.8%, 1%, 1.2%, 1.4% and 2%. The reaction was carried out at 800°C. 1.2% Gd<sub>2</sub>O<sub>3</sub> was found to be best suited to have high catalytic performance, minimum coke forming ability. Gd addition weakens the NiAl<sub>2</sub>O<sub>4</sub> phase on the catalyst and hence

enhances performance due to the reduction of Ni.

Brian Ashley developed a patented catalyst comprised of Ni on Rhenium promoter (Re) [21]. Different metal core catalysts can be alloyed with Co, Fe, Cr, etc. An electrotherm tube furnace was used for the reaction at 700°C, 750°C. In the feed stream, the ratio was CH<sub>4</sub>:CO<sub>2</sub>:Ar = 1:1:8. Re promoted catalyst performed well by 10% at 750-800°C. When the temperature was reduced to 700°C and an additional Re 0.2% was added, conversion of CH<sub>4</sub> and CO<sub>2</sub> doubled [21].

Al Fatesh, et al. studied the effects of promoters like Ca, Ce, and Zr on Ni/γ-Al<sub>2</sub>O<sub>3</sub> [22]. It was found that 3%Ni/γ-Al<sub>2</sub>O<sub>3</sub> promoted with 0.15% Ce and 0.05% Ca gave the best performance and resulted in very less coke formation. The CH<sub>4</sub> and CO<sub>2</sub> conversions were found to be 94.1% and 98.3% respectively at 850°C. Al Fatesh also developed catalysts with Sr as a promoter on 5wt% Ni and 5wt% Co on γ-Al<sub>2</sub>O<sub>3</sub> [23]. DRM reaction was carried out at 700°C. The corresponding results with Sr promoter at 700°C are listed in the Table 1.

Sr promoter (%)	CH <sub>4</sub> conversion (%)	CO <sub>2</sub> conversion (%)
0.0	86.1	84.5
0.25	85.8	84.2
0.50	84.7	84.2
0.75	84.9	82.3
1.0	83.1	81.9

**Table 1:** CH<sub>4</sub> and CO<sub>2</sub> conversion at 700°C with different wt percent of Sr promoter [23]

K. Świrk, et al. also studied Y modified Ni catalysts with DLH. Co-precipitation with yttrium (III) nitrate hexahydrate resulted in increased specific surface area, smaller Ni crystallite size, enhanced reducibility, and higher distribution of weak and medium basic sites as compared to Y-free material [24]. The reaction temperature was in the range of 600-850°C. 1.5 weight percent Y was found to be the most efficient Y concentration for stability, activity, and least deactivation of the catalyst. K. Świrk studied the effect of low Y concentration on DLH. Low Y concentration led to smaller Ni crystallite, decreased Ni reducibility, and also decreased the number of basic sites. 0.4 weight% of Y results in 84% CH<sub>4</sub> conversion and 87% CO<sub>2</sub> conversion at 700°C [25]. The catalyst remained stable after 5 hours of reaction run.

### Effect of operating variables – Temperature and Pressure

William L. Luyben designed a process plant for dry reforming of methane and considered various design variables like temperature, pressure, feed ratio, etc. to study the effect on conversion and selectivity [26]. When feed is in

the ratio of 1:1 no CO<sub>2</sub> recovery system is required and hence operating cost decreases. When pressure is increased, conversion of reactants drops so the pressure of 1 atm is most suitable for DRM. The maximum temperature allowed is 1000°C to avoid the formation of Nickel carbide on the surface of the catalyst which causes catalyst deactivation.

Rego de Vasconcelos B et al. suggested calcium hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> as supporting material for Ni [27]. Calcium hydroxyapatite is thermally stable and decomposes above 1000°C. Hence, using this catalyst no sintering takes place. Ni size used is 10-20 nm. The pressure is 1.6 bar. Catalyst is highly active and stable for 90 hours of the test. 700°C is the most suited temperature for high reactant conversion.

Andrzej Stankiewicz, et al. synthesized Pt/C catalysts for DRM and studied the effect of catalysts at different temperatures 600°C, 700°C, and 800°C. This was a microwave-assisted DRM. With the increasing power of the microwave, the temperature increased. As the temperature increased, conversion increases, and H<sub>2</sub>/CO ratio approaches unity at 800°C.

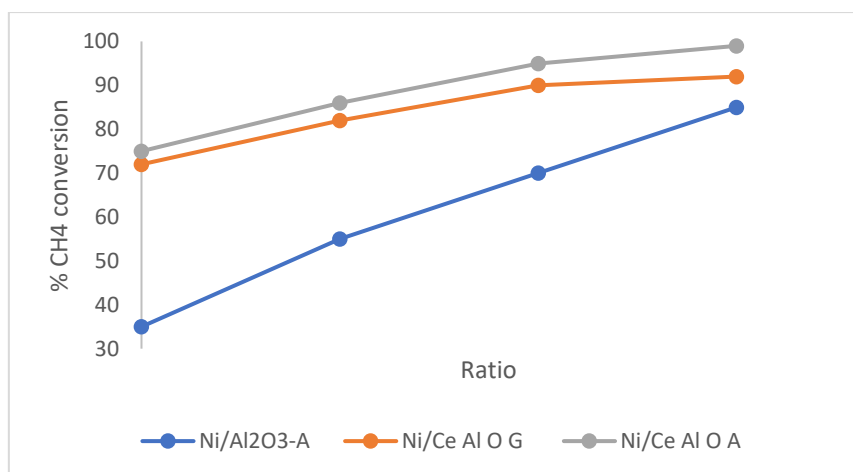
Also, with increasing temperature, the conversion of reactants increases [28].

Clarke Palmer, et.al, used molten metal alloys as a catalyst [29].  $\text{CH}_4:\text{CO}_2$  ratio was maintained as 1:1 to get Hydrogen selectivity of 97%. A bubble column reactor is used. The carbon formed in the reaction floats on the surface of the melt and can be easily separated. The metal used is Indium (In). Ar gas is purged in the bubble column. When temperature increases, CO selectivity decreases as described by Clarke Palmer.

### Effect of reactant ratio and inert

Evaporation-induced self-assembly method was used by Qinhong Wei, et al. to synthesize

Ce modified alumina support after which Ni was incorporated into alumina framework by citric acid auto reduction method [30]. In the reactant gas mixture,  $\text{O}_2$  was introduced which drastically increased methane conversion but decreased carbon dioxide conversion. Three catalysts were compared – Ni/ $\text{Al}_2\text{O}_3$ -A, Ni/Ce-Al-O-G, and Ni/Ce-Al-O-A; where, Ni/ $\text{Al}_2\text{O}_3$ -A this formed by the auto-reduction method, Ni/Ce-Al-O-G this is oxygen introduced and G is for general impregnation method and Ni/Ce-Al-O-A this is oxygen is introduced and auto-reduction method is used. With  $\text{CH}_4:\text{CO}_2:\text{O}_2 = 1:1:0.5$  conversion of  $\text{CH}_4$  was almost 100%. Carbon deposit: Ni/ $\text{Al}_2\text{O}_3$ -A (18.3%) > Ni/Ce-Al-O-G (4.4%) > Ni/Ce-Al-O-A (4%)



**Figure 2:**  $\text{CH}_4$  conversion with different ratio of  $\text{CH}_4:\text{CO}_2:\text{O}_2$  [30].  
 Ratio = 1:1:0, 1:1:0.15, 1:1:0.3, 1:1:0.5

### Nano-catalysts

Takeshi Fujita, et.al developed nanoporous Ni for DRM [14].  $\text{Y}_2\text{O}_3$  has been used as a supporting material. Ni/  $\text{Y}_2\text{O}_3$  maintained high performance and suppressed carbon deposits. At 450°C, 59% conversion of methane and carbon dioxide was seen and analyzed by characterization methods.

Yasar Vafaeian, et al. used Ni/ZSM-5 catalyst with an average Ni size of 43 nm as analyzed by TEM. Transmission electron microscopy (TEM) detects the size of the ultrathin film on the surface [31]. The particle size when less

than 100 nm i.e in the nano regime, the coke formation tendency decreases. Ni doping of 3-8 weight percent was used. The impregnation method was used via ultrasound irradiation. Reduction in particle size and particle size distribution is attributed to ultrasound energy during synthesis [32]. Out of which 8% Ni proved to be the best in terms of stability and resistance to coke formation.

Youngdong Song, et.al performed DRM with Ni-Mo nano-catalysts on MgO surface [33]. Mo alone is not suitable for DRM but when Ni-Mo is used improves conversion and yield. Ni:Mo

was always 5:1 ratio. Helium atmosphere was given to the reactor and 50 mg catalyst loading was present. Temperature of the reactor was 800°C. Ni nanoparticles size less than 7nm were used. It was found that above 7nm carbon deposition takes place.

Meirong Lu, et.al synthesized interface-based catalyst- BN Nanoceria interface-based Ni catalyst [34]. Bao, et al.[35] suggested that syn gas formation is enhanced at the interface between metal and boron nitride (BN). So Meirong Lu, et al. confined Ni between nanoceria (NC) and boron nitride (BN). This prevented coke formation and sintering of Ni nanoparticles. OH<sup>-</sup> ions formation was fast which helped prevent coke. A tubular quartz reactor was used at 750°C. Ni/NC conversion drops after 20 hours but Ni/NC/BN conversion remains constant.

Takami, et.al suggested that plasmonic metal nanoparticles accelerate DRM [36]. Wibow, et.al showed that SrTiO<sub>3</sub> photocatalysts can be

used for photocatalytic DRM [37]. Yohei Cho, et.al developed semiconductor-supported catalysts [38]. Rhodium (Rh) and Ruthenium (Ru) nanoparticles are deposited on semiconductor support. Tantalum-based oxynitride (TaON) and nitride (Ta<sub>3</sub>N<sub>5</sub>) with Rh nanoparticles were efficient for DRM. But Ta<sub>3</sub>N<sub>5</sub> has less thermal stability than TaON and hence Rh/TaON performed better than Rh/Ta<sub>3</sub>N<sub>5</sub>.

Swirk K, Zhang H, et al., made NiO-Y<sub>2</sub>O<sub>3</sub> nanostructure catalyst that was carbon resistant [39]. Yttrium loading was 3,4,8 weight percent. Double layered hydroxides (DLH) were synthesized by the co-precipitation method. When Yttrium content increases, basicity increases. Here NiY<sub>4</sub>-DLH i.e 4 weight percent Y showed the highest catalytic activity. The reaction carried out at 700°C. By Raman Spectroscopy data, Yttrium 8 weight percent gave superior coke resistance but conversion was not to the mark.

Catalyst	CH <sub>4</sub> conversion (%)	CO <sub>2</sub> conversion (%)	H <sub>2</sub> /CO ratio
NiY <sub>3</sub> -DLH	85	90	0.99
NiY <sub>4</sub> -DLH	84	90	1.00
NiY <sub>8</sub> -DLH	58	68	0.87

**Table 2:** Comparison of NiY-DLH catalysts with different Y weight% [39].

### Alumina supported catalysts

N.N Gavrilova, et.al have developed a Tungsten carbide (WC) catalyst on alumina surface (Al<sub>2</sub>O<sub>3</sub>) [6]. 2.86% WC/ Al<sub>2</sub>O<sub>3</sub> pellet 5.5 cm in length was developed. Here the temperature of the reaction can be lowered by about 100°C. The reaction rate constant is 30 times higher than the traditional catalyst used for DRM. During the reaction, water is formed as initial selectivity shows the same rate of formation for hydrogen and water. After which, CH<sub>4</sub> + H<sub>2</sub>O → CO + 3H<sub>2</sub> reaction is taking place. This reaction is possible only in membrane catalysts.

Ni catalyst supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub> supports, and found that the activity and selectivity were dependent on the nature of the support and increased in the order Ni/TiO<sub>2</sub> <

Ni/SiO<sub>2</sub> < Ni/Al<sub>2</sub>O<sub>3</sub>. The low activity of the Ni/TiO<sub>2</sub> catalyst was attributed to strong metal-support interactions. During reduction, TiO<sub>2</sub> molecules go to the surface of Ni particles, covering active sites, and hence a decrease in the surface free energy is seen [40].

The effect of plasma using a (10% wt.) Ni/γ-Al<sub>2</sub>O<sub>3</sub> calcined at different temperatures (300, 500, and 800°C) Results shows that plasma has indeed a positive effect on the conversion of methane and even without any catalyst the experimental setup by itself allowed a maximum conversion of methane in the range of 50% was reviewed by Jean M.L [41].

Chunshan Song and Wei Pan utilized the CO<sub>2</sub> from electric power plants for the production of syn gas[42]. Ni catalysts were used and tri reforming of methane was performed. The

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process had 97% CH<sub>4</sub> conversion and more than 80% CO<sub>2</sub> conversion with a 1.5-2 ratio of H<sub>2</sub>:CO. The ability of catalysts to enhance the conversion of CO<sub>2</sub> is as follows:

Yen Chen, et.al used Al promoted Ni/Palygorskite (Pal) catalyst developed by the co-precipitation method [43]. Palygorskite consists of 65.5% SiO<sub>2</sub>, 14% MgO, 5.4% Al<sub>2</sub>O<sub>3</sub>, 3.2% Fe<sub>2</sub>O<sub>3</sub>, 0.9% impurities, ignition losses are 11%. (all percent are weight percent). Ni content was 8 weight percent. Using only Ni/Pal only 5% conversion of methane was observed after 45 min. When the catalyst is Al promoted conversion enhances. Different content of Al was used – 2%, 5%, 8%, 15%. Fixed bed quartz reactor with catalyst packing was used.

Catalyst activity: Ni<sub>8</sub>/Al<sub>8</sub>/Pal > Ni<sub>8</sub>/Al<sub>5</sub>/Pal > Ni<sub>8</sub>/Al<sub>15</sub>/Pal > Ni<sub>8</sub>/Al<sub>2</sub>/Pal > Ni<sub>8</sub>/Pal [43]  
Ni<sub>8</sub>/Al<sub>8</sub>/Pal and Ni<sub>8</sub>/Al<sub>15</sub>/Pal formed no carbon. Strong interaction between Ni and Al<sub>2</sub>O<sub>3</sub> results in the formation of small Ni crystallites. Ni<sub>8</sub>/Al<sub>8</sub>/Pal is the best-suited catalyst with roughly 100% methane conversion and an H<sub>2</sub>/CO ratio of 0.98. When Al content is less than 8 weight percent, carbon deposition takes place which deactivates the catalyst [43].

Liu J-Lin, et al., conducted DRM in a Spark Plasma Reactor with Ni/Al<sub>2</sub>O<sub>3</sub> catalyst [44]. A high AC voltage supply with a frequency of 5 kHz was given. The distance between the electrodes was 10 mm. the reactor encompasses stainless steel catalyst holders. N<sub>2</sub> is used as an inert gas. It was observed that as methane in the feed increases coking tendency increases. Even

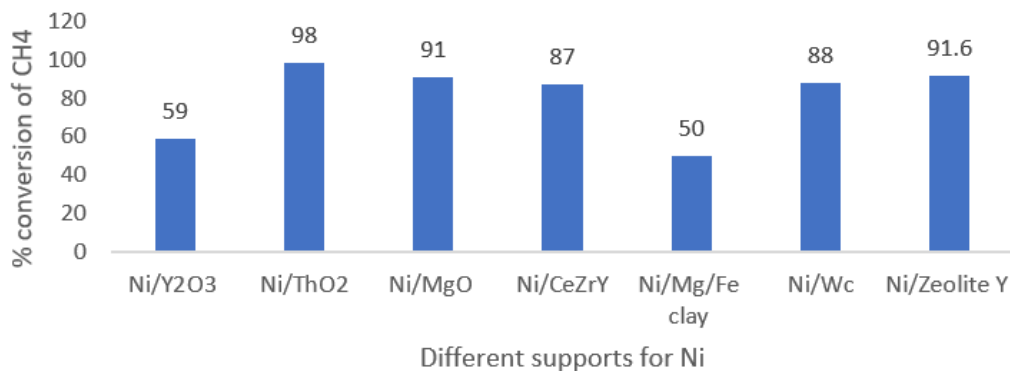
at 50% CH<sub>4</sub> severe coking was observed leading to plasma destabilization. 20% of the input energy is utilized in plasma for DRM endothermic reaction.

### **Zeolite supported catalysts**

Zeolites have gained attention nowadays due to their highly porous structures. They are mainly alumino- silicates. Ningbo Gaoa, et.al studied DRM over Ni-Ce/ZSM-5 catalyst [45]. Different Ni loading was used 1%, 5%, 10%, 20%. Higher the Ni loading more was the conversion of CH<sub>4</sub> and CO<sub>2</sub>. A fixed bed quartz reactor at 650-800°C was used.

Apanee Luengnaruemitchai, et.al studied zeolite-supported Ni catalysts, zeolite being thermally stable, has a high affinity for CO<sub>2</sub>, and enhances activity and stability [9]. 7% Ni loading gave the highest activity but also deposited carbon and deactivated the catalyst after the reaction. 91.6% conversion of CH<sub>4</sub> was obtained. ZeoliteY proved to be best to prevent coke formation and this support has a BET area of 606.5 m<sup>2</sup>/g. A cheaper catalyst with strong potential would confine Ni and Co particles in the mesopores of SBA15 zeolite [46].

Albazari, et.al used Ni-Ce/SBA-15 [47]. The reaction temperature was 650°C giving 99% conversion of CO<sub>2</sub> and almost 100% conversion of CH<sub>4</sub>. Ce:Ni ratio is maintained at less than 0.04 to prevent pore-blocking due to carbon deposits.



**Figure 3:** Conversion of CH<sub>4</sub> over supported Ni catalysts.

### Bimetallic catalysts

Ferreira AC, et.al have shown that actinide bimetallic catalyst synthesized from Uranium (U) and Thorium (Th) can stimulate the activation of CO<sub>2</sub>, prevent deactivation of the catalyst, and Uranium oxide formed helps in oxidation of carbon deposits [48]. Here 98% conversion of methane is possible and selectivity to syngas is more than 98%. Reactions are as  $2\text{Ni}.\text{ThO}_2 + 2\text{H}_2 \rightarrow 2\text{Ni}.\text{ThO}_2 + 2\text{H}_2\text{O}$  and  $\text{NiO}.\text{UNiO}_4 + 3\text{H}_2 \rightarrow 2\text{Ni}.\text{UO}_2 + 3\text{H}_2\text{O}$ . Here ThO<sub>2</sub> after the reaction is stable but UNiO<sub>4</sub> reduces to UO<sub>2</sub> (U<sup>6+</sup> to U<sup>4+</sup>). The reactions take place at 550-750°C.

Turap Y et al. synthesized Co-Ni alloy on CeO<sub>2</sub> as a bimetallic catalyst [49]. Co here enhances oxygen adsorption due to high oxygen affinity. Ni content was 10%. Fixed bed quartz reactor at 600-850°C was used for the reaction time of 60 minutes. The atomic ratio of 0.8 of Co:Ni gave the highest conversion of methane and carbon dioxide. Comparing Ni-Co/CeO<sub>2</sub> and Ni/CeO<sub>2</sub>, more carbon deposit was found on Ni/CeO<sub>2</sub>.

Bimetallic catalysts synthesized by the wet impregnation method have gained attention. Pan C, et al. synthesized Ni-Pd bimetallic catalyst [50]. SiO<sub>2</sub> was used as a support material. Ni:Pd was in the ratio 4:1. The reaction temperature was 700°C and reaction time was optimized to 60 min. H<sub>2</sub> selectivity was 98.4% and Pd was beneficial to the

reduction of NiO due to the hydrogen spillover effect [51].

Ismagilov, et al. developed Ni-Co on glass fiber catalyst [52]. At 750°C temperature, the conversion of CO<sub>2</sub> was 90% and that of CH<sub>4</sub> was almost 100%. A small amount of carbon deposit was observed – around 0.13%.

### Novel catalysts used in DRM

Very few researchers have developed catalysts with ores. Keisuke Abe, et.al used limonite laterite ore (FeOOH) as a catalyst [53].

This ore can be dehydrated to get porous Fe<sub>2</sub>O<sub>3</sub>. The reaction is  $2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ . This reaction proceeds at 573K. This ore also contains some Ni and 90% conversion of CO<sub>2</sub> is achieved. After reactions, no carbon deposits on the catalyst were found.

Solar energy is considered as its solution, which requires an efficient photocatalytic DRM (PDRM). However, most catalysts explored for PDRM are not efficient, about 4% of the total solar energy. Pt/blackTiO<sub>2</sub> catalyst with a light-diffuse- reflection- the surface of a SiO<sub>2</sub> substrate, which created an efficient visible light PDRM at relatively low temperature [54]. But these types of catalysts have not been studied in much more detail and research is on the way.

Huang J, et al. used freeze drying to synthesize Ni catalyst [55]. Layered double hydroxides were used. Ni catalyst supported on Mg-Al



oxide. A fixed bed reactor at 800°C was used for the reaction. To estimate carbon deposits, the bed was oxidized by 5% by volume O<sub>2</sub>/N<sub>2</sub> and total CO<sub>2</sub> and CO formed was quantified.

Katarzyna Świrk, et.al [5] developed double-layer hydroxides called hydrotalcites (HTs) which are potential carriers for metals. Then Mg<sup>2+</sup> and Al<sup>3+</sup> have been introduced on these carriers by co-precipitation. 5% by weight Zr is added to the catalyst to enhance stability but this limits the activity of the catalyst. Here Ni can be used which helps in decrease in reducibility of the catalyst as compared to Mg and Al. Along with Zr small amount of Y helps in increasing the activity. Also, Y improves the dispersion of Ni and decreases basicity.

Carbide catalysts have been developed and studied by Jun Guo, et al.[56]. NiMo<sub>2</sub>C catalyst was synthesized from (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O and Ni(NiO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O with Ni:Mo ratio of 2:3. A fixed bed quartz reactor at 1073K was used. No decline in NiMo<sub>2</sub>C catalytic activity was observed in 35 hours. If only Mo<sub>2</sub>C catalyst is used it deactivates due to Mo<sub>2</sub>C bulk oxidation by CO<sub>2</sub>.

Ingale P., et al. synthesized catalysts with AlO<sub>x</sub> coating on NiO/SiO<sub>2</sub> via molecular layer deposition [57]. Alucone deposition on the catalysts initially showed lower activity due to less Ni content due to the presence of alucone by molecular layer deposition. Very few carbon deposits of 0.8% were found on spent catalysts. After the reaction, the deactivation of alucone coated catalysts was 12-18% which was much lower due to 3-6 layers of alucone.

Yanzhao Cui, et.al performed tests for partial oxidation of methane and dry reforming of methane using molybdenum phosphide catalyst in the ratio 1:1[58]. Microreactor assembly was used for reactions. It was found that molybdenum phosphide catalyst is suitable for partial oxidation of methane than dry reforming of methane. Ruckenstein, et al. used Ni on alkaline metal oxides like MgO, SrO, BaO [59]. 700°C was the reaction temperature which gave 91% and 98% conversion of methane and carbon dioxide respectively.

Sun et al. synthesized Ni–CaO–ZrO<sub>2</sub> catalysts with different pore structures to be used as catalysts for DRM [60]. The catalyst with a mesoporous framework with a specific surface area of 210 m<sup>2</sup>/g showed both high activity and high stability. Also, no deactivation was observed after 100 hours and 700°C. The enhanced efficiency and resistance to coking were attributed to the confinement effect of the mesoporous structure which prevented Ni particles from sintering. These mesoporous materials exhibit higher activity as well as stability for DRM with retention of the mesostructure. The high specific surface area and large and uniform pore sizes inherent to these materials contributed to their superior performance. Also, the confinement effect of the mesoporous matrixes stabilized the Ni active sites during the reaction [61].

## Catalyst preparation methods

### Precipitation and Co-precipitation method

In precipitation method, active metal solution is precipitated by using a precipitating agent as metal carbonates and hydroxides, etc. It includes two distinct processes namely nucleation and growth. A majority of the bimetallic catalysts are synthesized by the co-precipitation method. Here, there is simultaneous precipitation of more than one component. Precipitation occurs in three steps: supersaturation, nucleation, and growth [62].

Katarzyna Świrk, et al.[5] and Yen Chen [43] have synthesized double-layered hydroxides and Ni/Palygorskite catalysts respectively by co-precipitation method. Wang S, et.al [63] synthesized Ni/MgO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts but these catalysts were less stable due to partial oxidation of Ni during the reaction. A base solution like NaOH is used and Na<sup>+</sup> ions i.e alkali metal ions could act as promoters and enhance the rate [17].

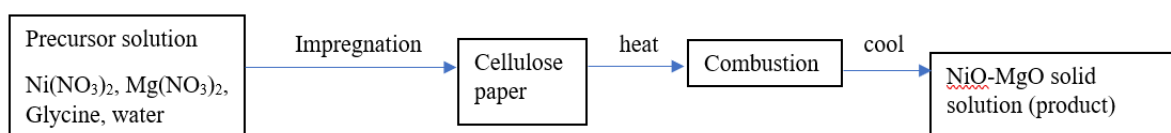
### Impregnation method

Many researchers have developed catalysts based on the impregnation method – wet and incipient impregnation. Impregnation method

has several advantages over precipitation method (i) Filtering and washing steps are eliminated (ii) Small metal loading are easily prepared (iii) Offers some control over the metal distribution on support etc. [1]. Pan C., et al., synthesized Ni-Pd bimetallic catalysts using the wet impregnation method [49]. Ni and Pd precursors –  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Pd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are used and deionized water is added. Mesoporous Silica is used as a support. Water is evaporated by sintering and powder is dried and calcinated. Oleic acid (OA) is also sometimes used and OA-assisted synthesis is performed.

### Reverse Micellar Method

$\text{NiCoO}_x/\gamma\text{Al}_2\text{O}_3$  was synthesized by Abbas Beheshti, et al., using the modified reverse micellar method [64]. Ammonium oxalate, nickel acetate, and cobalt acetate are mixed in water to make 3 solutions. A mixture of cetyltrimmonium bromide, hexanol, and hexane was prepared and added to the 3 solutions. Finally, all the solutions are mixed and stirred for 48 hours to get the catalyst. Centrifugation is done, washed with methanol and chloroform after which  $\gamma\text{Al}_2\text{O}_3$  is added and calcined at  $400^\circ\text{C}$ . This catalyst is highly stable and has high activity.



**Figure 4:** Cellulose paper assisted synthesis flow diagram [67].

### Atomic Layer Dispersion method

Gould T.D, et.al synthesized Ni-Pt catalyst on  $\text{Al}_2\text{O}_3$  support by Atomic Layer Deposition method [68]. Here the precursor is vaporized to transfer it on the support and hence a layer of the precursor is formed on the support. The pressure maintained is less than the vapour pressure. The particle size used by Gould T.D et.al was less than 3 nm which helped more and effective dispersion and also strong metal interaction.

### Solution Combustion Synthesis (SCS) and Paper assisted synthesis (PACS)

In this process, since we are considering Ni as the main metal for catalysts in DRM, nickel nitrate is heated in presence of glycine/urea. After which it is dried and a thick reactive gel is formed. Again when the gel is heated, combustion reaction ignites, and self-propagation through the medium takes place as synthesized by Wolf.E., et al.[65]. Ismagilov, et al. also synthesized Ni-Co catalyst on glass fiber by SCS method [49]. Danghyan V, et al., synthesized NiO-MgO catalysts by paper-assisted SCS for dry reforming of methane [66]. Catalysts formed are highly stable as small Ni crystallites easily.

Varma A., et.al synthesized NiOMgO catalysts by impregnating the reactive gel into cellulose paper [67]. The cellulose paper had a pore size of  $6\mu\text{m}$ . This was then dried at  $80^\circ\text{C}$  and further heated at  $200^\circ\text{C}$  for self-ignition. 10 weight% Ni in NiOMgO prepared by PACS was most stable and active as compared to 10NiOMgO/SCS catalyst which developed 26% by weight carbon after reaction with methane conversion of only 35%.

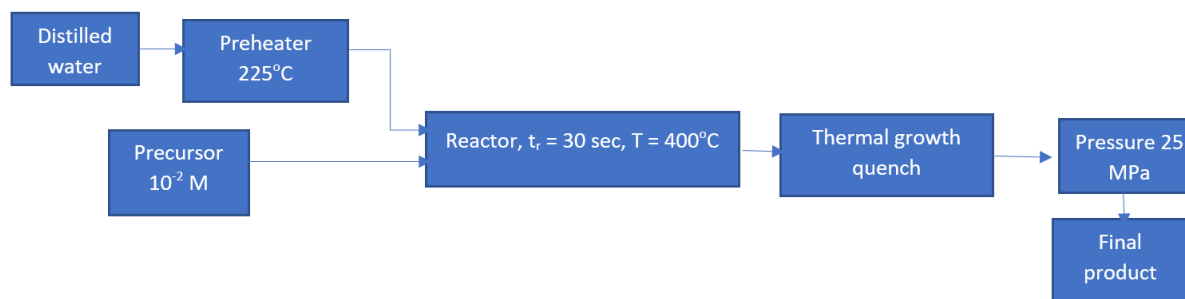
### Solvothermal process

Solvothermal synthesis is defined as a chemical reaction taking place in a solvent at temperatures above the boiling point and

pressures above 1 bar. The medium used in a solvothermal synthesis can be anything water, alcohol, or any other organic or inorganic solvent [69]. Brigitte Botello Frias, et al. used a supercritical solvothermal method for the synthesis of ceria-zirconia nanostructured

supports for catalysts [70]. A stainless steel reactor was used for synthesis. Two injection points one for deionized water and one for the precursor-ethanol mixture. The reactor temperature was set at 400°C and pressure was 25 MPa. Inside the reactor, the residence time

was 30 seconds and after which the mixture was quenched and taken in a suspension followed by centrifugation to get nanoparticles. These samples were calcined at 800°C for 6 hours and then Ni was incorporated by wet impregnation method.



**Figure 5:** Solvothermal process flow diagram for Ce-Zr nano-supports [70].

## Catalyst Deactivation in Dry Reforming of Methane

### Deactivation

As mentioned earlier, the deactivation of catalysts in dry reforming of methane reaction is a major cause of concern. The deactivation takes place due to carbon (coke) formation on the catalysts and due to sintering of the catalysts. Sintering is nothing but the local temperature is approximately  $1/3^{\text{rd}}$  to  $1/2$  the catalyst melting temperature. Some stabilizers  $\text{Al}_2\text{O}_3$ , Magnesia, Chromia increase the melting point of catalysts [71].

Many researchers have been working to tackle this problem of deactivation mainly coke formation. Confinement of Ni between supports, metal carbide catalysts, different support materials, stabilizers has been used to curb this coke formation problem. Ce modified mesoporous silica-supported Ni catalysts provide high resistance to coke, increases the life and activity of catalyst [72]. Silica mesoporous support has a high surface area, high pore volume, large pore size which enhances contact between reactants, decreases mass transfer efficiency and Ni-based alloys on silica have high resistance to carbon deposits [73]. F. Pompeo, et al. utilized Li-SiO<sub>2</sub> as

support for Ni. Also, Ni/SiO<sub>2</sub> was studied. It was found that on Li promoted support no

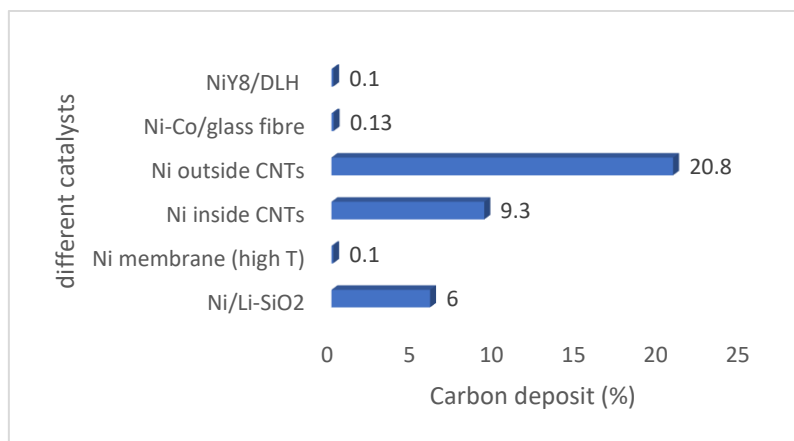
carbon deposits were found whereas, on only SiO<sub>2</sub>, 6 weight percent carbon was found [74]. Many structured catalysts like monoliths, foams, and perovskite provide versatile structural properties which help in the reaction dynamics control and help in enhancing the performance and efficiency of catalysts [75].

Carbide deactivation is mainly attributed to bulk oxidation [76]. Zhiwei Yao, et al. synthesized Ni/W and Ni/Mo catalysts, and further, they were carburized to get carbide catalysts – Ni/Mo<sub>2</sub>C and Ni/WC [77]. Ni/Mo<sub>2</sub>C catalyst showed a rapid decline in the performance in 5 hours whereas Ni/WC was stable for 12 hours giving 84-88% conversion of CH<sub>4</sub>. No coke deposit was found on both the catalysts but Ni/Mo<sub>2</sub>C underwent particle sintering. The conversion of methane drops rapidly using Ni/Mo<sub>2</sub>C catalyst due to sintering.

Now a days carbon and carbon materials like carbon nanotubes (CNTs), graphene, fullerenes, etc. Wang D, et al., deposited Ni nanoparticles inside and outside CNTs by the wet chemical method [78]. Argon gas was used as inert along with the reactants. CH<sub>4</sub>:CO<sub>2</sub>:Ar = 4.5:4.5:1. Results showed that the catalytic

activity of outside-CNTs was lower. Inside-CNTs were stable and gave 83.4% and 70.2% conversion of methane and carbon dioxide

respectively. Characterization results showed 9.3% carbon deposits on inside-CNTs and 20.8% carbon deposits on outside-CNTs.



**Figure 6:** Carbon deposits on different catalysts.

The addition of alkaline metals to catalysts brings Lewis basic sites on the support and efficiently curbs the carbon deposition by a reverse CO disproportionation reaction [79]:  $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ . Recently it was found that Ni nanoparticles with a size less than 8 nm are resistant to coke formation but are thermodynamically less stable and hence they get easily aggregated above 700°C [80]. As mentioned earlier Co has an affinity for oxygen and hence it slows down the reduction of Ni and stabilized the catalyst [81]. In a theoretical study, it was revealed Co has a low energy barrier for activation of methane and on the Co-Ni surface CH<sub>4</sub> activates preferentially [82]. On La<sub>2</sub>O<sub>3</sub> support many times there is poor dispersion of metals which can be improved by partial substitution of La by Ca, Ce, Sr [83] which would help in decreasing coke forming ability.

Ideally, the H<sub>2</sub>/CO ratio should be equal to 2. A higher value indicates the formation of solid carbon, a lower value indicates the presence of a reverse water-gas shift reaction. The percentage of carbon formed should be as low as possible. Ideally, the CO/CO<sub>2</sub> ratio should be equal to 1. A higher value indicates the oxidation of the carbon deposited on the

Support. The conversion of methane and carbon dioxide should be equivalent [84].

### Characterization

It is important to characterize catalysts for the DRM reaction from the perspective of morphology, carbon deposition, type of carbon, phase changes, active site and support behaviours, stability, catalyst chemistry, etc. To gather this information, a wide variety of common techniques are used, including those listed below:

- Active phases of the catalyst before and after reaction: X-Ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) spectroscopy, X-ray fluorescence (XRF) spectroscopy, and atomic absorption spectroscopy (AAS).
- Metal dispersion, metal particle size, and the state of the metal on supported catalysts: Transmission electron microscopy (TEM), scanning electron microscopy (SEM), XRD, and CO chemisorption.
- Formation of carbon deposits and their behaviour temperature-programmed oxidation (TPO), temperature-programmed hydrogenation (TPH), thermogravimetric analysis (TGA), differential thermal analysis (DTA), mass spectroscopy (MS), and

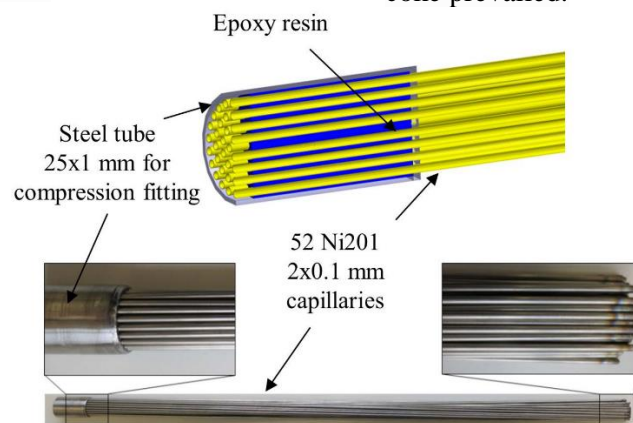
temperature-programmed surface reaction (TPSR) [31].

## Reactors used for Dry Reforming of Methane

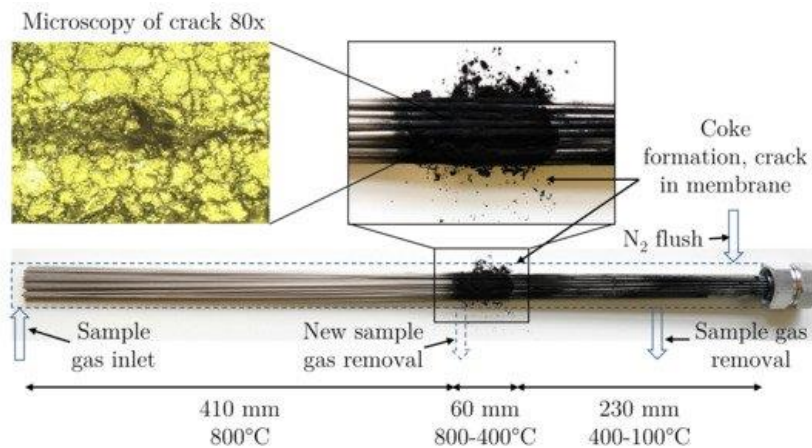
### Membrane Reactor

The term membrane reactor is for those processes wherein the membrane functions as more than simply a reactive membrane - a membrane matrix used for catalyst immobilization [85]. Considering IUPAC definition, a membrane reactor is a device for simultaneously performing a reaction – steam reforming, dry reforming, autothermal reforming, etc, and a membrane-based separation in the same physical device. Hence, a membrane not only is a separator but also is a part of the reaction [86].

Jonas M. Leimert, et al. developed a membrane reactor with the capillaries made from Ni (Ni201 Material no. 2.4068) [87]. The membrane bundle consisted of 52 single capillaries with 2 mm diameter and 0.1 mm thickness. The length of the tube was 750 mm but the total heated length was 400 mm. The membrane bundle area was 0.13 m<sup>2</sup>. This reactor was proposed in replacement of Pd membranes where the operating temperature required is high. Methane conversion was found to be 70%. Membrane systems at low temperatures show carbon formation leading to membrane degradation [88]. Jonas M. Leimert, et al. found that in the regions where the temperature was 800°C, no coke formation was seen whereas in the regions where the temperature is in between 400-800°C or less coke prevailed.



**Figure 7:** Membrane reactor [87]



**Figure 8:** Coke formation in reactor (T = 400-800°C) [87].

Yang K.Z, et al. compared three different reactors – Fixed bed reactor (FBR), Straight through transport reactor (STTR), and Membrane straight through transport reactor

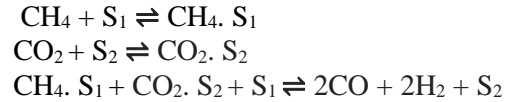
(MSTTR) [89]. The catalyst used was Ni/Al<sub>2</sub>O<sub>3</sub>. In STTR, either an inert gas or the reactant itself transports the catalyst through the reactor. With this reactor, any possibility of catalyst decay/selectivity disguise is virtually eliminated because the catalyst and reactants are fed continuously [90]. FBR gave the lowest coke deposit (15%) but also the lowest conversion of reactants. The highest catalytic activity was found in MSTTR. 55% CH<sub>4</sub> conversion and 95% CO<sub>2</sub> conversion but coke formation were highest (18%). The maximum yield of H<sub>2</sub> was seen in STTR. In MSTTR, after a certain reactor length, the hydrogen flow rate was decreased due to diffusion of H<sub>2</sub> out of the tube with silica membrane [89]. Silica membrane being semi-permeable other species like CO, CO<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> also pass out.

**Fixed Bed Reactors**

A fixed bed reactor (FBR), also known as a packed bed reactor consists of a bed of solid catalysts packed inside. In literature, most of the experiments are performed in a fixed bed reactor. A fixed bed reactor is economical than a membrane reactor and is easy to operate [91].

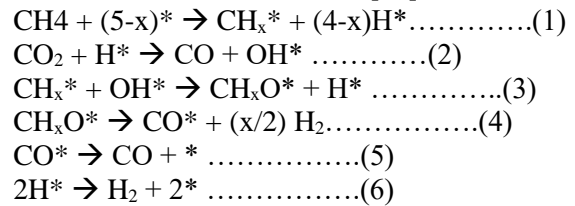
**Mechanism of Dry Reforming of Methane**

Considering Langmuir Hinshelwood Approach for Dry Reforming of Methane reaction with the surface reaction as the Rate Determining Step (RDS) and S<sub>1</sub>, S<sub>2</sub> as active sites we have the following mechanism: [92]

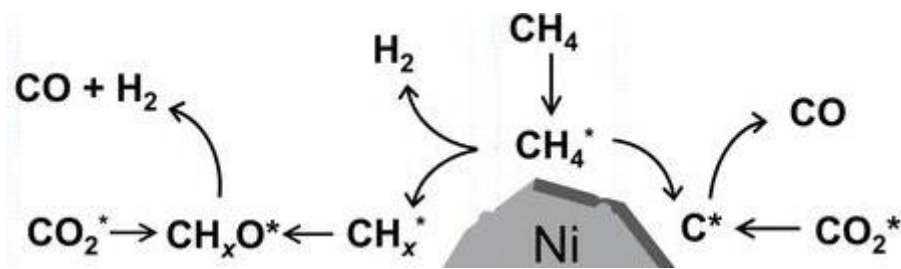


Some researchers also suggest that CH<sub>4</sub> is first adsorbed at an active site to yield CH<sub>x</sub> species, which is a rate-determining step. CO<sub>2</sub> is converted to CO by the reverse water-gas shift reaction. H<sub>2</sub> and CO are produced via the reaction of H<sub>2</sub>O with CH<sub>x</sub> species.

The mechanism is as follows: [93]



The above mechanism suggests that H\* created in step (1) is essential for the adsorption and activation of CO<sub>2</sub>.

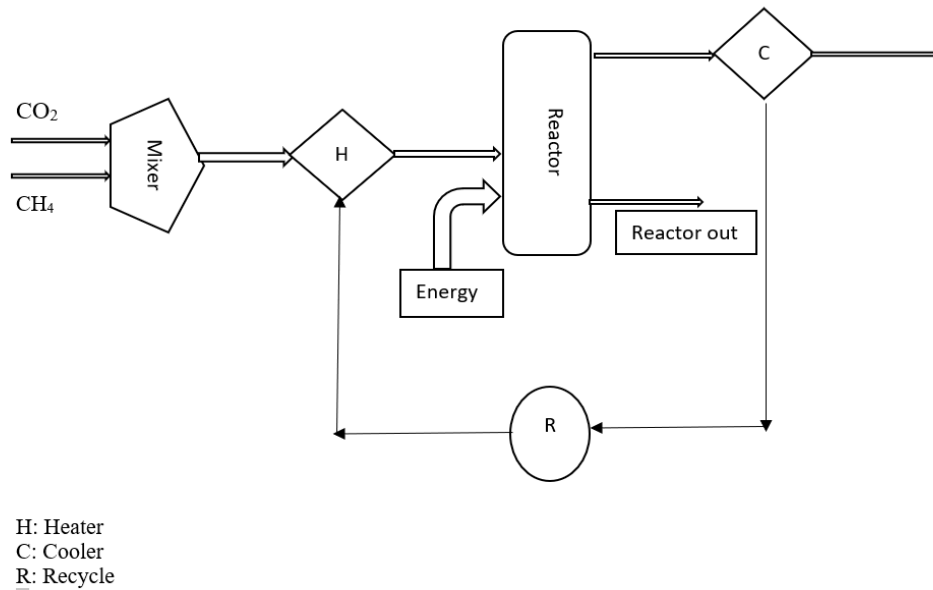


**Figure 9:** Reaction Mechanism scheme of DRM with supported Ni catalyst [94].

**Simulation of DRM in DWSIM**

DWSIM is an open software for chemical process industry simulation. Dry Reforming of Methane is simulated in DWSIM. Using a

reactor, feed stream (CH<sub>4</sub> and CO<sub>2</sub>), products (H<sub>2</sub> and CO), and catalyst the process is simulated at 800°C and 1.01325 bar. Catalyst used is Ni (density = 8900 kg/m<sup>3</sup>). A heterogeneous catalytic reaction model is used.



**Figure 10:** DWSIM Flowsheet of Dry Reforming of Methane

Using reaction kinetics of DRM, we have



Rate =  $k_{\text{DRM}} * ((P_{\text{CH}_4} * P_{\text{CO}_2}) - (P_{\text{H}_2}^2 * P_{\text{CO}}^2) / K_{\text{pDRM}}) / (((1 + K1 * (P_{\text{CH}_4} + K2 * P_{\text{CO}})) + (1 + K3 * P_{\text{CO}_2}))$  [95].

Where P is the partial pressure.

From the literature,  $K1 = 0.50 \text{ bar}^{-1}$ ,  $K2 = 9.71 \text{ bar}^{-1}$ ,  $K3 = 26.21 \text{ bar}^{-1}$

$k_{\text{DRM}} = 2.79 * 10^3 \exp\left(\frac{-225613.58}{R} * \left(\frac{1}{T} - \frac{1}{1123.15}\right)\right) \text{ mol/g}_{\text{cat}} \text{ hr. atm}$

$K_{\text{pDRM}} = 147.9317$ ,  $k_{\text{DRM}} = 905.3$ ,  $R = 8.314 \text{ J/mol K}$

Considering diameter of particle = 2 mm and Void fraction = 0.4

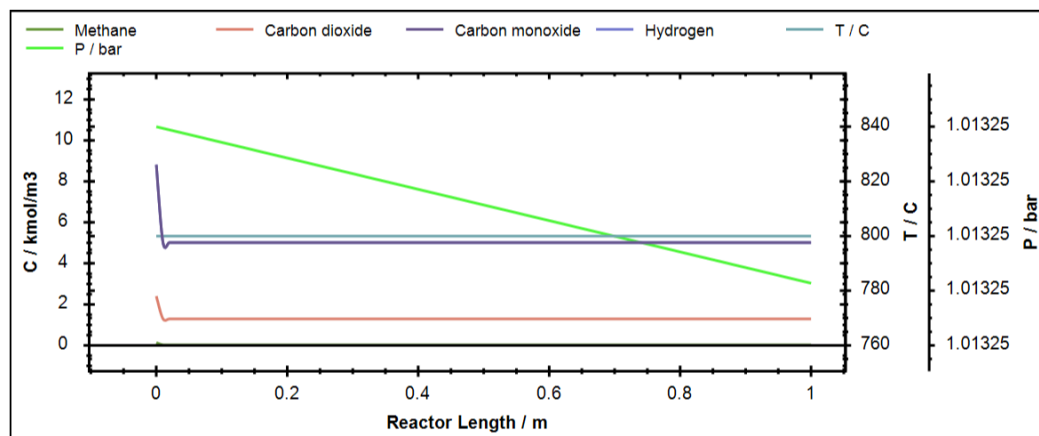
As particle size decreases, pressure drop increases so size is in mm.

CH <sub>4</sub> mole fraction	CO <sub>2</sub> mole fraction	T (°C)	CH <sub>4</sub> conversion (%)	CO <sub>2</sub> conversion (%)	H <sub>2</sub> /CO ratio
0.5	0.5	800	92.58	92.58	1.0
0.4	0.6	800	98.69	65.97	1.0
0.3	0.7	800	99.71	42.73	1.0
1.0	1.0	800	92.58	92.58	1.0

**Table 4:** Effect of variation of mole fraction on reactant conversion.

So, it can be seen that with the increasing mole fraction of CO<sub>2</sub> in the feed the conversion of CH<sub>4</sub> increases but that of CO<sub>2</sub> decreases.

Ideally, all the mole fraction ratios give H<sub>2</sub>/CO ratio of 1.0 based on the stoichiometry of the reaction.



**Figure 10:** Concentration profile for DRM in DWSIM.

Now, when molar ratio of CH<sub>4</sub> and CO<sub>2</sub> is 1:1, with increase in pressure, the conversion of the reactants drops.

Pressure (bar)	Conversion of reactants (%)
1.0	92.67
2.0	86.71
3.0	81.83
4.0	77.66

**Table 5:** Effect of pressure on reactant conversion.

### Conclusion

Thus, it can be inferred that Dry Reforming of Methane (DRM) is a very suitable process to convert greenhouse gases – CH<sub>4</sub> and CO<sub>2</sub> into valuable products like CO and H<sub>2</sub>. This process hence tries to solve the environmental issues to some extent. The endothermic nature of this process is the reason for carbonaceous deposits on the catalyst which deactivates the catalyst and hence limits the use. Nickel alone gets easily deactivated so Ni-Co catalyst is widely used for DRM. Many times, Ni on other supports like Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, MgO, SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> help reducing deactivation to some extent. Various promoters like Y, Zr, Gd, alkaline earth metals are used to avoid carbon deposits. The small size of Ni (approximately < 5 nm) proves to be better performing due to better dispersion on the support. The molar ratio of CH<sub>4</sub>/CO<sub>2</sub>, the operating temperature, and pressure have considerable influence on the product molar ratio CO/H<sub>2</sub>, catalyst deactivation, equilibrium

conversion of reactants, and side reactions like methane decomposition, Boudouard reaction,

and water gas shift reaction. The optimum temperature for DRM is found to be in the range of 650-900°C. The pressure is 1 atm. The feed molar ratio should be CH<sub>4</sub>:CO<sub>2</sub> = 1:1. The reaction is simulated on DWSIM software and few plots of pressure variation, mole fraction variation are plotted to verify the experimental analysis by simulation.

The above compilation of literature would try to give a pathway for new research and development in the field of dry reforming methane. The future scope of this process

includes the commercialization of the process to utilize the green-house gases and the development of a catalyst that is highly stable which doesn't get deactivated by carbon deposition and sintering to be used in process industries.



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