Chapter 1

Introduction

1.1 Hydrogen Energy

Hydrogen is a key component for building a sustainable energy future since it is a clean energy carrier that possesses high adaptability. There has been a huge increase in the amount of greenhouse gas emissions, especially COx, that have been released into the atmosphere as a result of the high energy consumption. In addition to this, the combustion of fossil fuels is also a big concern [1-4]. It's a point of concern towards the energy sector that based on existing energy-supplying techniques such as the combustion of fossil fuels, are we able to sustain life in the future? This requires the world to have an efficient energy system by minimizing the concentration of harmful gases in the atmosphere which is released mainly due to the combustion of fossil fuels and also needs an alternative and innovative way to produce energy [4-6].

To overcome this problem, one of the possible innovative ways of an efficient energy system is to use a Proton exchange membrane fuel cell (PEMFC). PEMFCs are promising resources for power applications due to no greenhouse gas emissions [7-10]. PEMFC uses a high purity hydrogen (>99.999%) as a fuel for power generation [11-13]. The combustion of hydrogen only produces water and hence it does not pollute the environment. However, the major challenge in using PEMFC is the safe storage and transportation of hydrogen. Hydrogen can be stored in gas form at high pressure (200-700 bar) in cylinders or it can be stored as a liquid at -253°C [13]. Both of these are energy and cost extensive processes. The alternate solution to storage and transportation of hydrogen is to generate it 'on-site' by using a source which is less expensive to store and transport. However, the major challenge of 'on-site' hydrogen generation are: safe generation of hydrogen, separation of hydrogen from other gases and generation and separation of hydrogen in a compact unit which makes it suitable for ‘on-site’ application and overall energy utilization. Therefore, it is vital to revisit the processes of hydrogen generation and separation which is suitable for ‘on-site’ application. [14-18]

1.2 Hydrogen Production Processes

1.2.1 Renewable Production Methods

There are several renewable methods to produce the hydrogen. Some of them are briefly explained below:

Electrolysis is a versatile and environmentally friendly way of hydrogen production that involves splitting of water molecules into hydrogen and oxygen using electricity. It’s ability to produce high-purity hydrogen and compatibility with renewable energy sources make it particularly attractive towards green hydrogen production [19-20]. The two basic types of electrolysers are alkaline electrolyser and proton exchange membrane (PEM) electrolyser. The electrolyte in alkaline electrolyser is an alkaline solution, most often potassium hydroxide (KOH). It operates at relatively high temperatures and pressure, often between 50-70 °C and 5-30 bar. Alkaline electrolysis is well-known for turning electrical energy into hydrogen with a reasonably high efficiency. It is a well-established technology that has been used in a variety of industrial applications [21-22]. Over time, the use of alkaline electrolytes, particularly KOH, can cause corrosion and degradation of materials and its components. A solid polymer electrolyte membrane is used in PEM electrolyzer that selectively enables protons to pass while separating hydrogen and oxygen from mixing. The operating temperature is lower, often between 60 °C, and the system operates at near ambient pressure.

Solid oxide electrolysis cells (SOECs) are high-temperature electrolyzers that produces hydrogen by splitting water vapor into hydrogen and oxygen, similar to solid oxide fuel cells (SOFCs) but in reverse mode. SOECs are energy efficient and may run on a variety of heat sources, such as waste heat from industrial processes or renewable energy sources [24-26]. The main issue is that SOFC operate at high temperatures, which can reduce material durability and increase expenses. SOECs are still in the process of development and commercialization. Electrolysers are predicted to play an increasingly crucial part in the transition to a greener and sustainable energy future as technology advances. However, electrolysis is a highly energy-intensive process with high-cost CapEx and OpEx limitations [22,23]. The cost of hydrogen generation through the electrolyser is currently quite high (~8-10 $/kg).

Biological hydrogen generation involves the use of microorganisms such as algae and cyanobacteria to produce hydrogen through the photosynthesis or fermentation processes. Microorganisms such as algae and cyanobacteria are used in biological hydrogen generation to produce hydrogen via photosynthesis or fermentation. Biological hydrogen production is still in the experimental stages, and it faces hurdles such as low production rates, scaling difficulties, and the necessity for ideal microbe growth conditions [27]. Photosynthesizing microorganisms, such algae and cyanobacteria, have the ability to spontaneously create hydrogen under certain conditions. This process is known as photobiological hydrogen generation. By using photosynthesis, these organisms use sunlight to fuel chemical reactions. They are able to redirect energy in order to split water into hydrogen and oxygen in specific environmental circumstances. This process is having Low efficiency and rates of hydrogen production. The oxygen sensitivity of hydrogenase enzymes prevents large-scale synthesis. A significant amount of research is required to enhance scalability and optimize the process for the stage of development.

Photoelectrochemical (PEC) water splitting combines photochemistry with electrolysis. When exposed to sunlight, specialized materials from electron-hole pairs drive the water-splitting mechanism. Because PEC directly harnesses solar energy for hydrogen production, it is a renewable and sustainable solution. It has off-grid and distributed application possibilities [28,29]. The efficiency of PEC cells, cost-effectiveness, and the availability of sufficient materials are all challenges. Continuous materials science and engineering research are required to increase PEC system performance and durability.

Thermochemical water splitting is extremely efficient, particularly when using high-temperature heat sources. High-temperature chemical reactions are used in thermochemical water splitting to break down water molecule into hydrogen and oxygen. Concentrated solar energy or nuclear heat sources can be used to power this technology. This is Currently in the experimental stage, there are still problems with material stability, cost, and efficiency that need to be resolved before being widely used.

Renewable hydrogen production has a bright future ahead of it, with governments, businesses, and academic institutions all over the world showing an increasing interest in and willingness to invest in it. Green hydrogen technologies are developing more quickly as a result of the drive to achieve net-zero emissions by 2050. Several nations have launched national hydrogen programs to encourage the production and use of hydrogen. Renewable hydrogen is anticipated to become increasingly important to the world energy grid as technology advancements drive down costs and boost efficiency. Because it may be used as a clean fuel, energy transporter, and storage medium, hydrogen is a vital component of a sustainable energy transition.

1.2.2 Steam Reforming Mechanisms

For ‘on-site’ hydrogen generation, steam reforming of hydrocarbons such as methane, methanol, ethanol, and glycerol is considered advantageous. Methanol is considered to be one of the most promising chemical commodities due to its high hydrogen-carbon ratio, low reforming temperature, easy availability, easy to store and lower boiling point. The lack of carbon-carbon bonds in the process lowers coke production. Therefore, methanol steam reforming is a practical and promising route for ‘on-site’ hydrogen generation [13,30-32].

Ethanol steam reforming (ESR) is an attractive and economical process which is used for hydrogen production. It is easily available from biomass, non-toxic, and easy to store. The CO_2 emissions generated during steam reforming can be absorbed via CO_2 capture mechanism [33,34]. Steam reforming of ethanol is an endothermic process. Therefore, high heat energy is required for hydrogen production. Hence, the main challenge is to minimize the energy requirement [35]. Catalysts play a crucial role in minimizing the amount of heat energy required. Various parallel reactions occur such as the decomposition of ethanol, dehydration, dehydrogenation, water gas shift reaction etc. One of the major disadvantages of steam reforming of ethanol is the coke deposition on the surface of the catalyst which may occur via the cracking of ethylene and ethanol decomposition [36-38]. The C-C bond in the ethanol is responsible for the highly endothermic nature of the reaction. The high-temperature conditions enhance the CO formation but for PEMFCs, the concentration of CO is a major issue, it should be less than 10 ppm to avoid the poisoning of Pt electrodes. So, it needs a final purification unit.

Methane (CH_4)/natural gas is also a widely used feedstock for steam reforming due to its prevalence as the primary constituent of natural gas, which is easily available and inexpensive [39]. Natural gas reforming meets approximately 50% of hydrogen demand, 30% is derived from chemical and refinery industries, and 20% is from gasification of coal and other resources [1,40]. Hence, steam methane reforming (SMR) is also a promising way for hydrogen production, which is a well-recognized and economically viable technology for large-scale industrial hydrogen production. In general, steam methane reforming is more cost-effective and efficient than methanol steam reforming, particularly when producing hydrogen on a big scale since it yields more hydrogen per unit of fuel. Furthermore, India already have more than 17000 km pipe line network of natural gas which makes methane more accessible. Therefore, steam methane reforming is an optimum choice for this study for on-site generation of hydrogen [41,42].

Steam methane reforming (Eq. 1.1) operates under harsh operating conditions such as high temperature (700-1000 °C) and pressure (up to 30 bar) followed by water gas shift reaction (Eq. 1.2). In the initial stage, methane reacts with steam to generate hydrogen and carbon monoxide (CO). The carbon monoxide generated in the initial reaction reacts with additional steam to yield additional hydrogen and carbon dioxide in the subsequent step (Eq. 1.2) [43-45].

Steam methane reforming reactions

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = 206\ kJmol^{-1} \qquad (1.1)$$

Water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ kJmol^{-1} \qquad (1.2)$$

However, the high temperature required for steam methane reforming also promotes the formation of carbon through methane decomposition (Eq. 1.3) and Boudouard reaction (Eq 1.4). High carbon formation also leads to the formation of CO by gasification of carbon (Eq 1.5). CO formation is also reported via reverse water gas shift reaction which is favorable at high temperature as per Le-Chatlier principle. These reactions reduce the efficacy of the whole process and becomes one of the major reasons for the catalyst deactivation [46] and possess major challenge for on-site generation of hydrogen.

Methane Decomposition reaction

$$CH_4 \leftrightarrow C + 2H_2 \qquad \Delta H = 75\ kJmol^{-1} \qquad (1.3)$$

Boudouard Reaction

$$2CO \leftrightarrow CO_2 + C \qquad \Delta H = -172.5\ kJmol^{-1} \qquad (1.4)$$

Carbon Gasification

$$C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H = 131\ kJmol^{-1} \qquad (1.5)$$

One of the main areas of current study has been the development of extremely active catalysts for low-temperature steam methane reforming which can minimize the catalyst deactivation by reducing the carbon formation and reverse water gas shift reaction.

1.3 Catalysts for steam methane reforming

In literature, precious metals such as Pd, Pt, Rh, Ru and Ir are tested for SMR process. These metals show high catalytic activity towards SMR. However, their high cost makes the nickel-based catalyst a source of attraction for steam methane reforming. Industrially, it is the commonly used catalyst owing to its cheap cost. Fig. 1.1 shows that out of reported work on SMR, 62% is on Ni based catalyst [47].

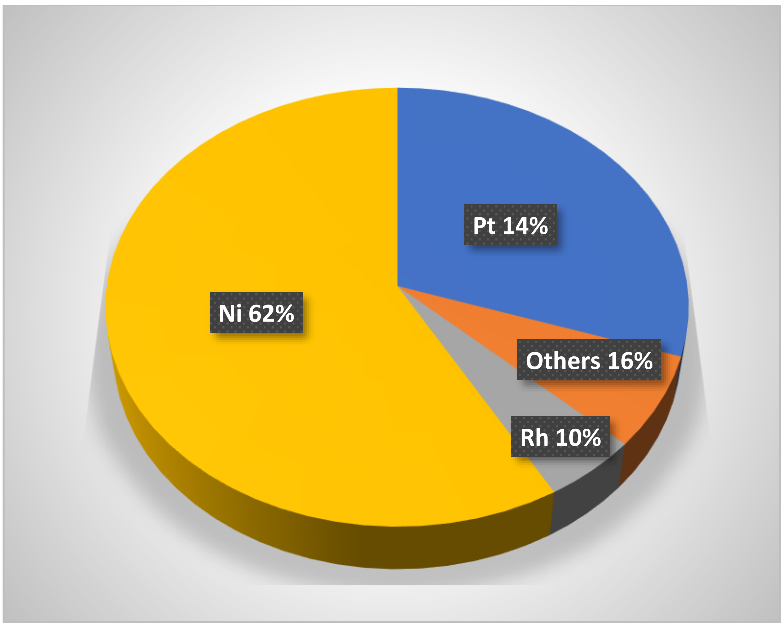

Fig. 1.1 Qualitative percentage distribution of different catalyst used for steam methane reforming in literature [47]

1.3.1 Literature review of steam methane reforming catalysts

Ni-based catalysts emerged as an attractive option due to its low cost and high activity for steam methane reforming. Various literature review has been reported on various parameters affecting the catalyst activity such as effect of supports, metal combinations, effect of promoters, metal loading, operating temperature, pressure, catalyst weight to feed ratio, etc.. Some of the key literatures are summarized in this section as mentioned below and in Table 1.1:

- Nieva et al [48] reported that Ni based catalyst activity depends on type of support which plays a key role in catalysis. Indeed, metal support is responsible for the dispersion of metal, sintering resistance etc. Some authors concluded the activity of Ni based catalyst in the following order $Ni/SiO_2 < Ni/Al_2O_3 < Ni/ZnAl_2O_4 < Ni/MgAl_2O_4$ during steam methane reforming at 600 °C. Due to carbon deposition Ni/SiO_2 deactivated easily as compared to other catalysts. Whereas, $Ni/ZnAl_2O_4$ shows high catalytic activity due to high sintering resistance and low carbon deposition. At 500°C, supports such as Al_2O_3

and SiO_2 allow oxidization of Ni based catalyst. Whereas, ZrO_2 helps to stabilize the Ni based catalyst and helps to obtain high methane conversion among all other supports owing to favor the hydroxyl group formation during steam methane reforming.

- Dan et al [49] proposed the work on Ni based catalyst for steam methane reforming reaction on Al_2O_3 support which was promoted by CeO_2 as promoter. They reported that it makes an enhancement in terms of methane conversion and decrement in coke formation.
- In recent years, a new approach for improving the catalyst activity can be seen from utilization of bimetallic catalyst. The two-metal combination can be utilizing effectively in terms of methane conversion. The dopant effect of one of the metals with catalyst support enhance the catalytic activity.

Table 1.1 Key Literature on steam methane reforming catalysts

Year	Catalyst	Preparation Method	Operating Conditions	Innovation	Performance Highlights	Application Potential	Reference
2024	TiO_2 Hollow Spheres	Template-assisted sol-gel	Reaction temperature: ~500°C	Spatially separated Pt and Rh_2O_3 co-catalysts enhance charge separation and activity	High charge separation efficiency; reduced SRM reaction temperatures.	Industrial-scale SMR and hydrogen production	Yamaguchi et al. [51]
2024	Ruthenium under Dynamic Charge	Surface functionalization	Frequency range: 10^6–10^{11} Hz	Dynamic oscillations in charge density to enhance TOF beyond Sabatier limitations.	Turnover frequency (TOF) increased by up to five orders of magnitude; lower operational temperatures.	High-efficiency hydrogen systems	Vempatti et al. [52]
2022	$LaFeO_3$ Perovskite	Solution combustion synthesis	~750°C, atmospheric pressure	Lanthanum ferrite perovskite offers excellent oxygen transport properties for methane reforming.	Enhanced coke resistance and improved activity.	Industrial hydrogen production	Zhang et al. [54]
2020	Fe-La-Al_2O_3	Impregnation	800°C, moderate pressure	Lanthanum-stabilized iron catalysts provided enhanced thermal stability and reduced deactivation.	High hydrogen selectivity and prolonged activity.	Decentralized hydrogen production	Zhang et al. [55]

2019	$Ni-Fe/La_2O_3-ZrO_2$	Wet impregnation	~750°C, steam-to-carbon ratio: ~3:1	Improved synergistic interaction between Ni and Fe on $La_2O_3-ZrO_2$ support.	Enhanced stability against sintering and higher methane conversion rates.	Hydrogen production for industrial applications	Wang et al. [56]
2005	Ni/Al_2O_3 with K, CeO_2, Mn promotion	Impregnation method	CO_2 reforming of methane; 700-900°C, atmospheric pressure, H_2/CO_2 ratio of 3	Promoted Ni/Al_2O_3 catalyst with K, CeO_2, and Mn to enhance CO_2 reforming stability	High stability and activity for CO_2 reforming of methane. Improved resistance to deactivation due to metal-support interactions.	Methane reforming, hydrogen production, CO_2 utilization	Nandini et al. [57]
2013	Cu-promoted Ni/SiO_2	Impregnation method	Methane decomposition; 600–750°C, atmospheric pressure	Copper promotion in Ni/SiO_2 catalyst for enhanced hydrogen production and CNT formation	Efficient hydrogen production and carbon nanotube synthesis from methane at moderate temperatures	Hydrogen production, carbon nanotube synthesis, renewable energy applications	Saraswat & Pant [58]

2017	Fe-Co/SiO_2	Impregnation method	Syngas (H_2/CO = 0.5–1.0) conversion to C5+ hydrocarbons; 250–350°C	Bimetallic Fe-Co catalyst for C5+ hydrocarbons synthesis from low H_2/CO ratio syngas	High selectivity for C5+ hydrocarbons and stable performance at low H_2/CO ratio	Liquid fuels synthesis, Fischer-Tropsch synthesis, renewable fuels	Pant & Upadhyayula [59]
2011	Ni/CeO_2 with La doping	Impregnation method	Tri-reforming of methane; 600-800°C, 1:1:1 (H_2/CO_2/N_2) ratio	La-doped Ni/CeO_2 catalyst for enhanced hydrogen production in methane tri-reforming	Higher hydrogen production and improved catalyst stability with La-doped Ni/CeO_2 catalysts	Hydrogen production, syngas reforming, clean energy	Pino et al. [60]
2023	Ni/Al_2O_3	Impregnation method	Tri-reforming of methane; 700-900°C, 1:1:1 (H_2/CO_2/N_2) ratio	Effect of metal loading on Ni/Al_2O_3 catalyst for tri-reforming of methane	Enhanced hydrogen production and catalyst stability with optimized Ni loading	Hydrogen production, syngas reforming, energy production	Gupta & Deo[61]
2020	Ni/Al_2O_3 with tailored metal-	Impregnation method	Tri-reforming of methane with	Tuning metal-support interaction to improve	Improved catalyst stability and hydrogen production	Flue gas utilization,	Kumar et al.[62]

	support interactions		flue gas; 700–800°C, 1:1:1 ($H_2/CO_2/N_2$) ratio	catalyst performance in industrial conditions	with optimized metal-support interactions	syngas reforming, hydrogen production	
2021	Ni/CeO_2	Co-precipitation method	Methane steam reforming; 600–900°C, 1:1 (H_2O/CH_4) ratio	Identifying active sites and metal-support interactions in Ni/CeO_2 catalyst for coke-free steam reforming of methane	Coke-free methane reforming, high hydrogen production, and enhanced stability	Methane reforming, hydrogen production	Salcedo et al. [63]
2017	Bimetallic Fe-Co/SiO_2	Co-precipitation method	Low H_2/CO syngas; 250–350°C	Enhanced bimetallic catalyst utilization for liquid fuel production from low H_2/CO ratio syngas	High efficiency in syngas conversion to liquid fuels with enhanced catalytic performance	Syngas conversion, liquid fuels production, renewable energy	Sonal et al.[64]
2013	Ni–Co catalysts	Co-precipitation method	Steam reforming of acetic acid; 450–550°C,	Bifunctional Ni–Co catalyst for steam reforming of acetic acid to produce hydrogen	High hydrogen production efficiency, with enhanced catalytic stability and coke resistance	Hydrogen production, biomass conversion,	Pant et al. [65]

			atmospheric pressure			renewable fuels	
2006	Ni	Unsupported nickel catalysts	Steam reforming of methane; 700–900°C, atmospheric pressure	Steam reforming of methane over unsupported nickel catalysts for hydrogen production	High catalytic activity for methane reforming and hydrogen production, but lower stability compared to supported catalysts	Hydrogen production, methane reforming	Rakass et al. [66]
1996	Ni-based catalyst	Impregnation method	Methane steam reforming; Low steam-to-carbon ratio	Highly stable Ni-based catalyst for methane reforming under low steam-to-carbon conditions	Improved methane conversion and hydrogen production with excellent stability at low steam-to-carbon ratios	Hydrogen production, methane reforming, energy production	Yamazaki et al.[67]
2009	Ni/Mo	Impregnation method	Methane steam reforming; 600–800°C, atmospheric pressure	Ni catalysts with Mo promoter for enhanced methane steam reforming	Enhanced catalytic activity and stability in methane steam reforming with Mo promoter	Hydrogen production, methane reforming, energy conversion	Maluf & Assaf [68]

2010	Rh/CeO_2-ZrO_2	Impregnation method	Methane steam reforming; 500-600°C, atmospheric pressure	Rhodium-supported on ceria-zirconia for low temperature methane reforming	Enhanced activity and stability for low temperature methane reforming	Hydrogen production, methane reforming, energy conversion	Halabi et al. [69]
2021	$Ni-Co/MgAl_2O_4$	Impregnation method	Ethanol steam reforming; 500-800°C, atmospheric pressure	Ni-Co catalyst supported on $MgAl_2O_4$ for ethanol reforming at varying temperatures	High ethanol conversion, selective production of hydrogen with good catalytic stability	Hydrogen production, biofuels, sustainable energy	Braga et al. [53]
2020	Ni/Al_2O_3	Impregnation method	Combined steam and dry reforming of methane; 600-800°C, atmospheric pressure	Ni catalyst for combined steam and dry reforming to produce hydrogen and syngas	Efficient syngas and hydrogen production with high selectivity and stability	Hydrogen production, syngas generation, energy production	Dan et al. [49]
2019	Zr-enhanced CeO_2	Co-precipitation method	Methane steam reforming; 700-	Zr-modified ceria supports for enhanced	Improved methane reforming stability and	Methane reforming,	Iglesias et al.[85]

	850°C, high pressure	stability in severe reaction conditions	resistance to sintering and deactivation	hydrogen production

1.4 Membrane Reformers

A membrane reformer (MR) is a device in which reaction and separation take place in a single unit. In MR, membrane separates one species (hydrogen in the current case) selectively from the product, which shifts the equilibrium of thermodynamically limited reaction towards the forward side (as per Le Chatelier's principle) and provides enhanced conversion beyond its thermodynamic limit. Further, it also produces ultra-pure hydrogen as the membranes are selective to only hydrogen. Hence, a suitably designed MR can reduce the cost of the overall process and can be very compact and makes it suitable for on-site application [70]. Fig. 1.2 shows the schematic representation of the membrane reformer. Integrated reaction-separation was first proposed by Professor Vladimir Gryaznov (Moscow University) in the year 1964. He proposed a method to carry out simultaneous evolution and consumption of H_2 in a dense tubular palladium membrane reactor where Pd is permeable to H_2 and also serves as a catalyst for the cyclohexane dehydrogenation to benzene. In the year 1990, a 4 Nm^3/h MR was developed by Tokyo Gas Co. Ltd with Mitsubishi Heavy Industries Ltd. In 2003, commercialized MR designs were reported by Reb Research and Consultancy (Prof. Buxbaum group). In addition to this, MR studies have been reported by ENEA (Prof. Sivano Tosti group), ITM-CNR (Dr. Angelo Basile group), Prof. Dittmeyer and Prof. Elnashaie group, fluidized membrane reactor by Prof. Kuipers and Prof. Sint Annaland group (University of Twente).

The system performance in case of a membrane reformer is both kinetically as well as diffusion controlled which thereby necessitates an optimal temperature, pressure and flow rate that will maintain stability of both the catalyst and the membrane. However, most of these works are performed for steam methanol reforming which is a low temperature process. Limited literatures are available on methane-based membrane reformer which is summarized in table 1.2.

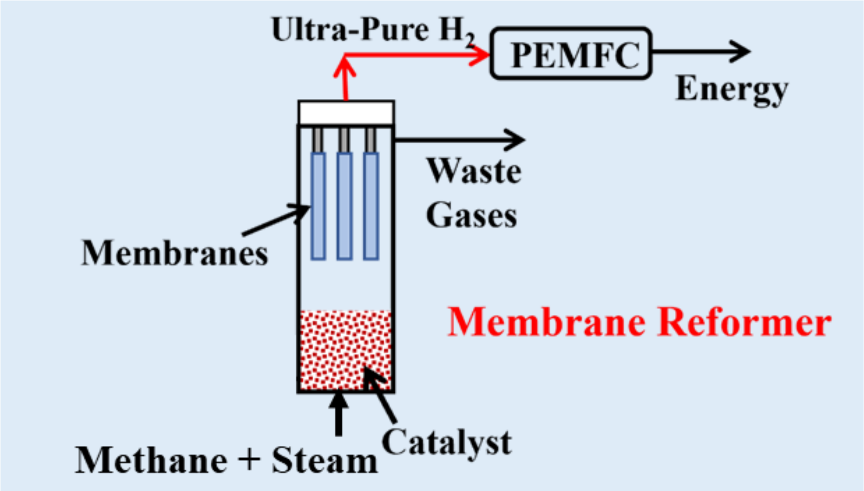

Fig. 1.2 Membrane reformer technology for hydrogen production via steam methane reforming

Table 1.2 Key literature on membrane reformer using methane

Catalyst	Reactor	Reaction condition	Observation	Remark	Author
Pt-Ni/CeO_2	Pd supported onto Alumina PBMR	T-440-525℃, P-10 bar, Methane feed flow-0.25NL/min	At Sweep flow 0.7NL/min H_2 yield > 80%, at 525 ℃	A substantial increase in conversion was observed due to increased H_2 transport across the membrane. Long terms deactivation of membrane and catalyst was no observed.	Patrascu and Sheintuch, 2015 [71]
Ni/Al_2O_3	Fixed Bed Membrane reactor	WHSV 349.6 kg_{cat} s/mol Temp- 500-700℃,	Methane conversion 47.4 at 873K, 500kPA Hydrogen recovery 28.1%	Membrane reactor model shows a good agreement with experimental data in terms of methane conversion and hydrogen recovery factor	Demarcoberardino et al., 2015 [72]
Ni/Al_2O_3	Reformer and membrane module (RMM)	850°C, steam-to-carbon ratio 3:1	High methane conversion and efficient hydrogen production	Membrane reactor demonstrated enhanced	De Falco et al. (2011)[73]

				selectivity and hydrogen recovery	
Pd–Ag	Pd–Ag membrane reformer	450–600°C, varying reaction pressures	Enhanced hydrogen recovery and methane conversion at middle temperatures	Membrane reformer showed pressure-dependent performance improvements	Basile et al. (2011)[74]
Pd–Ag	Multi-tube Pd–Ag membrane reactor	400–500°C, steam-to-carbon ratio 3:1	High hydrogen production and selectivity at moderate temperatures	Multi-tube Pd–Ag membrane reactor enhanced hydrogen purity and yield	Tosti et al. (2010) [75]
Pt/Al_2O_3	Pd-based membrane reactor	Oxidative steam reforming of ethanol	High hydrogen production efficiency with selective membrane separation	Pd-based membrane reactor showed enhanced hydrogen yield in oxidative steam reforming	Santucci et al. (2011) [76]
Pd/Pd–Ag	Pd/Pd–Ag membrane reactor	Water-gas shift reaction	Simulation and experimental studies showed high efficiency	Pd and Pd–Ag membranes exhibited superior performance in water-gas shift reactions	Basile et al. (2001)[77]

-	Integrated dehydrogenation-hydrogenation membrane reactor	Not specified	Modeling and simulation of integrated membrane reactor for dehydrogenation-hydrogenation process	Introduced novel integrated membrane reactors for simultaneous hydrogenation and dehydrogenation	Elnashaie et al. (2000)[78]
-	Membrane reactor	Low temperature, 300–500°C, steam-to-carbon ratio 3:1	Simulation showed efficient low-temperature methane reforming with membrane assistance	Membrane reactor simulation predicted enhanced hydrogen yield at low temperatures	Kyriakides et al. (2013)[79]
Palladium	Compact steam reformer with Pd membrane	650–700°C, steam-to-carbon ratio 3:1	High hydrogen production with compact reformer using palladium membrane	Compact Pd-based membrane reformer showed efficient hydrogen production	Dittmeyer et al. (2010)[86]
Ethanol	Fluidized bed membrane reactor	800°C, steam-to-carbon ratio 3:1	Simulated efficient hydrogen production via autothermal reforming in a fluidized bed membrane reactor	Simulation study suggested that the fluidized bed membrane reactor provides high hydrogen yield	Gallucci et al. (2010)[80]

-	Fluidized bed membrane reactor	Steam-to-carbon ratio 3:1, 850°C	High hydrogen purity and selective methane steam reforming using fluidized bed membrane reactor	Experimental study validated simulation models for fluidized bed membrane reactors	Patil et al. (2007)[81]
Pd/Ag	Dense Pd/Ag membrane reactor	650–750°C, steam-to-carbon ratio 3:1	High hydrogen production and methane conversion with Pd/Ag membrane	Dense Pd/Ag membrane reactor demonstrated high methane conversion and hydrogen selectivity	Gallucci et al. (2004)[82]
Pd-based catalyst	Fluidized bed membrane reactor	700–750°C, steam-to-carbon ratio 3:1	High hydrogen yield and selective methane reforming using Pd-based fluidized bed membrane reactor	Pd-based fluidized bed membrane reactor showed high hydrogen purity and methane conversion efficiency	Roses et al. (2013)[83]
-	Autothermal packed-bed membrane reformer	700–800°C, steam-to-carbon ratio 2:1	Model-based optimization showed improved hydrogen generation efficiency	Optimization strategy enhanced hydrogen production and reactor performance	Simakov & Sheintuch (2011)[84]

Ni-based catalyst	Hydrogen-permeable membrane reactor	700°C, steam-to-carbon ratio 3:1	High hydrogen purity and yield through membrane separation	Membrane reactor significantly increased hydrogen selectivity and purity	Tong & Matsumura (2006)[45]

Though membrane reformers look attractive, it is still an upcoming technology which is yet to be standardized as per the requirements and dimensions of a potential applicant such as a portable generator, car engine or industrial scale production. The contrary requirement of reaction (high temperature, low pressure) and membrane separation (low temperature, high pressure) makes the integration even more challenging. Reforming being endothermic reaction requires high temperature and low pressure. However, membrane separation requires high pressure and low temperature. Some of the key challenges of membrane reformers are listed below:

- When reforming is done at low temperature, hydrogen concentration is also reduced which reduces the partial pressure of hydrogen in feed to the membrane and hence separation efficiency of membrane.
- The selectivity of Pd/Pd-alloy membrane (which is commonly used for hydrogen separation) is theoretically reported to be infinity. However, pure Pd membrane is thermally not stable at a temperature below than 300 °C. Further, preparation of 100% dense membrane is still a challenge which needs to be overcome.
- It is well established in the literature that CO has inhibition effect on Pd-based membrane and hence higher concentration of CO reduces the hydrogen permeability through the membrane and can also harm the membrane. This is vital incase of steam methane reforming as the primary reaction produces CO. Hence, it is crucial to synthesise a catalyst which shows low CO selectivity.
- Carbon formation can also reduce the membrane permeability as it can be deposited on the membrane which will make membrane ineffective. Therefore, the catalyst used in methane-based membrane reformer should have low or zero carbon selectivity. It is important to mention that even the amorphous carbon is not desirable as it can be deposited on the membrane.

- Conventionally, SMR is performed at high temperature, however, high temperature operation is not suitable for on-site device due to the safety issues. Further, it enhances the startup time of the device. Therefore, it is important to synthesize a catalyst which shows high catalytic activity at low temperature.
- Membrane stability at high temperature is also a challenge mainly due to different expansion coefficients of different metals used in membrane with support and intermediate layer. This issue becomes more critical at high temperature and affects the performance of the membrane.

1.5 Motivation of study

Membrane reformers are interesting process intensified units which have immense potential to emerge as a new technology for small scale portable hydrogen generators utilizing the existing infrastructure of natural gas pipe line. The major challenge in the development of this technology is to obtain maximum hydrogen recovery, high hydrogen selectivity, minimize startup time and low temperature and pressure operation.

Steam reforming of methane requires reaction temperatures in the range of 700–1000°C which typically produces hydrogen (~70% by mole), the rest being CO, CO_2, unreacted H_2O and methane along with some carbon. However, in order to decrease the startup time, studies are targeted to achieve adequate conversion at even lower temperatures (500-700°C). Various metal-metal and metal-support interactions are therefore studied to identify best performing catalysts for low temperature steam reforming of methane. Further, in membrane reformers, reforming catalysts are intertwined with membranes which together control the performance of this system. Integration of endothermic steam reforming with membrane separation necessitates membranes which can sustain higher temperatures. With evident superior thermal stability and acceptable tolerance to chemical attack. Although the overall concept of membrane reformer looks very simple, integrating a high temperature and low-pressure steam reforming reaction with low temperature and high-pressure membrane separation process is a major challenge. As the focus of the current study is limited to the synthesis of suitable catalysts for steam methane reforming, the efforts are made to synthesize a low temperature, low CO and C selective catalyst. Further, the reduction of startup time is also targeted to make the device suitable for on-site application.

In the present work, hydrogen generation via steam methane through membrane reformer is studied for Ni-based catalysts. The effect of different support and support morphology are studied to enhance the catalytic activity targeting low CO selectivity, and startup time. Catalyst testing is performed with varying operational parameters such as weight hour space velocity (WHSV, $kg_{cat}/mol_{methane}.s$)), temperature and steam-to-methane (S/M) ratio. Further, active metal% and bimetallic and trimetallic compositions are varied to study the product selectivity for the optimal reaction. Finally, scaleup studies are performed to find the suitable catalysts for large scale operation.

1.6 Objectives

The overall aim of the current study is to develop a suitable catalyst for generation of hydrogen via steam methane reforming through membrane reformer. The specific objectives of the study are as follows:

- Synthesis, characterization and testing of monometallic catalyst for the generation of hydrogen using steam methane reforming
  - Effect of various supports and its morphology
  - Effect of various metals on supports
- Synthesis, characterization and testing of bimetallic/trimetallic catalysts
  - Effect of various metal combinations
  - Optimization of various parameters such as W/F, GHSV, WHSV, S/M ratio
  - Effect of operating conditions
- Scale-up studies for 1kW and 3 kW power production

1.7 Structure of thesis

In ***Chapter 2***, an overview of the several catalyst synthesis methods as well as characterisation techniques, including BET, XRD, SEM, EDS, TEM, XPS, and FTIR are explained. These methods are crucial for examining the catalysts structural, chemical, and physical characteristics. Furthermore, experimental framework is also described, providing a thorough technique for the catalyst's synthesis and testing. Additionally, a list of the catalysts employed in the study is provided with their metal loadings in the investigation. A strong basis for comprehending catalyst preparation, characterization and the experimental methodology in catalytic investigations is established in this chapter.

In ***Chapter 3***, effect of various supports such as Al_2O_3 and CeO_2 is observed. The gamma phase of alumina is converted to theta phase by calcined at high temperature (970°C).

Nickel based monometallic catalyst supported on theta alumina is also synthesized. Additionally, effect of various morphologies of ceria support such as nanocube and nanorod have been seen. These are doped with nickel to synthesize monometallic Nickel based catalyst supported on ceria supports. Catalytic activity of various shapes of ceria is also compared with commercial ceria activity with same metal loading. Characterization of synthesized monometallic catalyst was done using SEM (Scanning electron microscope), TEM (Transmission electron microscope), XRD (X-ray diffraction), BET (Brunauer Emmette teller).

In ***Chapter 4***, Effect of bimetallic catalyst is observed on Ni based monometallic catalyst on both the supports alumina and ceria. Carbon formation is observed on monometallic Ni based catalyst with respect to time which is the main cause of deactivation of catalyst. Iron, lanthanum and cobalt promoted Ni based bimetallic catalyst is tested for steam methane reforming to reduce the CO selectivity. CO selectivity gets reduced by the incorporation of promoters. Addition of promoters also increased the conversion at low temperature (500°C). The aim of this study is getting maximum conversion at low temperature with minimum CO generation. Characterization of bimetallic catalyst is done using XRD, SEM, EDS, BET techniques.

In ***Chapter 5***, Effect of trimetallic catalyst is observed on Ni based bimetallic catalyst with the addition of Iron, lanthanum and cobalt to further minimize the CO selectivity for the membrane reformer technology. Zero CO selectivity is observed with the trimetallic catalyst with maximum conversion at low temperature (500°C). Synthesis of trimetallic catalyst also increases the stability of catalyst for at least 130 hours without any CO formation at low temperature which is the main cause of deactivation of catalyst. Ni-Fe-La, Ni-Co-La and Ni-Co-Fe catalyst is tested for steam methane reforming for hydrogen production in methane membrane reformer. Characterization of trimetallic catalyst is observed with XRD, SEM, EDS, FTIR, XPS, TEM analysis.

In ***Chapter 6***, Scale up study of methane membrane reformer is performed using trimetallic catalyst having best catalytic activity with maximum conversion at low temperature (500°C) with zero CO selectivity. The reactor inner diameter changed from 11.74mm to 6.35cm to be upscale for the industrial applications. The Ni-Co-La/Al_2O_3 catalyst is used in the upscale reactor in bulk amount. The operating conditions optimized for upscaling studies. Comparative study is also done with small scale reactor at same conditions by keeping the residence time same. Finally, the fresh and spent catalysts for upscaling study is being characterized using various techniques such as XRD, SEM, BET, FTIR, XPS, TEM.

In ***Chapter*** *7*, conclusions and recommendations for this study is mentioned based on the analysis. Best of Trimetallic catalyst Ni-Fe-La/Al_2O_3, Ni-Co-La/Al_2O_3, and Ni-Co-Fe/Al_2O_3 is tested for upscale studies. The effect of CO selectivity is observed at various temperature from 500-800°C. Zero CO selectivity is observed for trimetallic catalyst with maximum conversion at low temperature (500°C). This catalyst can be used for steam methane reforming for large scale applications also.

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