Abstract

The rapid increase in the world industrialization has led to a significant rise in energy consumption demands. There have been attempts to utilize alternative and renewable energy sources as the next generation of energy carriers. Among many sources of energy, hydrogen has garnered a significant attention because of its high energy storage capacity (140.7 kJ/mol) and environment friendly combustion process which generates only water as the byproduct. However, storage and transportation are a significant challenge in the pathway of hydrogen as clean energy carrier due to its low density and high flammability. On-site or on-board hydrogen generation can resolve the issue of storage and transportation limitations. There are various hydrogen production pathways: coal combustion, electrolysis, dry reforming, cracking of fuels and steam reforming. Electrolysis can be used for onsite or onboard hydrogen generation. However, electrolysis is highly energy intensive process with high cost (2.5 \$/kg H_2) whereas DOE USA has a target of (1 \$/kg H_2 in 1 decade). Membrane reformer is a technology which can also be used for onsite or onboard hydrogen production due to its compactness and low cost. Generally, methanol is used as a feed in membrane reformer for hydrogen production due to its easy storage and transportation. Alternatively, natural gas/methane can also be used to reduce the cost of hydrogen production combined with CCUS. This makes the process cost effective and controlled the CO_2 emission also. India, already have a natural gas pipe line network of more than 17000 km. This can be utilized to generate on-site hydrogen via steam reforming route in a membrane reformer.

At a high temperature and pressure, steam methane reforming (SMR) is an endothermic reaction involving steam and methane. During this phase, the water gas shift reaction also occurs, increasing H_2 generation and reducing the CO selectivity by converting it into CO_2. To obtain high methane conversion, precious metals such as Pd, Pt, Rh, Ru and Ir have been tested in literature.

These catalysts have shown promising results for SMR. Although higher activities can be attained with precious metals, the catalyst cost limits the feasibility of these catalysts at commercial scale. Hence, non-precious metals such as Co, Ni, La and Fe have also been investigated at much lower metal loadings. Due to its low cost and high activity, Ni/Al_2O_3 has been the most extensively used catalyst for SMR. However, coke formation and Ni particle sintering are two major problems for Ni based catalysts. Deposition of coke on the surface of catalyst blocks the pores which makes it challenging for long run operations by reducing the catalyst activity. Industrially, coke deposition is avoided using high stoichiometric ratio of steam/methane but this can lead to high pressure drop and high energy requirement. 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 affect the performance of membrane reformer. This is vital in case of SMR as the primary reaction produces CO. Hence, it is crucial to synthesise a catalyst which shows low CO selectivity, low temperature operation and low startup time for membrane reformer application.

In current work, efforts have been undertaken to investigate novel promoters and additives that reduce CO selectivity and improve catalytic viability over time. A series of studies performed focusing on Ni based monometallic, bimetallic and trimetallic catalyst for steam methane reforming on alumina and ceria supports. The complete characterization of these catalysts are performed by using XRD, SEM, EDS, BET, XPS, FTIR, TEM. A series of optimization studies have been performed to find the effect of independent variables such as reaction temperature, W/F, Steam to water ratio, residence time and life cycle analysis.

Initially, effect of various supports such as Al_2O_3 and CeO_2 is observed on catalytic activity of Ni based monometallic catalyst. Additionally, effect of various morphologies of ceria support such as nanocube and nanorod have been investigated. These Shapes 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 with same metal loading. Thereafter, different metals like Ni, La, Fe and Co based monometallic catalysts on both Al_2O_3 and CeO_2 supports are synthesized and tested in packed bed reactor of internal diameter 11.74mm. It is observed that Ni/Al_2O_3 and Ni/CeO_2 showed high catalytic activity towards steam methane reforming. However, both these monometallic catalysts showed high CO selectivity at higher temperature where conversion was high. At low temperature CO selectivity for mono metallic catalysts was low but it shows quite low conversion (20%). Hence, it necessitates the investigation for bimetallic catalyst.

Iron, lanthanum and cobalt promoted Ni based bimetallic catalyst is tested for steam methane reforming to reduce the CO selectivity, low temperature operation and low startup time. 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 was getting maximum conversion at low temperature with minimum CO generation. Effect of trimetallic catalyst is also 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 (55%) 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. Zero CO selectivity is observed with all the trimetallic catalysts at low temperature.

Finally, scale-up studies are performed using trimetallic catalyst having best catalytic activity with maximum conversion at low temperature (500°C) with zero CO selectivity. The reactor inner diameter was changed from 11.74mm to 63.5mm. The Ni-Co-La/Al_2O_3 catalyst is used in the upscale reactor in bulk amount (350 gm). The experiments were performed for different temperature, W/F, S/M ratio for different capacity. It is found that Ni-Co-La/Al_2O_3 catalysts shows similar performance in upscaled reactor as of the laboratory scale reactor. At 550 °C temperature for larger diameter (63.5mm ID) column Ni-Co-La/Al_2O_3 catalyst shows zero CO selectivity and 60% conversion. This makes it suitable for membrane reformer application. Hence, current work recommends the use of Ni-Co-La/Al_2O_3 catalyst for membrane reformer applications at low temperature.