

Study of Steam Methane Reforming Catalysts for Membrane Reformer



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by

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Chapter 7

Conclusions and Future Perspectives

7.1 Conclusions

This chapter concludes the overall study by analyzing the results. Evaluating the catalytic efficacy of monometallic, bimetallic, and trimetallic Ni-based catalysts supported on both alumina and ceria was the main goal of the current study on steam methane reforming (SMR) to get zero CO selectivity and maximum conversion at low temperature and then upscale it for the commercial applications. First of all, Ni based monometallic catalysts were prepared on both alumina and ceria supports. Both the supports showed good catalytic activity towards steam methane reforming as alumina has high surface area and ceria having excellent redox properties. Additionally, Ni shows good properties in activation of methane molecules but monometallic Ni based catalyst shows deactivation after some time due to coking and high CO selectivity. To reduce the CO selectivity, promoters such as La, Fe and Co is incorporated with Ni based catalyst to make it bimetallic. The reduced CO selectivity is obtained with bimetallic catalysts with all the promoters in bimetallic catalysts. The objective of this study is to get low CO selectivity (ideally zero CO selectivity) and getting maximum conversion at low temperature. Further, lower startup time is also targeted for commercial application. Lanthanum is reported to lower the start-up time of the reaction. Cobalt is reported to reduce the coke deposition. The promoters also enhanced the water gas shift reaction to reduce the CO selectivity. For membrane reformer application, the CO content should be low as it affects the performance of membrane. Therefore, to further reduce the CO selectivity, trimetallic catalysts such as Ni-Fe-La, Ni-Co-La and Ni-Co-Fe catalysts were prepared on both the alumina and ceria supports. All the trimetallic catalysts showed zero CO selectivity at low temperature (below

550 °C). These catalysts were tested for high stability test for at least 130 hours continuous operation. No deactivation was observed with trimetallic catalysts after 130 hours of operation at 700°C. When compared catalyst activity of all trimetallic catalysts, Ni-Co-La/Al₂O₃ showed highest conversion at low temperature with zero CO selectivity at laboratory scale (reactor ID 11.74 mm).

This outcome demonstrates the advantages of adding cobalt and lanthanum in addition to nickel. While cobalt probably contributes to the catalyst increased resistance to carbon deposition and the development of a more active reaction site, lanthanum serves as a promoter, strengthening the metal-support relationship. The total catalytic performance in the steam reforming reaction is improved as a result of these metals synergistic interaction. Therefore, Ni-Co-La/Al₂O₃ catalyst is further tested at larger scale in 63.5 mm ID reactor. The Ni-Co-La trimetallic catalyst demonstrated high catalytic activity in the laboratory-scale packed bed reactor (11.74 mm inner diameter), shows high methane conversion rates with no degradation over time. This finding implies that, in the reaction conditions characteristic of SMR, the trimetallic catalyst is both persistent and effective.

The performance of the catalyst was then assessed in a bigger reactor with an inner diameter of 63.5 mm by scaling it up. The catalyst performance remained consistent even under conditions typical of industrial-scale operations, as seen by the striking concordance between the results obtained in the bigger reactor and those observed in the smaller reactor by keeping the residence time same in both the reactors. The performance of this scale-up indicates that the Ni-Co-La trimetallic catalyst has the stability and dependability required for realistic, extensive use in SMR operations.

The trimetallic Ni-Co-La catalyst appears to be a viable option for large-scale membrane based steam methane reforming, as at large scale also this catalyst shows zero CO selectivity till 550 °C and good conversion (~50%) in traditional reactor. The conversion at

lower temperature will further improve when the same catalyst will be used in membrane reformer where thermodynamic equilibrium will be tailored due to simultaneous generation and separation of hydrogen. Hence, it can be concluded that Ni-Co-La catalyst is suitable choice for methane-based membrane reformer application. The key conclusions of study are mentioned below in points:

- The analysis of steam methane reforming performance highlights the superior activity of monometallic Ni-based catalysts, supported on Al_2O_3 and CeO_2 , due to their high methane conversion and enhanced stability. However, challenges such as deactivation and high CO selectivity remain critical. Therefore, introducing Ni based bimetallic systems with promoters like Fe, La, and Co can address these issues by synergistically improving catalytic performance. Fe can enhance coke resistance and promote water-gas shift activity, reducing CO selectivity. La improves oxygen storage capacity, low start up time and thermal stability, while Co increases methane activation and facilitates hydrogen production. Both alumina and ceria supported Ni based catalyst shows 100% conversion at high temperature (above 750 °C). However, CO selectivity was very high (>80%). Hence, it is not suitable for membrane reformer application. At low temperature (550 °C) CO selectivity for Ni/ Al_2O_3 catalyst was low (<30%), however, the conversion at this temperature was quite low (20%).
- A bimetallic Ni-based catalyst with promoters (Co, Fe, La), supported on Al_2O_3 and CeO_2 , is able to achieve high methane conversion with lower CO selectivity, offering an optimal balance of activity, stability, and selectivity for efficient steam methane reforming. Ni-La/ Al_2O_3 provides higher conversion (~50%) at low temperatures (500°C). It also gave low CO selectivity (~15%) at lower temperatures

(500 °C). These qualities made it a suitable catalyst amongst the investigated catalysts for membrane reformer application.

- Ni-Co bimetallic combination also shows high conversion as compared to other cobalt bimetallic catalysts but this catalyst is deactivating after 12 hours of study. Overall, Ni-La, Ni-Fe and Ni-Co bimetallic combinations shows high catalytic activity with low CO selectivity. Ni-Co bimetallic catalyst shows zero CO selectivity at low temperature (500 °C) but conversion is low. This can be concluded that trimetallic catalysts with these combinations can even provide high conversion at low temperature with zero CO selectivity by providing high stability.
- The catalytic activity of trimetallic catalysts Ni-Fe-La/Al₂O₃, Ni-Co-La/Al₂O₃ and Ni-Co-Fe/Al₂O₃ are investigated for steam methane reforming. These catalysts were analyzed at temperature ranges from 500-800°C, 1 bar pressure in packed bed reactor of I.D 11.74mm. All trimetallic catalysts shows zero CO selectivity at low temperature. The effect of La and Fe on Ni-Co combination is studied. It is observed lanthanum and iron both lowers the CO selectivity of the reaction by making Ni-La and Ni-Fe alloy respectively. However, lanthanum is a good promoter than iron with Ni-Co combination in terms of lowering the CO selectivity. Ni-Co-La/Al₂O₃ catalyst lowers the CO selectivity as compared to Ni-Co-Fe/Al₂O₃ catalyst with high stability throughout the reaction. Therefore, Ni-Co-La/Al₂O₃ catalyst was tested for life time analysis. The stability of catalyst is also improved for at least 130 hours with constant conversion (~45% at 500°C). Therefore, trimetallic Ni-Co-La/Al₂O₃ catalyst shows promising results for steam methane reforming. The strong metal-support interaction with Al₂O₃, lanthanum promotion, and the bimetallic Ni-Co system work in concert to give the Ni-Co-La/Al₂O₃ catalyst its improved low-temperature performance and zero CO selectivity in methane steam

reforming. La increases basicity and water-gas shift activity, allowing for effective CO conversion to CO₂, whereas the Ni-Co alloy suppresses carbon production while improving CH₄ activation. Even at lower working temperatures, these elements work together to provide clean hydrogen and high methane conversion.

- In small reactor (I.D 11.74mm), this catalyst is tested for best operating conditions. At the same operating conditions such as residence time, catalyst Ni-Co-La/Al₂O₃ is tested for scaled-up reactor (I.D 11.74mm to 63.5mm) for steam methane reforming (SMR) reactions employing a packed bed reactor. The difficulties and opportunities related to flow rates, performance optimization, and catalytic particle size are studied through catalyst testing and research in upscale reactor. Almost same methane conversion, hydrogen production, and resistance to carbon deposition are observed by the trimetallic catalyst (Ni-Co-La/ Al₂O₃) at scaled up reactor. At low temperature (550 °C) high conversion (~50%) is achieved with zero CO selectivity even in scale up reactor for 1 and 3 kW capacity. However, at higher kW, CO selectivity rises at higher temperature. Finally, the results of this work highlighted the trimetallic catalyst activity in upscale reactor (I.D. 63.5 mm) is same as obtained in small reactor of I.D 11.74mm. It can be concluded that this catalyst can be used in upscale reactor for the membrane reformer application at low temperature.
- The Weisz–Prater criterion assesses whether internal diffusion is restricting the reaction by using measured values of the rate of reaction, or obs.

$C_{WP} = 2\eta \times \Phi^2$ (Where C_{WP} is Weisz–Prater modulus, η is effectiveness factor and Φ is thiele modulus)

η is 0.988, Φ is 0.415 (Calculated using Langmuir hinshelwood approach)

With a Weisz-Prater criteria (C_{WP}) value of 0.17, this catalytic system appears to have low internal diffusion restrictions. The reported kinetics mostly reflect the intrinsic chemical reaction rather than mass transfer resistance inside the catalyst since $C_{WP} \geq 1$, indicating that pore diffusion does not substantially impair the reaction rate. Since the C_{WP} is smaller than 1, at 0.17, diffusional restrictions are absent.

7.2 Recommendations and future perspectives

Here are some recommendations for this work on "Study of Steam Methane Reforming Catalysts for Membrane Reformer" are mentioned below:

- **Temperature and Pressure Range:** To make sure the catalyst is effective throughout a wider operating range, a thorough examination of different high pressures should be conducted, even though the catalyst exhibits maximal conversion at low temperatures. The combinational effect of optimum temperature with high pressure system ($P > 3$ Bar) can also be tested so that the trimetallic catalyst can also be used in existing systems for steam methane reforming for commercial applications.
- **Scaling Strategy:** Keep researching the effects of scaling on mass and heat transport limitations, as increasing the reactor size from 11.74 mm to 63.5 mm did not alter catalytic activity for these operating conditions. By closely observing temperature gradients and reactant distribution within the scaled-up reactor, we can make sure that the scaling maintains the same high conversion and selectivity. To confirm, there will be no heat and mass transfer limitations by scaling it further, Thiele modulus and effectiveness factor are some critical parameters to determine the scale up it further which can be consider in future. Moreover, Reducing CO

selectivity can also be tested by scaling it up more than 3 kW with different metal combinations.

- **Catalyst Bed Distribution and Packing:** In larger reactors, maximizing catalyst bed distribution and packing are also critical parameters defining the efficiency. Because of inadequate heat and mass transport, non-uniform packing may result in decreased performance and efficiency. Therefore, when this will be further scale up, non-uniform packing can lead to adequate catalytic efficiency.
- **Cost-Effectiveness:** Conduct a cost-benefit analysis of using these trimetallic catalysts compared to existing alternatives, especially considering the cost of materials and any potential scalability challenges. The metals used in the study are cheap in cost. But total metal loading can be reduced. As we are getting almost 100% conversion for most of the catalyst at higher temperature. Therefore, Overall, less metal loading can also be checked for upscale studies. So that effect of various parameters can also be seen clearly with less metal loading.
- **Sustainability evaluation:** Considering the low CO selectivity attained in the steam methane reforming process when conducting an environmental impact evaluation. Calculate the decreases in greenhouse gas emissions and need to evaluate the process total industrial energy efficiency.
- **Kinetic Modeling:** Kinetic modelling explains how the reforming process will behave, reacts and improve kinetic models using the experimental data. For larger-scale applications, this will aid in further optimizing the reactor design and operating conditions. Simulation and modelling can also be done in packed bed reactor for scale up studies.
- **Computational Fluid Dynamics (CFD) Simulations:** To maximize the temperature distribution and flow patterns inside the enlarged reactor, CFD

simulations is also critical parameter. These simulations can enhance performance prediction and lower scaling-related hazards.

- **New Metal Combinations:** To improve performance even more, look at different trimetallic combinations. We have focused on iron, lanthanum and cobalt for metal combinations. Other transition metals or rare earth elements, for instance, could provide extra advantages in terms of stability, activity, or selectivity. Therefore, other metal combinations can also be tested for steam methane reforming for scale up studies.
- **Catalyst regeneration:** Investigate catalyst regeneration techniques to increase catalyst life, such as employing regeneration cycles or lowering coke formation is required. Catalyst regeneration can be done by passing steam, increase reduction time and by recovering the support. This process will further reduce the overall cost of catalyst with increased efficiency.

These suggestions help to direct future advancements in reactor scaling up, catalyst development, and the process wider use in actual steam methane reforming operations for commercial applications.