

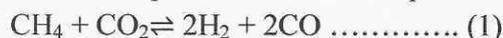
Thesis abstract

Index No. 20/21/Chem./27

Title of the Thesis: *Development of Perovskite and Spinel Based Molecular Level Nanocomposite Catalysts of Conventional and High Entropy Metal-Oxides for Dry Reforming of Methane*

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The goal of this thesis is to synthesize some promising catalysts (perovskite and spinel oxides) for dry reforming of methane (DRM) reaction. DRM is a catalytic process that uses two powerful greenhouse gases, carbon dioxide (CO₂) and methane (CH₄) to synthesize syngas (H₂+CO), which is a useful feedstock for the preparation of chemicals and fuels. This reaction not only resolves the need for sustainable energy but also reduces greenhouse gas emissions. A number of industries that significantly rely on the use of hydrogen and syngas are given financial and environmental advantages through utilization of DRM reaction. The chemical equation for the DRM process is as follows:

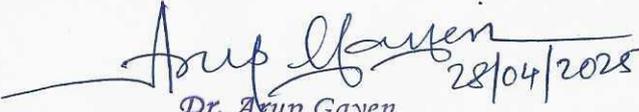


Despite its potential outcome, quick catalyst deactivation from sintering and carbon deposition are serious issues to commercialization of DRM reaction. Effective catalysts, mostly based on noble metals (Ru, Rh, Pd, and Pt) and transition metals (Ni, and Co), supported on a variety of materials to improve stability and activity, are the subject of recent studies. The design of modern catalysts, including the use of promoters and bimetallic systems, have been demonstrated to impart improved catalytic efficiency and reduced carbon deposition. Even though DRM provides a sustainable method of producing syngas and lowering greenhouse gas emissions, its actual implementation will depend on resolving technical issues with catalyst stability and performance. To fully realize the impact of this promising technology, more research and innovation on catalyst development and process optimization are indispensable. For this research work, some catalysts based on perovskite and spinel oxides have been synthesized following various approaches and deployed these catalysts for DRM reaction.

Chapter 1 provides a concise overview published in the literature on nanostructured metal oxide-based catalysts for DRM reaction, emphasizing the several relevant concerns.

Chapter 2 enunciated the many preparative methods utilized to synthesize the different catalyst components, along with the justification for selecting sol-gel citrate combustion as the optimal synthesis pathway. We have then summarized the working principle of the wide range of modern sophisticated characterization techniques that have been used to observe the physicochemical nature of the materials. These techniques include powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) temperature programmed reduction (TPR), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The gas-solid heterogeneous catalyst testing process have been discussed at the end of this chapter.

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Chapter 3 deals with the synthesis, characterization, and catalytic activity of $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.1-0.8$) perovskite nanomaterials. The current study provides a thorough analysis and comprehension of the DRM reaction employing Cu-doped LaNiO_3 , offering a new perspective on its catalytic activity. The phase of pure $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ catalysts, in particular, $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$, shows high catalytic activity towards the DRM reaction (97% CH_4 and 98% CO_2 conversion) with H_2/CO ratio ~ 1.2 . Remarkably, the catalytic activity remains unchanged even after 100 h, despite the fact that the first perovskite phase mostly breaks down into component phases following the DRM. Based on extensive characterization of as-prepared and aged catalyst materials, we have explained the prolonged activity of the disintegrated perovskite catalysts in the context of nanocomposite formation at the molecular level in the reforming atmosphere along with the availability of Ni^0 and NiO .

Chapter 4 discusses the study of dry reforming of methane of the double perovskite series, with general formula $\text{La}_2\text{Ni}(\text{TM})\text{O}_6$ (where, $\text{TM} = \text{Cr, Mn, Fe, and Co}$). All these catalysts show significant catalytic activities towards DRM reaction. It has also been seen that $\text{La}_2\text{NiMnO}_6$ exhibits the highest DRM activity and its CH_4 and CO_2 conversion are 97% and 99%, respectively, along with a considerable H_2/CO ratio (0.9) after 10 h of reaction. The catalyst shows nearly similar DRM activity up to 100 h run time of DRM. After the reaction, the aged phase of the catalyst can be recovered to its original phase by heat treatment at ~ 800 °C for 3 h.

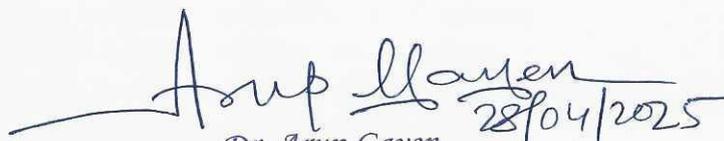
Chapter 5 gives an analysis of DRM activity of high entropy oxide perovskite series $\text{Ln}(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ (where $\text{Ln} = \text{La, Ce, Pr, Nd, Sm and Gd}$). All these catalysts demonstrated a significant catalytic activity towards the DRM process. Out of all the synthesized catalysts, $\text{La}(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ was found to exhibit the highest DRM activity. After 10 h of DRM reaction, its CH_4 and CO_2 conversions are 86% and 90%, respectively with a H_2/CO ratio close to unity. For 100 h of DRM reaction, this catalyst exhibits almost identical DRM activity and the catalyst phase form on ageing in the DRM atmosphere can be heat-treated for 3 h at 800 °C to regenerate to its initial phase.

Chapter 6 discusses the investigation of DRM activity of the high entropy oxide spinel systems $\text{MM}'_2\text{O}_4$ (where $\text{M} = \text{Mn, Fe, Co, Ni and Cu}$ in equimolar proportion, $\text{M}' = \text{Al, Cr, Mn, Fe, and Co}$). All the as-prepared samples of this series have shown promising DRM activities. $(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Al}_2\text{O}_4$ spinel oxide was found to be the most active catalyst in the series, having 97% CH_4 and 99% CO_2 conversions, respectively for 100 h of DRM. After ageing, the catalyst was degraded, but the degraded phases of the catalyst were successfully regenerated by heat treatment for 3 h even at lower temperature than the synthesis temperature. The regenerated phase also demonstrated a similar DRM activity with the as-prepared and aged samples.

Finally, we have summarized the key research findings and highlighted certain significant insights in **Chapter 7**. We have also pointed out the plausible future directions in this crucial and developing field of multifunctional nanostructured oxide materials.

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