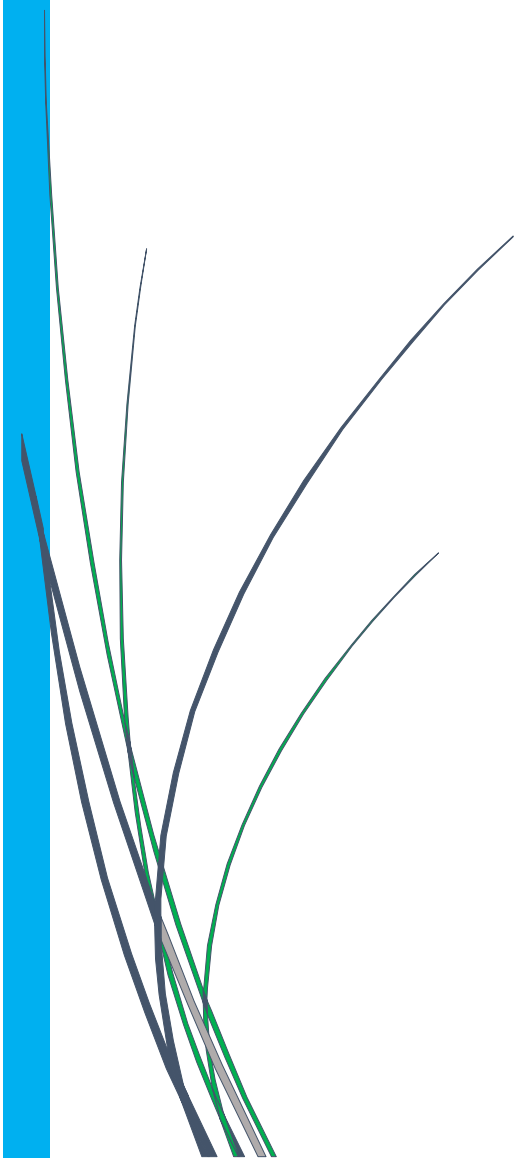
Chapter:9 Conclusions and Recommendations



9.1 Conclusion

The ESR with Ni, Co and $NiCo_2O_4$ revealed that the synergistic effect of Ni and Co significantly affected the ethanol conversion and selectivity of H_2, CO, CH_4, CO_2, CH_3CHO and C_2H_4. On the basis of product gas distribution, the dominant reactions for Ni and Co catalysts were decomposition and dehydrogenation of ethanol respectively. The synergistic effect of Ni and Co in $NiCo_2O_4$ spinel inhibited the formation of double carbon containing product such as C_2H_4 and CH_3CHO. So, the C-C bond scission ability also gets promoted.

Further, detailed study of unsupported cobalt with time on stream at 723K in Co^0 state with (111) plane found that the catalyst remained stable for 19h in terms of H_2 selectivity. The absence of CoO state in used catalyst indicated reduction of oxide phase to elemental state during ESR performance. The activity of the catalyst starts decreasing after 19h and the main reason for activity loss was due to carbonaceous deposition. The presence of Co metal at the tip and in between of carbon nano filament is confirmed by SEM-EDS analysis of used catalyst. It supported the tip growth as well as Y- junction carbon growth phenomenon of carbon filament formation with Co catalyst.

The catalyst reformulation study of the deactivated Co catalyst by nano-casting method has shown an advantage of high temperature ESR. The proposed way of catalyst synthesis has a significant advantage regarding catalyst regeneration, perovskite catalyst preparation, and cost effective renewable hydrogen generation. The Co metal catalyst itself produced hydrogen and further utilization of Co-C nanofilament in active perovskite based composite catalyst synthesis had cost effective approach. The synthesized perovskite composite can be reused for hydrogen generation after carbon deactivation, because perovskite catalysts have high thermal stability.

The performance of ZSM-5 without any active metal species gave only 23.7% ethanol conversion even at 923K with enormous amount of C_2H_4 generation. But, the presence of active metal with ZSM-5 has shown near to 97% ethanol conversion at lower temperature 723K. The product distribution varied with temperature and the type of active metals used. The C_2H_4 selectivity is found dominant at low temperature ESR which may be owing to acidity of catalyst.

The CeO_2 supported catalysts can be used industrially for hydrogen production via ESR. The pre-treatment condition of Co/CeO_2 significantly affects the selectivity of the product gases. In case of H_2 reduction, the metallic Co (111) plane is prominently available for ESR. However, H_2 reduction treatment is found most effective for ESR, but pretreatment of a catalyst by CO with air, a redox condition also has comparable activity.

The simultaneous precipitation of oxides of Co, Ni and Ce also occured directly from their nitrate precursors. The role of solvent is important here because in presence of water, the precipitation of CeO_2 does not occur even at 455K for 6h treatment. The absence of impurities in the CeO_2-P confirmed that high purity based nano materials can be easily synthesized in a single step. This is one of the best cost-effective methods since it does not require any precipitants for precipitation, washing solution and high temperature calcination. In this study, the produced active metal catalyst has shown their activity for ESR. This method can be considered as one of the best green approaches to catalyst synthesis and hydrogen generation.The study of Ni, Co and Ni-Co was found active in ESR and the co-existence of both of the metal has positive effect on product gas selectivity.

9.2 Scientific contributions

The notable scientific contributions that this research made to the area of ESR are as follows:

- The carbon nanofilament formation mechanism, tip growth phenomenon and Y-junction phenomena are confirmed with Co during ESR.
- The comparable activity analysis of non-noble active metal Ni and Co supported over perovskite-spinel, ZSM-5, and CeO_2 are investigated.
- The method of reformulation of high temperature catalyst from the deactivated Co catalyst is developed.
- The pre-treatment effects of redox and reducing atmospheres on nano Co/CeO_2 have positive effect on ESR performance.
- Novel route of catalyst synthesis is discovered by solvothermal reaction and it is termed as solvothermal precipitation.
- The disruption of spinel structure of $NiCo_2O_4$ in presence of ethanolic solution of Cerous nitrate by the solvothermal precipitation method is reported.
- CeO_2 supported bimetallic Ni-Co catalysts synthesized by the solvothermal precipitation method show significant ESR performance.

9.3 Recommendations

This study is able to clear the concept of Ni and Co catalytic activity with various supports, carbon formation, reformulation of deactivated catalyst and pretreatment (redox atmosphere) effects. However, the possible mechanism involved in synthesis of catalyst by solvothermal precipitation is not clear. Further, studies of the mechanism can provide insight in the solvothermal precipitation method. The mechanism of transition reaction and identification of catalytic sites leads to the better catalyst reformulation for ESR.