Chapter 6: Summary and Path Forward (Recommendations for future work)

6.1: Summary

Global warming is a serious environmental issue. Mitigating it requires decreasing the carbon footprint by moving towards renewable resources and utilizing and valorizing CO_2 to useful products wherever possible.

Hydrogen is a very useful commodity for the manufacture of chemicals, petrochemicals, fine and specialty chemicals, pharmaceuticals, fuels and as a standalone source of energy. Its production by SMR (Steam Methane Reforming) leads to significant emissions of CO_2. The best means to mitigate this is to produce it by electrolysis using renewable energy. However, this requires enormous resources. The steam reforming of ethanol and the dry reforming of ethanol can be useful as interim measures. The former utilizes a renewable feedstock whereas the latter augments it by utilizing CO_2 as a co-reactant. Both these processes require the use of multi-component heterogeneous catalysts. While mono and bi-component catalysts have been studied extensively in the literature, there is a paucity of literature on studies of ternary and quaternary catalysts. When multiple components are incorporated into a catalyst there is a strong possibility of mutual interaction which changes the inherent characteristics of these materials, which in turn influences catalyst reactivity.

The key objective of this work is to investigate a set of 17 supported Ni catalysts comprising binary, ternary and quaternary supports for steam reforming and dry reforming of ethanol. The catalysts are thoroughly characterized. An attempt is made to correlate the activity of the catalysts with their characteristics such as microstructure, acidity, OSC (oxygen storage capacity), Ni metal dispersion and interactions between the different components of the catalyst (solid solutions).

The alumina and magnesia components of the supports show a clear influence on specific surface area and pore volume. Zirconia also imparts hydrothermal stability to alumina. Supporting Ni on these supports does not change the microstructure drastically. However, there is a linear decrease in specific surface area and pore volume with increasing Ni content of the catalyst.

Ni dispersion correlates well with the combination of BET specific surface area and the degree of reducibility of NiO of the catalysts. Catalytic activity appears to be influenced largely by the chemical moiety/intrinsic nature of the catalyst due to the specific interaction of Ni with the composition of the support. These interactions apparently influence the energetics of the reaction. However, a good relation is observed between Ni surface area and activity for catalysts with similar composition.

Changes in the XRD pattern from crystalline to amorphous, and changes in lattice 'd' spacing in HR-TEM indicate the formation of solid solutions between the components of the supports. This affects physico-chemical properties of the catalyst. Magnesia also forms a solid solution with Ni resulting in high catalyst activity for both ESR (Ethanol steam reforming) and EDR (Ethanol dry reforming). NiO (in calcined catalysts) shows smaller crystallite size on ternary supports containing Mg and quaternary supports which are rich in Mg. This correlates with higher activity in ESR and EDR.

Magnesia and zirconia have contrasting effects on the acidity of the catalyst. Nickel imparts Lewis acidity to the catalysts. Catalysts with higher acidity show faster deactivation in short duration run due to coke formation.

Zirconia enhances the OSC of ceria. Its content shows a linear relationship with the OSC of the support. OSC slows the deactivation of ternary Al-Zr catalysts (within this series) and also in quaternary catalysts.

TPR indicates the presence of two types of NiO species in catalysts containing Al or Mg alone or a combination of Mg and Zr or balanced content of Al and Zr. Catalysts containing a combination of Al and Mg or all three (Al, Mg and Zr) show only one species of NiO which reduces at relatively higher temperatures. Catalysts of Al and Zr with composition skewed in favor of Zr also shows a single NiO species which reduces at lower temperature than the other catalysts which show single NiO species. The reducibility of Ni is affected significantly by Mg in binary and ternary catalysts containing this element.

Dispersion measurements by O_2 titration are significantly lower for binary and ternary catalysts containing Mg, which is primarily due to the poor reducibility of Ni on these supports. HRTEM of fresh reduced catalysts does not show a significant difference in Ni particle size between catalysts of different compositions. The structure sensitivity of the catalyst for these reactions is observed when a correlation of particle size of Ni(0) is made with activity (conversion of ethanol) for catalysts with similar composition. When the catalyst (support) composition changes, the inherent/intrinsic chemical nature of Ni also changes due to interaction with the support. This apparently changes the energetics of the reaction over these catalysts and hence this predominates over metal dispersion as a factor for reactivity. The results indicate that both ESR and EDR reactions may be structure sensitive. Dispersion of Ni correlates well with BET surface area and degree of Ni reducibility. Catalysts containing Mg show higher catalytic activity despite poor reducibility and poor dispersion. Thus, they appear to have higher intrinsic activity which may be due to the formation of solid solution between Ni and Mg.

OSC shows a benefit in slowing deactivation in both ESR and EDR. It appears to contribute to the slower deactivation of quaternary catalysts.

A clear influence of catalyst composition on activity and product selectivity is observed in the case of binary and ternary catalysts. Conversion of ethanol and H_2 yield increase with reaction temperature. Catalysts containing Mg show better activity than those which contain Al, or Zr or a combination of Al and Zr presumably due to the formation of Ni-Mg solid solution with higher intrinsic activity. The composition of the catalyst influences the set of reactions taking place in ESR. The correlation of molar ratios of H_2/CO, H_2/CO_2 and H_2/CH_4 are elegantly used for identifying reaction mechanisms on catalysts with different compositions. The trends indicate that the ESR reaction proceeds mainly by reforming ethanol through a water-lean stoichiometry. The WGS (Water Gas Shift) reaction predominates on catalysts that do not contain Mg, whereas the Boudouard reaction predominates on catalysts that contain Mg. Explaining the trend of H_2/CH_4 with increasing temperature requires a switch to steam reforming of methanol at water-rich conditions occurring simultaneously with the methanation of CO. Consumption of water in WGS appears to limit the availability of water for steam reforming although an S/C of 3 is maintained at the reactor inlet. Ethylene formation correlates with the acidity of the catalyst indicating that it forms by the dehydration of ethanol.

Two regimes of catalyst deactivation are observed on all catalysts. This is identified by carrying out short and long-duration runs. The first, with a relatively fast decrease in conversion and a higher rate of coke laydown followed by a significantly slower decrease in activity as well as a slower rate of attendant coke laydown. The magnesia-based catalysts show slower deactivation than zirconia-based catalysts in short duration runs and the reverse in long duration runs because of differences in deactivation mechanism. Magnesia based catalysts deactivate by both coking and Ni metal sintering whereas the zirconia-based catalysts deactivate predominantly by coking alone in ESR. However, sintering is observed in EDR even in catalysts which do not sinter in ESR.

Deactivation is also significantly slower at higher temperatures. Some sintering of Ni is also observed in the case of binary and ternary catalysts containing Mg, as evidenced by HRTEM. Decay trends in ESR correlate well with the coke content of the catalyst indicating that coke deposition is the major cause of catalyst deactivation. Whereas sintering appears to be the dominant cause of deactivation in EDR.

The quaternary spent catalyst i.e., 7.5%Ni-AMZ-22-44-22 can be regenerated back to its original activity by controlled coke burn. Higher temperature, 650°C, was required for complete regeneration indicating that at least some of the coke is refractory in nature. HRTEM does not show any significant increase in Ni particle size in ESR. Catalyst 7.5%Ni-AMZ-0-89-0 showed sharper deactivation than the remaining catalysts in an 80 hour run due to the sintering of Ni which is supported by HRTEM in ESR.

Spent catalysts containing Al or Zr or their combination show larger coke content. This also correlates with the trend of acidity. The morphology of coke differs for catalysts with different compositions. A diverse variety of coke such as filamentous, octopus type filamentous, encapsulating filamentous, rod-like, bamboo and whisker type is observed on these catalysts. Coke is formed by both tip and base growth mechanisms based on the composition of the support. Quaternary catalysts and ternary Al-Mg or Zr catalysts with balanced composition show base growth.

Trends of activity for ethanol conversion, concerning catalyst composition in EDR are like those observed in ESR. Catalysts containing Mg show higher activity and H_2 yield.

Correlation of H_2/CO, H_2/CH_4 and conversion of ethanol/conversion of CO_2 are elegantly used to identify the reactions taking place. Like ESR distinct differences are observed in EDR for catalysts that contain Mg or Zr. Catalysts containing Zr promote Boudouard reaction rather than WGS. Methane appears to form by methanation of CO at H_2 lean conditions concurrently with the Boudouard reaction. Catalysts containing Mg show differences in mechanism with reaction temperature. At reaction temperature $\geq 650^{o}C$ they appear to form methane by methanation of CO at H_2 lean conditions whereas at $<650^{o}C$ the Boudouard reaction occurs concurrently like that in catalysts containing Zr.

The yield of ethylene correlates with acidity and hence is higher in catalysts not containing Mg. Coke deposition also correlates with the catalyst composition. Catalysts containing Mg form lesser Coke and deactivate relatively slowly. Two regimes of deactivation, first slow and then fast are observed like that in ESR. Deactivation is also slower at higher temperatures, also like in ESR. Unlike ESR coke deposition is not the major cause of catalyst deactivation in EDR because the nature of coke is filamentous in the latter case. Sintering of Ni metal takes place in EDR even in catalysts where it does not happen in ESR.

Overall, quaternary catalyst rich in Mg 7.5%Ni-AMZ-22-44-22 shows good performance in both ESR and EDR. It presents slow deactivation and also shows complete restoration of activity upon regeneration by controlled combustion for ESR. Slow deactivation is attributed to a combination of better resistance to sintering of Ni, attenuated acidity and OSC. The complete regenerability of this catalyst is attributed to insignificant sintering of Ni during use for ESR.

To summarize, this study demonstrates that Ni supported on multicomponent supports of Al, Mg and Zr show significant differences in characteristics (microstructure, acidity, OSC, metal reducibility, metal dispersion and metal-support interaction). These differences influence reactivity for ESR and EDR (activity, product selectivity, catalyst stability and associated reactions taking place). Deactivation behavior and morphology of carbon deposited on spent catalysts are also influenced. The multi-component support imparts diverse properties which influence the overall performance of the catalyst. Catalyst characteristics are correlated with reactivity for ESR and EDR to a reasonable extent.

This study demonstrates the need for testing catalysts over extended durations to identify correct trends. It also demonstrates the importance of using H_2-TPR as a complementary technique for correctly interpreting results of metal dispersion by chemisorption technique. It teaches that correlation of activity with dispersion should be done for catalysts of similar composition which have similar intrinsic activity. HR-TEM provides unbiased results of metal dispersion compared to chemisorption technique.

6.2: Path Forward (Recommendations for future work)

The current study shows the influence of different components of support and their interaction with Ni on reactivity for ESR and EDR. Alumina enhances microstructure; however, its acidity and the encapsulating type of coke are detrimental to its performance.

Magnesia forms a solid solution with Ni which leads to higher inherent activity. It also attenuates acidity and thus contributes to slower deactivation. However, it works well in combination with alumina or zirconia rather than as a standalone support.

Zirconia enhances OSC and slows deactivation. However, its amphoteric nature tends to lay down higher coke of the catalyst. That notwithstanding this catalyst shows good stability.

Thus, it is clear that multicomponent supports constituting all three of these components in optimal concentrations lead to catalysts with improved performance.

Increasing the content of Mg and Zr in ternary Al-Mg and Al-Zr catalysts improves performance. Variation of composition is studied in these two ternary catalyst systems. However, the same is not studied in the case of ternary Mg-Zr catalyst. The MgO: ZrO_2 weight ratio was not varied. It was maintained at 1:1. This catalyst shows less coke laydown and slower deactivation than ternary Al-Zr catalysts with a balanced composition. Since the results of this study indicate that the presence of magnesia in the support leads to slower deactivation due to lower acidity and increasing zirconia in the support also slows deactivation (due to OSC and resistance to metal sintering), it would be worthwhile to study this combination in further detail by varying compositions to identify an optimum.

The quaternary catalysts show good performance due to the contribution of beneficial effects of all three (Al, Mg and Zr) components in the support. Further fine tuning of composition could be done to optimize the composition.

A significant fraction of ethylene is formed on these catalysts. Decreasing this requires attenuation of acidity. This could be done by dopants such as alkali metals or by thermal treatment. This could be attempted going forward.

Similarly, significant methane is also formed. Attempts should be made to mitigate this or to convert it further to syngas by modifying the catalyst.

Further studies should focus on long-duration runs for studying catalyst stability because short-duration runs can be misleading as seen for binary Mg catalyst (7.5%Ni-AMZ-0-89-0) which showed poor stability in long-duration (80 hours) runs.

Sintering appears to be a dominant mechanism of deactivation in EDR. Further work should be directed towards overcoming this problem.

The current study demonstrates that activity can be correlated with dispersion when the composition of the support is similar, where intrinsic activity is not very different. When comparing catalysts that comprise supports of different compositions, changes in inherent chemical nature due to specific interaction between metal (Ni) and components of the support predominate over metal dispersion. A Density functional theory (DFT) study to identify differences in the energetics of ESR and EDR of catalysts of different support compositions and correlate this with catalyst activity would be very useful.

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