Summary

Hydrogen is an important chemical commodity that is used extensively in the production of fertilizers (ammonia), refining of petroleum-based fuels (Gasoline, Diesel, Jet fuel), petrochemicals and fine and speciality chemicals that are used in many walks of life [1]. H_2 is being used as rocket fuel and even in automobiles. Global warming and the need to avert potential catastrophe have brought H_2 into the domain of sustainable fuels such as standalone or derived fuels and chemicals (Power-to-X) including the hydrogenation of CO_2 to replace fossil fuels [2]. It is also important to note that hydrogen itself is an indirect greenhouse gas and its emissions need to be monitored and controlled [3].

A massive R&D effort is ongoing around the Globe to replace conventional methods of production of hydrogen such as steam reforming of methane (SMR) with sustainable routes such as electrolysis using renewable energy. Mandatory regulation is already replacing conventional routes in the industry with eco-friendly methods such as electrolyzers. However, achieving net zero emission of CO_2 requires a concerted effort from various sectors because of the emission of CO_2 by different sectors. The energy sector accounts for about 73% of emissions. Breakup is 24.2% industry, of which the chemical and petrochemical industry accounts for 3.5%. Transportation is 16% of which road transport accounts for 12%. Energy used in buildings 18%, electricity and heat generation 8% etc. Direct emission from the chemical industry as a by-product is 5.2% out of which 2.2% is from chemical and petrochemical plants. Agriculture and forestry land use 18% [4].

Significant capital investment for the installation of infrastructure for renewable energy as well as significant improvement in the chemical efficiency of alternate routes is required to offset emissions from the energy and chemicals sector. This calls for considerable investment (US $ 27.5 Trillion) time and effort [5].

Meanwhile, dependence on conventional methods of producing H_2 is currently indispensable. Alternatives such as existing methods (SMR) combined with CC (CO_2 capture) immediately, and CCU (CO_2 capture and utilization) in the near to midterm are needed to contribute to the Net zero emission effort.

Replacing methane with a renewable raw material such as ethanol or the dry reforming of methane (or ethanol) can decrease the carbon footprint. Commercial

technology for dry reforming of methane is available viz. Linde Dryref® technology [6] with BASF's Ni oxide based Synspire® catalyst [7] and Chiyoda's noble metal-based CT-CO_2AR® technology [8]. However, there is no commercially operating plant with this technology to date. Dry reforming of ethanol combines the use of renewable raw material with utilization/valorization of CO_2 which is a further step towards decreasing the carbon footprint until the infrastructure of new ecofriendly technologies is created. The current study is a step towards this end. It encompasses a study of catalysts for steam reforming of ethanol as one part and the dry reforming of ethanol as a second part of the study.

Coke formation is considered a key factor that affects the commercialization of catalytic steam and dry reforming of ethanol [9, 10]. Although noble metal-based catalysts are advantaged in terms of activity and coke formation, their cost is a deterrent to their commercialization. A variety of oxides are studied as carrier for these applications. However, there is a paucity of systematic studies where composition of the support is systematically varied to understand its effect ternary and quaternary carriers [9, 10]. Hence, catalysts comprising nickel supported on binary, ternary and quaternary compositions of catalyst supports are prepared, characterized and tested for these reactions in the current study. The composition of rare earth lanthana and ceria is fixed, whereas the composition of magnesia, alumina and zirconia is varied systematically.

Chapter 1 introduces the topic. It highlights the importance of H_2 as a chemical intermediate and fuel. The existing methods of production and alternate methods that are being pursued to meet the target of net zero emission of CO_2 by 2050 are briefly covered. The challenges therein and the need to depend on conventional methods such as steam reforming in the near and midterms are highlighted. The advantage of replacing methane with ethanol for its steam or dry reforming are highlighted in the context of carbon footprint. This is the key motivation for this study. A summary of work carried out so far and reported in published literature is surveyed. The approach followed and gaps therein are identified. The current work is carried out to add to the body of knowledge to fill the gaps to the extent possible for enabling the development of more efficient catalysts for these applications.

Chapter 2 covers the preparation and characterization of the supports in detail. The method of support preparation is described in detail as also the techniques used for characterization. Effect of catalyst composition on characteristics of catalysts such as their microstructure, (hydro)thermal stability, crystallographic phase using X-Ray diffractometer (XRD), acidity using ammonia temperature programmed desorption (NH_3-TPD), oxygen storage capacity (OSC), are studied. These results are correlated with the reactivity of these catalysts for Ethanol Steam Reforming (ESR) and Ethanol Dry Reforming (EDR) in subsequent chapters.

Preparation of the support is described in detail. Thirteen supports comprising combinations of rare earth, alumina (Al_2O_3), magnesia (MgO) and zirconia (ZrO_2) as binary, ternary and quaternary compositions are prepared by coprecipitation. A total of 13 supports with varying compositions are studied. The supports are characterized by their composition, XRD phases, microstructure, Differential Scanning-Thermogravimetric (DSC-TG) of as-synthesized dried catalysts, oxygen storage capacity (OSC), Fourier transform infrared (FTIR) bands of as-synthesized catalysts for structure, acidity, and hydrothermal stability.

Varying the support composition significantly influences the above properties, such as specific BET surface area, pore volume and pore size distribution. Alumina has a profound influence on specific BET surface areas and isotherm types. Zirconia, magnesia and rare earth provide hydrothermal stability to alumina. A significant difference in pore size distribution is observed between the binary supports on one hand and the ternary and quaternary on the other.

The acidity of the catalyst is determined by NH_3-TPD. These trends are correlated with product selectivity, coke formation and catalyst deactivation. Unexpected changes in acidity indicate the formation of solid solution which is also confirmed by XRD. Acidity is correlated with by-products such as ethylene and coke laydown in ESR and EDR.

Since the catalyst operates under hydrothermal conditions (high temperature and moderate pressure in the presence of water vapor) the effect of hydrothermal aging of these composites at 750°C, 4 hours is also studied.

XRD studies are carried out to demonstrate the formation of solid solutions and the influence of catalyst components on crystallite growth upon hydrothermal ageing.

The effect of catalyst composition on OSC is determined. Zirconia has a strong influence.

The breakup of acidity into acidic, basic, and amphoteric characters is done using a model test reaction (decomposition of 2-methylbut-3-yn-2-ol (MBOH)). This is correlated with the catalyst composition. The composition of the catalyst is correlated with catalyst deactivation for this reaction. Physico-chemical characteristics of these supports are correlated with characteristics of supported metal catalysts in chapter 3 and with activity and reactivity for ESR (ethanol steam reforming) and EDR (ethanol dry reforming) in chapters 4 and 5.

Chapter 3 covers the preparation and characterization of supported metal catalysts. Ni is supported on the supports as the active phase. Ni content is varied in select catalysts to understand the effect of its content. The catalysts are prepared by incipient wetness impregnation. The results of characterization are correlated with the composition of the support. The decrease in specific surface area and pore volume with the incorporation of Nickel Oxide (NiO) is quantified. This relation is observed to be linear with the content of NiO.

Trends of weak and strong acidity and acid strength are correlated with the catalyst composition. The contribution of Lewis acidity from the Nickel impregnated onto the support is observed in the catalysts. Acidity is correlated with the formation of by-products such as ethylene and coke laydown in ESR and EDR in subsequent chapters.

Temperature-programmed reduction studies show that the ease of reduction of Ni depends on the catalyst composition, thus indicating differences in metal-support interaction. Overall, catalysts that contain Zr reduce at lower temperatures ($<500^{o}C$) than those that contain Mg. Binary Al or Mg catalysts and ternary Al-Zr catalysts with balanced composition show bimodal character of oxide reduction. Ternary catalysts of Al-Mg and all quaternary catalysts reduce at higher temperatures ($>500^{o}C$). Significant differences in reduction temperature are seen between binary catalysts on one hand and ternary or quaternary ones on the other which indicate the formation of solid solutions of Al-Zr (interaction between components of the support).

Interaction of Ni with support components (including the formation of solid solution with Mg) influences the degree of reduction of Ni, which in turn influences the dispersion of Ni. Overall, the dispersion of Ni correlates well with specific BET surface area for catalysts with a high degree of reducibility, thus both parameters influence the dispersion of nickel as determined by O_2 chemisorption. Multiple linear regression confirms good correlation. HRTEM shows that ternary catalysts of Al and Zr show smaller Ni(0) particle size than Al-Mg catalysts. These catalysts also show slower deactivation than the latter as seen in ESR studies covered in chapter 4.

An attempt is made to correlate these (of the catalyst) characteristics with performance for ESR and EDR in subsequent chapters.

Chapter 4 covers studies of steam reforming of ethanol (ESR). The 17 catalysts whose method of preparation is described in Chapters 2 and 3 are evaluated for their performance in ESR reaction. The results clearly show how catalyst composition influences product selectivity. Catalysts containing Mg or a combination of Al and Mg show higher ethanol conversion, and slower deactivation in short-duration runs, but deactivate relatively faster than catalysts containing a combination of Al and Zr or all three components Al, Mg and Zr in long-duration 80 hours runs. This is due to differences in the rate of coke laydown in these catalysts during the initial hours on stream compared to longer operation.

Dispersion of Ni influences catalytic activity within catalysts of similar composition of supports, whereas difference in inherent chemical character influences activity of catalysts of different compositions of support.

Correlation of trends of ratios of H_2 product with CO, CO_2 and CH_4 are examined to understand underlying reactions. They show that the reaction proceeds by steam reforming of ethanol through a water lean route. Further, CO participates predominantly in WGS (Water Gas Shift) reaction in catalysts that do not contain Mg whereas it participates in the Boudouard reaction in the case of catalysts that contain Mg. Methane is formed by the methanation of CO concurrently with steam reforming at water-rich conditions. Thus, catalyst composition influences product selectivity.

The acidity of the catalysts correlates reasonably well with the formation of ethylene and to an extent with coke laydown. The differences in product selectivity exhibited by binary and ternary catalysts are diluted in quaternary catalysts which contain all three elements (Al, Mg and Zr).

While Mg-containing binary and ternary catalysts show higher yield of H_2 they also deactivate faster than ternary Al-Zr catalysts.

Two distinct regimes of catalyst deactivation, short and long-term are observed, with the former being much faster than the latter. Reaction temperature influences the deactivation rate for all catalysts. It is significantly slower at the higher reaction temperature. The trend of deactivation with catalyst composition changes with reaction temperature indicating that different reactions could be involved.

Oxygen storage capacity slows deactivation in catalysts containing Zr. A trend is observed with increasing zirconia content (which increases OSC). The quaternary Mg-rich catalyst shows complete recovery of performance upon regeneration by coke burn indicating that the cause of deactivation is predominantly coke deposition by either or both of CO disproportionation and ethylene polymerization. High resolution transmission electron microscopy (HRTEM) shows that Ni sintering is insignificant in this catalyst.

Coke morphology of spent catalysts is influenced significantly by catalyst composition. Morphologies varying from filamentous to rod-like to encapsulating to whisker-type coke are observed. Thus, catalyst composition influences coke morphology. Coke content varies between 9-13 wt% in spent catalysts in long-duration runs despite which high conversions are observed. This is attributed to the filamentous or whisker/tentacle morphology of coke which keeps Ni particles accessible to the reactants. A correlation between catalyst composition and reactivity could be demonstrated.

Ternary Al-Mg catalysts show relatively higher activity but tend to deactivate faster. Ternary Al-Zr catalysts show relatively lower activity but higher stability. All the quaternary catalysts show slower deactivation and activity intermediate between ternary Al-Mg and Al-Zr catalysts. Quaternary 7.5%Ni-AMZ-22-44-22 can be regenerated back to its initial activity. Thus, it is advantageous to use quaternary supports for this application.

Chapter 5 is devoted to the dry reforming of ethanol (EDR) reaction. EDR has the double advantage of using a renewable feedstock and also utilizing/valorizing CO_2. Thus, it has a lower carbon footprint than ESR. The same 17 catalysts which were evaluated for ESR were also evaluated for EDR.

Similar to ESR, Mg-containing catalysts show higher conversion of ethanol and higher yield of H_2. Conversion of ethanol shows trends which are very similar to those of steam reforming of ethanol. Catalysts containing Mg show higher conversion of ethanol followed by quaternary catalysts and lastly ternary Al-Zr catalysts. Thus, the correlation of activity (ethanol conversion) with catalyst characteristics is likewise. The trend of conversion of CO_2 also follows that of ethanol. However, the quaternary catalysts show CO_2 conversion which is almost similar to that of ternary Al-Mg catalysts. The correlation of the molar ratio of H_2 with CO and CH_4 and the ratio of conversion of ethanol/conversion of CO_2 is used to identify the mechanism by which the products form. The analysis indicates that catalysts containing Zr promote the Boudouard reaction concurrently with the methanation of CO at water lean conditions. In contrast, catalysts containing Mg appear to follow the same mechanism as those containing Zr at temperature <650°C and predominantly by methanation of CO under water lean conditions at >650°C.

Ethylene yield is higher for catalysts with higher acidity viz. (catalysts that do not contain Mg). This is consistent with the expectation because the dehydration of ethanol is an acid-catalyzed reaction. Deposition of coke also trends reasonably with the acidity of the catalyst.

Similar to ESR, deactivation is significantly slower at higher temperatures. It correlates moderately with coke content on spent catalysts. The contribution of OSC (oxygen storage capacity) in slowing deactivation is also evidenced in EDR.

The morphology of coke for ternary Al-Zr catalyst AMZ-44-0-44 and quaternary Mg-rich catalyst AMZ-22-44-22 is very different from that observed in ESR.

Catalyst AMZ-22-44-22 could be completely regenerated by coke burn.

Overall, catalyst activity correlates well with crystallite size of NiO, ethylene formation correlates with acidity, and coke formation correlates with acidity for catalysts containing Al or Zr. In the case of Mg-based catalysts, coke appears to form due to the Boudouard reaction. A trend between catalyst composition and reactivity could be demonstrated. Quaternary 7.5%Ni-AMZ-22-44-22 shows good stability and it can also be regenerated back to its initial activity. Thus, it is advantageous to use quaternary supports for this application.

Chapter 6 compiles the major inferences drawn in the remaining chapters (3-5). The results clearly show the influence of the composition of the support and interaction of Ni with the composition of support on reactivity for ESR and EDR. Suggestions for pursuing these studies are also made on the basis of the results obtained from the current study and the gaps therein.

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