Chapter 1: Introduction

Hydrogen is an important compound. Conventionally it is used as a reactant in hydrogenation, hydrodesulfurization, hydrocracking and hydroisomerization which yield fuels, lubricants, monomers (such as ethylene from selective hydrogenation of acetylene) and speciality chemicals such as API (Active pharma ingredients), fragrances and flavor chemicals. As per [1], major uses of hydrogen are ammonia production (50%), petroleum processing (37%), methanol (8%), organic transformations for specialities, double bond saturation, desulfurization and denitrification (air pollution control), Oxygen (O_2) scavenger to remove oxygen to prevent oxidation and corrosion (Nuclear reactors), as a clean fuel (automobiles, spacecraft, as a coolant in electrical generators, Fuel cells etc.

Apart from its use as a reactant, it is used as a reaction environment in many refinery and petrochemical catalytic processes (such as dehydrogenation of alkanes to alkenes) to retard catalyst deactivation through fouling by coke.

With global warming increasing at an alarming rate, efforts are on to resort to fuels that do not generate Carbon Dioxide (CO_2) as a by-product or from utilities for the generation of heat. Hydrogen is such a fuel. It has a high energy density on a weight basis (120.7 MJ/kg) [2]. Its production from renewable energy by electrolysis of water and use in automobiles instead of conventional carbonaceous fossil fuels such as gasoline, diesel, Natural Gas results in a scenario where generation of CO_2 is avoided. This route of producing hydrogen relies on renewable sources such as solar, wind, tidal hydroelectric and geothermal energy. The hydroelectric is well established but is dependent on nature (monsoon rain) and geography. These methods require huge infrastructure and land (in the case of solar) and attendant cost which is estimated at trillions of US dollars [3] to achieve net zero emission of CO_2. Wind energy has a high degree of variability which requires the use of hybrid systems to tide over lean periods. Solar power as a source is much more predictable in tropical countries.

Significant research is ongoing to capture and convert CO_2 to useful chemicals. The objective is to contain CO_2 levels at net zero by the year 2050. This requires large quantities of hydrogen as a co-reactant for conversion to fuels and other useful compounds. CO_2 capture in itself is a challenging area of development.

Conventionally, on-purpose hydrogen is produced by the steam reforming of fossil fuels viz. steam methane reforming (SMR) or steam reforming of naphtha followed by WGS (Water Gas Reaction) to convert Carbon Monoxide (CO) to Hydrogen (H_2) and CO_2. However, these are non-renewable sources. Besides, steam reforming produces large quantities of CO_2 as a by-product. Using renewable feedstock offsets, the emissions to an extent due to CO_2 recycling. Thus, it is important to develop processes based on renewable sources such as ethanol.

Other sources of hydrogen are the steam cracking of naphtha and the catalytic reforming of naphtha which produce H_2 as a by-product. The thermo-catalytic decomposition of methane produces H_2 and CNT (Carbon Nano Tubes) as products. The latter route produces H_2 without the co-production of CO_2 as a by-product. However, these are thermo-catalytic processes and CO_2 is produced from the (fossil) fuels which are combusted to produce the heat required for the reaction.

Electro-catalytic processes are advantaged in this respect provided the electricity required for these processes is produced from non-fossil routes (solar, wind, tidal, hydroelectric, geothermal). Electrolysis is already used commercially for producing hydrogen instead of SMR. However, currently, the electricity required is produced mainly from thermal power stations which use fossil fuels and release significant CO_2 into the atmosphere. Electrochemical/electrocatalytic reforming of ethanol, the use of membrane reactors, structured reactors and plasma reforming are some new technologies that are cited as under development [4].

Ethanol is produced from molasses which is a byproduct of the sugar industry which in turn uses sugarcane and beet as renewable feedstock. Substituting SMR with Ethanol Steam Reforming (ESR) contributes to the conservation of fossil fuels and partial abatement of Green House Gas (CO_2) since plants fix CO_2 during photosynthesis. Steam reforming of ethanol has been widely studied but the major challenge in its commercialization is the lower yield of H_2 and the use of a high steam/carbon ratio to retard coke deposition compared to SMR. The use of noble metals such as Rh as catalysts gives competitive yields but attracts high costs. The current cost of Ni metal is 18.92 Euro/kg versus 131800 Euro/kg for Rh (May 2023 LME data).

Dry reforming is a reaction wherein CO_2 is used instead of steam for reforming hydrocarbons and oxygenates. It decreases the net quantity of CO_2 released into the atmosphere. Technology for dry reforming of methane is offered by Linde (DryRef® Process) which uses a nickel-based catalyst from BASF (Synspire® G1-110 / G2-120) [5] and by Chiyoda (CT-CO_2AR® process) [6] which uses their own noble metal-based catalyst. In these processes, part of the CO_2 produced as a by-product during reforming is recycled back to the reactor as CO_2 feed. However, there are no commercial operating plants based on these technologies at present.

Dry reforming of ethanol contributes to both, the substitution of fossil feedstocks with renewable feedstock as well as the utilization of CO_2, which decreases the impact of global warming. Thus, it has a double advantage.

Considering the current state of alternate technology and infrastructure required for producing non-conventional renewable electricity, the use of steam reforming to produce hydrogen is inevitable in the near to medium term. SMR with CCS (carbon capture and storage) is considered a good near-term option to mitigate the emission of CO_2 to the atmosphere until other technologies ramp up.

Thus, the use of renewable feedstock such as ethanol and its dry reforming with CO_2 could be used to conserve fossil fuels and also mitigate CO_2 emissions, thus contributing to Green House Gas abatement.

Both steam reforming and dry reforming are endothermic processes and hence require high reaction temperatures to enable economically feasible yields. The enthalpy of reaction for steam reforming of ethanol is +174 kJ/mol at 298K whereas that for dry reforming of ethanol is +296.7 kJ/mol at 298K. The former reaction gives 6 moles of H_2 per mole of ethanol with H_2/CO molar ratio of 3, whereas the latter gives three moles of H_2 with H_2/CO molar ratio of 1. This affects its end use. Significant research efforts have been made in both these areas and mono, bi and tri-component catalysts have been studied for both ethanol steam reforming (ESR) [7] and ethanol dry reforming (EDR) [8,9]. Process economics has been a key hindrance in the commercialization of these technologies. The other major factor is the limited availability of a concentrated stream of CO_2 as a reactant for dry reforming and the H_2/CO ratio which is low for dry reforming of methane. This affects the utility of the stream for downstream applications.

Wood Group UK Ltd., which is a Global expert and technology licensor for catalytic H_2 production have evaluated the substitution of methane with liquid renewable streams. They opine that the existing configuration of an SMR plant is adequate for ESR with minor modifications. Hence retrofitting existing SMR plants is readily feasible. They concede that hydrogen yields of hydrogen from steam reforming of bioethanol are lower than that of SMR, but the process is more energy efficient. They further mention that it is not competitive at current bioethanol prices [10]. They mention that the economics of ESR is favorable against electrolysis. Corresponding studies for the techno-economic feasibility of dry-reforming ethanol were not found in the literature.

SMR is a well-established technology with over 95% of global H_2 produced by this route. Yield of H_2 is ~74% [11]. The commercial process uses Nickel supported on alumina-based support. Various components are added to the support to tailor properties such as thermal stability, mechanical strength, acidity, and oxygen storage capacity. The key reaction is the direct reforming of Methane (CH_4) to CO and H_2. Other reactions which take place are WGS which enhances the productivity of H_2 with the co-production of CO_2 and the Boudouard reaction which forms coke by disproportionation of CO is a competing reaction.

Unlike SMR, where coke formation and WGS are important side reactions, the steam reforming of ethanol proceeds through many pathways such as direct reforming with steam, decomposition, hydrogenolysis, dehydration and dehydrogenation which yield methane in addition to syngas, ethylene, and acetaldehyde. Aldol condensation with subsequent dehydrogenation forms acetone. The CH_4 and CO formed undergo steam reforming and WGS to yield H_2. Dry reforming and methanation of CO also take place. In addition to reaction conditions and residence time, the intrinsic activity of the catalyst also plays a large role [12]. This calls for multi-component catalysts whose properties are tailored to maximize H_2 production.

In addition to Ni, a host of other non-noble metals such as Co, Cu, Zn and Fe and noble metals such as Rh, Pt, and Pd as well as their bimetallic combinations have been studied [7].

A host of carriers is also reported in the literature for the steam reforming or dry reforming of ethanol. These are MgO [13], CeO_2 [14], CeO_2-ZrO_2 [15], ZrO_2 [16], Lanthana [17], Al_2O_3-La_2O_3 [18], CeO_2-Al_2O_3 [19], Al_2O_3-ZrO_2 [20], Alumina-magnesia [21]; Y_2O_3-ZrO_2 [22], Lanthana or Zirconia [23], RE-$MgAl_2O_4$ [24]. As seen from this list most supports are monocomponent or bicomponent. Alkali metal oxides such as Potassium [25] and alkaline earth metal oxides such as SrO_2 [26] are also reported as promoters in the literature. H_2 yields comparable with SMR are reported in some literature for ESR. However, the latter is plagued by a higher degree of coking compared to SMR. S/C (Steam:Carbon molar ratio) in the range of 5-6 (which is much higher than stoichiometry) is used in much of the published literature to retard coking. Interestingly some literature reports the use of S/C ratio of 1.5 – 2.0 with low attendant coking and selectivity of 60% for H_2 for Ni supported on cerium-samarium mixed oxide nanowires [27]. Gas Hourly Space Velocity is significantly lower than SMR in most of these studies. However, scaling up the nanowire catalysts economically for commercial service could be difficult.

The performance of these catalysts is tabulated in references [4, 7]. While noble metals are highly active, cost is a deterrent. Noble metal catalysts prepared by impregnation are reported to present maximum selectivity to H_2. Materials with basic character are reported to decrease coke formation [7]. Base metals like Ni and Co with H_2 selectivity close to noble metal catalysts ($\geq$80%) are reported for ESR [7].

The various components of the catalyst are reported to attenuate acidity, improve thermal and hydrothermal stability, promote oxidation of coke through lattice oxygen and minimize sintering of the active phase.

Materials with a chemically basic character (calcium or strontium oxide, magnesia) decrease acidity which is important for minimizing the formation of ethylene through the dehydration of ethanol. Olefins are known to promote coke formation through oligomerization, hence low ethylene translates to less coke. Materials with redox properties (such as ceria) are known to store lattice oxygen, which is reported to combust coke (coke scavenging) and thus clean up the surface of the catalyst. Transition alumina tends to hydrate back to boehmite under hydrothermal conditions, thus hydrothermal stability is important. Promoters such as rare earth especially La or Zr are reported to impart this stability.

Thus, it is clear from the literature that the catalyst is preferably multicomponent to serve different functions. When multiple components are incorporated into a catalyst formulation it is important to understand changes in their individual effects due to the interaction between these components. Most of the studies reported in the literature are with mono or bicomponent supports. A few ternary supports are also reported.

Quaternary supports are not reported in the literature. Thus, there is a paucity of literature on the interaction effects of various components which are necessary to impart multifunctionality to steam and dry reforming catalysts. Further, a systematic study of preparation, characterization and performance evaluation of catalysts encompassing single component supports and their combinations into multicomponent supports for ESR and EDR is lacking in literature.

The main objective of the current study is to prepare mono, bi and multi-component supports by combination of the mono-component supports and study the interaction effects between different components in binary, ternary and quaternary catalyst formulations, and their impact on ESR and EDR. The components of the support are selected on the basis of an extensive literature search. Various characterization techniques such as surface area, pore volume, pore size distribution, acidity of the support, oxygen storage capacity, morphology of support, XRD crystallographic phases, reducibility of active metal and dispersion of active metal are studied. These properties are correlated with performance for ESR and EDR. Catalyst deactivation and catalyst regeneration are also studied. ESR was chosen as the target reaction because of its potential to substitute fossil feedstocks with renewable feedstock and thus contribute to the mitigation of global warming. EDR was chosen because, in addition to the use of renewable feedstock, it utilizes CO_2 as a reactant and thus contributes to the goal of net zero emission of CO_2.

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