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Catalysts for Hydrogen Generation from Renewables

Chapter 1: Introduction:

Hydrogen is a valuable commodity. It is used as a reactant in hydrogenation, hydrodesulfurization, hydrocracking and hydro isomerization which yield fuels, lubricants, monomers, petrochemicals, and specialty/fine chemicals. As per [1], major uses of hydrogen are ammonia production (50%), petroleum processing (37%), methanol (8%), organic transformations for specialties, double bond saturation, desulfurization, and denitrification (air pollution control), O_2 scavenger to remove oxygen to prevent oxidation and corrosion (Nuclear reactors), as a clean fuel (automobiles, spacecraft, as coolant in electrical generators, Fuel cells.

With global warming increasing at an alarming rate, efforts are on to resort to fuels which do not generate CO_2 as a by-product, or from utilities for generation of heat. Hydrogen is such a fuel. It has a high energy density on weight basis ($120.7\ kJ/g^{-1}$) [2]. Its production from renewable energy (Green Hydrogen) by electrolysis of water for substitution of conventional carbonaceous fossil fuels is important for arresting global warming. This route relies on natural sources such as solar, wind, tidal hydroelectric and geothermal energy. Implementing them require huge infrastructure and land (in case of solar) and attendant cost which is estimated at trillions of US dollars [3] to achieve net zero. Significant research is on-going to capture and convert CO_2 to useful chemicals. The objective is to contain CO_2 levels at net zero by 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. Electro-catalytic processes are advantaged provided the electricity required for these processes is produced from non-fossil routes (solar, wind, tidal, hydroelectric, geothermal). Current conversion efficiencies are low. Electrolysis is already used commercially for producing hydrogen instead of SMR. Electrochemical / electrocatalytic reforming of ethanol, use of membrane reactors, structured reactors and plasma reforming are some new technologies which are cited as under development [4].

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

Dry reforming of methane is a reaction wherein CO_2 is used instead of steam for reforming of hydrocarbons and oxygenates. It decreases the net quantity of CO_2 released to the atmosphere. However, the methane is a fossil fuel. 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 a proprietary noble metal-based catalyst. In these processes part of the CO_2 produced as by-product is recycled back to the reactor as CO_2 feed. This technology is yet to be fully commercialized.

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

Considering the current state of alternate technology and infrastructure required for producing 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 emission of CO_2 to the atmosphere, until other technologies ramp up.

Thus, use of renewable feedstock such as ethanol and dry reforming with CO_2 could be used to conserve fossil fuels and also mitigate CO_2 emissions, thus, contributing to GHG (Greenhouse gas) abatement.

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

Wood Group UK Ltd. opines that hydrogen yields 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], however economics of ESR is favorable against electrolysis at the moment.

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. Key reaction is the direct reforming of CH_4 to CO and H_2. Other key reactions which take place are WGS (water gas shift) methane decomposition, gasification of coke and the Boudouard reaction. The latter three influence coke laydown on the catalyst.

Unlike SMR, where coke formation and WGS are important side reactions, the steam reforming of ethanol proceeds through a number of pathways such as direct reforming with steam, decomposition, hydrogenolysis, dehydration and dehydrogenation of ethanol, besides WGS, which yield methane, ethylene, coke and acetaldehyde in addition to syngas. In addition to reaction conditions and residence time, the intrinsic activity of 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, Pd as well as their bimetallic combinations have been studied [7].

A host of carriers is also reported in 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], La or Zr [23], RE-$MgAl_2O_4$ [24]. As seen from this list most supports are mono-component or bi-component. Alkali metal oxides such as potassium [25] and alkaline earth metal oxides such as SrO_2 [26] are also reported in literature. H_2 yields comparable with SMR are reported in some literature for ESR. However, the latter is plagued by higher degree of coking compared to SMR. S/C (Steam: Carbon molar ratio) in the range 5-6 (which is much higher than stoichiometry and economically undesirable) is used in much of the published literature to retard coking. Interestingly some literature reports use of S/C 1.5 – 2.0 with low attendant coking and selectivity 60% for H_2 for Ni supported on cerium-samarium mixed oxide nanowires [27]. GHSV is significantly lower than in SMR in most of these studies. Further, scaling up the nanowire catalysts economically for commercial service could be difficult.

Performance of these catalysts is compiled 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 (≥80%) is reported for ESR [7].

The role of different components of the catalyst such as attenuation of acidity, improvement of thermal and hydrothermal stability, promotion of oxidation of coke through lattice oxygen and minimization of sintering of the active phase has been identified mainly through studies with mono and bi-component catalysts. Transition alumina tends to hydrate back to boehmite under hydrothermal conditions, thus hydrothermal stability of the support is important.

Thus, it is clear from literature that it is desirable to formulate catalysts which are multicomponent in order to serve different functions. When multiple components are incorporated into a catalyst formulation (multi-component) it is important to understand changes in their individual effects due to interaction between these components. Most of the studies reported in literature are with mono or bi-component supports. Few ternary supports are also reported. Quaternary supports are not reported in literature. Thus, there is a paucity of literature on interaction effects of various components which are necessary to impart multi-functionality to steam and dry reforming catalysts.

The main objective of the current study is to study interaction effects between different components in multi-component (binary, ternary and quaternary) catalyst formulations and their impact on physico-chemical properties and performance for ESR and EDR. ESR was chosen as the target reaction because of its potential to substitute fossil feedstocks with renewable feedstock and thus contribute to mitigation of global warming. EDR was chosen because in addition to use of renewable feedstock, it utilizes CO_2 as a reactant and thus contributes to the goal of net zero emission of CO_2.

Chapter 2: Multi-component supports- Binary / Ternary / Quaternary

Based on literature survey it is inferred that key components of steam reforming catalysts for ESR and EDR are alumina, magnesia, zirconia, ceria, lanthana as components constituting the support and preferably nickel (because of lower cost) or noble metals such as Pt or Rh as the active phase. Accordingly, systematic sets of binary, ternary and quaternary catalysts were prepared.

Concentrations of lanthana and ceria were fixed at 5.5 wt% (nominal) in all the catalysts. The three binary catalysts comprised one of Al or Mg or Zr along with lanthana and ceria. Likewise, combinations of Al-Mg, Mg-Zr and Al-Zr constituted the ternary supports. Supports with balanced and skewed concentrations of these components were included. The quaternary supports constituted combinations of all three components, Al, Mg and Zr along with fixed concentrations of lanthana and ceria. A total of thirteen supports were prepared and characterized for their composition (ICP-OES), thermogravimetry (DSC-TG), microstructure (surface area, pore volume and pore size), acidity (NH_3-TPD), FTIR (dried samples) crystallographic phase (P-XRD), OSC (oxygen storage capacity), thermal stability by hydrothermal aging and acid-base character by decomposition of MBOH (2-methyl-3-butyn-2-ol).

Physicochemical properties such as BET specific surface area, pore volume and pore size distribution (unimodal versus bimodal) and isotherm type were strongly influenced by composition. Alumina was a key contributor to BET specific surface area, whereas Magnesia to pore volume in the multi-component catalysts. Binary catalysts presented unimodal pores whereas ternary and quaternary catalysts presented bimodal pores. Type of isotherm depended on presence or absence of alumina in the catalyst composition. Quaternary catalysts showed larger pores which is beneficial for diffusion of reactants and products. Quaternary catalysts showed significantly slower deactivation in EDR than ternary Al-Zr which have relatively smaller pore size, and comparable deactivation to ternary Al-Mg catalysts whose pore size is similar to that of quaternary catalysts. The ternary Al-Mg catalysts with moderate surface area (125-150 m^2/g) showed best performance for both ESR and EDR. These catalysts also have pore volume on the higher side (0.4-0.55 ml/g) and relatively larger pores 110-120 Å. Hence microstructure is an important property in both these reactions.

Hydrothermal aging studies indicated that lanthana and ceria contributed to retention of surface area of alumina based binary catalyst. Ternary Al-Zr supports, and Zr-rich quaternary catalysts showed good retention of specific surface area after hydrothermal aging due to formation of solid solution of Al-Zr.

Acid strength of individual components (Al and Zr in binary catalysts) was significantly moderated in ternary Al-Zr, Al-Mg and Mg-Zr and quaternary catalysts. Total acidity of Al-Zr ternary catalysts was enhanced over that of the individual components. Similarly, the acidity of Mg was enhanced significantly in ternary Al-Mg and Mg-Zr catalysts (relative to binary

Mg). Strong acidity of Zr was further enhanced in ternary Al-Zr catalysts presumably due to formation of solid solution. The acidity of Al (relative to binary catalyst) did not change significantly in ternary Al-Mg catalysts. Presence of Mg decreased selectivity to ethylene, slowed catalyst deactivation and decreased coke formation in both ESR and EDR. These trends correlate broadly with total acidity of the catalysts. Zr in ternary catalysts led to increased yield of ethylene which affected H_2 yield at higher temperatures. Thus, moderate acidity such as displayed by ternary Al-Mg or quaternary Mg-rich catalysts is desirable for product selectivity to H_2 and CO.

P-XRD showed that all catalysts containing Mg component present smaller crystallite growth upon hydrothermal aging (750°C, 4h) whereas ternary Al-Zr and quaternary catalysts rich in Al or Zr show high crystallite growth of zirconia. All three binary catalysts show lowest crystallite growth. Spinel formation in ternary composites of Al-Mg and solid solutions in Al-Zr catalysts appear to be responsible for this behavior.

Solid solution formation between Al and Zr imparted hydrothermal stability, influenced acidity and acid strength and the retention of specific surface area.

ZrO_2 enhanced the OSC (oxygen storage capacity) of ceria linearly up to a ZrO_2/CeO_2 molar ratio 15.3. This retarded deactivation of the ternary Al-Zr catalysts with skewed composition (in favor of Zr) in ESR and EDR studies.

Results of decomposition of MBOH correlated well with those of NH_3 TPD. Catalyst composition influenced product selectivity of acid and base catalyzed reactions. Compositions containing MgO presented amongst the slowest deactivation, whereas those containing zirconia presented faster deactivation across all the series, binary, ternary and quaternary. Presence of zirconia in ternary and quaternary composites partially offset the desirable character of magnesia.

Chapter 3: Supported Metal catalysts

A total of seventeen supported metal catalysts were prepared by incipient wetness method using the set of thirteen supports described above. Nickel content was maintained at nominal 7.5 wt%. Nickel concentration was varied in the case of balanced Al_2O_3-MgO and Al_2O_3-ZrO_2 ternary systems. They were characterized by N_2 physisorption for microstructure, pulse chemisorption for dispersion of nickel, NH_3-TPD for acidity, XRD for phase and crystallite size, TPR for metal reducibility. These catalysts were evaluated for the steam reforming of ethanol (presented in Chapter 4) and the dry reforming of ethanol (presented in chapter 5).

The trend of specific surface area and pore volume of these catalysts was largely similar to that of the supports with which they were prepared. Specific surface area and pore volume decreased linearly with the concentration of Nickel impregnated on the supports.

Mixed trends were observed in acidity relative to the support. The presence of Nickel in the catalyst increased acidity of the catalysts in binary MgO and the quaternary catalyst rich in MgO. The ternary catalysts either showed marginal change or a decrease in acidity relative to the support. The trends of relative acidity between the catalyst compositions were very different from that of the supports. It was strongly influenced by the presence of Nickel. Nickel lends Lewis acidity to the catalyst.

Results of Temperature programmed reduction indicated presence of more than one reducible species in certain catalyst compositions. Binary Al showed two distinct peaks whereas Mg and Zr did not. The latter two did not show peak at high temperature (≥500°C). In ternary catalysts all the Al-Mg catalysts showed a single high temperature peak irrespective of whether composition was balanced or skewed. Whereas, ternary Al-Zr catalysts with balanced composition showed two peaks but catalysts with skewed composition showed only one peak at low temperature. Thus, binary alumina showed significantly stronger metal support interaction (MSI) than magnesia and zirconia. Amongst ternary catalysts Al-Mg showed stronger MSI than Al-Zr catalysts, but weaker than Mg-Zr. Quaternary Mg-rich catalyst showed strongest MSI followed by zirconia-rich and alumina-rich catalysts which is very different from the trend of binary catalyst. Formation of spinel and solid solution appears to be responsible for the variations in trends with composition. MSI decreased with increasing Nickel content as expected. Strength of MSI showed an inverse relation to the ease of reducibility of NiO, which is as expected. In turn, specific surface area of Nickel metal was influenced significantly by ease of reducibility of NiO.

Presence of Mg suppressed reducibility of NiO in binary Mg, ternary Mg-Zr and ternary balanced Al-Mg catalysts due to formation of solid solution. Al-Zr ternary catalysts showed higher reducibility than Al-Mg catalysts. The quaternary catalysts showed complete reducibility of NiO. These trends influenced specific surface area of Nickel along with BET specific surface area.

Specific surface area of Nickel ranged from 9.3 to 34.5 m2/g Ni. It decreased in the order Al>Zr>>Mg for binary catalysts, Al-Zr>Al-Mg>Mg-Zr for ternary catalysts and Al-rich>Zr-rich>Mg-rich for quaternary catalysts. It correlated reasonably linearly with the BET surface area of the catalysts and with the ease of reducibility of NiO. Multiple linear regression showed a positive correlation with a correlation constant of 0.8703 which may be considered a reasonable value for multicomponent systems. Correlation with reducibility was stronger than with BET surface area. Ternary Al-Mg catalysts deviated presumably due to spinel formation.

Distinct trends in XRD crystallite size of NiO were observed with composition. XRD crystallite size of NiO in calcined catalysts was significantly smaller in Al binary catalysts than the other two. In ternary systems crystallite size increased in the order Balanced Al_2O_3-MgO < skewed Al_2O_3-MgO < skewed Al_2O_3-ZrO_2 < Bal Mg-Zr< balanced Al_2O_3-ZrO_2. Ni content did not show appreciable trends with crystallite size. The quaternary catalysts showed the trend XRD crystallite size (of NiO) MgO rich < Al_2O_3 rich < ZrO_2 rich. These trends correlated inversely with MSI. Stronger MSI led to smaller crystallite size. A limited trend was observed between XRD crystallite size and BET specific surface area indicating that MSI had stronger influence on metal oxide agglomeration upon calcination than specific surface area of the support. The catalysts were evaluated for their performance in ESR (Ethanol Steam Reforming). The results form the content of Chapter 4.

<u>Chapter 4: ESR (Ethanol Steam Reforming)</u>

Steam reforming of ethanol was studied with the above catalysts. The catalyst was sized to 0.5-1.0 mm size fraction. Reaction conditions were H_2O: Ethanol 3 (molar ratio), atmospheric pressure, LHSV $8h^{-1}$, N_2: Ethanol 1.0 (molar ratio). Reaction temperature was studied at five levels, 550°C, 600°C, 650°C, 700°C and 750°C. Time on stream was 8 hours. Select runs were carried out for a duration of 80 hours on stream at 650°C and 700°C at the above conditions.

Conversion of ethanol increased with increase in reaction temperature. Distinct differences in conversion were observed with catalyst composition at the lower temperature end 550-600°C of the temperature range studied. Amongst the binary catalysts the magnesia sample showed highest ethanol conversion followed by alumina and zirconia in that order (Mg>Al>Zr). The magnesia binary catalyst showed highest conversion (at 2h on stream) across the entire set of catalysts in the temperature range 550-650°C. The magnesia catalyst also presented the slowest decay in conversion with time on stream. This is in spite of its lower BET specific surface area and lower reducibility of NiO which results in lower specific surface area of Nickel. The magnesia catalyst also presented significantly lower acidity.

Likewise, the ternary catalysts containing Mg in their composition showed better activity and slower decay of conversion with time on stream. The trend of activity was Skewed Al-Mg > Balanced Al-Mg = Balanced Mg-Zr>Al-Zr. Conversion depended on Nickel content. While the catalysts containing 10wt% Nickel showed higher conversion than those containing 7.5 and 5 wt% Nickel, it was difficult to distinguish between the latter two. All three quaternary catalysts showed similar conversion of ethanol. Hence, the advantage of Mg which was observed in binary and ternary catalysts was diluted therein. Between the series the trend for ethanol conversion at 550°C was binary Mg > skewed Al-Mg > Balanced Al-Mg = Mg-Zr > Balanced Al-Zr > Quaternary catalysts > skewed Al-Zr > Binary Al > Binary Zr. Trend of specific surface area of Ni was Balanced Al-Zr > Binary Al > Skewed Al-Zr > Binary Zr > Balanced Al-Mg > Skewed Al-Mg > Quaternary Al-rich > Mg-Zr > Quaternary Zr-rich > Quaternary Mg-rich > Binary Mg. A comparison of the trends shows that the catalysts with higher dispersion show lower activity. This trend indicates that the reaction may be structure sensitive. This is also reported in literature [30]. Thus, catalysts with low to moderate specific surface area of Nickel (9-25 m2/g Ni) and lower acidity (0.165-0.187 mmol NH3/g cat strong acidity) show better conversion of ethanol.

The binary Mg based catalyst, ternary Al-Mg based catalyst and quaternary Mg-rich catalyst showed higher yield of H_2 than the remaining catalysts. The binary Mg based catalyst and ternary skewed Al-Mg based catalysts showed the highest H_2 yields amongst the entire set of catalysts. Between the series the benefit of Mg to H_2 yield was still observed in ternary Mg-Al and quaternary Mg-rich catalyst. Similar trend was observed for CO and CO_2 yields. The yield of H_2 for binary Mg and ternary Al-Mg catalysts with composition skewed in favor of Mg (39-49-0 and 29-59-0) was about 63-65% at 550°C and 70-71% at 750°C. In comparison binary Zr and ternary Al-Zr catalysts gave a H_2 yield 54-55% (550°C) and about 59-60% (750°C). The quaternary catalysts gave yield of H_2 57-58% (550°C) and 63-66% (750°C). The yield of H2 reported in literature for Ni catalysts supported on similar mono and bi-component supports at S/C 3 and 550-650°C varies from 65 – 82% [36]. Hence, the yield of H_2 achieved in the current study is in the ballpark range of what is reported for non-noble metal Ni based catalysts.

Catalysts which showed higher yield of H_2 also showed higher yield of CO and CO_2. However, trend with reaction temperature differed. It increased for yields of H_2 and CO_2 but decreased for yield of CO. This indicates occurrence of WGS reaction. However, the binary zirconia catalyst and the ternary catalysts containing Al-Zr showed a disproportionate relation between decrease in CO and increase in CO_2 as reaction temperature was increased. The former decreased significantly while the latter remained almost constant. Attendant CH_4 was also lower on these catalysts whereas carbon formation and H_2/CO (molar) were higher. A possible explanation for this behavior is competition from the decomposition of ethanol which produces a higher H_2/CO ratio (3 molar ratio) along with carbon, and without producing CO_2.

Yield of CH_4 and C_2H_4 with catalyst composition was different from that of the remaining products. Catalysts containing Mg showed higher yields of CH_4. The binary Mg and ternary Al-Mg and Mg-Zr catalysts showed higher selectivity than ternary Al-Zr catalysts. The distinction disappeared in case of quaternary catalysts. All the catalysts showed an increase in selectivity to methane with increasing reaction temperature. There was an unusual increase in the yield of methane at ≥700°C.

Catalyst compositions containing Al, Zr or their combination showed higher yields of C_2H_4 which is clearly related to acidity of the catalysts. The balanced ternary Al-Zr catalysts showed higher yield of ethylene than the skewed Al-Zr ternary catalysts. The relatively higher alumina in this catalyst appears to contribute to this. Selectivity to ethylene showed mixed trends with reaction temperature. While it increased with reaction temperature in the case of binary Al and ternary Al-Zr catalysts, it showed maxima in case of ternary Al-Mg catalysts.

The H_2/CO mole ratio was observed to increase from about 2 to 4 for temperatures 550-650°C for most of the catalysts. The ratio ranged from 4-6 at 700°C and from 9-12 at 750°C for binary Al and Zr catalysts and ternary Al-Zr catalysts. These catalysts also showed higher coke deposits compared to the remaining catalysts. They also showed a decrease in CO yield and almost independence of corresponding CO_2 yield with increase in temperature, which is attributed to competition from decomposition of ethanol as explained above. The H_2/CO mole ratio was similar across all three series of catalysts at reaction temperature ≤650°C. The higher ratio observed for Al-Zr ternary catalysts at higher reaction temperature (≥700°C) was not observed in quaternary catalysts including the Zr-rich catalyst. The presence of Mg apparently subdues it in this series. Thus, consumption of CO by WGS and/or Boudouard reaction appears to depend on the composition of the catalyst.

Trend of yield of acetaldehyde and acetone was clear in the case of binary catalysts where it decreased in the order Mg>Zr>Al. Ternary Mg-Zr showed higher yield than the remaining catalysts. No trends were observed between the quaternary catalysts. Yield of acetaldehyde decreased with increasing reaction temperature whereas yield of acetone largely showed a maximum at 600-650°C.

The coke content of the spent catalysts ranged from 3.1-6.9 wt% for on stream time 8h. Assuming a linear rate of deposition of coke, the rates ranged between 27 to 60 mg/(h g cat). These values are comparable with values reported in literature for similar Ni based catalysts, which range from 16 – 149 mg/(h g cat) [36]. Trend of coke content with composition was Mg<Zr<Al for the binary catalysts, Al-Mg<Mg-Zr<Al-Zr for ternary catalysts and Mg-rich<Zr-rich<Al-rich for the quaternary catalysts operated for 8h on stream. Thus, the ternary and quaternary catalysts largely followed the trend of Mg and Zr in the binary compositions. However, coke content of quaternary Mg and Zr rich catalysts was significantly lower than that of the remaining catalysts (excepting binary Mg). This series also shows moderate MSI, low to moderate dispersion and relatively larger pore diameter. Thus, they hold potential for showing high stability. Ternary catalysts containing Mg showed significantly lower coke than binary Al or Zr catalysts. Between the series the trend was binary Al ≥ Ternary Al-Zr > Quaternary Al > Binary Zr > ternary Al-Mg > Quaternary Zr > Quaternary Mg > Binary Mg. The coke formation correlated well with trend of acidity of the binary catalyst compositions. However, there was poor correlation between acidity and coke in case of ternary and quaternary catalysts. Coke content showed a good positive correlation with decay in conversion of ethanol at 750°C. Thus, coking appears to be the major cause of deactivation at this temperature. There was no correlation between coke and decay in conversion at 550°C indicating that nature of coke precursor species is dependent on reaction temperature. It is pointed out that coke deposits in an axial profile in the catalyst bed [28], hence there can be dilution effect due to mixing when the catalyst bed is discharged. The measured coke content is thus expected to be on conservative side than actual due to this.

Trend of slope of decay in conversion with time on stream differed with temperature. Meaningful trends with catalyst composition were only observed at 750°C. The magnesia catalysts presented the slowest decay in conversion with time on stream amongst the binary series, followed by zirconia and then alumina. Both the ternary catalysts based on Al-Mg and quaternary catalysts rich in Mg showed slower decay of conversion with time on stream than the Al-Zr (ternary) and Al rich or Zr rich catalysts (quaternary). Between the series the binary Mg, skewed Al-Mg and quaternary Mg-rich catalysts showed significantly less coke than the remaining catalysts. ternary. Reasonable correlation was observed between decay rate and coke formation at 750°C. Catalysts showing higher acidity showed faster deactivation.

The catalysts with 10% Nickel content showed better activity than those containing 7.5 or 5% Nickel which is in line with expectation. Decay constants decreased with increasing Nickel content for the 44-44-0 series in the tests carried out at750°C.

Decay of conversion with time on stream decreased in ternary catalysts with increasing ZrO_2/CeO_2 molar ratio. Thus, OSC (oxygen storage capacity) was observed to have a positive influence on catalyst stability.

Similarly, decay of conversion with time on stream was significantly slower at 750°C than at 550°C. This is similar to reports in literature where removal of C by reverse Boudouard reaction or gasification of coke is proposed as the reason [29]. However, yield of CO_2 increases with increase of reaction temperature which is not consistent with these mechanisms. The exact mechanism could not be determined. However, the yield of methane increased significantly at ≥700°C which supports hydrogenation of coke to methane as a likely mechanism. La and Mg/alkaline promoters are reported to promote gasification of coke. This mechanism cannot be ruled out because WGS activity also occurred simultaneously.

Chapter 5: EDR (Ethanol Dry Reforming)

The same set of 17 Nickel based catalysts were tested for the dry reforming of ethanol. Reaction conditions were Ethanol: CO_2 1 (molar ratio), N_2: Ethanol 0.4 (molar ratio), atmospheric pressure, LHSV $8h^{-1}$. Reaction temperature was studied at five levels, 550°C, 600°C, 650°C, 700°C and 750°C. Time on stream 8 hours.

Similar to the ESR activity, differences in trends of EDR for the conversion of ethanol with catalyst composition could be better distinguished at the lower temperature end 500-600°C. Conversion of ethanol increased with reaction temperature for all catalysts. Trend for binary catalysts was Mg>Zr>Al. The order was different from that of ESR for Zr and Al catalysts, where it was Mg>Al>Zr. In the case of ternary catalysts, the trend was Al-Mg=Mg-Zr>Al-Zr, which was similar to that of ESR. Activity increased with increasing Nickel content for both the balanced Al-Mg (44-44-0) and balanced Al-Zr (44-0-44) series. The quaternary catalysts showed the trend Mg-rich > Zr-rich ~ Al-rich which is different from that of ESR. Trends with respect to catalyst composition were the same across the temperature range 550-650°C. This was similar to ESR.

Between the series the binary Mg catalyst showed highest conversion of ethanol. The ternary Al-Mg, Mg-Zr and all the quaternary catalysts showed near comparable conversion with each other but lower than that of binary Mg. The ternary Al-Zr catalysts showed the lowest conversion. Whereas, in ESR the ternary Al-Zr showed conversion similar to balanced Al-Mg catalysts but lower than skewed Al-Mg catalysts. The adverse effect of Zr on conversion was largely absent in quaternary catalysts for EDR.

These trends are largely similar to those of ESR, catalysts with low or moderate Nickel specific surface area and low acidity show better conversion. Hence structure sensitivity appears to play a role in EDR too.

The CO_2 conversion decreased with increasing reaction temperature for all the catalysts. However, distinct differences were observed with increase in reaction temperature for catalysts containing Mg and those not containing Mg. These are: i) yield of H_2 increased for catalysts containing Mg whereas it either decreased or remained constant for those that did not contain Mg ii) the yield of CO decreased relatively less than for catalysts not containing Mg iii) simultaneously, H_2/CO (molar) was lower and showed maxima with increasing temperature in catalysts containing Mg iv) and yield of ethylene was significantly smaller in catalysts containing Mg. The decrease in conversion of CO_2 accompanied by a decrease in yield of CO, increase in yield of H_2 and H_2/CO passing through maxima in catalysts containing Mg is attributed to the WGS (water gas shift reaction). This reaction is exothermic and favored at relatively lower temperature thus presenting maxima in H_2/CO. The decrease or small dependence of yield of H_2 with temperature in ternary Al-Zr and quaternary Zr-rich catalysts along with increase in H_2/CO and ethylene yield and decrease in conversion of CO_2 is attributed to increase in competing reactions, dehydration of ethanol along with the disproportionation of CO (Boudouard reaction) in these catalysts. The former reaction correlates with higher acidity of these latter catalysts.

The activity for conversion of CO_2 in EDR could be better distinguished at the low temperature end 550-650°C than at the higher temperature end. Activity trends (conversion at 2nd h on stream) at 550°C were binary magnesia showed highest conversion followed closely by alumina and then zirconia (Mg ~ Al >> Zr). This trend changed with increase in temperature. It was Mg > Zr > Al at temperature ≥650°C. Amongst the ternary catalysts the trend was Al-Mg > Mg-Zr ~ Al-Zr at 550°C. CO_2 is known to have affinity for materials with basic character and this appears to have favored conversion in the catalysts containing Mg. There are reports in literature which show that basic materials activate CO_2 favorably [31]. Unlike trends of ESR, clear increase of activity was evident with increasing Ni content for the balanced Al-Mg (7.5% Ni-44% Al-44% Mg – 0% Zr) series. Between the series the trend for conversion of CO_2 was similar to that of conversion of ethanol. The quaternary catalysts showed higher conversion than ternary Al-Zr catalysts and almost comparable conversion to ternary Al-Mg catalysts. The adverse effect of Zr on conversion was again absent in quaternary catalysts presumably due to presence of Mg.

Trend of H_2 yield in EDR was Mg > Al > Zr for the binary catalysts and Mg-Zr ≥ Al-Mg > Al-Zr for the ternary catalysts. The ternary catalyst with 5wt% Nickel supported on 44-44-0 support (balanced ternary Al-Mg catalysts) showed significantly lower yield of H_2 than catalysts containing 7.5 and 10wt% Nickel. Thus, trend was observed with Nickel content. Whereas the 44-0-44 series (balanced ternary Al-Zr catalysts) did not show any significant trend with Nickel content. Further, amongst the binary catalysts the Al based catalyst showed a decrease in H_2 yield with increasing temperature whereas the Mg and Zr catalysts showed an increase. This can be attributed to the propensity of the binary Al catalyst to form ethylene through dehydration of ethanol. Similar behavior is reported in literature [35]. H_2 yield of ternary catalysts showed an increase with increasing temperature for the Al-Mg and Mg-Zr catalysts whereas it either decreased or did not show appreciable change with temperature for the Al-Zr catalysts. In the case of quaternary catalysts H_2 yield increased with temperature for the Mg rich catalyst while it remained largely independent of temperature in case of the Al-rich and Zr-rich catalysts. As explained above this is attributed to an increase in competing reaction dehydration of ethanol along with the disproportionation of CO (Boudouard reaction) in these catalysts. This also correlates with their higher acidity. Between the series H_2 yield of quaternary catalysts was higher than that of binary Zr or ternary Al-Zr catalysts and slightly less than ternary Al-Mg. Binary Zr and ternary Al-Zr presented amongst the lowest H_2 yields. The binary Mg catalyst (0-89-0) gave the highest yield of H2 66% (550°C) and 73% (750°C). This was followed by the skewed Al-Mg catalysts 66.5% (550°C) and 69.1% (750°C). The ternary Mg-Zr catalyst gave H2 yield 63.6% (550C) and 69.7% (750C). Yield of ternary Al-Zr catalysts ranged from 62-63% (550C) and 56-62% (750C), The quaternary catalysts showed H2 yield 64-66% (550C) and 63-68% (750C), Thus the ternary Al-Mg and Mg-rich quaternary catalysts gave yields close on the heels of the binary Mg catalyst.

Trend of yield for CO was Mg > Al > Zr for the binary catalysts. It was Al-Mg ~ Mg-Zr > Al-Zr for the ternary catalysts. There was no trend with Nickel content of the catalyst. The quaternary catalysts did not present any significant trend with respect to catalyst composition. Between the series CO yield of quaternary catalysts was higher than that of binary Zr or ternary Al-Zr catalysts but lower than ternary Al-Mg. Binary Zr and ternary Al-Zr gave the lowest CO yields. While all the catalysts showed a decrease in the yield of CO with increasing temperature, those containing MgO showed a significantly smaller decrease than those not containing MgO (Al-Zr series). The decrease with increasing temperature is attributed to WGS activity as explained above. This also correlates with the decrease in conversion of CO_2 with increasing reaction temperature.

The H_2/CO molar ratio varied from 1.6 to 3.59. It increased with increase in temperature for all the catalysts. Binary catalysts showed the trend Zr > Al > Mg. Ternary catalysts showed the trend Al-Zr > Al-Mg ~ Mg-Zr. The quaternary catalysts did not show any clear trend with composition. Thus, similar to trend of ESR the catalysts showing higher acidity show higher coke and C_2H_4 formation along with higher H_2/CO molar ratio, indicating a shift in selectivity to decomposition of ethanol at higher temperature on these catalysts. The Al-Zr ternary catalysts show higher acidity which leads to dehydration of ethanol. The water produced as by-product appears to promote WGS which leads to higher H_2/CO ratios. Between the series the quaternary catalysts showed values of H_2/CO intermediate between binary Zr or ternary Al-Zr and ternary Al-Mg. The ratio was lower than that of binary Zr or ternary balanced Al-Zr catalysts but higher than Al-Mg ternary catalysts.

Trend of yield of C_2H_4 for binary catalysts was Al > Zr > Mg. For ternary catalyst it was Al-Zr >> Al-Mg ~ Mg-Zr. For quaternary catalysts the trend was similar to the binary series Al > Zr > Mg. Between the series the beneficial effect of Mg in decreasing ethylene yield was evident in both ternary Al-Mg and quaternary Mg-rich catalysts, which gave lowest yield of C_2H_4 after binary Mg. Binary Mg gave the lowest yield of ethylene amongst all the catalysts. The ethylene yield of quaternary Mg rich catalyst was lower than that of balanced ternary Al-Mg catalysts. The binary Mg catalyst showed a decrease in yield of ethylene with increase in temperature whereas the Al and Zr catalysts showed an opposite trend. The Al-Mg ternary catalyst showed maxima in ethylene yield with increasing temperature whereas the Al-Zr series showed a clear increase. The quaternary catalysts showed behavior similar to the ternary catalysts. Mg-rich quaternary catalyst showed maxima in ethylene yield with temperature. The trend for yield of ethylene showed some correlation with strong acidity of the catalysts. However, correlation was poor in the case of Al-Mg ternary catalysts. The trends were similar to those of ESR.

Trend for yield of methane was Al > Mg > Zr for the binary series, Al-Mg > Al-Zr > Mg-Zr for the ternary series. The ternary series did not show any specific trend with Ni content. The quaternary catalysts showed the same trend as the binary series Al-rich > Mg-rich > Zr-rich. All the catalysts showed an increase in yield of methane with increase in temperature. The increase was significantly higher at ≥700°C. Binary Zr showed the lowest yield. The ternary Al-Mg catalysts and binary Al gave the highest yields.

Specific trends with catalyst composition were not observed for yields of acetaldehyde and acetone. The yield of acetaldehyde showed a decrease with increase in temperature whereas acetone showed mixed trends with increase in temperature which could not be correlated with catalyst composition.

Coke content varied from 4.5 to 8.5wt%. Assuming a linear rate of deposition of coke, the rates ranged between 39 to 74 mg/(h g cat). Coke content for a given catalyst was higher than that in ESR studies for the same time on stream. Trend for binary catalysts was Mg < Zr < Al. For ternary catalysts it was Al-Mg < Mg-Zr < Al-Zr. Skewed Al-Zr ternary catalyst (29-0-59) showed significantly less coke than 39-0-49 (which has lower Zr content) and the balanced Al-Zr ternary catalysts (44-0-44). This is attributed to its higher OSC (oxygen storage capacity). Amongst the quaternary catalysts trend was Mg-rich < Zr-rich < Al-rich, which is similar to that of the binary catalysts. Between the series, the quaternary catalysts formed coke higher than that of ternary Al-Mg catalysts and comparable to that of ternary Al-Zr catalysts. In comparison the quaternary catalysts formed coke comparable to Al-Mg and lower than Al-Zr catalysts in the case of ESR. Thus, that advantage was not observed in EDR. The binary Al and quaternary Al-rich catalysts showed amongst the highest coke formation amongst the three series. This correlated with the higher acidity of these catalysts.

Similar to trends of ESR, decay of conversion with time on stream was slower at higher temperature than at lower temperature. Differences were observed in trend of deactivation with temperature. Meaningful trends with catalyst composition were only observed at 750°C.

Amongst the binary catalysts trend with catalyst composition at 550°C was Al < Mg < Zr, whereas it was Mg << Al << Zr at 750°C. Amongst the ternary catalysts trend at 550°C was Al-Mg < Mg-Zr < Al-Zr for catalysts with balanced composition. At 750°C the trend was Al-Mg < skewed Al-Zr < Mg-Zr << balanced Al-Zr for catalysts with the same Nickel content (7.5 wt%). Thus, catalysts with lower acidity showed slower deactivation. Contribution of OSC in decreasing deactivation was clearly observed at 750°C for the skewed Al-Zr catalysts - ternary Al-Zr showed a trend of decrease in deactivation with increasing ZrO_2:CeO_2 molar ratio. Thus, similar to trend of ESR, OSC contributed to slowing down deactivation in EDR. Binary Zr and ternary balanced Al-Zr showed significantly higher decay constants than the remaining catalysts. Deactivation decreased with increasing Mg content in Al-Mg catalysts. Both the 44-44-0 and 44-0-44 series showed trend of decreasing deactivation with increasing Nickel content. Decay constants decreased with increasing Nickel content. The quaternary catalysts showed the trend Mg-rich << Zr-rich < Al-rich at 550°C whereas the trend was Mg-rich < Al-rich < Zr-rich at 750°C. Between the series all three quaternary catalysts showed slower deactivation at 750°C, which was comparable to ternary Al-Mg catalysts. Hence, the effect of Zr which showed higher deactivation in binary and ternary Al-Zr catalysts was masked by the presence of Mg in quaternary catalysts. Binary Mg showed lowest deactivation whereas binary zirconia showed the highest amongst the three series. Ternary Al-Zr showed higher deactivation than binary Al.

Chapter 6: Conclusions

Commercial ESR catalysts are multi-component compositions. The role of individual components of the catalyst is established through studies on monocomponent and bicomponent catalyst systems which is reported in literature. However, there is scarce literature regarding how these roles are affected in multi-component, such as ternary and quaternary catalyst compositions. This work provides insights on this aspect.

Nickel supported on binary, ternary and quaternary supports comprising a combination of lanthana and ceria along with one or more of Al, Mg and Zr are prepared, thoroughly characterized and evaluated for ESR and EDR. The supports are prepared by co-precipitation and the supported metal catalyst by incipient impregnation. Ternary catalysts comprised both balanced and skewed compositions. The Nickel content is varied in one set of Al-Mg and Al-Zr ternary catalysts. A total of 17 catalysts are studies.

The characteristics of individual components and their interaction effects in multi-component catalysts, which in turn influence physico-chemical properties are identified. The characteristics of the catalysts are further correlated with reactivity for ESR and EDR.

The Al and Mg components contribute distinctly to microstructure. Alumina contributes strongly to specific surface area whereas magnesium to pore volume of ternary Al-Mg catalysts. Pore size, its distribution and isotherm type are influenced by catalyst composition. The advantage of high surface area of alumina is negated by its acidity which favours dehydration of ethanol to ethylene, which can further polymerize to coke. The higher pore size of quaternary catalysts appears to contribute to slower deactivation.

P-XRD confirms the formation of Al-Mg spinel and Al-Zr solid solution in ternary and quaternary catalysts. This influences microstructure, acidity, and hydrothermal stability of the catalysts.

The combination of Ceria-zirconia enhances OSC (oxygen storage capacity) which has positive influence of decreasing deactivation in both ESR and EDR. However, this advantage is negated/decimated by their higher acidity which catalyzes dehydration of ethanol which is detrimental to performance. Overall, these catalysts show poor conversion and lower H_2 product yield.

Acidity and acid strength of supports are strongly influenced by catalyst composition. Moderate acidity is beneficial for performance. Strong acidity produces undesirable by-products (ethylene and coke). The results of NH_3-TPD correlate well with trends of product selectivity of decomposition of MBOH and product selectivity in ESR and EDR.

Metal dispersion (specific surface area of Nickel) changes with composition of catalyst. It is influenced by BET surface area and ease of reducibility of NiO of the catalyst. The reducibility is in turn influenced by metal support interaction (MSI). All the catalysts containing Mg show relatively lower specific surface area of Nickel due to low reducibility. This is attributed to formation of Mg-Ni solid solution [33]. However, they show the best performance for ESR and EDR. Correlation of specific surface area of Nickel with conversion of reactants indicates that these reactions are structure sensitive. Catalysts with low and moderate specific surface area of Nickel (binary Mg, ternary Al-Mg, and quaternary catalysts) show better performance (higher H_2 yields and slower deactivation) in both ESR and EDR than the binary Al or Zr or the ternary

Al-Zr which have higher dispersion. This indicates that these reactions are structure sensitive. Grulek et.al. also report that ESR is structure sensitive [30]

Catalysts containing Mg (which are less acidic and present lower specific surface area of Nickel) show better ethanol conversion, higher yield of H_2, slower deactivation and less coke formation (better performance) in ESR. Similar trend is observed for EDR. However, quaternary Mg-rich catalyst showed H2 yield close to that of ternary Al-Mg and binary Mg catalysts in EDR. The conversion of CO_2 is also higher in these catalysts in case of EDR. CO_2 is known to be activated by materials with basic character [31]. Thus, these results are consistent with published literature in this respect.

Product selectivity clearly depends on catalyst composition. All catalysts containing Mg favor WGS which enhances yield of H_2 with increase in temperature in both ESR and EDR. Whereas on ternary Al-Zr and quaternary Zr-rich catalysts decomposition of ethanol appears to be favored in ESR, the dehydration of ethanol to ethylene along with the disproportionation of CO appears to be favored in EDR with increasing reaction temperature. WGS favors H_2 yield in catalysts containing Mg whereas dehydration of ethanol is detrimental to yield of H_2 in catalysts containing Zr.

While catalysts containing Zr show faster deactivation of the catalyst due to coke laydown, they show significant higher H_2/CO mole ratio at ≥700°C in both ESR and EDR. This is beneficial for applications such as production of methanol.

The beneficial characteristic of higher ethanol and CO_2 conversions and higher H_2 yield in binary Mg catalysts is also retained in ternary and quaternary catalysts containing Mg for both ESR and EDR.

Excepting for Al-Mg ternary catalysts, yield of ethylene correlates well with acidity of the catalyst. Both acetaldehyde and acetone are observed in the product. Their yields could not be correlated with catalyst composition probably because they are reaction intermediates and the operating temperature used in this study is rather high.

Trend of methane yield is similar in ESR and EDR. Al-Mg catalysts show higher yield.

While binary Mg shows good results overall, some drawbacks are low reducibility of Ni which results in low Nickel surface area. This can limit long term service life of the catalyst. The low H_2/CO ratio of this catalyst (in both ESR and EDR) limits its end application. Brucite

[$Mg(OH)_2$] can form under reaction conditions due to presence of moisture. This segregates from the support due to volume expansion and leads to loss of mechanical properties (crush strength) of shaped/formed catalysts [34]. This can be overcome in Al-Mg catalysts where spinel formation stabilizes the Mg and prevents its segregation as Brucite. However, the Al-Mg ternary catalysts too give low H_2/CO. The ternary Al-Mg catalysts show comparable yield of H_2 besides higher H_2/CO in ESR in catalysts with balanced composition (which is desirable for production of methanol). Further, the quaternary Mg rich catalyst shows comparable to slightly higher H_2 yields than binary Mg and ternary Al-Mg catalysts in EDR. It also shows comparable deactivation to these catalysts perhaps due to the added advantage of OSC from presence of zirconia. Thus, quaternary catalyst composition hold merit for further exploration.

Low activity of binary alumina and zirconia for ethanol conversion in ESR and of Al in EDR is markedly improved in their ternary and quaternary catalysts. Similarly, the low activity of binary Zr for CO_2 conversion is markedly improved in ternary and quaternary catalysts. Similar trend is also observed for H_2 and CO yields in ESR and EDR.

Fast deactivation behavior of binary Al and Zr is significantly decreased in ternary and quaternary catalysts in both reactions. Deactivation is significantly faster at lower temperature 550°C than at 750°C in both ESR and EDR. This observation is consistent with reports in literature [29]. However, the actual mechanism by which this is occurring is unclear. The yield of methane increases significantly at ≥700°C, which supports the hydrogenation of coke precursors to methane. This reaction is reported in literature [32]. An alternative is the gasification of coke to syngas by water leading to formation of equimolar H_2 and CO. However, yield of CO decreases with temperature and H_2/CO increases significantly with increasing temperature in the current study, which is not consistent with this reaction. However, it cannot be ruled out due to the simultaneous occurrence of WGS reaction which converts CO to CO_2 and H_2. Conversion of ethanol shows clear dependence on Ni content of the catalyst in EDR.

These distinct transitions in reactivity, selectivity and deactivation behavior between the binary, ternary and quaternary catalysts clearly demonstrate interaction between individual components of the supports in the multi-component catalysts.

Thus, this work is a comprehensive study of multi-component catalysts and correlates catalyst composition with structure/characteristics and activity of the catalyst for ESR and EDR. As seen, all physico-chemical properties change significantly in multi-component (ternary and quaternary) catalysts when compared to binary catalysts. Distinct trends are observed between activity and composition with reaction temperature. Catalysts with lower acidity and low-moderate dispersion show better activity indicating that structure sensitivity (Nickel specific surface area) and acidity of the catalyst (and hence the propensity for coke formation) play a dominant role in activity of these catalysts. Distinct trends which are observed in binary catalysts are progressively diminished in ternary and quaternary catalysts due to interaction between the individual components of the support such as solid solution or spinel formation. However, the quaternary catalysts still showed distinct trends within themselves and between the binary and ternary series.

This work is useful in understanding interactions between individual components of the support and their further interaction with Nickel. It provides insights for further improvement of these catalysts.

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List of Publication Related to Thesis:

1. Multi-component oxide composites for carriers in catalytic applications. Aliakbar M Vora, Ran Bahadur Yadav, Arun G Basrur; IJACT, 18 (5), 2021, 1607-1622.

List of Conference/Workshop/Seminar Related to Thesis:

1. National Conference on Frontier of Catalysis Science & Technology and its applications. (FOCSTA-2020), 10th and 11th January 2020.
   Topic: Ethanol Reforming for Hydrogen Generation on Nickel Based Catalyst.
   Poster presentation: PP-2
   Aliakbar M Vora et. al.

2. 2nd International Symposium on Functional Nano Material in Industrial Applications; UCLAN, 2022, 14th to 16th July 2020.
   Topic: Ethanol Bi-Reforming for Hydrogen Generation on Nickel Based Catalyst.
   Poster Presentation: P-5-01
   Aliakbar M Vora et. al.

List of Conference/Workshop/Seminar non-related to Thesis:

1. Challenges and Opportunities in designing Nanoarchitectonics of Nanoporous Carbon Material for Industrial Applications, (16-20th September 2020), Department of Materials and Metallurgical Engineering Maulana Azad National Institute of Technology, Bhopal
   Participated: Aliakbar M Vora

2. Conference on Advances in Catalysis for Energy and Environment, Tata Institute of Fundamental Research (TIFR), Mumbai, 31st October to 4th November 2022.
   Participated: Aliakbar M Vora

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