Chapter-1 : PREAMBLE

1.1 Introduction

Catalysis touches all walks of life. Noble metals such as Pt, Pd, Rh, Ru are widely used as catalysts in different areas in industry such as refining, commodity/bulk chemicals, specialty/fine chemicals, petrochemicals manufacture, sustainable/green chemistry and emissions control/pollution abatement. They are known for their high activity (Turnover frequency) and excellent product selectivity. Scarcity (low abundance in Earth's crust) relative to transition metals and high price are disadvantages. These are key drivers for the development of non-noble metal based catalysts.

A disadvantage with Non-noble metals is their lower productivity and product selectivity relative to noble metals. This requires considerable effort to develop catalysts which can match up to noble metals.

Transition metals of the 1st Transition series such as Cr, Fe, Co, Ni, Cu and Zn are well known for their catalytic activity as main component or promoters, and are used in many Industrial processes viz. ammonia synthesis, FT (Fischer-Tropsch) synthesis, paraffins dehydrogenation, SMR (Steam reforming of methane), hydrodesulfurization and selective hydrogenation and hydrodeoxygenation and many organic process transformations.

Of these Co, Ni and Cu standout. They are widely used for catalytic hydrogenation. An interesting aspect of these is that Cu has an electronic configuration which is different from that of Co and Ni. There is a paucity of studies which compare them on equitable basis from this perspective.

Supported metal catalysts consist of porous high surface area oxides which serve as support, on which the active metal component is dispersed. These materials tend to have acidity and metal (such as redox) functionalities. These influence product selectivity and stability of catalysts. Hence it is important to understand their effects and adjust them in industrial catalysts.

A vast majority of these catalysts are heterogeneous (formed / shaped) materials for use in fixed bed flow reactors where pressure drop is an important consideration. Ease of separation of the used catalyst from products of reaction is a common consideration to flow and batch reactions. Formed catalysts can be prepared by different methods. Cost is an important consideration in selection of the method of catalyst preparation for commercial implementation.

The current work addresses the above aspects through a study of Co, Ni and Cu (non-noble metals) supported on zirconia-alumina bicomponent supports. Deposition-precipitation is examined as a simple method of preparation of the bicomponent supports. The catalysts are prepared by deposition-precipitation, characterized thoroughly and evaluated for transformation of styrene oxide and the hydrodeoxygenation of m-cresol with the objective of distinguishing their catalytic behavior, in light of copper having a different electronic configuration than Co and Ni. The former reaction produced phenylacetaldehyde and 2-phenylethanol which are important perfumery and flavor chemicals. They fall in the class of Specialty/Fine Chemicals. The latter reaction yields aromatics, cyclic saturates and cyclic oxygenates which are useful in producing petrochemicals, textiles and fuels. They fall under the general class of Bulk/Commodity chemicals.

Catalysts are materials which enhance the rate of reaction by lowering the activation energy barrier of the reaction through an alternate pathway. All catalysts undergo multiple repeated catalytic cycles wherein reactant is transformed to product through a reaction intermediate involving the catalyst. Thus, on a short timescale the catalyst apparently does not undergo any change at the end of the catalytic cycle. However, catalysts undergo slow changes in their physical and chemical characteristics which decrease their efficacy with time. These changes, which are referred to as deactivation, are partially reversible in some cases, which enable regeneration of the catalyst for reuse in a few subsequent cycles. In other cases, these changes are irreversible and the catalyst charge needs to be replaced with a fresh lot. Catalysts enable higher productivity with better product yield at less severe reaction conditions than the corresponding thermal non-catalytic reactions.

Catalysts are broadly classified into homogeneous, heterogeneous, heterogenized homogeneous and enzymes (biocatalysts). Enzymes are the oldest catalysts known to mankind. Fermentation was practiced to produce vinegar in Ancient Egypt, Babylon and old kingdom times as early as circa 2450 and 2401 BCE[1]. Jons Jackob Brezelius coined the term “Catalysis” in 1835[2]. Wilhelm Ostwald is credited with providing the modern definition of Catalysis[2]

Catalysis touches practically every walk of life either directly or indirectly. Some important examples are basic amenities such as food (fertilizers - ammonia), water (treatment to remove fluoride, arsenic and hardness) which is strictly adsorption, shelter (polymers used in construction and interiors), clothing (polyester, nylon), medicines (API’s), fuels and energy (hydrotreating and cracking of petroleum to produce gasoline, diesel, aviation fuels with low sulfur, nitrogen compounds), SMR and electrocatalysis to produce hydrogen, transportation (fuels and engineering plastics used in automobiles), pollution abatement (automobile and stationary power plant emissions control), catalytic wet air oxidation and photocatalysis for destruction of dyes and dye intermediates, GHG abatement (renewable fuels such as biodiesel, green diesel, dry reforming and CO_2 to chemicals) gadgets and entertainment (engineering plastics), lifestyle (flavors, perfumes, furnishings, paints).

The practice of catalysts has been documented as early as 1552 for the production of ether from alcohol using H_2SO_4 as the catalyst[2]. Production of sulfuric acid by the lead chamber process (1746), and later by the contact process (1831)[3], Chlorine by Deacon process (1875)[4], Ostwald's nitric acid process by the oxidation of ammonia (1901)[5] and Haber-Bosch process for ammonia (1913)[6] are some important early processes which use catalysts.

Chronologically, early industrial catalytic processes were dominant in the area of production of mineral acids (1746-1901) which themselves served as efficient homogeneous catalysts. Production of ammonia (1913) which is used in fertilizers followed. Methanol which is a useful source of monomers and fuels from syngas route (coal gasification route) followed in 1923. The 20th century saw phenomenal growth in catalytic processes for oil refining and petrochemicals. The use of catalysts for specialty and fine chemicals industry took off in the 1950's.

Some important events which shaped and fueled the growth of catalysis are listed below:

- Mankind's move from a nomadic style of living to settlements and the population explosion fueled the need for fertilizers to grow more food (ammonia), petrochemicals, transportation fuels, polymeric fabrics (polyester, nylon) for clothing.
- World wars I & II saw a significant development in oil refining (catalytic cracking, alkylation, isomerization) to produce high quality aviation fuel. Growing international trade by land, sea and road called for growth in transportation fuels.
- The global boycott of South Africa due to their practice of apartheid led to the development of coal based technologies for achieving self-sufficiency in transportation fuels and chemicals. Fischer Tropsch and GTL processes were developed as a result.

- Global pandemics such as polio, the flu, cholera, typhoid, the plague, AIDS etc. promoted development of antibiotics and vaccines. The API's required for preparing medicinal formulations come from catalytic processes.
- Constantly improving standard of living drove development of polymers, fibers, dyes, paints, pigments, flavors and fragrances, FMCG (beverages, personal care products like toiletries, cosmetics), medicines etc.
- Recognition of ill effects such as spread of disease due to pollution of rivers, smog, acid rain, respiratory diseases due to automotive emissions led to catalytic solutions for automotive and stationary emissions control, hydrotreating, phasing out of lead and benzene in gasoline.
- Changing weather patterns / global warming due to GHG emissions has led to the current trend of moving away from fossil fuels to achieve carbon neutrality. It has revived the growth of electrocatalysis and photocatalysis for splitting of water to produce green hydrogen and producing renewable energy from non-fossil routes. And the valorization of CO_2.

Competition has prompted improvement in product yields and decrease in cost of production, which call for improved catalysts. Logistics and ready availability of alternate raw materials are other important factors which led to new routes of production and thus influenced the development and growth of catalysts. The need for Process intensification has led to the development of structured catalysts, tandem catalysts, cascade catalysis and ceramic catalytic membranes.

Patenting of catalyst formulations and their method of preparation is yet another important factor which drives catalyst development to compete without incurring patent infringement. The Global catalyst market is pegged at US$ 35 Bn (2020) and projected to grow to US$ 57 bn (2030) at a CAGR of 4.9%. Precious metal catalysts are valued at US$ 12 bn[7]. The contribution of catalysts to the Chemical industry is estimated to be US$ 5.7 tn (2020).

Ease of separation and recovery of the catalyst from the product of reaction is an important consideration in catalytic processes. It is for this reason that heterogeneous catalysts are predominantly practiced in industry even at the expense of loss of some activity due to diffusional resistances. This eases pressure drop across the reactor in fixed bed reactors thereby decreasing energy costs. The active metals in the spent catalyst are valuable and they are reclaimed by hydrometallurgy or pyrometallurgy for recycling. Heterogeneous nature of catalysts ensures ease of recovery of the spent catalyst for this purpose. Almost 70-80% of catalysts used industrially are heterogeneous in nature[8].

Heterogeneous catalysts consist of a high surface area porous material which is inherently active for the reaction, or supported metal catalysts wherein an active metal is supported on this substrate. Major materials which are used as active components in catalysts are precious metals (Pt, Pd, Rh, Re, Ru), base transition metals (Ni, Co, Cu, Fe, Sn, Mo, W), aluminosilicates (zeolites), amorphous silica alumina, alumina and titania. Silica, alumina, carbon, titania and clays are used as supports. The oxides of 'p' block elements generally serve as important catalyst promoters.

Heterogeneous catalysts are used in a wide variety of chemical reactions such as Catalytic Cracking, Hydroprocessing (Hydrotreating, hydrocracking, hydrodewaxing), polymerization of olefins, isomerization, alkylation, oxidation, ammoxidation, ammoximation, hydrogenation, dehydrogenation, deoxygenation, reforming, C-C coupling, hydroformylation, nitration, sulfonation etc. Amongst these, catalysts for refining petroleum such as catalytic cracking and hydroprocessing are used in large volumes.

Catalytic hydrogenation is an important reaction which is used extensively in industries such as agrochemicals, petrochemicals, oil refining, pharmaceuticals (API), renewable chemistry, oleochemicals, fragrances and flavors. It is widely used for manufacturing chemicals such as ammonia, cyclohexane, specialty chemicals such as fatty alcohols, oxo-alcohols, cinnamyl alcohol and for hardening of oils and fats to improve shelf life. It is also used for polishing applications to remove impurities such as S, N and O containing compounds from hydrocarbon feedstock to produce clean fuels. Selective hydrogenation of acetylene is used to improve yields of ethylene from steam cracking route. It also serves to overcome catalyst fouling in downstream sections due to the acetylene which is a very reactive molecule. In recent times hydrogenation of CO and CO_2 to produce substitute natural gas, fuels and chemicals, the hydrodeoxygenation of oxygenated compounds in biomass to produce green diesel and other chemicals has gathered momentum to meet the objective of carbon neutrality by year 2050. This is aimed at GHG abatement.

Precious metals and base metals are used extensively in the manufacture of specialty chemicals involving hydrogenation. They are used either as bulk catalysts (Raney Nickel, Pt or Pd sponges) or metals supported on carriers such as carbon, alumina or silica etc.

Precious metals are predominantly used in catalysis by virtue of their high activity (high Turnover number) and product selectivity. However, they are significantly less abundant in the earth's crust when compared to base metals such as Iron, Nickel, Cobalt, Copper. Relative abundance of Pt is 0.0000005% whereas that of Nickel is 0.00845. Hence, the latter are significantly economical than the former (1000 to 4000x cheaper on mole basis)[9].

A patent study over the period 1910 – 2015, which used patent database PatBase®, covering over 100 issuing authorities worldwide, indicates significantly more patenting in the area of heterogeneous catalysts for hydrogenation since year 2005. As per these patents impregnation dominates as the method of incorporating active metals in heterogeneous catalysts, followed by precipitation[10]. The growth rate of patents based on individual metals as active components for hydrogenation is cited in this study for the period 2011-2015. The growth rate of base metals is higher than that for noble metals such as palladium, ruthenium, rhodium, osmium, iridium or platinum. The growth rates based on patents are shown in parenthesis after each metal: Nickel (7.1%), Copper (4.9%), Cobalt (6.6%) and Iron (9.4%), noble metals as listed above (3.8-4.8%)[10]. It is interesting to note that amongst the base metals Nickel, Cobalt and Copper are the elements which are mainly used in catalysis apart from Mo and W (which are mainly used in hydrotreating/hydroprocessing). Global trade in supported nickel catalysts was to the tune of US$ 1.25 bn (2020) [11]. Similar information is not available for cobalt and copper catalysts.

Nickel, cobalt, copper and iron exhibit good activity for catalytic hydrogenation. Catalysts based on these metals are widely used for the manufacture of commodity chemicals and purification applications such as synthesis of ammonia, Fischer Tropsch synthesis, substitute natural gas, methanation, saturation of edible oils and fats, hydrodesulfurization, hydrocracking, selective hydrogenation of pyrolysis gasoline etc[12]. However, noble metals are still widely used in many applications such as manufacture of cyclohexane by the hydrogenation of benzene, selective hydrogenation of acetylene or MAPD (methyl acetylene and propadiene) from C_2 and C_3 hydrocarbon streams, 2nd stage hydrocracking, hydroisomerization of lubes and for the manufacture of specialty chemicals (API's, fragrances and flavors) and automotive emissions control. Hence, there is scope for exploring the use of non-noble metals as catalysts in these areas.

Some interesting differences between Co, Ni and Cu are:

- While all three elements belong to the first transition series, Cu presents an atypical electronic configuration and its Fermi level does not overlap with the d band. Its effect on reactivity is not studied so far for catalytic reactions.
- The Fermi level of Cu does not overlap with the d band of Cu. It is 0.1 eV lower than the d band. Whereas, the d bands of both Ni and Co overlap with the Fermi level[13].
- Quaino et.al.[13] have shown from model Hamiltonian, quantum statistics and DFT calculations, that, an overlap of the d band and the Fermi level is one of three important criteria for good catalytic activity in hydrogen electrocatalysis.
- Co, Ni and Cu belong to the first transition series of the periodic table. The electronic configuration of Cu ($4s^13d^{10}$) shows anomalous behavior from that of Co ($4s^23d^7$) and Ni ($4s^23d^8$) in that, the 3d orbital is completely filled before the 4s orbital (which is half filled).
- The Allen scale electronegativity increases from Sc (1.19) to Co (1.84) and Ni (1.88) and then decreases for Cu (1.85) and Zn (1.59). The Pauling scale also shows a similar trend.
- Cu tends to have I and II (lower) oxidation states, where as Co tends to have II, III, IV, V and Ni II, III, IV (higher) oxidation states. The higher oxidation states are observed in organometallic complexes. Oxides of lower oxidation states tend to have more ionic character and hence tend to have basic chemical character [14]

Thus, it would be interesting to compare the catalytic behavior of these three elements under a common set of conditions of catalyst preparation and performance evaluation using model reactions. This aspect forms the main focus of this work.

Further, when active metals are supported on carriers they present interesting properties as described below. These properties are useful in determining structure-activity correlations for continued development of catalysts:

- Metal dispersion (distribution of the active metal on the surface of the carrier) is an important property of supported metal catalysts. It is determined by pulse chemisorption of a probe molecule in flow through mode or by static chemisorption which is carried out under vacuum. Probe molecules such as hydrogen or CO or oxygen or NO are used depending on affinity with the metal. They chemisorb on the active site with a specific stoichiometry which is then used to back calculate the extent of metal dispersion. An option is to measure metal particle / cluster size as a representation of dispersion by transmission electron microscopy (TEM). This requires taking multiple micrographs at different locations. Particle size is determined by measurement and averaging of individual particles. This can also be done automatically using a photo-analyzer based software. Dispersion is a reflection of the surface area of active metal (as opposed to the BET specific surface area of the catalyst which is determined by physisorption and which includes surface area of the support as well). The surface area of the active metal has a direct influence on activity. It is very relevant to structure insensitive reactions wherein activity depends only on the extent of dispersion. In these cases, near atomic dispersion of the active metal is desired. In the case of structure sensitive reactions, the activity is influenced by specific location of the active metal sites, such as, terrace sites or edge sites or corner sites. The distribution of active metal sites at these locations depends on the cluster size of the atoms of the active metal. Thus, in the case of structure sensitive reactions, achieving desired cluster size is more important than atomic level dispersion of the active phase.

- The spatial distribution of active metal along the geometric dimensions of the catalyst particle is determined by SEM-EDAX (Energy dispersive analysis of X-rays). This has an important bearing on the type of reaction at hand. An eggshell distribution, where majority of the active metal is located at the outer periphery of the catalyst particle is preferred for reactions which are sequential in nature. In these cases, reaction intermediates are the desired product and prolonged contact with the catalyst can drive further reactions which are undesirable. This distribution is also desirable for reactions which are highly exothermic. These reactions are limited by external mass transfer from the bulk gas phase to the surface of the catalyst and most of the reaction takes place at the surface of the catalyst particle. Similarly, an egg-yolk distribution is favored for reactions which are negative order or when poisons are present in the feed stream. A uniform distribution is favored in remaining cases.
- Location of the active metal on the surface or sub-surface regions of the catalyst at microscopic scale (5-10 nm) can also affect activity and product selectivity. This is determined by X-ray photoelectron spectroscopy which has an approximate surface depth of 5 nm. If an active metal is located in the sub-surface regions it can affect its activity adversely. XPS also provides

information about metal-metal and metal-support interactions through shifts/changes in binding energy.

- Studies of reducibility of the active metal provides an idea of the availability of the active metal in its ‘active’ metallic form which is necessary for metal catalyzed reactions. This is determined from H_2-TPR (hydrogen temperature programmed reduction) studies wherein the amount of hydrogen consumed as a function of temperature during the experiment is determined and used for estimating degree of reducibility of the precursor such as oxide to metal. TPR also provides information of MSI (metal support interactions). The peak temperature of reduction increases as the MSI increases. While adequate MSI is necessary to minimize sintering of the active metal during use, too high MSI can affect reducibility of the active metal therein affecting activity. TPR also provides information of hydrogen spillover. This is important in hydrogenation reactions where this augments activity.
- Supports such as alumina, silica, titania, zirconia, carbon, magnesia etc. have inherent acidity or basicity. This acidity changes when an active metal is loaded on these supports and when the catalyst is subjected to post synthesis thermal treatments such as calcination. Presence of impurities such as alkali or alkaline earth compounds which can be introduced during preparation of the catalyst also affects acidity. Acidity is important for reactions which are acid-base catalyzed. It can affect activity, selectivity (by catalyzing side reactions) and stability (by formation and deposition of undesired coke precursors). Total acidity and acid strength are determined by Temperature programmed desorption of ammonia. Individual Brönsted and Lewis acidity are determined by FTIR of pyridine adsorbed on the catalyst. Model reactions such as transformation of isopropanol, methylbutanol, isomerization of butene etc. are also used to access acidity of solids.
- During preparation of supported metal catalysts, the precursor salts of the active metal decompose during calcination to form oxides. These oxides can be identified by X-ray diffractometry, provided they are sufficiently crystalline, by using the Braggs equation. Crystallite size of these oxides can be determined using the Debye-Scherrer equation. A smaller crystallite size corresponds to better dispersion of the active phase on the support. Orientation of crystal planes can also be identified. Preferred orientation of planes is reported to influence activity of catalysts[15].

- Catalysis being a surface phenomenon, textural properties of the catalyst such as specific surface area, pore volume, pore diameter are important for their performance. These can be determined by Nitrogen physisorption in the case of microporous and mesoporous solids and by mercury porosimetry in the case of mesoporous and macroporous solids. Good specific surface area with mesoporosity is generally desired. The latter is important for ease of diffusion of reactant and product molecules. Microporosity is important only for shape selective catalysis where the pore size is tailored to approximate the dynamic molecular size. This is important in selective preparation of the para isomer in di-substituted benzenes such as xylenes or diethyl benzenes[16].
- Raman spectroscopy is another useful technique for general characterization such as determining chemical structure, type of carbon, crystallinity, phase, polymorphs, particle size etc.
- DTA(DSC)-TG (Differential thermal analysis (Differential scanning calorimetry) and Thermogravimetry) is useful for determining changes in mass (weight loss or gain) and heat changes (exothermic or endothermic) when a sample is heated. Thermal decomposition of solids which results in weight loss is generally endothermic in nature. Coupling the DTA-TG with a Mass spectrometer enables analysis of gases evolved during calcination (evolved gas analysis). It provides useful information about the chemical nature of the as synthesized catalyst prior to calcination. It is also useful in deciding calcination conditions of the catalyst. DSC (Differential scanning calorimetry) can also be used for determining specific heat capacity by ASTM E1269-11 method.
- Bifunctional nature due to combination of metal function and acid-base function of the catalyst is important for reactions such as dehydrocyclization and hydroisomerization. Some applications are reforming of naphtha to aromatics or gasoline, isomerization of EB to xylenes, hydroisomerization of lubes to decrease pour point, hydrocracking of VGO. A proper balance of metal:acid function is important for these reactions. The ratio of these functions also dictates product selectivity in cases where individual competing reactions are catalyzed by either of these functions.

Catalyst supports are prepared either by precipitation, sol-gel, hydrothermal or pyrogenic routes. Alumina, silica, titania, magnesia, amorphous silica-alumina are generally prepared by the former two methods. Zeolites are prepared by hydrothermal techniques whereas fumed silica, fumed alumina and activated carbon are prepared by the pyrogenic route.

Sol-gel consists of preparation of a sol (or mixed sol for multi-component materials) using organometallic precursors (such as alkoxides) and organic solvents. The sol is then hydrolyzed by adjusting the pH through addition of an aqueous acid or base to form a gel. The gel is subsequently aged, dried and calcined. Precursors containing alkali metals are avoided. Thus, the product does not contain these impurities and has high purity. The presence of organic solvents results in higher surface area and pore volume in general. It adds to cost of chemicals and also to processing.

Precipitation can be carried out in a number of different ways. Variants therein are strike precipitation which is generally done by adding a basic precipitant or precursor to an acidic precursor till the final pH becomes slightly alkaline (7-9.5), sufficient to bring about precipitation. Reverse strike precipitation consists of adding an acidic precursor/precipitant to a solution of a basic precursor. The advantage is traversing a relatively smaller range of pH throughout the precipitation process in the latter case. Precipitation at constant pH is another variant where an acidic precursor and a basic precursor/precipitant are simultaneously fed to a liquid heel (usually water). The entire process is carried out at a reasonably constant pH. PFHS (Precipitation from homogeneous solution) is another technique wherein a solution of acidic precursor is mixed with the precursor of a base (such as urea) which hydrolyses readily at elevated temperature. The mixture is stirred and rapidly heated to a temperature where the base hydrolyses and brings about precipitation. Yet another variant is deposition precipitation which is particularly useful for preparing bi-component supports. It is similar to strike or PFHS methods with the difference that one of the support constituents is present in the form of a solid powder and the second constituent is precipitated over this powder at a certain pH. PFHS does not present an opportunity to vary the pH significantly whereas strike pH or constant pH do. Hence, the latter are resorted to for a study of the effect of pH on properties of the precipitate. Deposition precipitation is particularly useful in situations where conventional precipitation can result in low surface area and pore volume for bi-component supports.

Supported metal catalysts can be prepared either by impregnation of the precursors of the active metals on to a porous high surface area solid support or by co-precipitation along with the support.

Impregnation is resorted to when the active metal can be loaded on the support within a maximum of 2-3 sequential steps. When the concentration of active metal exceeds this requirement, severe pore plugging can take place if the catalyst is prepared by impregnation. In such situations the catalyst is prepared by co-precipitation, even at the expense of minor loss of accessibility of the active phase which gets embedded in the support structure. Catalysts prepared by impregnation are expected to present better accessibility / availability of the active metal to the reactants compared to catalysts prepared by co-precipitation. MSI (Metal support interaction) effects can be expected to be relatively less in these catalysts compared to those prepared by co-precipitation. Yet another option is compounding, wherein the solution of active metal precursors is blended with a solid powder such as pseudoboehmite prior to forming/shaping the material into shapes such as extrudates.

One of two methods of impregnation is generally used. SEA (Strong Electrostatic Adsorption) or CEDI (Charge Enhanced Dry Impregnation)[17]. They are especially useful when the support is in the form of small granules or shaped particles such as cylinders, spheres, extrusions such as plain cylinders or trilobes or quadralobes etc. with the smallest dimensions in the millimeter scale.

SEA is effective when a single active metal is used and its concentration is lower than the equilibrium adsorption capacity of the support. The PZC (point of zero charge) of the support is also an important consideration in selecting the active metal precursor. The pH of the solution is adjusted such that the surface charge of the support is opposite that of the ionic form of the metal precursor (cationic or anionic species) to enable adsorption by attractive electrostatic forces and also at a pH where the electrostatic forces of attraction between the ions of the metal precursor and the support are strongest. A significant excess of impregnation solution relative to the solid is used to minimize shifts in pH. The concentration of H^+ or OH^- ions (depending on pH of the impregnation solution) is also such that it overcomes pH shifts. A competing ion is used to minimize spatial gradients in the concentration of active metal along the cross section of the carrier particle. While very good dispersion is achieved on formed supports by this method, one has to deal with disposal of significant quantities of impregnation solution with trace concentration of metal ions. This is undesirable from an effluent standpoint.

CEDI on the other hand becomes indispensable when the concentration of the active metal to be loaded exceeds the equilibrium adsorption capacity of the support. It can also be used as a substitute for SEA when the concentration of active metal is lower than the adsorption capacity of the support. It is also useful when a mixture of active components is impregnated simultaneously. In this case the volume of the impregnation solution is just sufficient to completely fill the pores of the support. Hence, a significantly higher concentration of acid / base needs to be used to prevent pH shifts. Large changes in pH can lead to premature precipitation of the precursor. The larger concentration of acid or base can lead to local dissolution of the support in some cases. It can also lead to corrosion of equipment (requires corrosion resistant equipment). An advantage is that there is no excess spent impregnation solution for disposal.

Drying is an important step in the preparation of catalyst materials prepared by precipitation. These materials can undergo significant shrinkage due to collapse of micropores during drying. This results in loss of surface area. Slow rate of drying helps to slow down this process to an extent. Supercritical drying, Freeze drying, replacement of aqueous solvent by organic solvents (which change surface tension) and the use of viscosity enhancers are some effective methods which help to minimize loss of surface area. However, they add to costs.

Drying is also important in the preparation of shaped supported metal catalysts. It involves removal of the solvent which is used to impregnate the active phase onto the support. The active phase which is impregnated onto the support can redistribute during drying. Drying of a support impregnated with solution of the active phase takes place in two regimes, a constant rate period and a falling rate period. There is sufficient liquid at the surface of the catalyst particle to sustain constant rate of drying during the former regime. When the quantity of liquid depletes to the extent where there is no free liquid at the surface of the catalyst particle drying shifts to the falling rate regime. Liquid from the interior of the catalyst particle diffuses to the surface through the pores due to capillary action. It carries the dissolved active metal precursor with it. This can result in a maldistribution of the active phase across the cross section of the catalyst particle. Chelates are used to retard this effect. The presence of chelates increases the viscosity of the solution in the pores as drying progresses. Thus, redistribution of the active phase during drying is minimized.

Calcination is another important step in the preparation of catalysts. It refers to thermal treatment of the dried catalyst in air. It converts the precursors of the active phase to corresponding oxides and fixes the active phase to the support. It also dictates the formation of crystallographic phases and polymorphs such as in alumina. Too high a temperature or too long a duration can cause loss of surface area of the support and the active phase due to thermal sintering.

The metallic form of the active phase is what catalyzes reactions in supported metal catalysts. Chemical reduction with molecular H_2 in vapor phase or with solution of compounds such as sodium borohydride or hydrazine which liberate hydrogen in liquid phase are used for reduction. Presence of moisture or oxygen enhances sintering of the active metal during reduction. It is important to properly dry the catalyst prior to reduction and also ensure a dry, moisture and oxygen free environment during reduction. Reduction is an exothermic process and the heat of reaction needs to be properly managed to prevent / minimize metal sintering. Catalysts which are reduced off-site need to be stabilized by forming an inert film of oxide or carbonate on the external surface of the reduced catalyst particle.

Adequate microstructure and bifunctional character are important properties in heterogeneous catalysis. It is important to assess both these properties in the exploration of new catalysts. This aspect has been systematically studied in this dissertation with catalysts based on transition metals Ni, Co and Cu which are supported on bicomponent carriers comprising of different mole ratios of zirconia:alumina. Methods of preparation such as co-precipitation and deposition-precipitation were evaluated to understand their effect on specific surface area, porosity and acid-base character of the carrier. The active metals Ni, Co and Cu were loaded by incipient/dry impregnation.

The preparation of 2-phenyl ethanol and phenylacetaldehyde by the hydrogenation and isomerization of styrene oxide respectively, and the hydrodeoxygenation of phenolics (m-cresol used as model compound representing phenolic compounds present in lignin) to useful chemicals such as BTX, phenol, xylenol, cyclohexanone or cyclohexanol were studied as representatives in this dissertation. Generic reactions are shown in Figures 1.1 and 1.2 below.

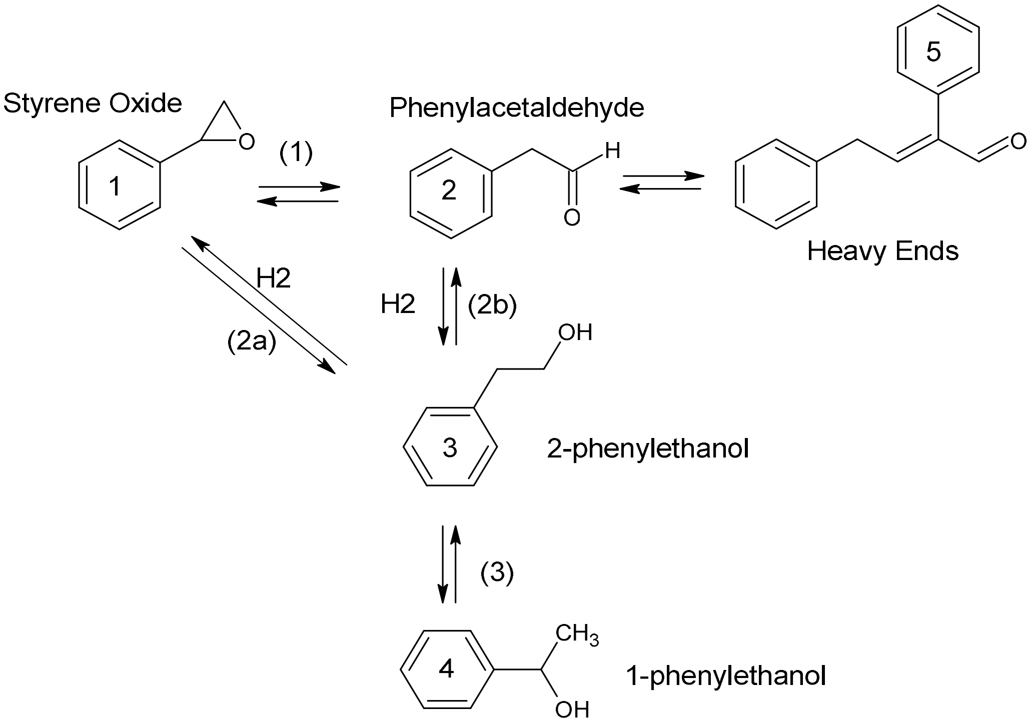

Figure 1. 1: Hydrogenation and isomerization of styrene oxide

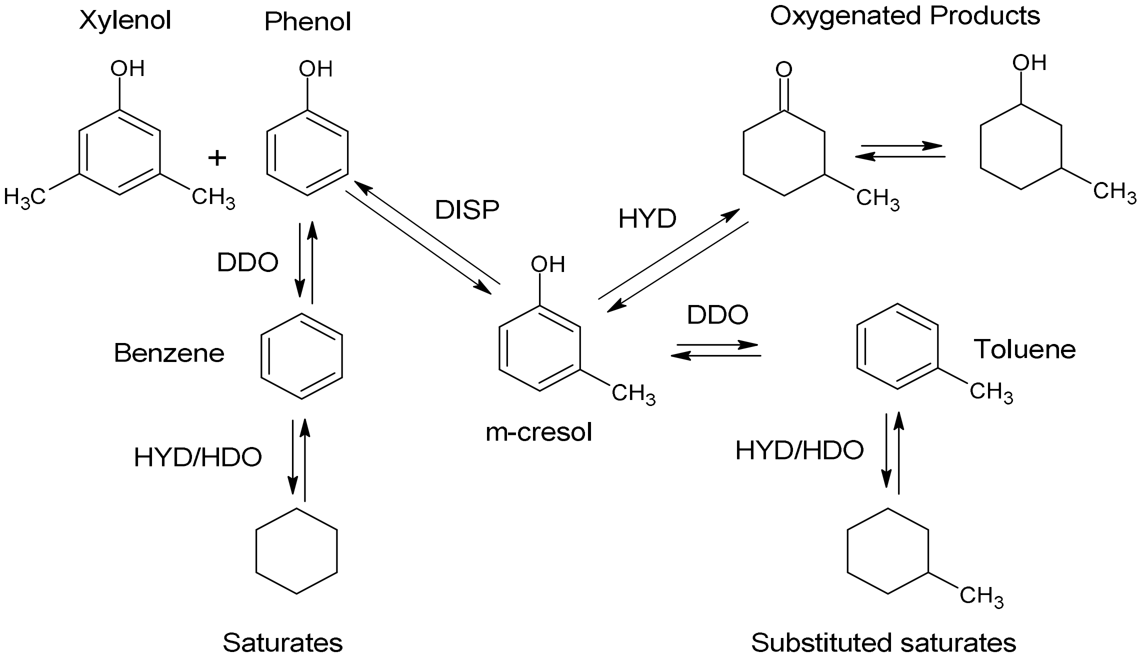

Figure 1. 2 : Hydrodeoxygenation of m-cresol

In this study bi-component zirconia-γ-alumina composites were prepared by two different methods. i) Deposition precipitation of zirconia onto a powder of γ-Al_2O_3 and ii) by co-precipitation from a mixture of the solutions of their nitrates. The effect of pH of precipitation was studied in both cases. The detailed chemical composition of the as synthesized catalysts (prior to calcination) was determined through characterization techniques such as DTA-TG coupled with MS (TGA-MS) and FTIR[18]. Different precursors of alumina such as aluminum trihydrate (ATH), pseudoboehmite (PSB) and γ-Al_2O_3 were also explored as substrates for deposition precipitation. They vary in their specific surface area and degree of hydroxylation. Effect of pH was studied over the range 7-9. The as-synthesized catalysts were characterized for their composition. The resultant bi-component zirconia-alumina supports were thoroughly characterized using the appropriate techniques listed above and were further evaluated for the decomposition of 2-methylbutanol.

The decomposition of 2-methylbutanol is a useful reaction for characterizing acid-base character of metal oxides[19]. It is based on the observation that acidic, basic and amphoteric sites convert it to different products, Acid sites form 3-methyl-3-butene-1-ene and prenal, basic sites form acetylene and acetone and amphoteric sites 3-methyl-3-butene-2-one and 3-hydroxy-3-methyl-3-butanone.

Based on these studies γ-Al_2O_3 was selected as a substrate for further studies. pH of deposition precipitation was fixed at 9. Supports with zirconia:alumina varying from 0:1 to 1:0 were prepared. A set of supported metal catalysts constituting nominal 12 wt% Co or Ni or Cu supported on zirconia-alumina carriers were prepared by the method of dry impregnation. The carriers used for preparation of these catalysts were prepared by deposition-precipitation at final pH 9. These catalysts were characterized using all the techniques listed above. They were also evaluated for two model reactions viz. the transformation of styrene oxide to 2-phenylethanol and phenylacetaldehyde and for the hydrodeoxygenation of m-cresol to hydrocarbons.

The first model reaction is the hydrogenation of styrene oxide to 2-phenylethanol (2-PEA). Styrene oxide also isomerizes to phenylacetaldehyde (PAA). Both these products are important perfumery chemicals in the fragrance industry and in the flavor industry. 2-PEA has fragrance and flavor of rose petals while the fragrance of PAA is described as “green floral odor” with a honey-like flavor. The former reaction requires a metal function while the latter requires an acid-base function. 2-PEA is generally prepared from alkylation of benzene through Friedel Crafts reaction[20] or through Grignard synthesis[21]as well as hydrogenation of styrene oxide[22] while PAA is prepared by the isomerization of styrene oxide[23]. Commercial catalysts used for producing 2-phenyl ethanol are Pd based. Studies using noble metal catalysts such as Pt or Pd are reported[24][25][26][27]. A number of studies have been reported with non-noble metal catalysts such as Raney nickel (bulk metal)[28], Ni, Co and Cu supported on various refractory supports[22][29][30][31]. Acid catalysts such as zeolites, Nafion or heteropoly acids are reported for preparing phenyl acetaldehyde[32]. The relative distribution of these two products and the cause of catalyst deactivation in this reaction is attributed to either strong acid sites which leads to coking[33] or basic sites which promote condensation reactions[31] Weak Lewis acid sites or sites with mild basic character could help in this regard.

Most of the studies on conversion of styrene oxide reported in literature are carried out in batch reactors[22][24][25][30]. Very few studies are reported in continuous flow mode[26][27][29]. The current studies were carried out in a continuous flow reactor. Further, while Co, Ni and Cu based catalysts are reported for this reaction, the studies are fragmented. A systematic study comparing the behavior of these three active metals under a given set of preparation and evaluation conditions is not reported in literature. Such a study will add value in understanding their behavior in light of the differences in their electronic properties. Most of the studies are with mono-component supports. Some studies with bi-component supports are reported[22], but a combination of zirconia-alumina is not reported in literature. Both alumina and zirconia are useful for acid-base catalysis. Zirconia has Lewis acidity while γ-Al_2O_3 has both Lewis and Brönsted acidity, which makes for an interesting combination. Thus, supported Co, Ni, Cu on bi-component zirconia-alumina were studied in this work.

Interesting trends in characteristics such as microstructure, crystallite size, surface concentration of active metals, metal-support interactions, acidity and preferred orientation of crystals were observed with zirconia content and the metals Co, Ni and Cu. These influenced trends of conversion and product selectivity.

The transformation of styrene oxide on these catalysts showed significant differences in activity and product selectivity between Cu on one hand and Ni and Co on the other. The Co based catalysts showed the highest activity for formation of 2-PEA, closely followed by Ni based catalysts. Zirconia favored selectivity to PAA. Combination of Cu with high zirconia enhanced formation of PAA and styrene. The Cu based catalysts showed low activity for 2-PEA but high activity for PAA. Conversion of styrene oxide and the selectivity to 2-PEA correlated with concentration of active metal on the surface as determined by XPS and acidity. Cu based catalysts also showed significantly higher selectivity for styrene than the Co or Ni catalysts. Spill over hydrogen and preferential orientation of crystal planes of Cu correlated with the formation of styrene. Styrene was observed to form by the hydrodeoxygenation of styrene oxide. Differences in MSI (metal support interaction) between the active metal components and the zirconia or alumina components of the support were also observed. Nickel showed a stronger MSI with alumina whereas copper showed stronger interaction with zirconia. Trends of process parameters such as space velocity, pressure, temperature and H_2/SO were in line with expectations from thermochemistry and reaction stoichiometry. A reaction schematic is proposed in chapter 4, which is based on the trends observed in this study.

The conversion of biomass to valuable chemicals is a sustainable alternative to fossil fuels for the manufacture of chemicals, due to its renewable nature. Cellulose and hemicellulose are relatively easily converted to materials such as paper, value added compounds such as cellulose ethers and esters, levulenic acid, γ-valerolactone and 2G ethanol, through the exploitation of the sugars, HMF and furfural platforms[34] The lignin component is however relatively difficult to valorize. Lignin accounts for 5-35% of the weight of biomass depending on the type of vegetation. It is present in higher concentrations in woody biomass. It is a low value by-product of the paper and pulp industry[35]. It is mainly used as fuel. Thus, efforts to valorize it to value added chemicals is important. Hydrodeoxygenation is a promising route for its valorization to chemicals such as BTX, cyclohexane, phenolics, xylenol, cyclohexanol, cyclohexanone and their methyl and dimethyl derivatives. These find use in the manufacture of fuels, aromatics, solvents, plastics, resins, adhesives, detergents, antioxidants, polyester and nylon. Key reactions involved in valorization of compounds present in lignin are direct deoxygenation (DDO), hydrogenation (HYD), hydrodeoxygenation (HDO), dealkylation and disproportionation which requires catalysts which are bifunctional[36][37]. Hydrodeoxygenation of phenol, phenol derivatives and biomass have been reported in literature. A variety of catalysts such as noble metal based catalysts: Pt/SiO_2 [38] , bimetallic Pt-Mo/Al_2O_3[39], Pt/Al_2O_3[40] and non-noble metal based catalysts such as supported metal oxide catalysts[41][42][43] and metal sulfide catalysts such as MoS_2, CoMoS and

NiMoS[44] on a variety of supports have been studied and reported for this reaction. Zhang et.al. have provided a comprehensive review covering these materials[45]. There is possibility to further explore non-noble metal catalysts for this reaction.

(Hydro)deoxygenation of m-cresol over supported metal catalysts: Ni, Co Cu on a set of five zirconia:alumina carriers with ZrO_2:Al_2O_3 varying from 0 to 1 was investigated in the present work. The reaction was studied out at 350°C, atmospheric pressure, WHSV 0.5 h^{-1} and H_2 : m-cresol 11.5 molar in fixed bed continuous flow studies.

Conversion of m-cresol was low, <10% which facilitated comparison of product selectivity of the catalysts and helped identify the routes by which these products formed. Disproportionation of m-cresol to phenol and xylenol was observed to be a dominant reaction. A reaction network based on the trends observed in this study is proposed in chapter 5.

Conversion increased with alumina content of catalyst, with the trend Ni>Co>Cu, which correlated with XRD crystallite size. Phenol, xylenol, cyclohexane, benzene and toluene were main products. Acid-base (support) functionality was evident from disproportionation of m-cresol. It correlated with zirconia content of catalysts and weak acidity. Toluene and benzene formation correlated with a combination of metal and acid function. Hence they appear to form by tautomerization or partial ring hydrogenation mechanisms culminating in a dehydration step. Aromatics formation correlated with oxophilicity to an extent. The combination of active metal and the support was observed to be sensitive for aromatics formation in the case of Co and Cu catalysts. Role of metal function was evident from formation of cycloalkanes, mainly cyclohexane and small quantities of cyclohexanone, cyclohexanol and their methyl substituted analogs. Cyclohexane appeared to form by hydrogenation of benzene. In addition to disproportionation, phenol also appeared to form by C-C hydrogenolysis of m-cresol exclusively on Ni catalysts rich in alumina. While formation of toluene was observed, its disproportionation to xylene was not observed. The concentrations of methyl cyclohexanes in the products was significantly lower than that of cyclohexane, which is consistent with literature report that substituents on the benzene ring retard kinetics of its hydrogenation[46]. Neat zirconia based catalysts showed poor performance due to lower acidity and lower surface concentration of active metals. Zirconia rich catalysts showed higher HDO (Hydrodeoxygenation) selectivity (to saturates) whereas alumina rich ones showed higher DDO/TAU selectivity (to aromatics). Co and Cu catalysts rich in alumina formed significantly higher selectivity to aromatics (70-75% selectivity) than Ni catalysts, but lower yields due to lower conversion. Product trends mainly correlated with surface concentration of active metals and acidity. Coke formation correlated with the formation of aromatics which is consistent with requirement of higher acidity. Copper catalysts showed trends which differed from those of Ni and Co catalysts. This correlated with differences in its MSI (metal support interaction), XRD crystallite size and electronic configuration relative to Ni and Co.

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