Chapter-6 : SUMMARY AND PATH FORWARD

The objective of this dissertation was to explore non-noble metal based bifunctional supported metal catalysts of Co, Ni and Cu supported on bicomponent zirconia:alumina for the transformation of styrene oxide and for the hydrodeoxygenation of m-cresol. The former reaction is useful in preparing fragrance and flavoring chemicals whereas the latter is useful for producing chemicals through sustainable routes by valorization of lignin. m-cresol which is similar to phenolic compounds found in lignin was used as a model compound for the latter reaction.

Non-noble metals are of interest in catalysis because of their substantially higher abundance in the earth's crust and their lower price compared to noble metals. Further, the combination of active metals Co or Ni or Cu with zirconia-alumina support has not been reported in published literature or patents for the two target reactions. Thus, the results would add to the body of existing knowledge.

Zirconia and alumina are amphoteric oxides. The former has Lewis acidity, whereas the latter has both Lewis and Brönsted acidity. Thus it should be possible to tune the acidity of the support by varying their molar ratio in bicomponent supports. Cu has an electronic configuration which differs from that of Co and Ni. This could influence metal functionality and hence reactivity and product selectivity of catalytic reactions. Thus, it is reasoned that supporting these transition metals on zirconia-alumina supports would make for an interesting study.

The target reactions chosen are i) transformation of styrene oxide to phenylacetaldehyde and 2-phenyl ethanol and ii) hydrodeoxgenation of m-cresol. Both these reactions are influenced by acid and metal function (bifunctional catalysis). The former is from the area of Specialty Chemicals and the latter from Bulk /commodity Chemicals.

Deposition precipitation was explored as a simple method of preparation. Alumina materials with widely differing properties were explored as substrates. The supported metal catalysts were prepared by dry impregnation of the active metals onto the support.

Detailed characterization was undertaken to understand the microstructure, acid and metal character of the catalysts and correlate them with reactivity for the two target reactions.

Learning from the study which add value are:

- Deposition-precipitation is evaluated for preparation of supported metal catalysts. The results indicate that it is a simple method of preparation which is useful for improving microstructure of oxides like zirconia which otherwise tend to have poor microstructure. However, high zirconia content (>50 mole%) leads to pore plugging which limits the application. In this study catalysts prepared by deposition precipitation performed better than those prepared by co-precipitation.
- Reactivity (peptizability) of alumina substrates used for deposition precipitation and their initial physico-chemical properties influence the support prepared by deposition precipitation. Clear differences in this regard are seen between supports prepared with Aluminum trihydrate (ATH), pseudoboehmite (AM) and γ-Al2O3 (GA) as substrates. The high reactivity of pseudoboehmite affects microstructure of the bicomponent zirconia-alumina support. The low initial surface area of ATH proved detrimental to microstructure of the bicomponent product. GA gave product with good microstructure. Strong interaction / solid solution formation between zirconia and GA was observed which influenced microstructure and acidity.
- N_2-physisorption, XRD, DSC-TG and NH_3-TPD proved to be useful characterization techniques. Properties such as acidity, metal XRD crystallite size, surface concentration of metals, metal support interaction and microstructure were correlated with performance for transformation of styrene oxide and the hydrodeoxygenation of m-cresol.
- Acidity of the bicomponent supports varied significantly with changes in zirconia:alumina ratio. Interaction between zirconia and the alumina substrate and Lewis acidity imparted by the active metal precursors contributed to these changes. This reflected as differences in product selectivity for both target reactions.
- Generally, the support is perceived as imparting acid function and active metals the metal function in supported metal catalysts. This study shows that residual unreduced metal oxides impart Lewis acidity to the catalyst. Acidity and metal functionality are in fact closely inter-related. While oxide materials (read ‘support’) affect acid catalysis directly, they can affect metal functionality indirectly. As shown in this study, catalysts rich in zirconia show low acidity. However, they also affect metal functionality through low

surface concentrations of active metals and preferential orientation of crystal planes (as in case of copper). In the specific case of transformation of styrene oxide both acid and metal functions were impaired which resulted in low STY (Space Time Yield) for both phenylacetaldehyde (PAA) and 2-phenyl ethanol (2-PEA) in catalysts with high zirconia content. Selectivity to products of TAU (tautomerization) and HDO (hydrodeoxygenation) reactions was observed to be closely governed by the combination of acid and metal function in the hydrodeoxygenation of m-cresol.

- The results reiterate the importance of a proper combination of acidity and metal functionality for achieving product selectivity such as between phenylacetaldehyde and 2-phenylethanol in transformation of styrene oxide and between aromatics (produced from TAU – tautomerization) and saturates (produced from HDO – hydrodeoxygenation) in hydrodeoxygenation of m-cresol.
- Reaction schemes were identified for both the target reactions. These provide useful information for modulating acidity and metal functionality in prospective catalysts for improving selectivity.
- The transition metals, Co, Ni and Cu are compared on an equitable basis using a set method of catalyst preparation and performance evaluation in this study. This enabled distinguishing inherent characteristics between them.
- Between the three active metals copper catalysts showed a distinctly different behavior. Copper catalysts showed stronger metal support interaction with zirconia whereas Co and Ni show stronger interaction with alumina. Copper catalysts showed poor metal (hydrogenation) function for both reactions which manifested as low STY (space time yields) of 2-PEA (even at low zirconia content in catalyst), and low yields for HDO, TAU and HYD (hydrogenation reactions) in hydrodeoxygenation of m-cresol. The different behavior of Cu based catalysts may be attributed to difference in its electronic properties relative to Co and Ni, as well as preferred orientation of crystal planes in Cu catalysts.
- Copper supported on carriers with high zirconia content also showed preferred orientation of crystal planes which enhanced the formation of styrene and suppressed the formation of 2-PEA in the transformation of SO (styrene oxide).
- While non-noble metal based catalysts are economically priced and are desirable from long term sustainability perspective, they do not match up to the performance of noble metal

catalysts for the transformation of styrene oxide. The selectivity of the former catalysts needs to be improved significantly. Selectivity to styrene needs to be decimated. Selectivity to 2-PEA or PAA can be enhanced by adjusting acidity or metal functionality.

- In the hydrodeoxygenation of m-cresol good selectivity could be achieved for either TAU or HDO by manipulating acidity. However, the poor metal function in zirconia rich catalysts resulted in poor product yields. The role of oxophilicity in promoting formation of aromatics (toluene from m-cresol) remained ambiguous.
- Overall, the effect of acid and metal function on product selectivity was elucidated for the target reactions.
- The study demonstrates use of a combination of characterization techniques such as CHN, TGA-MS, ICP-OES and Flame photometry to elucidate chemical composition of as-synthesized multicomponent oxide materials.
- The study also demonstrates the use of catalyst characterization techniques for correlation of catalyst characteristics with reactivity for the target reactions. Such as, besides the routine microstructure and acidity, effect of surface concentration of active metals (by XPS) for hydrogenation activity, preferred orientation of crystal planes (by XRD) for selectivity to styrene and 2-PEA. Correlation of metal support interactions with sintering of active metals.

Thus, the study has addressed the objectives with which it was started, viz.

- To study use of non-noble metal catalysts (Co, Ni and Cu) on an equitable basis for producing useful chemicals and compare their performance characteristics in relation to their physico-chemical characteristics. These metals are available in relative abundance and are lower priced than noble metals, which makes them attractive for substituting noble metals in catalysis.
- To explore a simple method such as deposition precipitation for preparation of bicomponent supports when one component tends to have poor microstructure and the other lends its microstructure to the benefit of the bicomponent supports. Alternate methods such as sol-gel or freeze drying are relatively expensive and/or need elaborate hardware.
- To appreciate whether the different electronic configuration of Cu relative to Co and Ni leads to differences in its characteristics and performance in catalyzing reactions.

<u>Path Forward</u>:

- Non-noble metal catalysts are attractive from cost and sustainability perspective. However, they lack the activity and selectivity of noble metal catalysts. Considerable improvements are necessary in this direction.
- Experimental studies could be complemented with DFT studies to further the understanding of interactions between supports and active metals and also interactions of reactants with the catalysts. These studies would be useful in developing improved catalysts.
- Alloying is known to change chemisorption behavior of active metals. Based on inputs from DFT studies suitable multi-metallic clusters such as Cu-Ni, Cu-Co, Ni-Co (between transition metals) or Pt(Pd)-Ni, Pt(Pd)-Co, Pt(Pd)-Cu (combinations of transition and noble metals) could be pursued for these reactions to improve product yields. Studies of surface and interface engineering to maximize certain facets which have high activity for a given reaction are actively pursued in the area of electrocatalysis[1]. Strategies such as alloying, doping, control of metal crystallite size, regulating composition in alloying is pursued to this end. Surface dealloying of Ni_xSi_y intermetallics has been reported to improve activity of Ni to better than that of Pd for H_2 storage by hydrogenation of unsaturated compounds such as ethylene, benzene and toluene[2]. DFT studies show that clusters of Ni partially embedded in the SiO_2 matrix bring out the high activity.
- Cascade catalysis in batch reactors has been explored by Sasu et.al.[3] This could be extended to Tandem catalysis in flow reactors for improving product selectivity.

6.1 References

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