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Summary and Future Directions

6.1 SUMMARY

In the present thesis entitled "***Supported Chiral Platinum Nanoparticles for Asymmetric Catalysis***", a variety of metal supported heterogeneous catalysts were synthesized and characterized. Carbon materials and polyamide were used as supporting materials. Natural source cinchona was used as a chiral modifier. Cinchona modified heterogeneous catalysts were applied for asymmetric synthesis. The most significant conclusions are summarized as follows.

- A set of carbon supported metal catalysts were synthesized using a modified wet impregnation method. Among the various catalysts, Pt loaded carbon materials (Carbon nanotubes, Graphene, Activated carbon and Carbon fibers) were characterized using different analytical techniques. SEM, TEM and AFM results showed the morphology and distribution of Pt nanoparticles on the surface of carbon materials. XRD results showed that the FCC structure of Pt was favoured. Absorption and transmission spectra in UV-IR demonstrate the interaction between Pt and carbon materials. Pt/C was screened for asymmetric heterogeneous hydrogenation of methyl pyruvate. Pt/MWNTs were most efficient catalyst and provided the highest enantioselectivity. The supremacy of Pt/MWCNTs was attributed to the high absorption of cinchonidine/substrate on atomically dispersed Pt nanoparticles loaded on nanochannels of MWCNTs which maximizes metal utilization. NMR study elucidated 1:1 substrate modifier complex, and cyclic voltammetry suggested irreversible adsorption of cinchonidine on Pt surface.

- A strategy was developed to prepare highly faceted Pt HNC/C catalysts using Tw20, and their catalytic activity was studied for the asymmetric hydrogenation of a carbonyl group. The Pt HNC loaded MWCNT catalyst showed the highest conversion and enantioselectivity, in the case of α-ketoesters, under optimized reaction conditions. The higher catalytic activity was attributed to Pt (111) hexagonal nanocrystals present at the nanochannels of the carbon nanotubes.

- Highly active Pt nanoparticles loaded chiral polyamide catalysts were synthesized for asymmetric hydrogenation of industrially important α-ketoester; ethyl 2-oxo-4-phenylbutanoate, under solvent free conditions. The CD and UV-vis spectroscopy are proved to be effective to examine the helical structures of polyamides and transferred the chirality from helical chiral polyamide support via atomically distributed platinum particles. The present study established a relation between enantioselectivity and dispersion of Pt nanoparticles on chiral polyamide. The dispersion is high in case of distant amide groups containing polyamide, which lead to highly isolated platinum nanoparticles that behaved like single atom catalysts. This results in high conversion and enantioselectivity.

- F-CD-BF_4 was synthesized and immobilized on carbon nanotubes, and heterogeneous catalysis of imines was carried out with allyltributyltin. It was observed that the reaction was much less sensitive towards air and moisture, due to F-CD-BF_4. Products were analyzed by NMR, polarimeter and HPLC.

- ❖ The successful catalysts (Pt/MWCNTs (3a), Pt HNC/MWCNTs (11) and Pt/polyamide (15e)) are reusable, without any significant loss of activity, even after ten cycles.

6.2 FUTURE DIRECTIONS

- o The current study provides an opportunity to develop large scale industrially viable asymmetric hydrogenation catalysts. The complete mechanism of the heterogeneous asymmetric catalysis is not clear yet, despite various studies. Investigation in this area will help to develop better and more efficient catalysis for other chemical transformations.

- o The Pt-functionalized carbon interaction can be explained by solid state NMR. It is very interesting to know about the change in chemical shift of Pt and carbon nuclei during the interaction. The change in oxidation state of Pt can be determined by XPS during the Pt loading and pre-treatment of the catalyst. Interaction of polyamide with ketoester or Pt can be explained by a time depended NMR study. To determine the exact percentage loading and leaching of metal, ICP analysis can also be carried out.

- o Further efforts can be directed towards understanding the exact mechanism of fluorinated cinchonidine mediated allylation of imine and the utility of F-CD-BF_4.