CHAPTER 4

SUMMARY AND CONCLUSION

Hydrotalcite (HT) support was synthesised by co-precipitation method as reported earlier. Similarly MgO, MgCr and MgAl mixed oxides were synthesised. The material was characterised by various physico-chemical methods such as XRD, BET surface area, TGA and SEM. The nature of the material was confirmed by XRD. BET measurement revealed high surface area of the material. TG analysis indicates the removal of water and carbondioxide at specific temperatures.

Hydrotalcite was used as a support for palladium catalysts. Hydrotalcite (HT) was impregnated with Pd by wet impregnation method and polyol reduction method. 0.5, 1, 2 and 5 wt.% Pd on HT support was prepared. All the supported catalysts were characterised by XRD, BET surface area, SEM, TEM, XPS, UV-Vis DRS, TPR and CO chemisorption studies. XRD data clearly indicates the presence of hydrotalcite phases. The surface area is found to decrease as the palladium loading increases. The surface morphology of the hydrotalcite material is clearly seen from SEM. The particle size of the metal is calculated from CO chemisorption and TEM. The metal dispersion, surface area is calculated from CO chemisorption studies. The metal environment is observed from Uv-Vis DRS. A two stage reduction is observed in all the hydrotalcite supported palladium catalysts. From the XPS spectra of reduced palladium catalysts two peaks Pd 3d$_{3/2}$ and Pd 3d$_{5/2}$ are found clearly in all the catalysts. The binding energy value of Pd
3d₅/₂ peak in hydrotalcite supported palladium catalyst is found to be around 335.6 eV which indicates that Pd is reduced to Pd metal.

The catalytic activity of the synthesised catalysts is tested for hydrogenation of nitrobenzene, dehydrogenation of cyclohexanol and combination reaction. Vapour phase hydrogenation of nitrobenzene is studied in the temperature range of 498-573 K over hydrotalcite supported palladium catalysts. The reaction parameters such as temperature, WHSV, time on stream were varied to optimize the reaction conditions. Effect of Pd loading (0.5, 1, 2 and 5 wt.% on HT support is studied, and observed that very low wt.% of Pd is sufficient for high conversion and selectivity at 498 K. This is due to high dispersion of Pd on the HT support which is revealed from CO chemisorption results. The above reaction is compared with other conventional supports such as MgO and γ-Al₂O₃ and concluded that among all the catalysts, hydrotalcite supported palladium catalyst is identified as the highly versatile for hydrogenation of nitrobenzene.

A novel combination reaction viz., hydrogenation of nitrobenzene and dehydrogenation of cyclohexanol is studied over 1 wt.% Pd/HT (imp) and 1 wt.% Pd/HT (EG) catalyst. In order to carry out the above reaction, individual reactions were also studied. A comparative study of the nitrobenzene hydrogenation reaction is done with 1 wt.% Pd/HT prepared by wet impregnation method and polyol reduction method using ethylene glycol as solvent, by varying reaction parameters such as temperature and time on stream. The conversion is found to be 78% at 498 K and the selectivity remains 100% at all temperatures. Dehydrogenation of cyclohexanol to cyclohexanone is studied over 1wt.% Pd/HT prepared by impregnation method and 1wt.% Pd/HT prepared by polyol reduction method. The reaction is studied in the temperature range of 498-548 K. Maximum conversion is found to occur at 523 K and the conversion is found to decrease at higher
temperature. After studying the individual reactions, combination reaction is attempted on the same catalysts. Dehydrogenation of cyclohexanol and hydrogenation of nitrobenzene is found to occur simultaneously in vapour phase conditions by maintaining the flow of nitrogen (10 ml min\(^{-1}\)). The reaction is carried out in the mole ratio 1:3 (NB:CY) and in the temperature range 498-548 K. The released hydrogen in the dehydrogenation of cyclohexanol reacts with nitrobenzene resulting in hydrogenation of nitrobenzene to aniline. Thus without any external supply of hydrogen it is possible to achieve aniline and hence it is a hydrogen economy reaction.

Selective hydrogenation of furfural to furfuryl alcohol is studied over 1 wt.% palladium catalysts using different supports such as hydrotalcite, Mg-Al mixed oxide, MgCr and MgO in the temperature range of 453-523 K. Among all the catalysts 1 wt.% Pd/HT shows maximum conversion of furfural and higher selectivity towards furfuryl alcohol at 498 K. Selective hydrogenation of acetophenone to 1-phenyl ethanol is studied over calcined hydrotalcite supported palladium catalysts in vapour phase conditions in the temperature range of 498-548 K. The maximum conversion and selectivity is found to occur over 1 wt.% Pd/HTA at 523 K. The product selectivity towards 1-phenyl ethanol is high and the selectivity towards ethyl benzene is found to be low. Based on the above observations, it is concluded that hydrotalcite supported palladium catalyst is found to be a highly active catalyst for the hydrogenation, dehydrogenation and combination reactions as it is a highly active base catalyst.