Chapter 6
Summary and conclusions

This thesis describes the preparation, characterization and catalytic evaluation of zirconia-supported Keggin heteropoly acids such as silicotungstic acid, phosphotungstic acid and phosphomolybdic acid. This chapter presents a brief summary of the work described in previous chapters and general conclusions arrived from the work.

Chapter 1 gives a general introduction about heteropoly acids (HPAs), its structure, classification, and catalytic properties. It also gives an introduction to supported-heteropoly acids and the conventional supports used for the preparation of supported-heteropoly acids. Further, this chapter gives an introduction to zirconia, its properties, and zirconia based solid acids. Finally, the aim of the thesis is given: to explore the possibility of the preparation of stable supported heteropolyacid catalysts.

Chapter 2 describes the procedure for the preparation of zirconia-supported heteropoly acids. The catalysts were characterized by different techniques such as surface area, X-ray diffraction, Raman spectroscopy, TG-DTA, XPS, FTIR pyridine adsorption, TPD of ammonia, DRUV-vis spectroscopy, $^{31}$P MAS NMR etc. Theory and experimental procedure employed for each technique is discussed in this section.

Chapter 3 describes the preparation of zirconia-supported silicotungstic acid catalyst with different STA loading (5-25 wt. %) and calcination temperature (600-850 °C), characterization by different techniques such as surface area, XRD, Raman spectroscopy, DTA, XPS, NH$_3$-TPD, FTIR pyridine adsorption, and DRUV-vis spectroscopy and application in veratrole benzoylation with benzoic anhydride and tert-butylation of phenol with tert-butanol. XRD results indicate that the presence of STA retards the crystallization of zirconia and stabilizes ZrO$_2$ in tetragonal phase. Characterization of the catalyst with optimum STA loading (15 %) by Raman spectroscopy showed the presence of zirconia-anchored mono-oxotungstate as the major tungsten species up to 750 °C. The catalysts showed both Brönsted as well as Lewis acidity and the catalyst 15 SZ-750 had the highest Brönsted acidity and total acidity.
Characterization of the catalysts by XPS shows that a monolayer of silicotungstate on zirconia was attained for the catalyst 15 SZ-750.

The activity of these catalysts depends on STA coverage and the catalyst with monolayer of silicotungstate on zirconia (15 SZ-750) shows the highest activity. Comparison of the catalytic activity of 15 SZ-750 with 15 SS-300 in veratrole benzoylation showed that STA supported on zirconia act as efficient and stable solid acid catalysts, while STA supported on silica gets leached into the reaction medium and catalyze the reaction homogeneously. These catalysts were also found to be efficient for tert-butylation of phenol. The deactivated catalyst could be regenerated by calcination with out appreciable lose in activity and selectivity.

Chapter 4 describes the preparation of zirconia-supported phosphotungstic acid catalysts with different PTA loading (5-20 %) and calcination temperature (650 to 850 °C), characterization by different techniques such as surface area, XRD, DTG-DTA, FTIR pyridine adsorption, NH$_3$-TPD and $^{31}$P MAS NMR spectroscopy measurements and application in the synthesis of linear alkyl benzenes by the alkylation of benzene with 1-octene and 1-dodecene and acylation of 2-MN with acetic anhydride. The catalyst with optimum PTA loading and calcination temperature (15 PZ-750) was prepared in different solvents and characterized by $^{31}$P MAS NMR spectroscopy. The XRD results indicate that PTA stabilizes the tetragonal phase of zirconia. The catalysts show both Brønsted and Lewis acidity and the catalyst 15 PZ-750 shows the highest acidity. $^{31}$P MAS NMR spectra show two types of phosphorous species, one is phosphotungstate which is in interaction with zirconia and the other is the decomposition product of PTA and the relative amount of each depend on PTA loading, calcination temperature and the solvent used for the catalyst preparation.

The activity of the catalyst in alkylation of benzene with 1-octene was found to depend on the solvent used for the catalyst preparation and solvents like methanol and DMF are the best for catalyst preparation. The catalyst with monolayer of PTA on zirconia (15 PZ-750) prepared in methanol showed the highest activity. In acylation of 2-MN, 15 PZ-750 catalyst showed deactivation due to product inhibition. The deactivated catalyst could be regenerated by calcination without appreciable loss in its activity and product selectivity.
Thus, 15 SZ-750 and 15 PZ-750 catalysts were found to be the most active catalysts and the activities of these catalysts were compared in benzylation of veratrole with benzoic anhydride and alkylation of diphenyl ether with 1-dodecene. In benzylation of veratrole, 15 SZ-750 catalyst showed different reaction profile compared to 15 PZ-750 catalyst, while in alkylation of diphenyl ether, both catalysts showed similar reaction profiles and 15 SZ-750 catalyst has higher activity than 15 PZ-750 catalyst. The kinetic profile of the reaction with 15 SZ-750 and 15 PZ-750 catalysts in veratrole benzylation indicated that product inhibition was more prominent with 15 PZ-750 catalyst. Thus, the higher conversion and greater deactivation resistance of 15 SZ-750 catalyst in benzylation of veratrole and also its higher activity in alkylation of diphenyl ether could be due to the presence of higher amount of strong Brønsted acid sites.

Chapter 5 describes the preparation of zirconia-supported phosphomolybdic acid catalysts with different PMA loading (5-25 %) and calcination temperature (500 to 750 °C), characterization by XRD and $^{31}$P MAS NMR spectroscopy measurements and application in the synthesis of linear alkyl benzenes by the reaction of benzene with 1-octene and 1-dodecene and tert-butylation of phenol with tert-butanol. The XRD results indicated that MPA stabilizes the tetragonal phase of zirconia. $^{31}$P MAS NMR spectra showed the presence of three types of phosphorous species, phosphomolybdate in interaction with zirconia, decomposition product of PMA and an unidentified species. FTIR pyridine adsorption on 15 MZ-700 catalyst showed the presence both the Brønsted and Lewis acidity.

The 15 MZ-700 catalyst showed the highest activity in alkylation of benzene with 1-octene and phenol with tert-butanol. In benzene alkylation, these catalysts deactivated mainly due to the formation of carbonaceous deposits on catalyst surface and phosphomolybdate reduction and the deactivated catalysts could be regenerated without appreciable loss in its activity and product selectivity. These catalysts were also highly active in tert-butylation of phenol but deactivated with time. In tert-butylation of phenol, catalyst deactivation was mainly due to the reduction of phosphomolybdate and leaching of PMA from the catalyst surface to the reaction medium.
Chapter 6 summarizes the conclusions made in this thesis.

Thus, the present work showed that heteropoly tungstic acids such as silicotungstic acid and phosphotungstic acid supported on zirconia acts as efficient and stable solid acid catalysts, while heteropoly molybdic acid such as phosphomolybdic acid supported on zirconia leaches to the reaction medium in presence of polar reactants.