CHAPTER 7

SUMMARY AND CONCLUSION

7.1 SUMMARY AND CONCLUSION OF THE PRESENT WORK

Catalysis is one of the most important tools of green chemistry as it minimises waste production in chemical reactions. Conventional synthesis of fine chemicals and pharmaceuticals utilizes stoichiometric equivalents of homogeneous catalyst such as mineral acids or Lewis acid catalysts. Selective oxidation reactions are pivotal transformation in organic synthesis which generates huge amount waste and the disposal is an environmental issue. Many of these transformations are currently performed both in the laboratory and industrial scale by the use of hazardous stoichiometric inorganic oxidants like Cr(VI) and Mn(VI) reagents. These acid and redox catalysts generate large amount of inorganic wastes. Further, the catalyst separation and reuse, disposable of the spent catalyst, corrosion and toxicity are series issues which lead to unfavourable ecological conditions. Solid acids find important application as heterogeneous catalyst. The surface area of the catalyst is an important factor because it increases the catalytic activity by exposing more active centers. Bronsted and Lewis acid sites present act as active sites in zeolites and zeotype molecular sieves. The linkage of SiO$_4$, AlO$_4$, PO$_4$ and other cations tetrahedra decides the framework shape and final structure type of zeolites and zeo-type molecular sieves.

The discovery of aluminophosphate (zeotypes) molecular sieves (AlPOs) widened the scope to tailormade neutral framework. However, the
The drawback of AlPO is its neutral zeotype. The incorporation of desirable heteroatom created active sites for several organic transformations. The framework incorporated PrAlPO-5 with different (Al+P)/Pr ratios were synthesized using appropriate precursors for aluminium, phosphorous and praseodymium in fluoride medium. The catalytic activity was evaluated in the oxidation of ethylbenzene and synthesis of campholenic aldehyde. Similarly, iron incorporated AlPO-5 molecular sieves with different Al/Fe ratios were synthesized and the catalytic activity was evaluated in the synthesis of biologically active 2,4-thiazolidinedione analogues. The summary and conclusions drawn from the study are delineated below.

The hydrothermal synthesis of PrAlPO-5 with different (Al+P)/Pr ratios viz., 25, 50, 75, 100, 150 and 200 was successfully accomplished in fluoride medium. The characterization using XRD, DRS-UV-vis, BET, and $^{27}$Al and $^{31}$P MAS-NMR techniques confirmed the incorporation of Pr in AlPO-5 framework.

The phase purity of PrAlPO-5 molecular sieves was confirmed by correlating the XRD patterns of PrAlPO-5 and XRD patterns of Pr$_6$O$_{11}$. The lattice parameters calculated for PrAlPO-5 were different from the parent AlPO-5. PrAlPO-5 showed higher surface area and pore volume than AlPO-5. All these observations confirmed the incorporation of praseodymium into the framework. The DRS-UV-Vis, ESR and XPS studies explained the electronic environment of praseodymium in PrAlPO-5. The appearance of two bands around 210 and 262 nm in DRS-UV-Vis spectra of PrAlPO-5 confirmed the presence of Pr$^{3+}$ and Pr$^{4+}$ species in tetrahedral environment. Further, the absence of peak between 415 and 590 nm in PrAlPO-5 confirmed the absence of extra-framework praseodymium species. The TPR-H$_2$ trace of PrAlPO-5 also confirmed the absence of praseodymium oxide species. The low temperature ESR studies confirmed the chemisorption of oxygen on
paramagnetic praseodymium species and unsymmetrical environment of praseodymium. The XPS spectrum of PrAlPO-5 confirmed the existence of praseodymium in +3 and +4 oxidation states. The incorporation of praseodymium substitution both Al and P in TO$_4$ tetrahedra was evidently proved from $^{27}$Al and $^{31}$P MAS-NMR spectra of PrAlPO-5. The SEM and TEM images established the presence of inter-particle voids in PrAlPO-5. The TPD-NH$_3$ study and the ex-situ pyridine adsorbed IR spectra revealed the nature and strength of acidity. Thus, the presence of both redox and acid sites in PrAlPO-5 was established. TGA and FT-IR spectra of PrAlPO-5 confirmed the complete removal of template.

The liquid phase aerobic oxidation of ethylbenzene over PrAlPO-5 with different (Al+P)/Pr ratios (25, 50, 75 and 100) demonstrated that the conversion of ethylbenzene and selectivity to acetophenone increased in the order: PrAlPO-5 (25) > PrAlPO-5 (50) > PrAlPO-5 (75) > PrAlPO-5 (100). This study also concluded that weak and moderately strong acid sites favoured side chain oxidation rather than ring hydroxylation. PrAlPO-5 (25) showed slightly higher selectivity to acetophenone (95%) and ethylbenzene conversion (95%) at 120 °C. The substituted ethylbenzenes altered the electron density around the benzylic hydrogen atom. Since benzylic oxidation was ascribed by hydrogen abstraction of the C-H bond, the electron density around benzylic hydrogen did not alter the selectivity to form the respective carbonyl compound.

PrAlPO-5 with different (Al+P)/Pr ratios viz., 75, 100, 150 and 200 were attempted in the synthesis of campholenic aldehyde from $\alpha$-pinene. The catalytic activity of the catalysts increased in the order: PrAlPO-5 (75) > PrAlPO-5 (100) > PrAlPO-5 (150) > PrAlPO-5 (200). The effect of reaction parameters such as reaction temperature, (Al+P)/Pr ratio, reaction time and solvent were optimised over PrAlPO-5 (75) for the synthesis of campholenic
aldehyde. The catalyst was found to play dual role both as redox and acid catalyst. The oxidation of $\alpha$-pinene occurred via chemisorbed oxygen on the praseodymium sites. The campholenic aldehyde formation was attributed to the isomerisation of $\alpha$-pinene oxide over Lewis acid sites of PrAlPO-5. This study concluded that weakly basic and non-polar solvents favoured the formation of campholenic aldehyde. This study also established the bifunctional nature of PrAlPO-5 catalysts.

The hydrothermal synthesis of FeAlPO-5 with different Al/Fe ratios (75, 100 and 150) was successfully accomplished in the fluoride medium. The characterization of the materials using XRD, DRS-UV-vis, BET, SEM, ESR, XPS, TPD-NH$_3$ and ex-situ pyridine adsorbed IR revealed the physico-chemical characteristics of the materials.

The powder XRD patterns of FeAlPO-5 catalysts displayed characteristic reflections of AlPO-5, which were indexed to $P6_{cc}$ space group. The increase of unit cell parameter from 11.51 to 11.82 Å with increase of Fe content was explained on the basis of atomic radius of Al and Fe. The atomic radius of Fe$^{3+}$ (0.49 Å) is larger than Al$^{3+}$ (0.39 Å), assuming the coordination number of both the atoms as four. This led to large Fe-O distance which ultimately changed the unit cell constant of the materials. Moreover, these observations suggested that Fe atoms were successfully incorporated into AlPO-5 framework. FeAlPO-5 samples exhibited type I nitrogen adsorption-desorption isotherms characteristics of microporous material. The UV-Vis DRS spectra of FeAlPO-5 samples revealed that most of the Fe atoms in AlPO-5 framework occupied tetrahedral position, which was further confirmed from the results obtained from ESR spectroscopy. The TPD-NH$_3$ study and ex-situ pyridine adsorbed IR spectra revealed the presence of mild Lewis acidic nature in FeAlPO-5.
The catalytic activity of FeAlPO-5 catalysts with different Al/Fe ratios was tested in the Knoevenagel condensation of aromatic aldehydes with 2,4-thiazolidinediones. The catalytic activity of the catalysts increased in the order: FeAlPO-5 (75) > FeAlPO-5 (100) > FeAlPO-5 (150). The reaction parameters such as reaction temperature, reaction time and solvent were optimised with FeAlPO-5 (75) for high conversion and selectivity. The Knoevenagel condensation of several substituted benzaldehydes and heterocyclic aldehydes with 2,4-thiazolidinedione under optimised reaction conditions using water-ethanol (4:1) mixture as solvent was successful. This study revealed that FeAlPO-5 is a good catalyst for green synthesis of a range of TZD analogues.

7.2 SCOPE FOR FUTURE WORK

The present investigation results concluded that Pr incorporated AlPO-5 is a convenient eco-friendly redox catalyst for aerobic oxidation of alkyl aromatics. PrAlPO-5 can be used not only as a redox catalyst but also solid acid catalyst. The bi-functional nature of PrAlPO-5 catalyst will open new prospect for potential application in the synthesis of fine chemicals. Further, it is also confirmed that FeAlPO-5 is an efficient catalyst for the Knoevenagel condensation. With suitable modifications and reaction conditions, it is expected these materials can be exploited for other organic transformations. Synthesis of ciprofloxacin analogues using FeAlPO-5 is in the pipeline.