Chapter 7

Summary and future scopes

7.1 Summary of the present work

The major findings of the thesis are highlighted chapter wise below:

Chapter 2

- A new series of three -SO_3H functionalized chlorometallates $[Dsim]_2[ZnCl_4]$, $[Dsim][FeCl_4]$, $[Dsim]_2[NiCl_4]$ was prepared as solid material from the reaction of 1, 3-disulfoimidazolium chloride with certain mole fractions of respective metal chlorides such as $ZnCl_2$, $FeCl_3$, and $NiCl_2$.
- All these acidic solids were characterized *via* FTIR, NMR, TGA, UV-Visible, PXRD, SEM, EDX, Raman, ICP-OES and CHN analysis. Also, their Hammett acidities were determined by UV-Visible Hammett plot method.
- They were tested as reusable heterogeneous catalysts for Mannich-type reaction in EtOH at atmospheric condition.

Chapter 3

- A new type of photo-activated HZSM-5 hybrid materials each of which loaded with five different percentages (such as 3%, 6%, 9%, 17% and 50%) of the semiconductor Ni(II) ionic salt $[Dsim]_2[NiCl_4]$ was prepared through wet impregnation method.
- All the loaded samples were subjected to various analyses such as FTIR, TGA, PXRD, SEM, EDX, BET, TEM, UV, Raman, Hammett acidity, photoluminescence and ICP-OES technique *etc.*
- Structural modification of HZSM-5 framework during preparation of composite materials were observed after thermal initiated dealumination followed by reinsertion and desilication of framework Al upon treatment with acidic salt which clearly described the retention of crystalline structure and stability up to 17% loaded material. The highest loaded material suffered destruction of framework.
- Photoluminescence spectra established 9% and 17% loaded materials as best photocatalysts due to low electron-hole recombination.
- These hybrid materials are investigated as possible heterogeneous photocatalysts for degradation of methylene blue (MB) at atmospheric condition involving H_2O_2/sunlight initiated Wet Hydrogen Peroxide Catalytic Oxidation Process (WHPCO).

- The highest degradation ability was achieved by 9% loaded material which was further supported by kinetic study as well as TOC (total organic carbon) determination.
- The catalyst was reused for three more cycles with a little loss of activity which was further characterized by PXRD and FTIR analysis.

Chapter 4

- A series of Brönsted-Lewis acidic 1, 3-disulfoimidazolium chlorozincate ($[Dsim]_2[ZnCl_4]$) ionic salt immobilized HZSM-5 materials was prepared in different w/w ratios (3%, 6%, 9% 17% and 50%) by wet impregnation method.
- These dual acidic materials were completely characterized by FTIR, TGA, PXRD, SEM, EDX, BET, UV, Raman, Hammett acidity, and ICP-OES technique *etc.*
- Their catalytic efficiency as dual acidic catalyst was tested for Fischer indole reaction of phenylhydrazine hydrochloride with aliphatic/aromatic ketones.
- Significant surface area and excellent thermal stability of these heterogeneous materials along with limiting hygroscopic nature upgraded their catalytic ability.
- Lewis acidity imparted by $ZnCl_4^{2-}$ enhanced the efficiency together with the Brönsted acidity of the catalyst.
- Easy recyclability of these catalysts made them reuse for ten cycles with minimum loss of activity. Later reused catalysts were studied by PXRD and ICP-OES analysis.

Chapter 5

- Ionic liquid derived polyoxometallate salts $[mdsim]_3[PM_{12}O_{40}]$ (where M = W and Mo) of two heteropolyacids $H_3PW_{12}O_{40}.nH_2O$ (PTA) and $H_3PMo_{12}O_{40}.nH_2O$ (PMA) were synthesized using 2-methyl-1, 3-disulfoimidazolium chloride [mdsim][Cl] ionic liquid and the corresponding heteropolyacids.
- These polyoxometalate ILs were characterized using different analytical techniques such as NMR, FTIR, TGA, UV-Visible, PXRD, DR-spectroscopy, SEM, EDX *etc.*
- Dual $-SO_3H$ functionalized thermally stable water insoluble salts were examined as heterogeneous catalyst for nitration of various aromatic

compounds using 69% HNO_3 at room temperature or heating condition without use of conc.H_2SO_4.

- ❖ Catalytic use of these hydrophobic POM salts introduced several advantages to aromatic nitration which include complete replacement of corrosive sulfuric acid, controlled use of 69% nitric acid, mild reaction procedure, and minimal release of reddish brown fumes of nitrogen dioxide, simple isolation of product, recycling of catalyst in heterogeneous phases, shorter reaction time and also release of less acid waste.
- ❖ These POMs were reusable for five consecutive cycles with retention of activity. The recycled catalyst was further characterized *via* PXRD and FTIR analysis.

Chapter 6

- ❖ Three new members of $–SO_3H$ functionalized dicationic ionic liquids based on N, N, N', N'-tetrasulfopiperazinium cation $[TSPi]^+$ and various counter anions $[X]^-$ (X = Cl, CF_3SO_3 & TsO) were prepared and fully characterized using ^1H NMR, ^{13}C NMR, FTIR, elemental and thermogravimetric analyses.
- ❖ $[TSPi][CF_3SO_3]_2$ with highest Hammett acidity value was screened as best acidic catalyst for synthesis of 2-amino-4, 6-diaryl pyrimidines from *in situ* generated Biginelli-like DHPMs through sequential condensation-aromatization reaction with phenylhydrazine.
- ❖ These newly synthesized 2-amino pyrimidine derivatives were confirmed by NMR, FTIR, elemental analysis and melting point.
- ❖ The acidic ionic liquid was recycled and reused for three more cycles with minimum loss of activity.

7.2 Future scopes of the present work

- ❖ This study discloses a greater number of ways towards the field of functionalized ionic liquids which will contribute in the synthesis of more ionic liquids with different structural variations and diverse physicochemical properties.
- ❖ Target oriented synthesis of new functionalized ionic liquids or ionic liquid based systems will have the multifaceted role in various applications like electrochemistry, photochemistry and many other industrial processes.

- Development of new photocatalytic systems involving chlorometallate ILs and polyoxometalate ILs for degradation of pesticides and harmful dyes.
- Synthesis of more number of task specific piperazinium dicationic ionic liquids with varied organic or inorganic anions and study their physical properties for electrochemical uses.
- Design of chiral ionic liquids and their catalytic uses in asymmetric synthesis.