

## *Chapter 7*

**Summary and future scopes of the present work**

## 7.1. Summary of the present work

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

### Chapter 1

- ❖ A new class of solid acids of 3-methyl-1-sulfonic acid imidazolium transition metal chlorides ([Msim][X]: where X = FeCl<sub>4</sub>, CuCl<sub>2</sub>, Zn<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> containing both Lewis and Brønsted acidic sites were prepared from the reaction of 3-methyl-1-sulfonic acid imidazolium chloride with equimolar amount of FeCl<sub>3</sub>, CuCl and ZnCl<sub>2</sub> at 60°C.
- ❖ All these solid acids were fully characterized via FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, Raman, P-XRD, SEM, EDX, BET, AAS and elemental analysis. The thermal stability of the solid acids was assessed using thermo gravimetric analysis. The relative Brønsted acidities of the acids were determined on an UV-Vis spectrophotometer via the Hammett plot.
- ❖ The catalytic activities of these solid acids were explored as heterogeneous catalyst for the synthesis of *bis*(indolyl)methanes using ethyl acetate as solvent at room temperature stirring within short time.
- ❖ The reusability of the solid acids was also studied using the model reaction and found to be reusable for three consecutive cycles with little loss in catalytic activity.

### Chapter 2

- ❖ Six acidic composites of Y-zeolite with 1, 3-disulfoimidazolium trifluoroacetate [Dsim][CF<sub>3</sub>COO] ionic liquid (IL) were prepared by mixing [Dsim][CF<sub>3</sub>COO] ionic liquid with NaY zeolite powder in six different percentage ratios (weight/weight) expressed as 3%, 5%, 10%, 20%, 50% and 80% in methanol
- ❖ The structural changes of the modified framework of zeolite were analyzed by FT-IR, P-XRD, SEM-EDX, TEM, TGA and BET techniques. The relative acidities of the composites were determined from the Hammett plot on an UV-Vis spectrophotometer.
- ❖ The maximum permissible limit found for loading of the IL over zeolite surface was 20%. Loading above this percentage was harmful for the zeolite framework

due to maximum dealumination as evidenced from the FT-IR and P-XRD patterns of the 50% (**f**) and 80% (**g**) loaded composites.

- ❖ Formation of EFAI species on loading of the acidic IL affected the Si/Al ratio of the composites which in turn may also affect the acidity scale of the composites.
- ❖ The strongly acidic 20% loaded composite (**e**) was evaluated as heterogeneous catalyst for synthesis of DHPMs derivatives under solvent-free thermal condition at 60°C and at ambient temperature using solvent-free grinding method.
- ❖ The reusability study for composite **e** indicates its high catalytic activity up to 6<sup>th</sup> consecutive cycles. FT-IR and P-XRD analysis data for reused catalyst collected after 6<sup>th</sup> cycle supports the integrity of the system.

### Chapter 3

- ❖ A new type of acidic hybrid material of NaY zeolite were synthesized by modifying the zeolite surface with 1-sulfonic acid-3-methyl imidazolium ferric chloride ([Msim][FeCl<sub>4</sub>]) ionic salt in six different weight/weight ratios namely, 0.03, 0.05, 0.1, 0.2, 0.5 and 1.
- ❖ These composites were fully characterized by Powder XRD, FT-IR, Raman, TGA, SEM-EDX, TEM, BET, ICP-OES and Hammett acid strength measurement methods.
- ❖ Loading up to the w/w ratio of 0.2 was found to be the maximum permissible limit for the zeolite framework without destruction as observed from the IR and PXRD studies. Acid mediated dealumination produces extraframework Al species within the zeolite structure.
- ❖ The zeolite structure got completely destroyed in case of composites **f** (w/w ratio of 0.5) and **g** (w/w ratio of 1) for maximum observation of acid initiated dealumination of framework Al to extraframework Al species
- ❖ The most acidic [Msim][FeCl<sub>4</sub>]/NaY=0.1 composite utilized as efficient reusable heterogeneous catalyst towards the sequential one-pot conversion of *in situ* formed Biginelli 3,4-dihydropyrimidin-2(1H)-one to multifunctionalized 2-amino-4-arylpyrimidines.
- ❖ The presented methodology proved to be a novel efficient route towards the development of pyrimidines in less time and would be applicable for the library

synthesis of 2-amino-4-arylpurimidine derivatives without using any oxidizing agents and solvents with easy purification.

#### Chapter 4

- ❖ Four different chlorometallates of disulfo-diisopropyl-ammonium ionic salt with complex ionic composition ; ([DSDIP]<sub>x</sub>[A]: where [A]= [FeCl<sub>4</sub>]<sup>-</sup>, [NiCl<sub>4</sub>]<sup>2-</sup>, [Zn<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup>/[Zn<sub>4</sub>Cl<sub>10</sub>]<sup>2-</sup>, [CoCl<sub>4</sub>]<sup>2-</sup> and x = 1, 2 were prepared from the 1:1 reaction mixture of disulfodiisopropylammonium chloride with four transition metal chlorides ( such as FeCl<sub>3</sub>, ZnCl<sub>2</sub>, NiCl<sub>2</sub> and CoCl<sub>2</sub>) in an inert atmosphere. The ionic salts were characterized with FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, Raman, TGA and electronic spectroscopy analysis.
- ❖ The anionic speciation of the synthesized chlorometallate salts were examined using the combined indicative studies of FT-IR, Raman and electronic spectroscopy.
- ❖ The acidity study revealed that the overall Brönsted and Lewis acidity order for these salts depend on the anionic speciation and also their tendency to form secondary co-ordination shell in association with other anionic species present in the ionic liquid salt.
- ❖ Out of the two acidic sites, the Brönsted acidic site has major role for catalyzing the three-step one pot synthesis of styrylpyrimidines involving Biginelli DHPMs under solvent-free thermal method using only 10 mol% of the strong Brönsted acidic [DSDIPA][FeCl<sub>4</sub>] (**IL I**).
- ❖ The reusability study for **IL I** revealed retaining of significant catalytic activity up to third consecutive cycle.

#### Chapter 5

- ❖ A series of structurally varied –SO<sub>3</sub>H functionalized PEG-6000 linked imidazolium/diphenylammonium based dication ionic liquids of four different anions (trifluoroacetate, trichloroacetate, acetate and hydrogen sulfate) were developed and characterized with various analytical tools.
- ❖ The catalytic efficiencies of these Brönsted acidic ILs were explored for the conversion of fructose to 5-hydroxymethylfurfural (HMF) in three different solvents, such as EtOAc, THF and CH<sub>3</sub>CN and analyzed with HPLC technique.

- ❖ The variation of acidic strength of the ILs did not affect the selectivity of HMF in the reaction. The dosage of the catalyst also had an impact on the outcome of the reaction.
- ❖ The efficient isolation of HMF by solvent extraction process depends on the loose H-bonding ability of anion of DIL with the HMF molecule during work-up step which may also be accounted for loss of catalytic efficiencies of the IL as observed in the recyclability study for **IL 5** up to 3<sup>rd</sup> run.

## Chapter 6

- ❖ A new series of triethylamine bridged basic tricationic ILs (**TILs**) of imidazolium/pyridinium were designed in combination with variation of three anions such as hydroxide, acetate and imidazolidide.
- ❖ The synthesized basic TILs were analyzed with FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, TGA and elemental analysis. The relative Brønsted basicity of the TILs was determined from Hammett plot using *p*-nitrophenol as acidic indicator.
- ❖ TGA analysis expressed thermal stabilities within the range of 100-150°C for these **TILs**.
- ❖ All the basic **TILs** were investigated as efficient reusable catalysts for preparation of functionalized alkenes through Knoevenagel condensation at mild condition irrespective of their measured Hammett basicity values.
- ❖ The **TILs** were stable in water and also efficiently catalyzed the functionalized alkenes in water at room temperature reaction.

## 7.2. Future scopes of the present work

- ❖ More systematic structural variations in the -SO<sub>3</sub>H functionalized or non-functionalized ILs will generate newer class of ILs with greater control over physicochemical properties.
- ❖ Apart from the catalytic uses, these functionalized or non-functionalized materials can be designed to be applicable as surfactant, chromatographic stationary phases, ligands in complex synthesis, mobile phase additives or electroosmotic flow modifiers in high-performance liquid chromatography, stabilizer in nano-synthesis and in capillary electrophoresis. They can also be employed in different industrial processes like metal ion extraction process,

removal of pollutants from refinery feed stocks, membrane separation process, electro depositions of metals, desulfurization of fuels etc.

- ❖ Investigation of biological activities of 2-aminopyrimidine derivatives and styrylpyrimidine derivatives.
- ❖ Development of efficient extraction process for separation of 5-hydroxy methyl furfural from the reaction mixture in presence of the DILs.
- ❖ Synthesis of chiral ionic liquids and their application in asymmetric syntheses.