

Abstract

Background of the present work

Ionic liquids represent a range of room temperature liquids or molten salts with significant physical properties like negligible vapour pressure, non-flammability, excellent solvating ability *etc.* These fascinating properties have been the basis of their evolution as solvent or catalyst in organic synthesis. Being compositionally diverse due to presence of a cationic and an anionic part ionic liquids possess functional variability. Depending on their nature of organic cations and organic or inorganic anions they can work accordingly. For example, in presence of Brønsted acidic group on cation makes them Brønsted acidic while Lewis acidic anionic counterpart contributes Lewis acidity and presence of both make them Brønsted-Lewis acidic in nature. Similarly they can be basic or neutral. An important class of Lewis acidic ionic liquids is chlorometallates bearing generally transition metal or Group IIIA metal chlorides as complex anion which showed variation in their physicochemical properties depending on the identity and concentration of metal species and thus specify their applications in different fields. Thus, tuning task specificity in ionic liquid has been quite interesting to the chemists to employ them as dual solvent-catalyst system and in other physicochemical processes as well. Moreover, metal based ionic liquids with semiconductor properties can be a great option for photocatalysis.

Despite all the excellent abilities of room temperature ionic liquids, researchers have been exploring several ways to upgrade their properties by modification through various means. To improve thermal, air and water sensitivity of the ILs, immobilization on high surface area materials like silica, alumina, zeolite, clay, polymer *etc.* through physical or chemical interactions has been adopted widely. Immobilized ionic liquids bring advantages like thermal stability, hydrophobicity and high surface area to the materials which in combination with specific properties of ionic liquid acts as promising candidate for versatile applications. The halometallate ionic liquids of transition metal with low band gap value have a scope to explore as photocatalyst in photocatalytic reactions like semiconductor metal oxide and metal salts. Therefore, limiting the disadvantage of moisture sensitivity and low thermal stability by immobilization they can be modified as good photocatalytic system for degradation of organic pollutant.

Another type of metal based ionic salt system is the organic-inorganic hybrids composed of organic cation from ionic liquid and anion of heteropolyacid with structural variety which has tunable functionality in cation as acidic, basic or neutral as well as polyhedral framework of anion due to possession of transition metal in higher oxidation state. This type of material is known as polyoxometalate generally consists of inorganic cations like H^+ , Na^+ or K^+ . But unlike inorganic cations, organic cations have the attractive ability of tuning their property which together with the active sites of polyanion of heteropolyacids results into very stable homogeneous or heterogeneous polyoxometalates. Thus, the polyoxometalate holds enough opportunity to develop new materials as catalyst.

Depending on the number of cations ionic liquids can be classified as mono, di, tri or tetra cationic. With increase in cationic sites their properties transform. Dicationic ionic liquids are comparatively more stable and have improved physicochemical properties as compared to monocationic analogues. Combination of two similar or different cations with various anions along with some bridging groups introduces many benefits to dicationic ionic liquids. However, literature reveals that almost all the dicationic ionic liquids have cations separated by a linker and somewhat have complex structure. There are only few reports on dicationic ionic liquids having dicationic site on the same molecule which inspires us to design such type of dicationic ionic liquids.

Organic reactions have their individual importance. N-heterocycles are key building blocks for many biologically and pharmacologically active compounds which consist of a huge array of important drug molecules. Similarly nitro aromatic compounds are also necessary feedstock for various dyes, perfumes, pharmaceuticals and many more. Another type of compounds that influence the environment by their harmful effects is organic pollutants such as organic dyes. To remove these toxic chemicals photocatalytic degradation using active photocatalysts is performed which break them into environment friendly minerals.

Objectives

[1] Synthesis and characterization of Brønsted-Lewis acidic chlorometallates of transition metal chlorides and exploration of their catalytic properties in organic synthesis.

[2] Immobilization of chlorometallate salts with low band gap value on porous support and utilize the composite materials as heterogeneous catalyst for photocatalytic degradation of organic pollutant as well as in the synthesis of heterocycles.

[3] Synthesis and characterization of organic-inorganic hybrid of polyoxometalate ionic liquid material and their uses as reusable heterogeneous acidic catalyst for nitration of aromatic compounds.

[4] Development of new methodology involving task specific acidic dicationic ionic liquids for synthesis of important N-heterocycles *via* one-pot approach.

[6] Characterization of all the synthesized organic compounds using proton NMR, ¹³C NMR and FT-IR spectroscopic techniques, elemental analysis, and also melting point determination.

Plan of work

[1] Synthesis of –SO₃H functionalized chlorometallate systems of different transition metal chlorides and apply them as reusable heterogeneous catalyst in the Mannich-type reaction.

[2] Determination of band gap of the synthesized chlorometallates for further use as photocatalyst.

[3] Immobilization of –SO₃H functionalized chlorometallate with low band gap value on to high silica zeolite surface and determine their catalytic activity as high surface area heterogeneous photocatalyst for degradation of organic dye molecule under sunlight irradiation using advanced oxidation process.

[4] Exploration of immobilized chlorometallate/zeolite materials as reusable heterogeneous catalyst in Fischer indole reaction.

[5] Synthesis of –SO₃H functionalized polyoxometalate organic-inorganic hybrid materials and determine their activity in the nitration of aromatics.

[6] Designing of new –SO₃H functionalized dicationic ionic liquids for the synthesis of various pyrimidine derivatives under mild reaction condition.

[7] Characterization of all the synthesized ionic liquid systems through various analytical techniques such as NMR, FTIR, TGA, UV-Visible, PXRD, Raman, SEM, EDX, TEM, BET, AAS, ICP-OES, photoluminescence, CHN *etc.*

Outline of the thesis

This work explains the synthesis of different Brønsted or Brønsted Lewis acidic ionic liquid systems and ionic salt immobilized zeolite composites, their characterization and applications in organic reactions. The thesis is divided into **seven chapters** and the chapter numbers from **2 to 6** are subdivided into **two sections**.

Chapter 1: General introduction of ionic liquid derived catalytic systems

This chapter offers a brief overview of importance and properties of different types of ionic liquids catalysts and their modified catalytic systems for potential uses in organic reactions depending on specific nature of them which are included in the thesis.

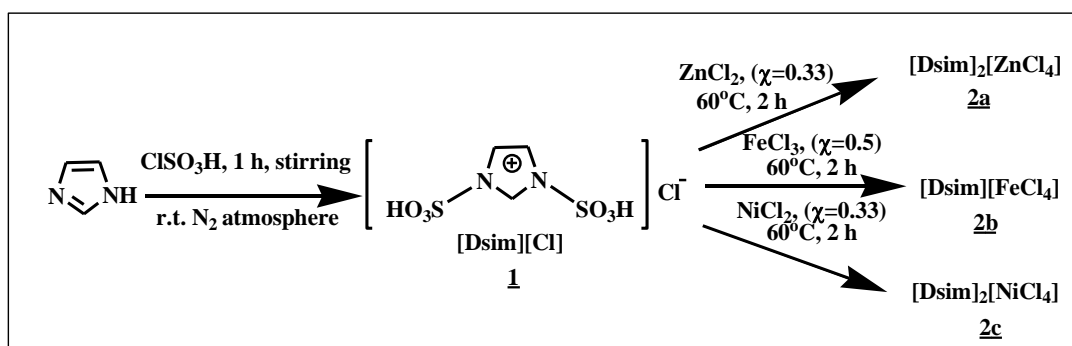
Chapter 2: Exploration of multifaceted acidic 1, 3-disulfoimidazolium chlorometallates as heterogeneous catalysts for preparation of β -amino carbonyl compounds *via* Mannich-type reaction

This chapter consists of two parts **Section 2A** and **Section 2B** with the following sub-headings.

Section 2A: Review of literature

This section gives general introduction of chlorometallate ionic liquids, their properties and review of different types of chlorometallates of Zn, Fe and Ni elements. Also, it includes a short note on importance of β -amino carbonyl compounds, their common synthetic roots and ionic liquid catalyzed synthesis procedures.

Section 2B: Results and discussion



Scheme 2B.1: Synthesis of 1, 3-disulfoimidazolium chlorometallates

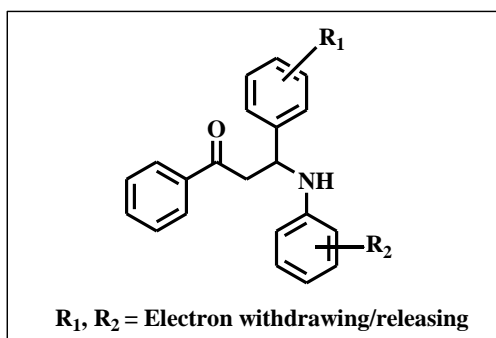


Fig.2B.1: Structure of β -amino carbonyl compound

This section contains synthesis of three $-\text{SO}_3\text{H}$ functionalized imidazolium chlorometallate salts of transition metal chlorides namely ZnCl_2 , FeCl_3 and NiCl_2 (**Scheme 2B.1**). They were characterized by 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. These ionic salts were tested as reusable heterogeneous catalysts for Mannich-type reaction in ethanol at atmospheric condition. Only 5 mol% of the catalyst was efficient enough to afford 82-96% yield of β -amino carbonyl compounds (**Fig.2B.1**). Easily recyclable ionic solids were reused for two more cycles without loss of noticeable activity.

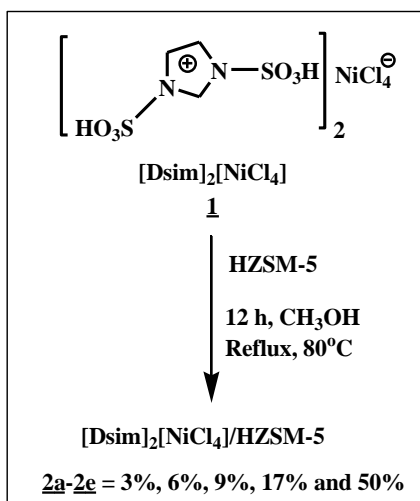
Chapter 3: Studies on 1, 3-disulfoimidazolium chloronickellate immobilized HZSM-5 framework as visible-light induced heterogeneous photocatalyst for degradation of organic dye using advanced oxidation process

This chapter consists of two parts **Section 3A** and **Section 3B** with the following sub-titles.

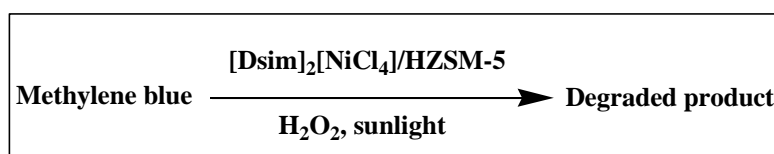
Section 3A: Review of literature

This section proceeds with description of zeolite structure, properties and mainly focuses on high silica ZSM-5 zeolite along with their framework modification through various techniques which make them advantageous to act as support material in development of different catalytic systems. This is followed by a review of literature on ionic liquid immobilized ZSM-5 catalysts. Apart from this a review of photocatalytic degradation of dyes *via* advanced oxidation process (AOPs) involving ionic liquid systems is included in this section.

Section 3B: Results and discussion



Scheme 3B.1: Preparation of [Dsim]₂[NiCl₄]/HZSM-5 composites



Scheme 3B.2: Dye degradation using advanced oxidation process

This section describes synthesis and characterization of 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 Ni(II) ionic salt [Dsim]₂[NiCl₄] through wet impregnation method (**Scheme 3B.1**). All the materials were analyzed by FTIR, TGA, PXRD, SEM, EDX, BET, TEM, UV, Raman, Hammett acidity, photoluminescence and ICP-OES techniques. These hybrid materials were investigated as possible heterogeneous photocatalysts for degradation of methylene blue (MB) at atmospheric condition involving H₂O₂/sunlight initiated Wet Hydrogen Peroxide Catalytic Oxidation Process (WHPCO) (**Scheme 3B.2**). These thermally stable less hygroscopic solids are reusable up to four cycles.

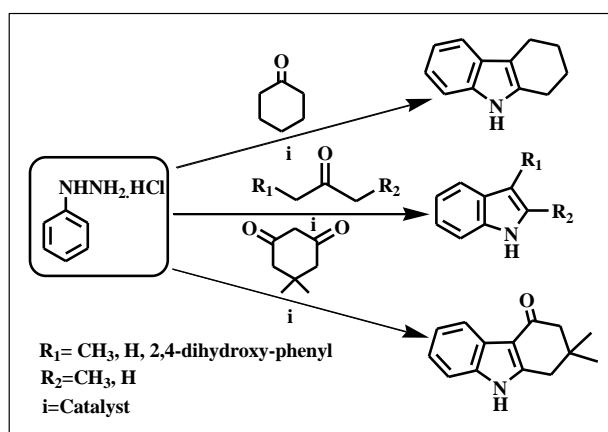
Chapter 4: Design of dual acidic 1, 3-disulfoimidazolium chlorozincate supported HZSM-5 materials and their catalytic use in the synthesis of indole derivatives

This chapter consists of two parts **Section 4A** and **Section 4B** with the following sub-titles.

Section 4A: Review of literature

This section covers a short note of chlorometallate ionic liquids which is followed by an introductory description of biological importance and various synthetic routes of indole derivatives. Further it focuses on methodologies adopted for Fischer indole synthesis and concludes with a review of ionic liquid mediated or catalyzed Fischer indole reaction.

Section 4B: Results and discussion



Scheme 4B.1: Fischer indole reaction

Brønsted Lewis acidic ionic salt 1, 3-disulfoimidazolium chlorozincate $[\text{Dsim}]_2[\text{ZnCl}_4]$ were immobilized onto HZSM-5 support by wet impregnation method similar to the **Scheme 3B.1** and various percentages of ionic salt loaded HZSM-5 materials were prepared i.e. 3%, 6%, 9%, 17% and 50%. These materials were also studied by FTIR, TGA, PXRD, SEM, EDX, BET, UV, Raman, Hammett acidity, and ICP-OES techniques. The stable acidic solids were utilized as catalyst for Fischer indole reaction of equimolar amounts of phenylhydrazine hydrochloride and various aliphatic or aromatic ketones at 80-90°C in neat condition to produce substituted indole derivatives with 80-94% yield (**Scheme 4B.1**). The efficient 17% ionic salt-loaded HZSM-5 composite was successfully reused for ten consecutive cycles with a slight loss of its activity. The recycled catalyst was further characterized using powder X-ray diffraction and inductively coupled plasma optical emission spectrometric techniques. Later the synthesized indole derivatives were analyzed by NMR, FTIR, CHN and melting point.

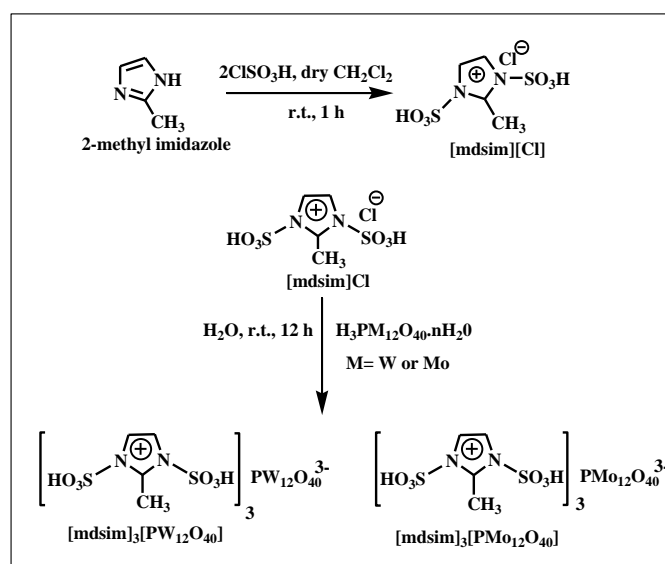
Chapter 5: A study on 2-methyl-1, 3-disulfoimidazolium polyoxometalate hybrid catalytic systems as safer alternative for sulfuric acid in nitration of aromatics

This chapter consists of two parts **Section 5A** and **Section 5B** with the following sub-titles.

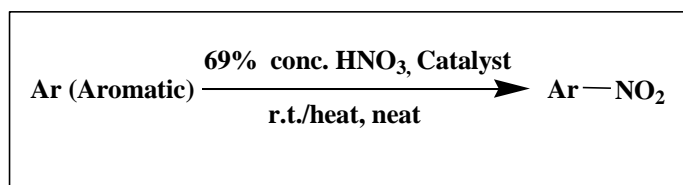
Section 5A: Review of literature

This section includes brief description of hybrid organic-inorganic polyoxometalates (POMs), -SO₃H functionalized polyoxometalate ionic salts and their importance as catalysts. Next part of the section discusses a review on nitration of aromatic compounds using ionic liquid system.

Section 5B: Results and discussion



Scheme 5B.1: Synthesis of N-SO₃H functionalized 1, 3-disulfoimidazolium POM-salts [mdsim]₃[PW₁₂O₄₀]³⁻ and [mdsim]₃[PMo₁₂O₄₀]³⁻



Scheme 5B.2: Nitration of aromatics

This section describes the synthesis of ionic liquid derived polyoxometalate salts [mdsim]₃[PM₁₂O₄₀] (where M = W and Mo) of two heteropolyacids H₃PW₁₂O₄₀.nH₂O (PTA) and H₃PMo₁₂O₄₀.nH₂O (PMA) using 2-methyl-1, 3-disulfoimidazolium chloride [mdsim][Cl] ionic liquid and the corresponding heteropolyacids (**Scheme 5B.1**). These polyoxometalates were characterized using different analytical techniques such as NMR, FTIR, TGA, UV-Visible, PXRD, DR-spectroscopy, and SEM-EDX. Dual -SO₃H functionalized thermally stable salts were examined as heterogeneous catalyst for nitration of various aromatic compounds within short time by 69% HNO₃ at room temperature or heating condition which avoids the use of additional conc.H₂SO₄ (**Scheme**

5B.2) as stoichiometric reagent. These nitro compounds were characterized by NMR, FTIR, CHN and melting point. Both the acidic salts were used as efficient catalyst for aromatic nitration which can be easily recycled and reusable up to four more cycles with retention of activity. These catalysts function as alternative solid substitute of conc. H₂SO₄ in nitration reaction.

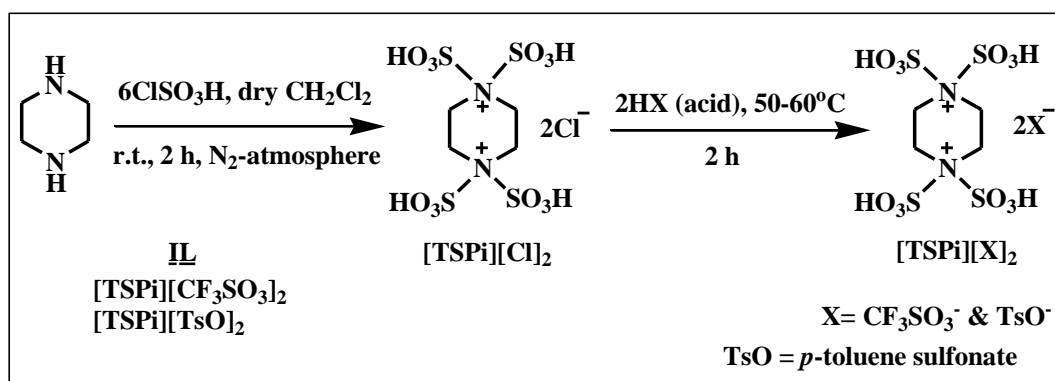
Chapter 6: N, N, N', N'-tetrasulfopiperazinium dicationic ionic liquids as prominent acidic catalyst for one pot synthesis of 2-amino-4, 6-diaryl pyrimidines

This chapter consists of two parts **Section 6A** and **Section 6B** with the following sub-titles.

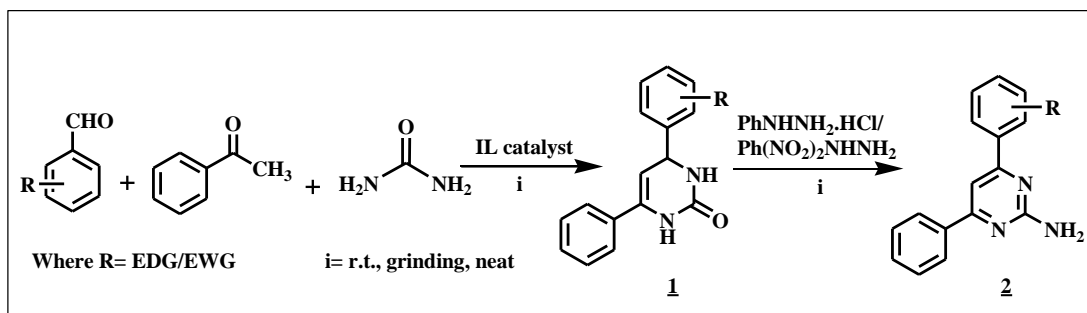
Section 6A: Review of literature

This section gives a comparison between monocationic and dicationic ionic liquid in terms of certain properties and points out dicationic ionic liquids (DILs) as better option in some cases. It explains the importance of piperazinium dicationic core and thus offers a review on piperazinium DILs. Rest of this section describes the biological and pharmacological importance of pyrimidine derivatives as well as their synthetic routes involving Biginelli-like reactions. A review on ionic liquid mediated or catalyzed Biginelli-like reaction to synthesize pyrimidine derivatives is mentioned here. Very few reports on ionic liquid catalyzed/mediated conversion of Biginelli-like dihydropyrimidones (DHPMs) to pyrimidines are found.

Section 6B: Results and discussion



Scheme 6B.1: Synthesis of [TSPi][X]₂ (X = Cl, CF₃SO₃ & TsO)



Scheme 6B.2: One pot two step synthesis of 2-amino pyrimidine derivatives

A new series of $-\text{SO}_3\text{H}$ functionalized dicationic ionic liquids based on N, N, N', N'-tetrasulfopiperazinium cation $[\text{TSPi}]^+$ and various anions $[\text{X}]^-$ ($\text{X}^- = \text{Cl}, \text{CF}_3\text{SO}_3$ & TsO (*p*-toluene sulfonate)) was synthesized and characterized with NMR, FTIR, TGA and elemental analysis. Brønsted acidity of these ionic liquids was measured by Hammett plot using UV-Visible absorbance spectra. Further they were examined as strong acidic catalyst for the synthesis of 2-amino-4, 6-diaryl pyrimidines through Biginelli-like reaction of acetophenone, aromatic aldehyde and urea followed by condensation with phenylhydrazine. This method involved one pot two step room temperature grinding in neat condition which afforded good to satisfactory yield within 16-30 min without isolation of the Biginelli dihydropyrimidinone intermediate. $[\text{TSPi}][\text{CF}_3\text{SO}_3]_2$ was found to be most efficient among the three homogeneous ionic liquids and reusable upto four times without loss of significant activity. Easy recyclability, simple and favorable reaction conditions represent the advantages of this method.

Chapter 7: Summary and future scopes