

Chapter 1

General introduction of ionic liquid derived catalytic systems

1.1 Ionic liquids: A brief overview as catalyst

Ionic liquids (ILs) have been explored as room temperature liquids or molten salts with enormous importance in organic synthesis as reaction medium or solvent-catalyst. The three generations of ionic liquids (**Fig.1.1**) namely (1) 1st generation in 1980s-chloroaluminates, (2) 2nd generation in 1990s-air and water stable ILs and (3) 3rd generation in 2000-task specific ILs [1] mainly composed of endless number of appropriate combination of cations and anions involving ionic-covalent interactions which led to modification of physical and chemical properties of the ionic material to achieve their required target specificity [2-7]. In organic reactions, they have been employed as benign solvent owing to diverse physical properties accordance to their ion-pair composition which includes viscosity, thermal stability, vapor pressure, non-flammability *etc.* Most of the ionic liquids have been studied as excellent homogeneous catalytic systems with greater catalytic ability and efficiency in the field of organic synthesis [1, 3 & 8]. A large number of heterogeneous catalytic systems have been developed to improve thermal, air and water sensitivity of the ILs after immobilization on high surface area materials like silica, alumina, zeolite, clay, polymer *etc.* through physical or chemical interactions [9-11].

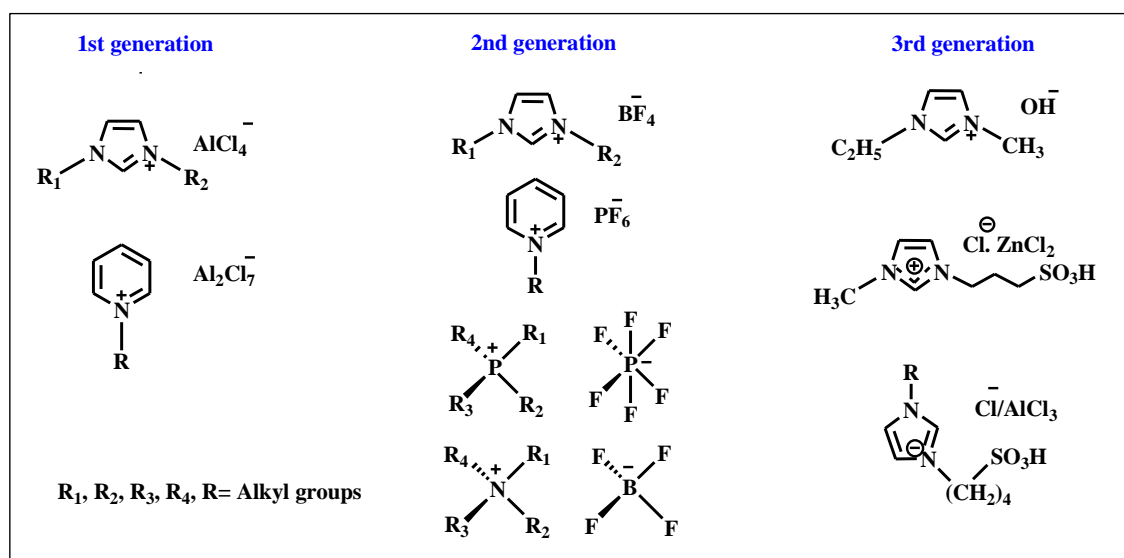


Fig.1.1: Three generations of ionic liquid

Further they can be widely divided into different categories according to the nature of their design (**Fig.1.2**).

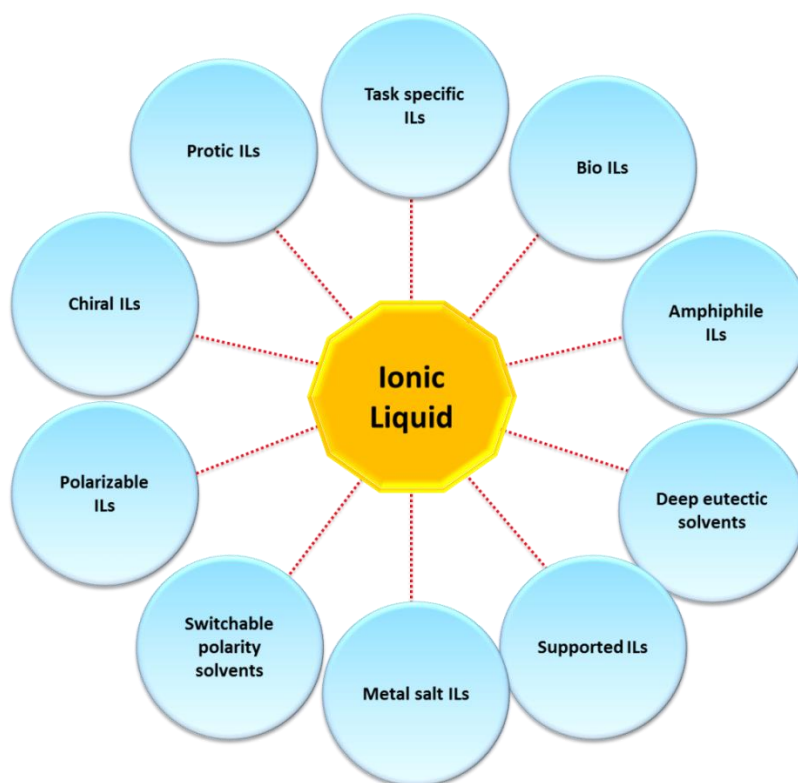


Fig.1.2: Types of ionic liquids on the basis of their design

Synthetic strategies of designing an IL catalyst consist of variation of ionic counter parts and involve suitable procedure to achieve the same. Properties like homogeneity and heterogeneity can be introduced by following specific predefined designs or the modified ones. Thus a vast array of IL catalysts has been growing since last few decades and extending its viability through the unlimited scopes they possess.

1.2 Ionic liquids derived catalysts: Basis and synthetic perspective

Catalysts designed from ionic liquids are multidirectional in terms of functionality. They have been synthesized according to the specific necessity regarding the application which they perform. The different types of ionic liquid material can be categorized as mono, di, tri, tetra cationic *etc.* based on the number of cations in their structure (**Fig.1.3**) [12]. In addition to that they can also be subdivided as acidic [13], basic [14], metal based [3], chiral [15], neutral [16, 17] ILs *etc.* according to their nature of cation or anion and also characteristic functional groups tethered to the ions for the definite target.

Impregnation of acidic, basic or metal based ionic liquids on porous support transfer the specific function of these ILs to its surface by distribution of active sites of the ILs which fulfill the need of efficient reusable heterogeneous catalyst [18]. This method eliminates

several limitations of IL catalysis in liquid state such as viscosity, hydrophilicity, non-recyclability and also thermal degradability. Depending on their characteristic task-specific nature, the ionic liquid derived materials are utilized in organic transformations [19-23], asymmetric synthesis [24] analytical process [25], surfactants [26], biomass conversion [27], electro catalysts [28], electrochemistry, photochemistry and other physicochemical processes [29-32]. These designs solely depend on the properties of those catalysts which are only aimed for some particular applications. For example, some room temperature ionic liquids exhibit good electrochemical stability within electrochemical window of 4.0-5.7 V. Such types of IL have been used as appropriate electrolyte in conducting polymer based electrochemical devices [33-35]. Metal based ionic liquids with semiconductor properties can be utilized as photocatalyst for various photochemical reactions. Thus owing to such diverse properties ionic liquids are the preferable candidates in the field of catalysis.

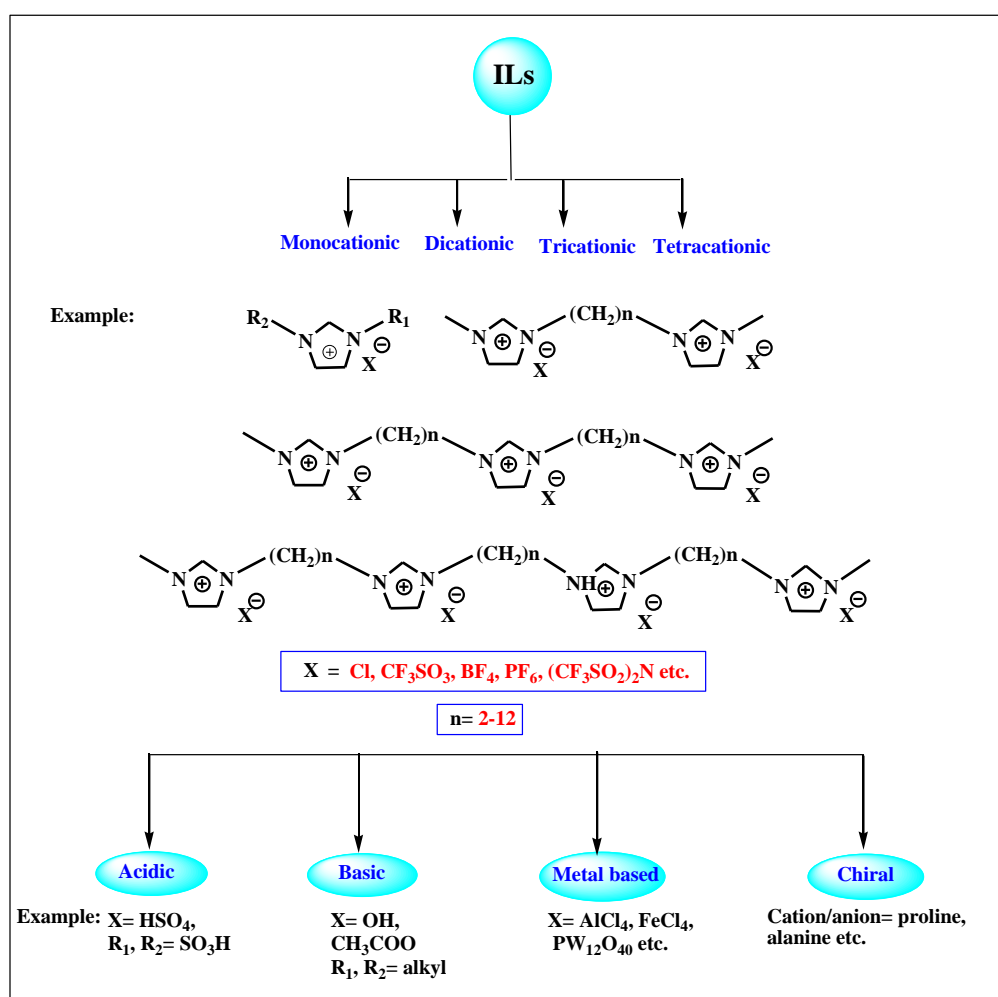


Fig.1.3: Classification of ionic liquids based on functionality with examples

This section offers brief description of some important types of ionic liquid catalysts including Brønsted and Lewis acidic, halometallates, supported ionic liquid phase, polyoxometalates and dicationic ionic liquids.

1.2.1 Brønsted and Lewis acidity in ionic liquids

Acidity of ionic liquids can be described as Lewis acidic (LA) or Brønsted acidic (BA) depending on the deficiency of electrons or presence of ionizable proton(s). Some of the ionic liquids contain more than one Brønsted or Lewis acidic sites and also possess combination of both acidic functionalities. The acidic proton(s) of Brønsted acidic ionic liquids (BAILs) are generally found on nitrogen and oxygen atom of the anion or cation or both ion-pairs. Many times these protons reside on acidic substituents like $-\text{COOH}$, $-\text{SO}_3\text{H}$ *etc.* which are tethered to the cation (**Fig. 1.4**). They are also sub-classified as protic ionic liquids (PILs) containing one or more acidic protons either on the cation, the anion or both the ionic components. The $-\text{SO}_3\text{H}$ functionalized BAILs are especially useful as efficient alternative recyclable liquid phase catalysts of Brønsted acids like H_2SO_4 , HCl *etc.* in organic reactions [36] Anchoring of $-\text{SO}_3\text{H}$ groups on ammonium, pyridinium or imidazolium cations can be done by introducing $-\text{N}$ alkyl sulfonic or $-\text{NSO}_3\text{H}$ groups with the cations of ILs in presence of variety of organic or inorganic anions or complex metal halide anions [37]. On the other hand, electron accepting ability of the Lewis acidic ionic liquids (LAILs) are commonly located in the complex metal based anions (**Fig.1.5**). They are synthesized after treatment of neutral ionic liquid with Lewis acidic metal salts. For example $[\text{FeCl}_4]^-$ anion obtained from the reaction of anhydrous FeCl_3 with neutral 1-butyl-3-methyl imidazolium chloride under anhydrous condition exhibits Lewis acidic properties [38].

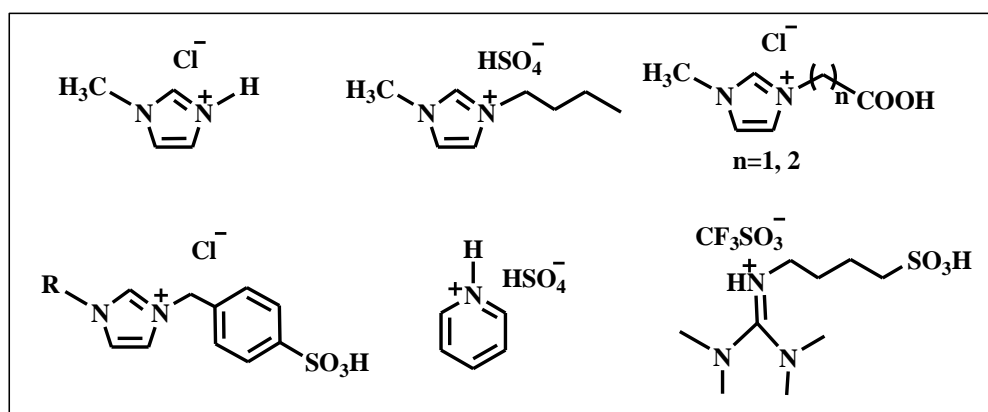


Fig.1.4: Brønsted acidic ionic liquids of different types

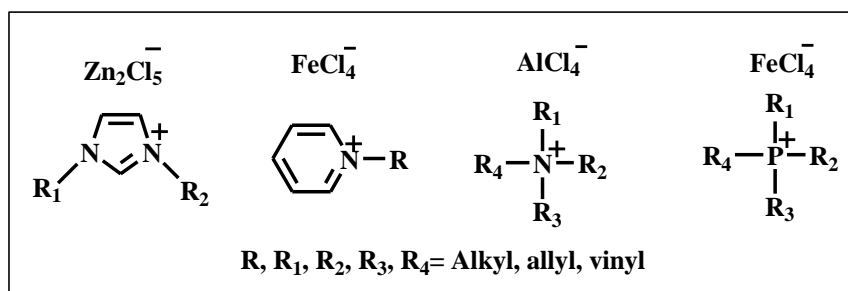


Fig.1.5: Structures of some Lewis acidic halometallates

Moisture sensitivity is one of the major limitations of chloroaluminate ionic liquids which cover a large number of Lewis acidic ionic liquids [39, 40]. Many attempts have been made to continuous search for moisture stable LAILs by mixing halide salts of transition metal (e.g. Fe, Co, Zn, Cu, Sn, Mn *etc.*) or Group IIIA metal (e.g. Ga, In) [41-44] or rare earth elements [45] in different ratios with neutral organic halides. Interestingly, some of them were isolated as molten salts or in solid state at room temperature with higher melting points [46-49]. Being very powerful Lewis acid they can actively take part in organic reactions.

1.2.2 Halometallates: Versatile approaches

Halometallates are formed by the reaction of a metal halide with an organic halide salt, and notably, in the early days the research was limited almost exclusively to air and moisture sensitive chloroaluminate(III) ionic liquids [4]. Reviews of literature mentioned a large number of halometallate ionic liquid systems with varied thermal and water sensitive nature such as chlorocuprate(I) [50], chlorogallate(III) [51], $[C_4mim][Cl-NbCl_4]$, $[C_4mim][Cl-ZnCl_2]$ [52], chloroferrate(II) [53], chloroindate(III) [54], chlorostannate(II) [55, 56], tetrachlorometallate(II) ($[MCl_4]^{2-}$, $M = Fe, Ni, Co, Zn$) [57], tetrachloroaurate(III) [58] *etc.* Anionic speciation leads to variation in physical properties like viscosity, electrical conductivity, Lewis acidity, moisture and thermal stability depending on the identity and concentration of metal species [59]. The nature of metal and mole fraction of metal chloride to organic chloride salts (χMCl_x) are two main factors that induce the anionic speciation in Group IIIA halometallate ILs and consequently determine their catalytic activity [60-66]. Due to their tunable properties, halometallate ILs were explored in the fields of electrochemistry, catalysis, and separation processes as well as in biomass processing [3-6, 67]. They have been extensively studied in various catalytic and physicochemical activities (**Fig.1.6**).

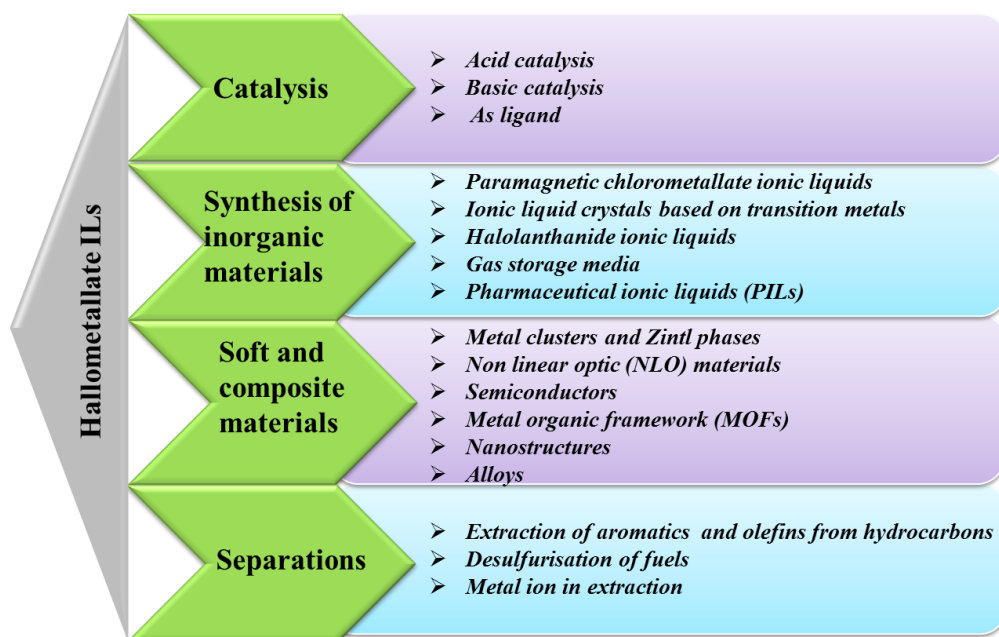


Fig.1.6: Various applications of halometallate ILs

1.2.3 Supported ionic liquid phase: Advances in catalysis

In spite of the excellent catalytic ability of room temperature ionic liquids or melts they have been facing several shortcomings because of high cost, hygroscopic nature, water miscibility and problem of recyclability in liquid state *etc.* Immobilization of ionic liquids on to various inorganic/organic supports creates very stable catalytic systems which limit the use of excess amount of expensive ionic liquids in catalysis. These immobilized or supported ionic liquids are known as supported ionic liquid phase (SILPs). Inorganic porous material such as silica gel, zeolites, clay are considered as better support for ionic liquids as they can preferably interact with the functionalized sites of the respective ionic liquids by covalent anchoring or by physisorption making the concentration of active species higher in the interface of the support [7, 68]. Also the larger surface area provides many advantages of heterogeneous catalyst (**Fig.1.7**).

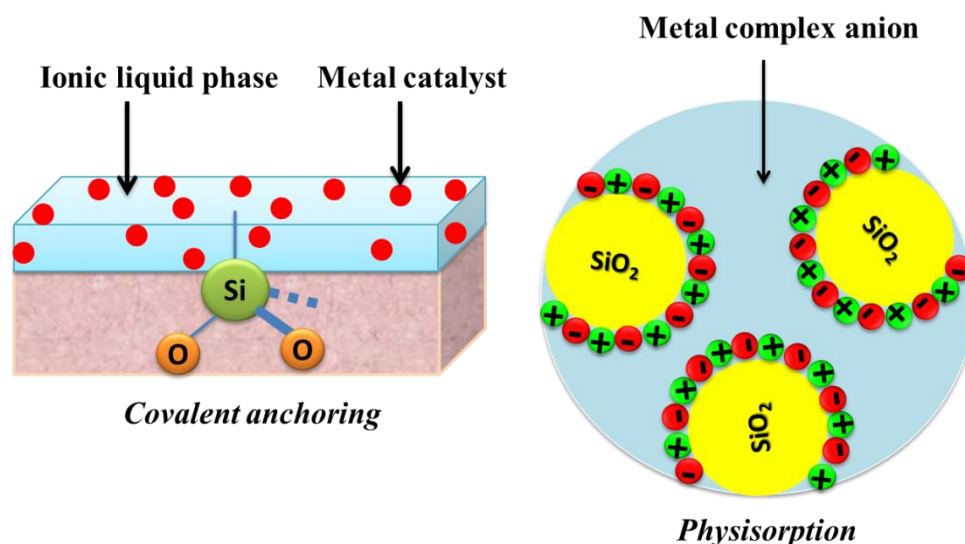


Fig.1.7: Schematic representation of SILPs

Olefin hydroformylation [7], gas phase hydroformylation of propene [69], Friedel-Crafts alkylation [70] are some examples of SILPs catalyzed reactions along with Rh and other metal complexes. The meso structured hybrid organic-inorganic silica materials containing imidazolium and Si-C covalently bonded moiety synthesized by conventional sol-gel procedures in the presence of surfactant template and tetraethyl orthosilicate have recently been used as supports to immobilize transition metal complexes such as Pd for Suzuki cross coupling reactions and for *in situ* formation of NHC-stabilized nanoparticles [71, 72]. Another type of support such as polystyrene functionalized resins synthesized from Merrifield resin produce SILPs with variation in linker length, the loading level of the IL portion and the nature of the IL anion [73]. Best catalytic properties were noticed for the materials with longest linker. Polyethylene glycol was also an efficient support for the ILs which have also been found to enhance catalytic reactions such as C-C coupling with Pd(OAc)₂, thus providing a ligand less recyclable system [74]. Thus, SILPs are the materials of greater ability as tunable catalysts.

1.2.4 Low band gap materials: Supported photocatalysts

Review of literature reveals that many transition metal oxide and other metal salts have been studied as homogeneous or heterogeneous photo catalysts for numerous organic reactions including photocatalytic degradation of organic pollutants e.g. dye, pesticide *etc.* [75, 76]. Semiconductor materials with low band gap values are widely employed as photocatalysts [77]. The use of heterogeneous photocatalysts provides easy separation of photo catalyst from reaction mixture without loss of much catalytic activity for next cycle of reaction for a large variety of reactions at different pH values. Semiconductor

heterogeneous photocatalysis involving advanced oxidation process (AOP) is a versatile, low-cost and environmentally benign treatment technology for a host of pollutants (**Fig.1.8**) [78, 79]. This semiconductor concept can also be applied for the halometallate ILs which have certain low band gap values due to metal halide anion and can be considered as semiconductor materials. As the halometallates face some disadvantages such as moisture sensitivity, low thermal stability, they can acquire advantages by modified into the SILPs. Those semiconductor halometallates immobilized on siliceous zeolite like ZSM-5 will have the ability to photocatalyze degradation of dye molecules in aqueous solution involving AOP under sunlight or UV light. Thus a new class of halometallate based SILP supported materials is the probable candidate for the photocatalysis.

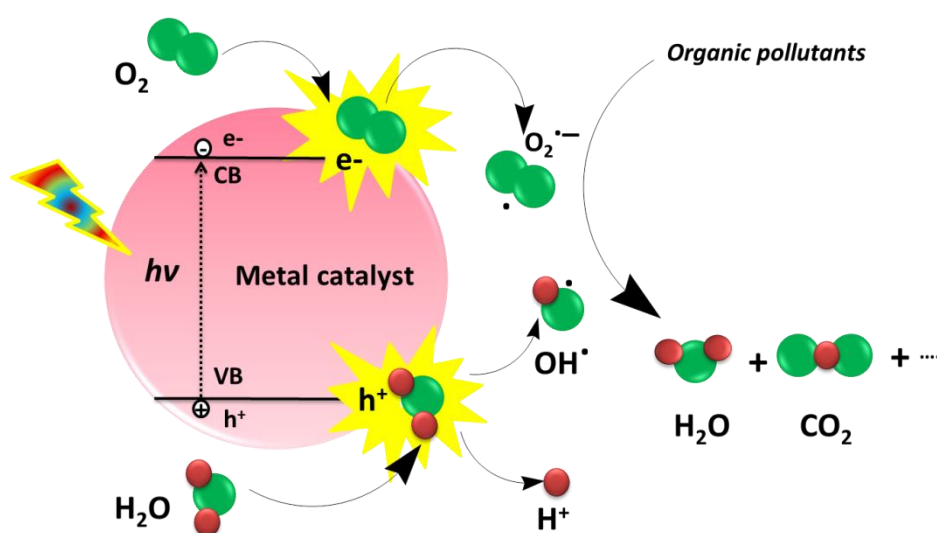


Fig.1.8: Representation of semiconductor band gap excitation and photocatalytic activity

1.2.5 Polyoxometalates: Heteropolyacid based catalysts

Polyoxometalates are the combination of cations and polyanion clusters [80] in which the oxo metal polyhedra of MO_x ($x = 5, 6$) are the basic construction units and M generally represents early transition metals (TMs) in their high oxidation state (e.g. W, Mo, V, Nb, Ta) which can be partly substituted by other metals (e.g. Al, Ti, Cr, Mn, Fe, Co, Ni, Zn, Zr, Ru, Pd, Ln, *etc.*) [81-83]. Parent acids of these POMs are mainly heteropolyacids centered with heteroatom containing only proton as their cation (HPAs). Unlimited numbers of organic cations deal in multiple ways to introduce different functionality in POMs as they are designable and flexible enough to tune into diverse properties. On the other hand, the limited numbers of inorganic cations include mainly H^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Ag^+ , *etc.* which are unlikely to undergo any modification. Ability of artificial

tuning and structural variations of polyhedral framework in POMs instigate nature like acidity, basicity, redox stability and chirality. Between Keggin-type and Dawson type POMs, Keggin types are the most tempting structures in catalysis due to their unique stability and have been well studied for decades (**Fig.1.9**) [84].

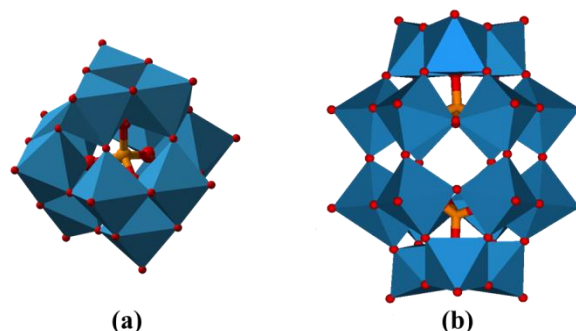


Fig.1.9: (a) Keggin structure ($XM_{12}O_{40}^{n-}$) & (b) Dawson structure ($X_2M_{18}O_{62}^{n-}$)

From the catalytic point of view, active sites in POMs/HPA are Brønsted acidic protons, basic oxygen atoms on the surface of POM anions and metals present in them. Most significant role is played by the metals in POMs/HPA as they are main active sites for almost all oxidative reactions, some acid catalyzed reactions and other reactions [85-87]. Thus multiple active site bearing POMs/HPAs have also attractive stability [88-90], photoactivity [91, 92], electrocatalytic ability [93, 84] which can also be used as excellent homogeneous and heterogeneous catalysts in plenty of reactions. While homogeneous catalysis is quite simple, heterogeneous catalysis by POMs/HPA is more complicated. There are three types of heterogeneous catalysis which are surface type, pseudoliquid bulk type and bulk type respectively (**Fig.1.10**) [94].

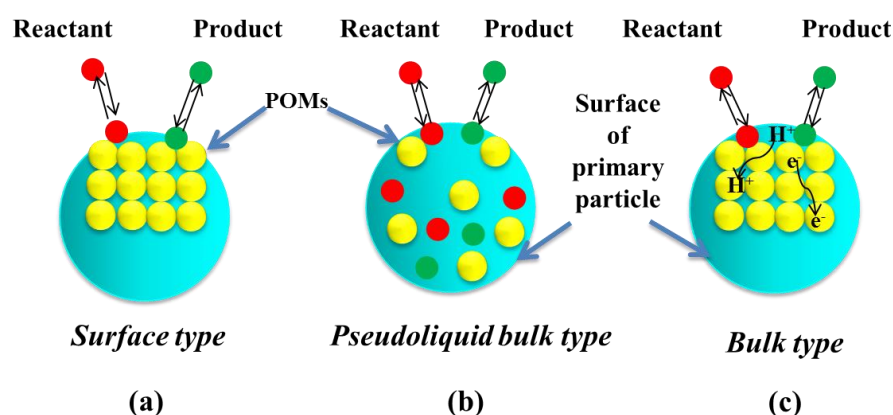


Fig.1.10: Three catalysis models of solid POM catalysts

Being stupendously active polyoxometalate anions can combine with ionic liquids resulting in very stable organic cation based POM salt which could be used in all above

mentioned catalytic processes. Thus ionic liquids expand their region by including the class of POMs/HPAs within it and hence widen the field of their applications.

1.2.6 Dicationic ionic liquids

The trend of ionic liquid synthesis initially started with monocationic ILs in presence of inorganic or organic counter anion which led to development of multicationic ionic liquids especially dicationic ionic liquids (DILs) consist of two charged head groups linked by a rigid or flexible spacer possessing wider liquid range temperature and better thermal stability [95]. The known DILs can be classified as homoanionic dicationic [96] and heteroanionic dicationic [97] ionic liquids which can be further categorized as symmetrical (germinal) [96] and asymmetrical DILs [98] for both homoanionic and heteroanionic DILs. The term ‘homoanionic’ indicates that the corresponding DIL consists of two identical anions along with a dication. Symmetrical or asymmetrical properties depend on the structure, composition and connectivity of ionic counterparts (**Fig.1.11**). The literature expressed melting point of some germinal DILs in the range of 450-673 K in contrast to corresponding monocationic ionic liquids below 373 K [99].

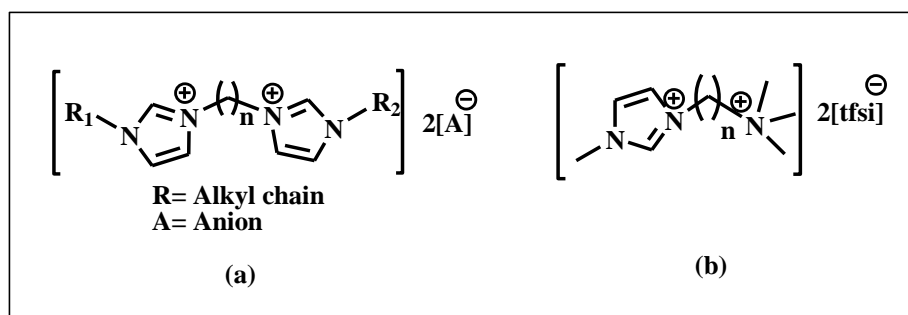


Fig.1.11: Examples of (a) symmetrical DIL & (b) asymmetrical DIL

Heteroanionic dicationic ILs are both symmetrical and asymmetrical containing two dissimilar anions (**Fig.1.12**).

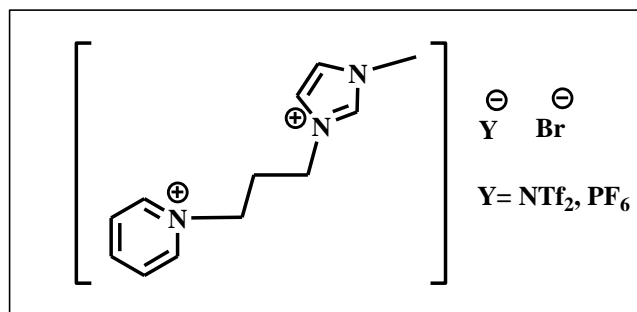


Fig.1.12: Example of asymmetric heteroanionic DIL

Implementation of dicationic ionic liquids in various fields has been limited till date. Though several DILs have been available in literature, but the range of their applications

is quite low. Having characteristics almost similar to monocationic ionic liquids, DILs display proficiency in catalysis. Above this, DILs can be used as supported ionic liquid membranes for gases such as CO₂ and CH₄ produced in fossil fuel and coal gasification [100]. Pyridinium, piperidinium, imidazolium and ammonium ionic liquids are most common DILs which have been found to be employed in catalytic processes such as hydrolysis/H₂ production [101], biodiesel production [102-104], esterification of carboxylic acid [105, 106], other chemical reactions [107-110] and also used as potential electrolytes [98, 111], structure-directing agents (SDA) for the synthesis of zeolite Beta [112], non-toxic and antimicrobial materials [113] *etc.* Owing to this multifaceted behavior, DILs open new doors to researchers to explore further.

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