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Magnetic ionic liquids: As multi-purpose catalysts

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Introduction

Ionic liquids (ILs) have been widely used as solvent, catalyst and reagent [1]. The first magnetic ionic liquid was reported by Hayashi and Hamaguchi [2-3]. These materials are liquids at room temperature and showing paramagnetic properties in the absence of any other magnetic particles. These paramagnetic properties were done by the anion, the cation or both of them. Magnetic ionic liquids were proportioned based on contain transition metal or lanthanide complexes in their anion structure. These tuneable fluids present unique physicochemical properties, resulting in responsive materials to an external magnetic field. Magnetic ionic liquids are because of outstanding thermal stability, excellent electrochemical properties, good solubility and recyclability; it has a broad application prospects in catalysis, separation, extraction, material synthesis and other fields. It is believed that the magnetic ionic liquids will be applied in a wide range of chemical-based sciences [4]. Herein the applications of magnetic ionic liquids (MILs) as efficient catalysts for the synthesis of organic (2-amino-4H-chromene, compounds such as 2-amino-4,8-dihydropyrano, 2-amino-4*H*-pyrans), 2-aminobenzothiazolomethylnaphthols, spiropyrans, 1-amidoalkyl-2-naphthols, tetrasubstituted



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

imidazoles, azidomethyl benzenes, ring opening of epoxides, 1- and 5-substituted 1H-tetrazoles, quinazolines, 1-benzyl-(o, m or p)-methylbenzene were shortly reviewed.



Scheme 1. The structures of some reported magnetic ionic liquids (MILs) with different anions.

Abstracts

(A) In 2019, magnetic ionic liquids pyridine sulfonic acid iron (IV) chloride [Py-SO₃H]FeCl₄ has been synthesized and its catalytic activities also studied as a novel catalyst for the synthesis of a wide range of O-heterocyclic compound (2-amino-4H-chromene, 2amino-4,8-dihydropyrano and 2-amino-4H-pyrans) [5].

(B) In 2019, Zolfigol et al. have introduced a novel magnetic phosphonium ionic liquid (MPIL) by reaction of tributylphosphine, ClSO₃H and FeCl₃. This catalyst was tested for the synthesis of 2aminobenzothiazolomethylnaphthols. The promising features of the mentioned catalyst are the benign nature of the protocols, the ease of reaction procedures, the strong catalytic activity and the timesaving with excellent yields of the target molecules [6].

(C) Mesoporous ionically tagged cross-linked poly vinyl imidazole sulfonic acid iron(IV) chloride [PVI-SO₃H]FeCl₄ has been synthesized and used as a dual role catalyst due to the presence of Lewis and Bronsted acidic tags (SO₃H and Fe³⁺ moieties) within its structure. The mentioned catalyst as a novel and reusable has been used for the synthesis of Nheterocycle compounds via reaction of various carbonyl compounds (A), amino compounds (B) and nucleophile compounds (C) under refluxing water [7].

(D) Moosavi-Zare *et al.* have introduced magnetic ionic liquid 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate {[Msim]FeCl₄} as an efficient catalyst, for the preparation of 1-amidoalkyl-2naphthols *via* a tandem reaction of β -naphthol with aromatic aldehydes and benzamide at 110 under solvent-free conditions. High yields and very short reaction times are the major advantages of the reported methodology [8].









(E) In another exploration, magnetic ionic liquid tri (1-butyl-3-methylimidazolium) gadolinium hexachloride, ([bmim]₃ [GdCl₆]) has been used as a green salt and reusable catalyst for the synthesis of tetrasubstituted imidazoles. The obtained products are interesting bioactive compounds, which they had been prepared in excellent yields and very short reaction times [9].

(F) The catalytic activity of the polyethylene glycol functionalized magnetic dicationic ionic liquid, PEG-MDI, as a polymeric, highly efficient, reusable nanostructured, mild and green catalyst has been studied in the nucleophilic substitution reactions of benzyl halides under refluxing water. PEG-MDIL has showed remarkable reactivity as a Lewis acidic agent and considerably accelerated the reactions. It seems that polyethylene glycol units in PEG-MDIL encapsulate alkali metal cations, much like crown ethers, and these complexes cause the anion to be necked and activated [10].

(G) The catalytic activities of the 1-butyl-3methylimidazolium tetrachloroferrate $[pbmim](FeCl_4)_2$ has been studied as novel catalyst for the ring opening of epoxides by the one-pot reaction of various epoxides and sodium azide in water under reflux conditions. The synthesis of bipolar magnetic imidazolium-based ionic liquid [pbmim] (FeCl_4)_2, consists of two steps. First, 1,3dichloropropane reacts with two *N*-methyl amidazole equivalents in methanol and under reflux conditions. Secondly, the ionic liquid anions of the imidazoliumbased dipole, Cl⁻, are easily converted to FeCl₄ anions by simple mixing with FeCl₃ in regular conditions [11].







(H) In 2013, chitosan supported magnetic ionic liquid (CSMIL) was proportioned by reaction of methyl imidazole, 1,2-dichloroethane, chitosan and FeCl₃. The product 1- and 5-substituted 1*H*-tetrazoles have been prepared from the condensation of nitriles or amin compounds and sodium azide, in the presence of a catalytic amount of chitosan supported magnetic ionic liquid (CSMIL) under solvent-free conditions. The obtained products are interesting bioactive compounds, which they had been prepared in excellent yields and very short reaction times [12].

(I) In 2013, Kumar and Saha have introduced a novel solid acid namely magnetic ionic liquid, [bmim]FeCl₄ as a highly efficient and reusable catalyst for the regioselective synthesis of quinazolines by the reaction of 2-aminoarylketone, aromatic aldehydes and ammonium acetate at moderate temperature under solvent-free conditions. The major advantages of the described catalyst, are green synthesis, short reaction times and excellent yields of products [13].

(J) In the another exploration, synthesis of polymeric ionic liquids (PILs) with paramagnetic anions based on tetrachloroferrate(III) (FeCl₄), have been introduced. PILs has been showed a strong response to a neodymium magnet. As a potential application, a microgel based on a paramagnetic PIL is used as a reusable catalyst in the Friedel-Crafts alkylation for 20 min, under refluxing toluene. The paramagnetic PILs can be easily separated and reused. The mentioned materials are interesting for green chemical processes [14].

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