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Manish Varyani, Praveen K Khatri, Suman L. Jain

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Amino acid derived ionic liquid supported iron Schiff base catalyzed greener approach for the aerobic oxidation of amines to nitriles

Manish Varyani,[a] Praveen K Khatri,[a] and Suman L. Jain[a*]

[a]*Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Mohkampur, Dehradun-248005 (India)*
Tel: 91-135-2525788; Fax: 91-135-2660202; Email: suman@iip.res.in

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ABSTRACT

Amino acid DL-threonine derived ionic liquid was treated with salicylaldehyde to give corresponding Schiff base which subsequently complexed with iron and used as a green catalyst for aerobic oxidation of amines under solvent-less conditions. The developed catalyst was readily synthesized, reusable and exhibited superior catalytic activity owing to the synergistic effect of ionic liquid moiety. The developed catalyst was found to be quite stable and could be reused for several runs without any significant loss in catalytic activity.

Owing to the growing environmental concerns and depletion of fossil fuels, utilization of renewable natural resources as starting materials in chemical industry is receiving considerable interest in recent decades. Natural amino acids and their derivatives provide the most abundant renewable natural sources which can be effectively used as feed stocks for producing valuable chemicals for various applications[1,2]. Ionic liquids owing to their excellent thermal stability, tunable solubility, efficient recycling and lower volatility have considerable to be green alternatives to volatile organic compounds in various chemical and bio-chemical transformations[3-9]. However, despite of their widespread applications, doubts have been raised about the genuine green nature of the ionic liquids. For example, some ILs are volatile, combustible, toxic, and also exert detrimental effects on the environment[10-14]. Thus, the development of environmentally compatible or biodegradable ILs is highly desired from environmental and economic viewpoints. After the first successful synthesis by Fukumoto et al. in 2005,[15] a number of amino acid-based ionic liquids have been prepared by using amino acids as anions or cations[16-22]. These ILs owing to their biodegradable characteristics and high biocompatibility are considered to be safer and environmentally benign alternatives of the functionalized task specific ionic liquids. Recently, metal complexes of Schiff bases, derivatives of *ortho*-hydroxy aldehydes and amino acids[23], have been developed and used for the biological applications. However, the potential of such ionic liquids for catalytic applications is remained unexplored.

Oxidation of benzylamines to corresponding nitriles is an important synthetic transformation as they have found widespread applications as important building blocks in dyes, natural products, herbicides, agrochemicals, pharmaceuticals, and various fine chemicals.[24-25] In addition, owing to the ease of functionalization, nitriles can also be converted into other functional groups, such as carboxylic acids, amides, aldehydes and heterocycles, etc.[26-28] Traditional methods for the preparation of benzonitriles on laboratory as well as on industrial scale are the Rosenmund–von Braun reaction of aryl halides[29-30] and the diazotization of anilines followed by subsequent Sandmeyer reaction.[31] However, these methods are associated with certain drawbacks such as the use of toxic cyanides and the generation of stoichiometric amounts of metallic wastes. Thus, the direct synthesis of nitriles *via* oxidative dehydrogenation of primary amines is an attractive approach for the clean synthesis of these important precursors. Apart from the use of stoichiometric oxidants which generate huge amount of undesirable waste[32-34] a number of catalytic methodologies has been reported in recent decades. Particularly, catalytic methods using molecular oxygen as an oxidant[35-36] are more desirable from the consideration of green and sustainable chemistry. So far the cobalt, copper, palladium, ruthenium and vanadium based catalysts have been reported for the aerobic oxidation of benzylamines to nitriles.[37-40] However, many of these catalytic systems have certain drawbacks such as high cost, poor product yields and use of toxic and volatile organic solvents. Catalytic aerobic oxidation of amines to nitriles in the presence of ILs has also been reported.[41] However, the use of pure ILs as reaction media can lead to product separation difficulties and metal immobilized IL's may lead to the leaching of metal thus affecting the recyclability of catalyst.

Herein we wish to report for the first time the use of tetrabutyl ammonium salt of amino acid Schiff base, derivative of salicylaldehyde and DL-threonine functionalized with iron (II) as