



Imidazolium chloride immobilized SBA-15 as a heterogenized organocatalyst for solvent free Knoevenagel condensation using microwave

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ABSTRACT

Heterogeneous organocatalyst, 1-methyl-3-[(3-triethoxysilyl) propyl] imidazolium chloride [MTE-SPImCl] immobilized SBA-15 (ILS) was synthesized by co-condensation method using microwave irradiation in which 1-methylimidazole (Im) was modified by organosilane (3-chloropropyl triethoxysilane). The ILS was thoroughly characterized by small angle XRD, N₂ adsorption desorption isotherms, TEM, SEM, TGA and FT-IR. The ILS showed 2D hexagonal short channeled disk type mesostructure which can provide facile to-and-from diffusion of substrates and products with enhanced activity. This heterogenized organocatalyst ILS had been investigated for the Knoevenagel condensation reaction of different aromatic and heteroaromatic aldehyde with ethyl cyanoacetate in solvent free conditions. The catalyst ILS was found to be efficient to catalyze the condensation effectively leading the completion of the reaction within 6 min using single mode microwave irradiation.

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1. Introduction

Ionic liquids have achieved great attention as a green solvent [1] in the fields of organic synthesis [2], nanoporous materials' synthesis [3,4], enzyme activation and catalysis [5] because of their unique properties such as non-volatility, non-flammability, polarity, solubility, and high thermal and chemical stabilities [6]. In the field of catalysis, ionic liquids (ILs) play the role of solvents and organocatalysts. In general, organocatalysis uses small organic molecules, composed of C, H, N, O, S and P atoms which play role as active site however, their high cost, and difficulty in recyclability and in the separation of products, cause limitations for their further applications at the industrial scale [7]. To overcome these shortcomings, supporting or immobilizing of organocatalyst ILs onto the solid supports termed as heterogenized IL organocatalysts have become as a green approach in their catalytic applications [8–15].

Since the discovery of ordered mesoporous silicates, a variety of ordered mesoporous materials with high surface area, large pore volume and large pore size have been synthesized using different surfactant templating methods to expand their practical applications in the area of heterogeneous organocatalysis by immobilizing organic functionalities [16,17]. The modified mesoporous

materials with various active sites had been extensively investigated in recent decade [18]. The organo-functional modification of mesoporous silica permits to tailor the surface properties, useful for various applications in the heterogeneous catalysis [19]. Generally the synthesis of functionalized mesoporous materials have two approaches: (1) the direct synthesis approach where in a silane containing functional group of ionic liquid was added to the synthetic mixture during the synthesis of mesoporous materials (2) the second approach is by post grafting wherein the organosilane is grafted after synthesis of mesoporous support [20,21].

Among the siliceous supports SBA-15 is promising candidate for the immobilization of organocatalyst due to its high surface area, porosity, uniform pore size distributions, and thermal stability [22]. In recent year our group reported several organic functional groups such as primary and quaternary amine, sulfonic acid, and amino acid (L-proline) functionalized mesoporous silica for organocatalytic applications in various reactions such as Knoevenagel, Henry reaction, Claisen-Schmidt condensation and diethyl malonate addition [23]. SBA-15 supported ionic liquids such as 1-methyl-3-propylimidazolium chloride (MPImCl) and 1-propylpyridinium chloride (PPyCl) ionic liquids have also been used as heterogeneous catalysts providing high yields in Knoevenagel condensation under solvent free conditions; however these are associated with longer reaction times due to conventionally, convective heating over heat baths or electric heating mantles, which have major adverse effect to the environment as well as consumption of energy for heating and cooling [24].

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