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Synthesis of 1,3-thiazolidin-4-one using ionic liquid immobilized onto Fe_3O_4/SiO_2/Salen/Mn

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ABSTRACT

An efficient and general method has been developed for synthesis of 1,3-thiazolidin-4-ones using magnetite nanoparticles immobilized Salen–Mn–ionic liquids as an efficient and recyclable catalyst. The inorganic, magnetic, solid base catalyst was characterized via N_2 sorption, TEM, VSM, TGA, XRD, FTIR, and UV–vis. Nanocatalyst can be easily recovered by a magnetic field and reused for subsequent reactions for at least 6 times with less deterioration in catalytic activity.

1. Introduction

The thiazolidin-4-one ring system is a core structure found in various synthetic pharmaceutical compounds, displaying a broad spectrum of biological activities [1–6]. Consequently, several synthetic methods have been developed for the synthesis of 4-thiazolidinones. The main synthetic routes to thiazolidin-4-ones involve cyclocondensation of azomethines (Schiff's base) with mercaptoacetic acid [7]. There are also reports using chemical agents, such as N-methylpyridinium tosylate [8] as desiccant, to assist the formation of thiazolidinone derivatives. The use of [BmIm]OH [9], Hunig's base [10], and Baker's yeast [11] has also been reported to expedite the cyclo-condensation of the azomethines and thioglycolic acid.

Ionic liquids (ILs) have emerged as promising homogeneous catalysts [12] because of their unique physicochemical properties including negligible vapor pressure, wide liquid range, high ionic conductivity and excellent solubility [13]. Although ILs possess some advantages but their practical applications have been restricted by some difficulties in its recovery which lead to economical and environmental problems. On the other hand, their high viscosity not only limits their mass transfer during catalytic reactions but also makes their handling difficult. Moreover, the use of relatively large amounts of ILs is costly and may cause toxicological concerns. These problems can be overcome by immobilization of ILs onto solid supports to obtain heterogeneous catalysts [14–16]. Thus, efforts have been made to immobilize them on diverse soluble and insoluble supports, such as inorganic solids [17–21], polymers [22,23], and nanoparticles [24–35]. Nowadays, magnetite nanoparticles, especially Fe_3O_4 nanoparticles have attracted increasing interest because of their unique physical properties including the high surface area, superparamagnetism, low toxicity and their potential applications in various fields. The Fe_3O_4 nanoparticles are easily prepared and surface functionalized and they can be recycled from the solution by external magnetic field. Hence, the catalyst supported on Fe_3O_4 nanoparticles can be easily separated from the reaction system and reused. In addition, the reported coupling reactions were mostly carried out in organic solvents, to begin with environmental benign, the development of highly efficient heterogeneous catalysts to facilitate coupling reaction in benign medium is highly desirable.

In this work, our interest in this area led us to explore the Salen/Mn/ionic liquid (IL) immobilized onto the surface of magnetic nanoparticles, which can be sufficiently applied even for the synthesis 1,3-thiazolidin-4-one and then can be easily separated from the reaction mixture to reuse. Herein, we wish to describe the synthesis of reusable magnetite nanoparticles supported Salen/Mn/IL and its catalytic activity in the multicomponent reaction (Scheme 1).

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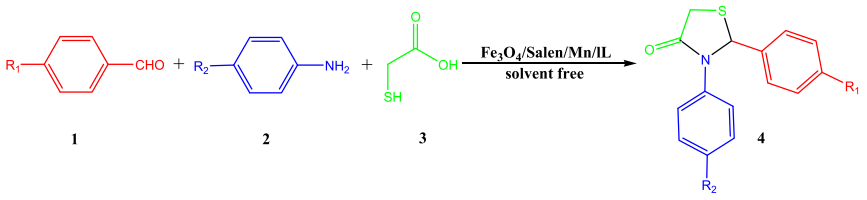
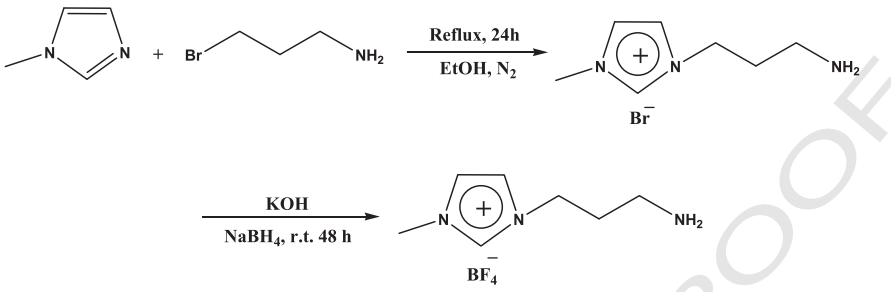


Scheme 1. Synthesis of 1,3-thiazolidin-4-one in the presence of Fe_3O_4/SiO_2/Salen/Mn/IL MNPs.



Scheme 2. Synthesis of the ionic liquid (IL) containing primary amine.

2. Experimental

2.1. Materials and methods

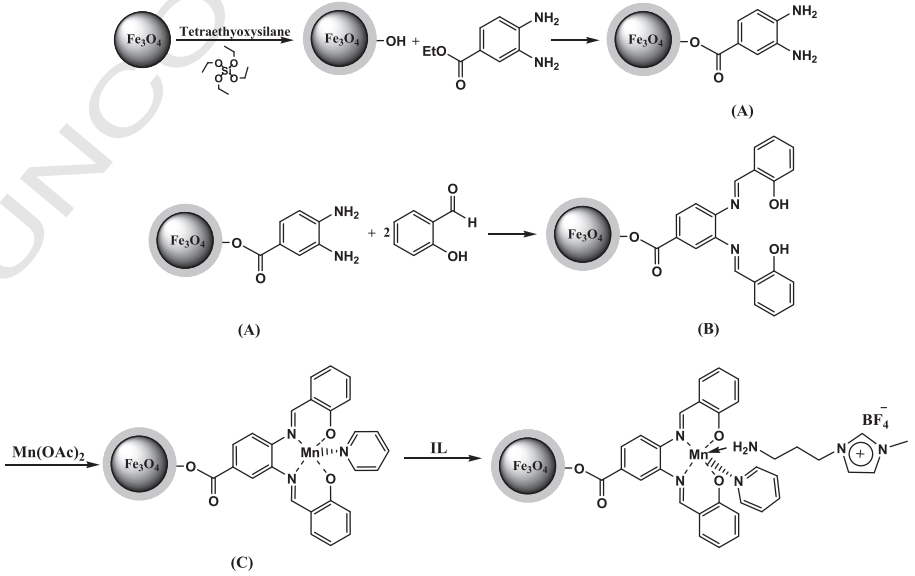
Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. Morphology was analyzed using high-resolution transmission electron microscopy (HRTEM) on a JEOL transmission electron microscope operating at 200 kV. The content of phosphorous in the catalyst was determined by OPTIMA 7300DV inductively coupled plasma (ICP) analyzer. Powder X-ray diffraction data was obtained using Bruker D8 Advance model with Cu Ka radiation. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min^{-1} under nitrogen. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (4 in., Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DRX-400 MHz instrument spectrometer using TMS as internal standard. The purity determination of the products and reaction monitoring was accomplished by TLC on silica gel polygram SILG/UV 254 plates.

2.2. General procedure for the ionic liquid

The IL was prepared as described previously [36], which was outlined in Scheme 2.

2.3. General procedure for the preparation of Fe_3O_4/SiO_2/Salen/Mn nanoparticles

Fe_3O_4/SiO_2/Salen/Mn nanoparticles were prepared by a simple method in our previous work [37].



Scheme 3. Schematic illustration of the synthesis for Fe_3O_4/SiO_2/Salen/Mn/IL nanoparticles.

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