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Self-assembled alkyl imidazolium based organosilica as efficient support for sulfonic acid catalyst in the synthesis of bis(indolyl)methanes

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ABSTRACT

A novel sulfonic acid-containing hybrid organic–inorganic material with ionic liquid framework (IL-OS-SO_3H) is prepared, characterized and applied as efficient catalyst for the synthesis of bis(indolyl)methanes. The IL-OS-SO_3H was prepared through hydrolysis and condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium iodide followed by grafting of 3-thiopropyl-trimethoxysilane and then oxidation of SH groups in the presence of hydrogen peroxide. This catalyst was characterized using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The IL-OS-SO_3H was successfully applied as powerful and reusable catalyst for synthesis of bis(indolyl)methanes at room temperature under solvent-free conditions. This novel catalyst could be recovered and reused at least eight times without significant decrease in catalytic activity and product selectivity.

1. Introduction

In recent years, ionic liquids (ILs) have gained considerable attention as being an environmentally friendly reaction media due to their special properties such as high thermal stability, low vapor pressure, peculiar ion environment, excellent polarity, high ion conductivity, unique solvation ability, wide liquidus range and wide electrochemical window [1–10]. These properties allow ionic liquids to be excellent candidates for plenty of applications in chemistry and material sciences [11–14]. However, since many of ILs are very expensive and cause toxicological concerns the broad developments of them are limited [4]. Moreover, for separation of product from IL-containing media, usually a large amount of organic solvents is needed. To overcome these restrictions, the immobilization of ILs on solid supports *via* either covalent attachment or noncovalent interactions has been applied to generate supported ILs which is recognized as a green approach in the catalytic processes [15–26]. Accordingly, in recent years, the application of supported ionic liquid in catalyst-mediated organic reactions is a trendy frontier of research.

On the other hand, the discovery and preparation of hybrid organic–inorganic materials have attracted much attention due to their widespread applications in catalysis, adsorption, chromatography, electrochemistry, gas storage, sensor technology and solid phase extraction [27,28]. Among these, bifunctional organosilica materials are of great importance due to high thermal and mechanical stability, containing organic functional groups inside both the body and surface, and excellent lipophilicity [29–33]. As an example, chemical grafting of n-propylsulfonic acids on organosilica supports, for the production of strong acidic sites, has been successfully applied as effective approach in catalytic processes [34]. The preparation of supported sulfonic acid catalysts has been achieved by oxidation of immobilized thiols [35–37]. To date, several materials have been used as support for catalytic sulfonic acid groups in several organic transformations [35–37].

On the other hand, bis(indolyl)methanes are an important class of organic compounds that have been very interested in pharmacology and fine chemistry worlds due to their diverse medicinal utility such as anti-cancer, antibacterial, anti-inflammatory and analgesic agents [38,39]. The synthesis of bis(indolyl)methanes has been traditionally achieved under homogeneous conditions in the presence of both Lewis and Bronsted acid catalysts such as trichloro-1,3,5-triazine [40], 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) [41] and pentafluorophenylammonium triflate (PFPAT) [42]. Due to problems of homogeneous systems such as catalyst recovery and product separation, several recoverable heterogeneous catalysts have also been reported in this matter. Some of recently developed catalysts are $Fe_3O_4@SiO_2@(CH_2)_3$-Urea-SO_3H/HCl [43], graphene oxide [44], $AlPW_{12}O_{40}$ [45], $ZrCl_4$ [46], $ZnCl_2/SiO_2$ [47], silica sulfuric acid (SSA) [48], $NH_4[NbO(C_2O_4)_2(H_2O)_x]\cdot nH_2O$ [49], hyper-cross-linked polyaromatic spheres bearing

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bromomethyl functionality (HCP@CH_2Br) [50], SBA-15-supported poly(4-styrenesulfonyl(perfluorobutylsulfonyl)imide) (PSFSI) [51] and cross-linked organic polymer containing-CO_2H (COP-A) [52]. However, the most of these reports suffer from disadvantages such as long reaction time, the use of large amounts of catalyst, the use of organic solvent and harsh reaction conditions. Therefore, the importance of overcoming these disadvantages is growing as attention and many efforts are being made to develop an efficient catalytic system for the synthesis of bis(indolyl)methanes.

In continuation of aforementioned studies and also according to importance of supported ILs and sulfonic acid based catalysts systems, herein, a novel sulfonic acid-functionalized ionic liquid based organosilica (IL-OS-SO_3H) is prepared, characterized and applied as powerful and durable catalyst for the synthesis of bis(indolyl) methanes at room temperature under solvent free conditions. The recoverability and reusability of the catalyst have also been studied under applied conditions.

2. Experimental

2.1. Preparation of IL-OS- SH material

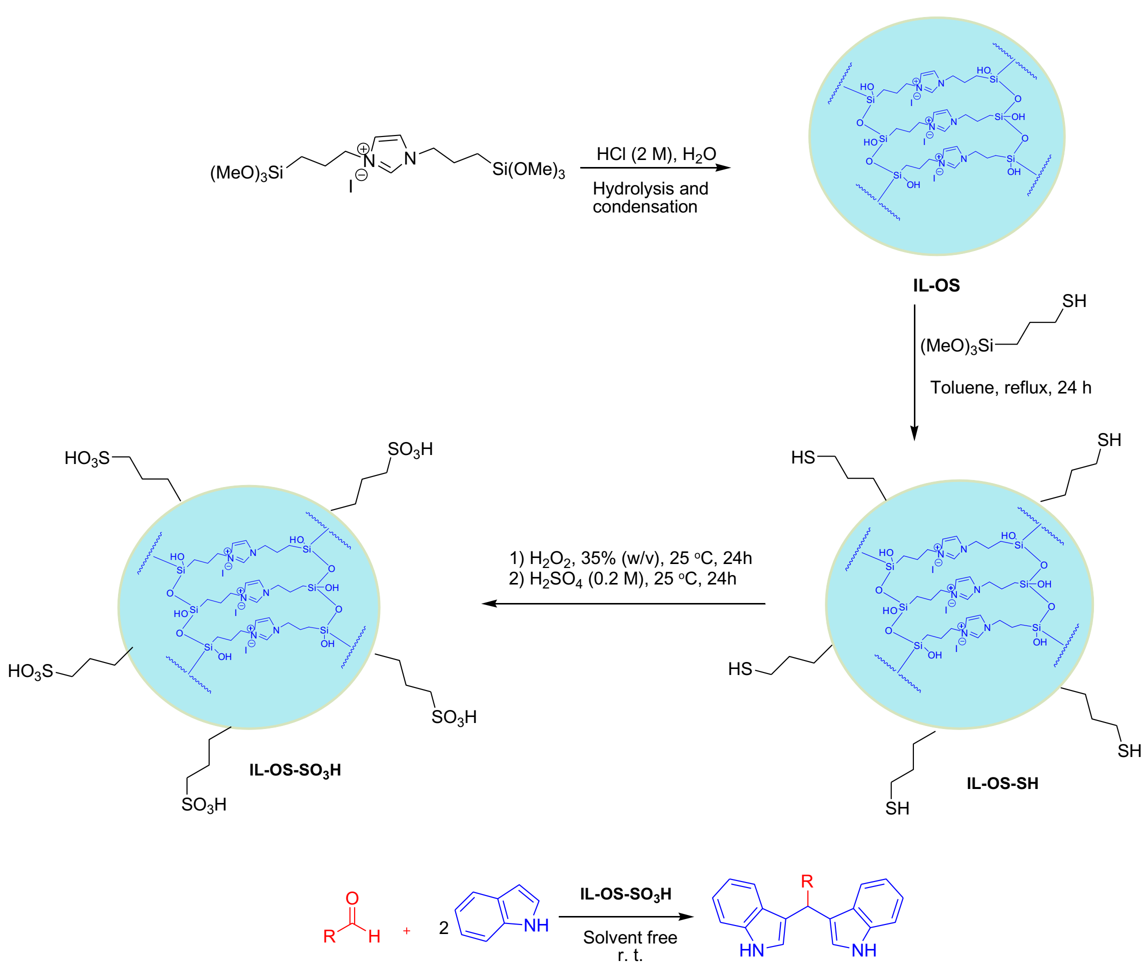
Firstly, the ionic liquid based organosilica (IL-OS) was synthesized *via* simultaneous hydrolysis and condensation of 1,3-bis(3-trimethoxysilylpropyl)-imidazolium iodide (30 mmol) in H_2O (30 mL) and HCl (2 M, 70 mL) at room temperature for 24 h [16]. The prepared IL-OS was then modified with 3-mercaptopropyl-trimethoxysilane through a grafting approach. In a typical procedure, IL-OS (1 g) was added to dry toluene (25 mL) at 25 °C and stirred for 10 min. After complete dispersion of IL-OS, 3-mercaptopropyl-trimethoxysilane (1 mmol) was added to the reaction vessel and the obtained mixture was refluxed under argon atmosphere for 24 h. The resulting material was filtered and washed thoroughly with dry toluene to remove unreacted mercapto-propyl-trimethoxysilane. The final product was dried overnight at 70 °C and gave a white powder denoted as IL-OS-SH (Scheme 1).

2.2. Preparation of the IL-OS-SO_3H catalyst

This material was obtained through oxidation of SH groups of IL-OS-SH in the presence of H_2O_2. Typically, IL-OS-SH (1 g) was added to a flask containing H_2O_2 (15 mL, 35%) and stirred at RT for 24 h. After oxidation treatment, the resulting mixture was filtered and washed completely with water and ethanol. Next, the obtained sample was acidified in 0.1 M H_2SO_4 solution (25 mL) for 2 h. The material was then washed thoroughly with deionized water, filtered, dried at 70 °C for 12 h and denoted as IL-OS-SO_3H.

2.3. Determination of acidity of the OS-IL-SO_3H catalyst

Sulfonic acid loading on the OS-IL-SO_3H surface was calculated by ion-exchange pH analysis [53]. For this, to an aqueous solution of NaCl (1 M, 0.025 L), 50 mg of IL-OS-SO_3H was added and the resulting mixture was stirred at room temperature for 60 h. Then, an inverse titration by NaOH (0.05 M) was carried out on the obtained solution. The loading of H^+ on the IL-OS-SO_3H surface



Scheme 1. Preparation of the IL-OS-SO_3H catalyst and its application in the synthesis of bis(indolyl)methanes.