

Acylation of sulfonamides using silica grafted 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium ionic liquids as catalysts

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Abstract

Heterogeneous immobilized ionic liquid catalysts were prepared via grafting of 1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate or bis{(trifluoromethyl)sulfonyl} imide ([NTf₂]⁻) on silica supports with different surfaces and pore size. In addition to the adsorption–desorption isotherms of nitrogen at –196 °C, the catalysts were characterized by TG-DTA, XPS, DRIFTS, DR-UV–vis, NMR, and XRD techniques. The catalytic behavior was checked in the acylation of three different sulfonamides: benzenesulfonamide, *p*-nitrobenzenesulfonamide, and *p*-methoxybenzenesulfonamide with acetic acid, acetic anhydride and maleic anhydride. These tests confirmed the acid Lewis properties of these catalysts.

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1. Introduction

Friedel–Crafts acylation is one of the most important reactions due to the multiple applications in organic syntheses [1]. Typically, this reaction is catalyzed by homogeneous Friedel–Crafts Lewis acid catalysts such as AlCl₃. However, the use of such homogeneous acid-catalysts has some major limitations including no possible reuse, air and moisture sensitivity and low product selectivity [2]. As a result one of the challenges in the field of catalysis is to replace this commonly used Lewis acid by a non-toxic, non-corrosive, easy to handle and environmentally friendly catalyst. Although heterogeneous acidic catalysts in the liquid-phase can alleviate these issues. Many of these materials, for example zeolites, often require higher reaction temperatures than those used under homogeneous conditions [3]. Also, the use of heterogeneous solid

acid catalysts may lead to different selectivities than those resulted using homogeneous AlCl₃ [4].

Ionic liquids have been suggested as a possible replacement for Lewis acid catalysts [5]. In addition to the known properties of these compounds like negligible vapor pressure, low toxicity, stability against water, they may exhibit tunable properties due to the possibility to change both the organic cation and the inorganic anion. As well as their use as liquids, Lewis-acidic ionic liquids have been immobilized on solid supports. Hoelderich and co-workers have immobilized ionic liquids based on FeCl₃, SnCl₂, and AlCl₃ for Friedel–Crafts processes [6–9]. In general, the immobilization of ionic liquids on solids brings many advantages for the catalytic system, such as the easier separation from the reaction media and the possible utilization of the catalyst in a continuous system [10].

The acylation of sulfonamides has a special place among organic syntheses because of the pharmacological importance of the sulfonyl acetamides moiety [11–15]. Almost all the acylation methodologies suffer from long reaction times, stringent conditions, use of halogenated solvents or the use of

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hazardous materials and catalysts. To avoid major environmental hazards and to satisfy growing stringent global environmental regulations, it is imperative to develop a truly catalytic process with minimal waste production.

The aim of this study was to investigate the acylation of three different sulfonamides: benzenesulfonamide (R = H), *p*-nitrobenzenesulfonamide (R = NO₂), and *p*-methoxybenzenesulfonamide (R = MeO) with acetic acid, acetic anhydride and maleic anhydride as the acylating agents using immobilized 1,3-dimethyl-3-(3-trimethoxysilylpropyl)-imidazolium tetrafluoroborate or bis{(trifluoromethyl)sulfonyl}imide ([NTf₂][−]) on silica supports as heterogeneous catalysts.

2. Experimental

Scheme 1 describes the preparation of immobilized ionic liquid catalysts. The ionic liquid **1** was reacted at 150 °C for 4 h under a nitrogen atmosphere with 3 chloropropyl-triethoxysilane in a molar ratio of 1:1 resulting 1,3-dimethyl-3-(3-triethoxysilylpropyl)-imidazolium chloride (step a). This was then treated with either sodium tetrafluoroborate or lithium bis{(trifluoromethyl)sulfonyl}imide in a ratio 1:1 for 2 days in dry acetone to give the corresponding derivatives **2** and **3** (step b). Then, pretreated silica gel was refluxed with a chloroform solution of compounds **2** and **3** at 65 °C for 26 h to give, after a condensation reaction, the modified support materials.

Silica with three different textural properties were used as the supports (**Table 1**). Samples with small surface area and very large pore size (K1 and K2) and with a rather high surface area but with mesopores were selected (K3). These properties were determined from the adsorption–desorption isotherms of nitrogen at −196 °C using Micromeritics ASAP 2000 apparatus after outgassing the samples at 120 °C K for 24 h under vacuum. The analysis of the isotherms was made using the BET and BJH formalisms. After modifying the supports by the IL grafting process both the surface area and the average pore size of the supports diminished.

In addition to the texture, the catalysts were characterized by TG-DTA, XPS, DRIFTS, DR-UV–vis, NMR, and XRD techniques. TG-DTA measurements were performed under ambient conditions using a SETARAM 92 16.18 instrument by heating the samples to 1273 K at a rate of 10 K min^{−1}. The XRD patterns were obtained with a SIEMENS D-5000

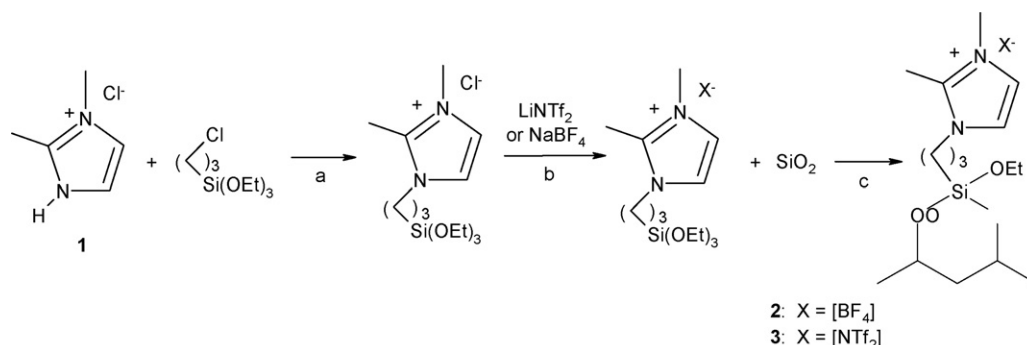
diffractometer operated at 40 kV and 50 mA, equipped with a variable-slit diffracted-beam monochromator and scintillation counter to ensure a strict monochromatization of the X-ray beam. The diffraction patterns were recorded in the range 0–80° 2θ using Cu Kα radiation (λ = 1.54183 Å). The XPS spectra were obtained with a Leybold Heraeus spectrometer with monochromated Al Kα radiation. The spectrometer energy scale was calibrated using the Au 4f_{7/2} peak (binding energy: 84.0 eV). For the calculation of the binding energies, the C 1s peak of the C-(C,H) component at 284.8 eV was used as an internal standard. The composite peaks were decomposed by a fitting routine included in the ESCA 8,3 D software. The superficial composition of the investigated samples was determined using the same software. The peaks assigned to F 1s, O 1s, Si 2p_{3/2}, N 1s, B 1s, S 2p, and C 1s levels were analyzed. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were collected on a Nicolet 4700 spectrometer (200 scans with a resolution of 4 cm^{−1}). Pure samples were placed inside a controlled environmental chamber attached to a diffuse reflectance accessory (Smart collector). DRIFT spectra were recorded at room temperature.

DR-UV–vis spectra were collected with a Specord250 (AnalytikJena). ¹H NMR of the analyzed ILs was performed on a 300 MHz AMX-Bürker spectrometer. TMS was used as internal standard and CD₃CN as solvent.

For the reaction, typically a mixture of sulfonamide (1 mmol), acylating agent (3 mmol) and catalyst (15 mg) in THF (4 cm³) as solvent were stirred and reacted in a closed system at 80 °C for 18 h. At the end of the reaction, the catalyst was filtered off and the product was separated from solvent by vacuum distillation at 80 °C as a crystalline solid. The product was then re-dissolved in the HPLC eluent and analyzed. The products were characterized by HPLC-MS technique. Blank experiments carried out in the absence of any catalyst showed no conversion of the investigated substrates under the investigated experimental conditions. Recycling experiments were carried as well. The separated catalyst was reused 5 times without any pretreatment in the same experimental conditions.

3. Results and discussions

¹H NMR analysis indicated that the step “a” in the preparation procedure (**Scheme 1**) was successfully achieved.



Scheme 1. The preparation of SiO₂ immobilized ionic liquid catalysts.

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