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Synthesis of a sulfonic acid functionalized acidic ionic liquid modified silica catalyst and applications in the hydrolysis of cellulose

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ABSTRACT

A sulfonic acid functionalized acidic ionic liquid modified silica catalyst was prepared in 68% overall yield from 3-chloropropyl silica by a simple two step method involving nucleophilic substitution of chlorine with imidazole, then condensation with 1,3-propanesultone and acidification using HCl. This silica supported acid catalyst was shown to be effective in the hydrolysis of cellulose (DP ~ 450) dissolved in 1-*n*-butyl-3-methylimidazolium chloride at 70 °C, producing glucose and total reducing sugars in 26 and 67% yields respectively.

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1. Introduction

Functionalized ionic liquids are a significant evolution in the ionic liquid arena and these materials have been developed for various special applications like catalysts, fossil fuel desulfurization reagents, lubricants and as monomers for the synthesis of ionic polymers [1–4]. The sulfonic acid group functionalized acidic ionic liquids are an important subgroup in the ionic liquid based catalysts class, and have been used in numerous types of reactions including, esterification [5,6], alkylation [7], nitration of aromatic compounds [8], Beckmann rearrangement [9], and alkene polymerizations [10]. These acidic ionic liquids can be used in neat or in a solvent in the catalysis applications and requires the separation of the catalyst during the isolation of the product. Immobilization of the functionalized ionic liquids have the benefits of combining the ionic liquid characteristics with the common advantages of immobilizations, such as ease of recycling and improved selectivity in applications involving catalytic activity. There are several reports on the preparation of ionic liquid covalently grafted silicas as chiral catalysts [11], esterification catalysts [12,13], and functionalized hydroxyapatite-encapsulated-Fe_2O_3 magnetic nanoparticles [14]. Yokoyama et al. has recently reported [15] the immobilization of a sulfonic acid functionalized ionic liquid catalyst and application of this catalyst for the esterification and nitration of aromatic compounds. In this study, vinyl substituted imidazolium ionic liquid has been grafted on to 3-mercaptopropyltrimethoxysilane modified silica gel by free radical polymerization using azodiisobutyronitrile (AIBN) as the initiator.

Among various interesting properties of ionic liquids, their ability to dissolve cellulose and lignocellulosic biomass has attracted the attention of a number of researchers in recent times [16,17]. In this regard imidazolium ion based 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl) are well known for their cellulose dissolution capabilities. However, hydrolysis and degradation of cellulose in the ionic liquid medium is a relatively less explored application for these systems. Zhao et al. has recently reported [18,19] the homogeneous phase hydrolysis of cellulose using concentrated sulfuric acid as the catalyst in 1-*n*-butyl-3-methylimidazolium chloride medium without any pretreatment. Furthermore, solid acid catalysts like HY-Zeolite are also known to be effective in the hydrolysis of cellulose in BMIMCl medium [20]. Recently, we have shown [21] that cellulose dissolved in Brönsted acidic ionic liquids 1-(1-propylsulfonic)-3-methylimidazolium chloride and 1-(1-butylsulfonic)-3-methylimidazolium chloride can be hydrolyzed at 70 °C under atmospheric pressure by the addition of 2.0 equivalents of water per glucose unit to give glucose along with other reducing sugars. In these experiments, the hydrolysis of Sigmacell cellulose (DP ~ 450) in 1-(1-propylsulfonic)-3-methylimidazolium chloride produced the highest total reducing sugar (62%) and glucose (14%) yields, and was attained with 1 h of preheating at 70 °C and 30 min heating at 70 °C, after adding water.

Our interest in the use of ionic liquid medium for the acid catalyzed hydrolysis of cellulose into glucose and fermentable sugars for the production of cellulosic-ethanol has led us to study the immobilization

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of sulfonic acid functionalized ionic liquids on silica surface. In this communication we report an efficient and simple two step preparation of imidazolium based acidic ionic liquid modified silica using 3-chloropropyl silica as shown in Fig. 1, and application of this catalyst for the hydrolysis of cellulose in BMIMCl medium.

2. Experimental

2.1. Materials and instrumentation

Fluka 60738 silica gel 60, 220–440 mesh (particle size 0.035–0.070 mm) was used for the preparation of 3-chloropropyl silica (**1**). (3-Chloropropyl)triethoxysilane, imidazole, 1,3-propanesultone, 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl), and Sigmacell® cellulose (DP ~ 450) were purchased from Aldrich Chemical Co. FT-IR spectra were recorded on a JASCO-470 PLUS IR spectrometer using KBr pellets. Thermogravimetric analysis was carried out in air using TA instruments TGA 2050 system. Elemental analysis was performed at QTI laboratories, New Jersey. Total reducing sugars (TRS) and glucose concentrations in aqueous solutions were determined using a Carey 50 UV–Vis spectrophotometer and 1 cm quartz cells.

2.2. Synthesis of 3-chloropropyl silica (1)

3-Chloropropyl silica (**1**) was prepared by using a modification of the method used by Adam et al. [22]. A mixture silica (10.0 g) and (3-chloropropyl)triethoxysilane (10.0 mL, 9.42 g, 42.5 mmol) in 15 mL of toluene was prepared and magnetically stirred for 15 min at room temperature, and then refluxed for 24 h. The reaction mixture was cooled, and the product was filtered and repeatedly washed with toluene (3 × 10 mL) and dried under reduced pressure at 100 °C for 8 h to produce 3-chloropropyl silica **1** (10.9 g).

IR 465, 699, 802, 1096, 1638, 2963, 3453 cm^{-1}

TGA: stable up to 270 °C, 5.5% weight loss with the decomposition of all organic structure at 660 °C. Chloropropyl group loading was calculated as 0.71 mmol/g by using thermogravimetric analysis data.

2.3. Synthesis of 3-(1-imidazole)propyl silica (2)

To a solution of imidazole (0.774 g, 11.38 mmol) in 25 mL of dry benzene, 50% sodium hydride in mineral oil (0.546 g, 11.38 mmol) was added and stirred under a nitrogen atmosphere at room temperature for 30 min to give sodium imidazole. Then 3-chloropropyl silica (**1**) (5.00 g, 3.55 mmol of Cl) was added and the mixture was refluxed under a nitrogen atmosphere for 24 h. The resulting product was filtered and washed with ethanol (3 × 20 mL) and dried under vacuum at 100 °C for 24 h to give 4.93 g of 3-(1-imidazole)propyl silica (**2**).

IR 475, 797, 1093, 1513, 1638, 2962, 3453 cm^{-1}

TGA: stable up to 224 °C, 7.5% weight loss with the decomposition of all organic structure at 550 °C. 3-(1-Imidazole)propyl group loading was calculated as 0.69 mmol/g by using thermogravimetric analysis data.

2.4. Synthesis of sulfonic acid functionalized acidic ionic liquid modified silica (3)

3-(1-Imidazole)propyl silica (**2**) (3.78 g, 2.61 mmol of imidazole group) was suspended in 5 mL of dry toluene and 1,3-propanesultone (0.320 g, 2.62 mmol) was added. The resulting mixture was stirred at 100 °C in an oil bath for 6 h, and then cooled to room temperature, filtered and washed with dry toluene (3 × 10 mL) to give imidazolium salt grafted silica. The intermediate was then treated with 36% w/w concentrated hydrochloric acid (0.266 g, 2.62 mmol) and allowed to stand at room temperature for 24 h. The resulting product was washed with ether (3 × 20 mL), dried under vacuum at 100 °C for 24 h to give 3.96 g of sulfonic acid functionalized acidic ionic liquid modified silica catalyst (**3**)

IR 463, 803, 1102, 1565, 1640, 2932, 3447 cm^{-1}

Found: C, 6.82; H, 1.49; N, 1.70%. Calc. for $SiO_2 \cdot 0.0486(C_9H_{16}N_2SO_2Cl) \cdot 0.1H_2O$: C, 7.01; H, 1.32; N, 1.82%.

TGA: stable up to 220 °C, 17.8% weight loss with the decomposition of all organic structure at 660 °C. Sulfonic acid group loading was calculated as 0.67 mmol/g by using thermogravimetric analysis data.

Determination of acidic sites: Titration of acidic ionic liquid modified silica catalyst (**3**) with 5.05 × 10^{-2} M aq. NaOH, using phenolphthalein as the indicator gave SO_3H group loading as 0.677 mmol/g.

2.5. Synthesis of sulfonated silica (4)

Sulfonated silica (**4**) was prepared by reacting silica with neat chlorosulfonic acid at room temperature, as shown in Fig. 2, following the literature procedure [23]. The acidic site loading in this sulfonated silica (**4**) was determined as 2.52 mmol/g by titration with 5.05 × 10^{-2} M aq. NaOH, using phenolphthalein as the indicator.

2.6. General experimental procedure for hydrolysis of cellulose using 3, 4, or H_2SO_4 as catalyst

Cellulose (0.030 g, 0.185 mmol of glucose unit of cellulose) was dissolved in 0.300 g of 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl) ionic liquid by heating at 80 °C for 4 h. Then catalyst (5–10 mol%), and deionized water (6.7 µL, 2.0 equivalents/glucose unit of cellulose) were added and the sample was warmed in a thermostated water bath for a pre-determined time for the hydrolysis of cellulose. Then the reaction was quenched by adding 10.0 mL of deionized water and transferred to a centrifuge tube and centrifuged at 3500 rpm for 6 min to precipitate and recover the acidic ionic liquid modified silica catalyst. The clear supernatant was collected and the acidic ionic liquid modified silica catalyst was repeatedly washed (dispersion in 3 mL of deionized water followed by centrifugation, three cycles) for recycling experiments. The supernatant and the washings were combined and the total reducing sugar (TRS) and glucose produced during the hydrolysis of cellulose were measured using the procedures described in the Sections 2.6 and 2.7. The average TRS and glucose yields produced in duplicate experiments are shown in Table 1 as entries 1–8.

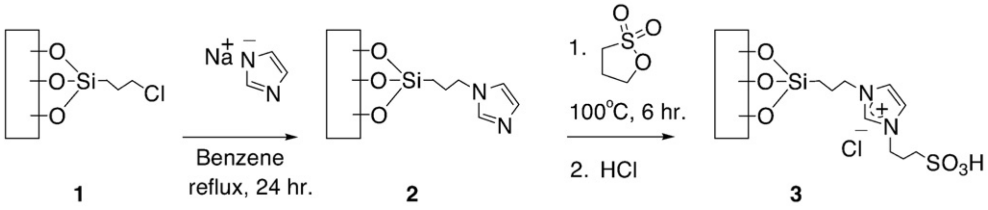

Fig. 1. Synthesis of sulfonic acid functionalized acidic ionic liquid modified silica catalyst (**3**).