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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.

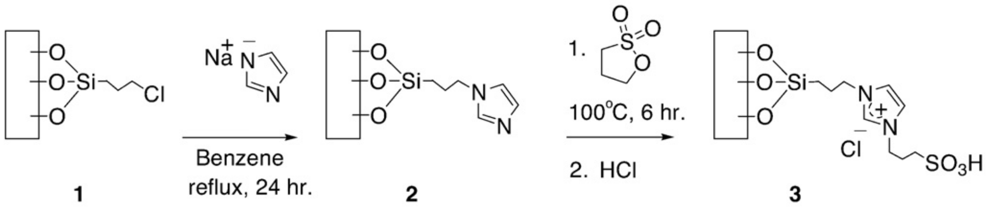

Fig. 1. Synthesis of sulfonic acid functionalized acidic ionic liquid modified silica catalyst (**3**).

Fig. 2. Synthesis of sulfonated silica (**4**).

2.7. Total reducing sugar (TRS) assay for cellulose hydrolyzate

2.50 mL of the clear solution from the centrifuge tube was transferred to a vial and 0.50 mL of DNS reagent [24] was added. The resulting solution was heated at 90 °C for 5.0 min to develop the red-orange color. Then the absorbance was measured at 550 nm using 1 cm quartz cells and Carey 50 UV–Vis spectrophotometer. TRS Concentration in the solution was calculated by employing a standard curve prepared using glucose.

2.8. Glucose assay for cellulose hydrolyzate

1.0 mL of the clear solution from the centrifuge tube was transferred to a vial, and 2.0 mL of glucose assay reagent [25] (Sigma-Aldrich Glu 20 kit) was added. The resulting solution was heated at 37 °C for 30 min, and reaction was quenched by adding 2.0 mL of 12 N H_2SO_4 to give a pink solution. Then the absorbance was measured at 540 nm using 1 cm quartz cells and Carey 50 UV–Vis spectrophotometer. Glucose concentration in the solution was calculated by employing a standard curve prepared using glucose.

2.9. Reuse of the sulfonic acid functionalized acidic ionic liquid modified silica catalyst (3)

The washed acidic ionic liquid modified silica catalyst (**3**) was collected and dried in an oven at 105 °C for 24 h. This recycled catalyst was used for the hydrolysis of cellulose using procedure 2.5 and the hydrolyzate was analyzed using procedures 2.6 and 2.7. The results of reusing the same catalyst sample in five cycles are shown in Table 2.

3. Results and discussion

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

Sulfonic acid functionalized acidic ionic liquid modified silica (**3**) was synthesized in two steps, and 68% overall yield as shown in Fig. 1.

Table 1
Average percent yields of TRS and glucose produced in duplicate experiments of hydrolysis of untreated cellulose using sulfonic acid functionalized acidic ionic liquid modified silica (**3**), H_2SO_4, sulfonated silica (**4**), and 1-(1-propylsulfonic)-3-methylimidazolium chloride (PSMIMCl).

Entry	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield (%)		Ref.
				TRS	Glucose	
1	**3**(5)[a]	70	2.0	26	10	This work
2	**3**(5)[a]	70	4.0	28	10	This work
3	**3**(10)[a]	70	4.0	52	15	This work
4	**3**(10)[a]	70	6.0	67	26	This work
5	**3**(10)[a]	70	10.0	55	19	This work
6	**3**(10)[a]	90	6.0	29	12	This work
7	H_2SO_4(10)[a]	70	6.0	38	6	This work
8	**4**(10)[a]	70	6.0	24	11	This work
9	PSMIMCl[b]	70	0.5	62	14	[21]
10	PSMIMCl[b]	70	1.0	42	7	[21]
11	PSMIMCl[b]	70	4.0	29	4	[21]

[a] 0.030 g of cellulose (DP ~ 450) dissolved in 0.300 g of 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl), and 6.7 µL of H_2O were added before the hydrolysis.
[b] 0.030 g of cellulose (DP ~ 450) dissolved in 0.300 g of 1-(1-propylsulfonic)-3-methylimidazolium chloride (PSMIMCl), and 6.7 µL of H_2O were added before the hydrolysis.

Table 2
Average percent yields of TRS and glucose produced in duplicate experiments reutilizing catalyst (**3**) for the hydrolysis of untreated cellulose (DP ~ 450).

Run	Yield (%)	
	TRS	Glucose
1	67	26
2	65	26
3	64	24
4	60	25
5	60	22

0.030 g of cellulose (DP ~ 450) dissolved in 0.300 g of 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl), and 10 mol% catalyst were used in all experiments. Reaction time: 6 h. Temperature: 70 °C and 6.7 µL of H_2O was added before the hydrolysis.

3-Chloropropylsilica (**1**) was first prepared by reaction of (3-chloropropyl)triethoxysilane with silica and then nucleophilic substitution of the chlorine with imidazole group gave 3-(1-imidazole)propyl silica (**2**). Condensation of 3-(1-imidazole)propyl silica (**2**) with 1,3-propanesultone produced the imidazole salt, which was treated with one equivalent of hydrochloric acid to give the sulfonic acid functionalized acidic ionic liquid modified silica (**3**). This is a simple two step linear synthesis of acidic ionic liquid grafted silica when compared with the earlier approach for the preparation of a similar catalyst [15].

3.2. Structural characterization of sulfonic acid functionalized acidic ionic liquid modified silica catalyst (3)

3.2.1. Elemental analysis and TG–DTG

Acidic ionic liquid modified silica (**3**) was characterized using elemental analysis, thermogravimetric–derivative thermogravimetric (TG–DTG) analysis, and FT-IR spectroscopy. The thermogravimetric analysis (TG) curve showed (Fig. 3) an initial weight loss of 2.4% up to 110 °C due to surface silanol groups and the adsorbed water in silica. Complete loss of all the covalently attached organic structure is seen in the 220–660 °C temperature range leaving SiO_2, and the organic fraction corresponds to 17.8% weight of the acidic ionic liquid modified silica. This decomposition of the organic structure occurs in two steps and the two peaks in the DTG curve at 390 and 532 °C, are related to 13.0 and 4.8% weight losses. The immobilized acid catalyst is apparently stable up to about 220 °C. By using the thermogravimetric data, the empirical formula of the catalyst can be calculated as $SiO_2 \cdot 0.0486\ (C_9H_{16}N_2SO_3Cl) \cdot 0.1H_2O$. Structural characterization for the catalyst **3** was supported by elemental analysis data shown in Section 2.4. These CHN analysis results are within ±0.19% of the CHN percentages calculated using thermogravimetric analysis based formula: $SiO_2 \cdot 0.0486\ (C_9H_{16}N_2SO_3Cl) \cdot 0.1H_2O$.

3.2.2. FT-IR

The FT-IR spectrum of the functionalized acidic ionic liquid modified silica (**3**) is shown in Fig. 4. The peak at 1565 cm^{-1} can be

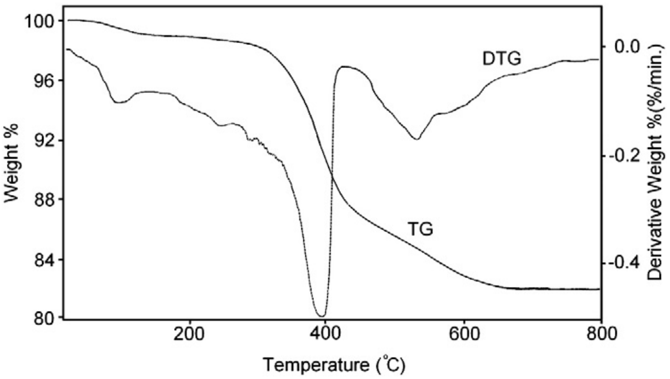

Fig. 3. TG–DTG of sulfonic acid functionalized acidic ionic liquid modified silica catalyst (**3**).

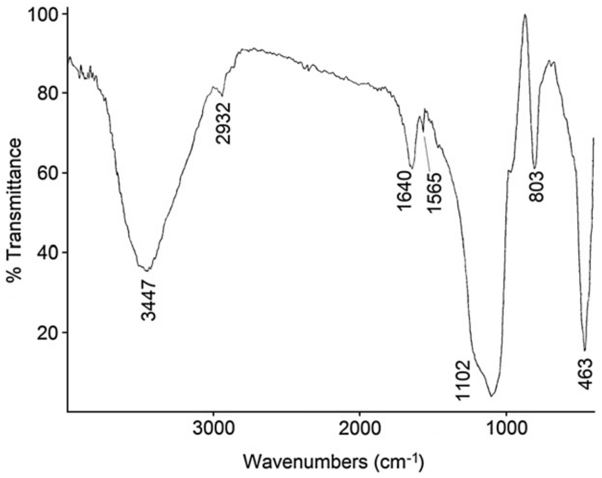

Fig. 4. FT-IR spectrum of sulfonic acid functionalized acidic ionic liquid modified silica catalyst (**3**).

assigned to the imidazolium ring, and Yokoyama has reported [15] a similar absorption at 1563 cm^{-1} for an imidazolium system attached to a silica surface through alkyl sulfide tether in their preparation of ionic liquid modified silica. The Si–O absorption of silica can be observed as a strong peak at 1102 cm^{-1}, whereas the weak absorption at 2932 cm^{-1} can be assigned to the C–H bonds in **3**. Furthermore, the broad absorption in the region of 3447 cm^{-1} is due to the Si–OH groups on the surface of the silica.

*3.3. Comparison of the catalytic activity of acidic ionic liquid modified silica catalyst **3** with other catalysts*

Hydrolysis of cellulose using acidic ionic liquid modified silica catalyst produced glucose and other reducing sugars. The TRS and glucose yields produced in these hydrolysis experiments are shown in Table 1. Initial experiments using 5 mol% of the catalyst **3** (entries 1 and 2) gave relatively low TRS and glucose yields, therefore the catalyst loading was increased to 10 mol% in the subsequent set of experiments. The highest TRS and glucose yields of 67 and 27% respectively were obtained in the experiment using 10 mol% of catalyst **3**, at 70 °C after a 6 h reaction time (entry 4). Heating the sample at 70 °C for a longer time (entry 5) or at a higher temperature (entry 6) failed to give better yields of TRS and glucose, indicating the importance of reaction time and temperature in the hydrolysis reaction. Furthermore, longer heating times (entry 5) and higher temperatures (entry 6) produced excessive charring of the sample, giving black residues, and thus lowering the TRS and glucose yields. The experiment using 10 mol% H_2SO_4 catalyst (entry 7) produced 38% TRS yield and low 6% glucose yield. Sulfonated silica (**4**) produced only 24% TRS and 11% glucose (entry 8), showing the importance of the imidazolium chloride tether. The higher catalytic activity of acidic ionic liquid modified silica catalyst (**3**) may be due to hydrogen bonding interactions of chloride ion with the hydrogens of cellulose OH groups. Entries 9–11 shows the results from our previous work on hydrolysis of cellulose using 1-(1-propylsulfonic)-3-methylimidazolium chloride (PSMIMCl) as the solvent as well as the catalyst. Even though, good TRS values are obtained in shorter times (entry 9; 62% TRS in 0.5 h) using PSMIMCl medium, glucose yields are comparatively lower in these experiments. Furthermore, longer reaction times like 4 h (entry 11) resulted in much lower TRS and glucose values.

*3.4. Reuse of the catalyst (**3**)*

The reusability of the catalyst (**3**) was tested by using the same catalyst sample in five catalytic cycles using 10 mol% of catalyst in the hydrolysis of cellulose at 70 °C for 6 h, and the results of these experiments are shown in Table 2. This catalyst recycling experiment shows that sulfonic acid functionalized acidic ionic liquid modified silica catalyst (**3**) can be reused for the hydrolysis of cellulose in BMIMCl medium with a small loss of catalytic activity.

4. Conclusion

In summary, we have demonstrated that sulfonic acid functionalized acidic ionic liquid modified silica (**3**) can be prepared in 68% overall yield from 3-chloropropyl silica (**1**), in a simple two step method by using nucleophilic substitution reaction of chlorine with imidazole anion and then condensation of the alkylimidazole silica with 1,3-propane sultone followed by acidification with HCl. The immobilized acidic ionic liquid catalyst (**3**) is shown to be effective in the hydrolysis of cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride at 70 °C and at atmospheric pressure. Additionally, the catalyst can be recovered through a simple separation protocol and can be reused with a small loss in the activity.

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