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Functionalized ionic liquids supported on silica as mild and effective heterogeneous catalysts for dehydration of biomass to furan derivatives

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Graphical abstract



HIGHLIGHTS

- A series of ILs covalently grafted silica have been prepared using ethanol solvent.
- Superior catalytic activity was achieved with IL-SO₃H-HSO₄/SiO₂ in biomass

conversion.

• IL-SO₃H-HSO₄/SiO₂ showed good catalytic stability.

Abstract

A series of functional ionic liquid supported silica nanoparticles with different acidity (ILs/SiO₂) have been prepared by covalent bonds using novel, non-toxic ethanol as solvent. Compared with using toluene or acetonitrile as solvent in traditional prepared method, the process represents a green, environmental friendly route to synthesize supported functional ionic liquid catalysts (SFILCs). These SFILCs, with the benefits of ionic liquid and the advantages of immobilization, were first systematically utilized in biomass dehydration reactions and proved to be efficient heterogeneous catalysts for the preparation of furan derivatives from various carbohydrates. However, the supported dual acidic functional ionic liquid catalyst (3-sulfobutyl-1-(3-propyltriethoxysilane)imidazolium hydrogen sulfate) was found to be more active and selective than other ILs/SiO₂ and the conversion of fructose, glucose, xylose, sucrose, cellobiose was up to 99%, 96%, 94%, 76% and 99%. Moreover, the reducing sugar (TRS) yield of microcrystalline cellulose dehydration was up to 77%.

Keywords: Carbohydrates; 5-HMF; Furfural; Ionic liquids; Immobilization.

1 Introduction

Since the global consumption of the liquid petroleum tripled in the ensuing years, continued reliance on petroleum feedstock will lead to an unacceptable amount of greenhouse gas emissions which has been the major concern.[1] Biofuel has potential to be sustainable substitutes as its economic, efficient, and environmentally benign properties.[2] Among current biofuel sources, furan derivatives, such as 5-hydroxymethylfurfural (5-HMF) and furfural, obtained from renewable biomass derived carbohydrates are versatile and key intermediates that are attracting much attention in biofuels chemistry and the petroleum industry.[3] Last few years have witnessed rapid progress in the conversion of biomass for the preparation of 5-HMF and furfural as a result of their versatile applications.[4]

Ionic liquids (ILs), viewed by some as a sort of novel reaction medium, have gained a variety of applications in catalysis as solvents, catalysts and catalyst carriers due to their non-volatility, wide temperature range for the liquid state, excellent solubility for organic and inorganic materials and structure tunability.[5] The acid group functionalized ionic liquid is an important subgroup in the ionic liquid based catalysts class, and has been used innumerous types of reactions over the past few years.[6] Studies involving the utilization of the acid (both Lewis and Brønsted) functionalized ionic liquids as catalysts for the dehydration reaction of biomass to 5-HMF have also been reported.[7, 8]

Although, homogeneous acid catalyzed biomass dehydration processes using acid functionalized ILs is quite effective but presents serious drawbacks in terms of separation and recycling of costly ILs, equipment corrosion as well as ILs toxicity.[9]

An approach to overcome these limitations is the development of supported functional ionic liquid catalysts (SFILCs) that require smaller amounts of ionic liquids and simultaneously minimize limitations associated to their viscosity, separation, corrosiveness and toxicity. SFILCs combine attractive features of homogeneous catalysis such as the uniform nature of the catalytic centers, high specificity and selectivity of the catalyst, with important features of heterogeneous catalysts, such as high interfacial surface area, high system stability, reusability and potential use in fixed-bed reactor.

Many work have focused on supported ILs on different materials, such as silica,[10] polymers,[11] and magnetic materials.[12] Compared to polymers and magnetic materials, silica is used as carriers for immobilizing ionic liquids widely for the reasons of lower price and availability. Furthermore, it was found that it could contain ionic liquids in comparatively high amounts, depending on the surface area of the silica. [13] There are several reports on the preparation of ionic liquids covalently grafted silica (ILs/SiO₂) and the application used as catalysts in carbohydrates conversion reactions.[14] However, unfortunately, the use of silica immobilizing acid functionalized ionic liquids in dehydration of other saccharides, especially in hydrolysis of cellulose is scarce. In addition, the traditional preparation method is using toluene or acetonitrile as solvent, which is harmful to both human body and environment.

In this study, a series of covalently-bound amorpous silica supporting acid functionalized ionic liquids (ILs/SiO₂) with different acidity and functional group were synthesized using ethanol as the solvent, which is a way of synthesize SFILCs in a green route under mild conditions and were utilized for a variety of sugars and cellulose conversion under mild reaction conditions. As well as this, the reusability of the immobilized acid functional ionic liquids was also investigated.

2 Materials and methods

2.1 Materials

Silica of porous particles (100–200 mesh) used as the support was purchased from the company of Qingdao Chemical Industry and microcrystalline cellulose (average particle size 50µm) from Sigma-Aldrich. Deionized water, acetonitrile (HPLC grade) and methanol (HPLC grade) were degassed ultrasonically prior to use. Phenol and furfural were redistilled before used. [BMIM]Cl was supplied by Center of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics (Lanzhou, China). All other chemicals used were of high purity and were used directly without further purification.

2.2 Synthesis of catalysts

2.2.1 Silica pretreatment and activation

Silica was activated by refluxing in acetone for 24 h at room temperature and then washed thoroughly. The sample was then dried at 100 °C overnight and was activated 4 h at 250 °C.

2.2.2 Synthesis of ILs

According to step 1 in Scheme 1, imidazole (2.72 g, 40 mmol) was heated at 95°C under a nitrogen atmosphere. After imidazole was melt, 3-chloropropyltriethoxy -silane (9.7 ml, 40 mmol) was added and the mixture was refluxed overnight under a nitrogen atmosphere. After the reaction, the mixture was extracted five times with anhydrous ether. The solvent was removed by rotatory evaporation under reduced pressure, and the product (N-(3-propyltriethoxysilane) imidazole chloride) was

obtained as a transparent viscous liquid (IL) (71% yield).

Detailed presentation of physical data of IL:

¹H NMR (300 MHz, CDCl₃): 0.60 (m, 2H), 1.15 (t, 9H), 1.96 (t, 2H), 3.61 (q, 6H), 4.22 (t, 2H), 7.48 (s, 1H), 7.51 (s, 1H), 8.74 (s, 1H);

¹³C NMR (75 MHz, CDCl₃): 11.2, 19.6, 54.2, 54.4, 60.2, 121.7, 124.5, 137.2.

Then, 5 g IL (18.3 mmol) was dissolved in ethanol (15 g) in flask and 1,4-butane sultone (1.87 mL, 18.3 mmol) was added dropwise into above solution under 15° C, then the final mixture was stirred at 30°C for 5 h and heated at 45°C for another 24 h under nitrogen flow (step 2 in Scheme 1). The mixture was evaporated under reduced pressure and extracted five times with diethyl ether. The diethyl ether was removed at a reduced pressure to get a viscous yellow liquid 3-sulfobutyl-1-(3-propyltriethoxy -silane) imidazolium chloride (IL-SO₃H) (64% yield).

Detailed presentation of physical data of IL-SO₃H:

¹H NMR (300 MHz, DMSO-d6): 0.50 (t, 2H), 1.11 (t, 9H), 1.74 (m, 4H), 2.50 (t, 2H), 3.59 (q, 6H), 4.20 (t, 2H), 4.41 (t, 2H), 7.61 (s, 2H), 9.05 (s, 1H);

¹³C NMR (75 MHz, DMSO-d6): 11.2, 19.5, 24.4, 33.3, 46.4, 49.8, 52.6, 59.0, 60.2, 122.0, 124.6, 136.2.

The **IL-SO₃H** (1.0 g) was dissolved in absolute ethanol (30 mL) and conc. H₂SO₄ (0.54 mL, 10 mmol) was added dropwise into the above solution as shown in step 3 sheme 1. The final mixture was stirred at 85°C for 24 h under reflux conditions. The solvent was removed by rotatory evaporation and the mixture was extracted five times with anhydrous ether under reduced pressure. The resulting transparent viscous liquid is 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate (**IL-SO₃H-HSO₄**) and used as the compared reaction.

¹H NMR (300 MHz, DMSO-d6): 0.50 (t, 2H), 1.11 (t, 9H), 1.74 (m, 4H), 2.50 (t, 2H), 3.59 (q, 6H), 4.20 (t, 2H), 4.41 (t, 2H), 7.61 (s, 2H), 9.05 (s, 1H);

¹³C NMR (75 MHz, DMSO-d6): 11.2, 19.5, 24.4, 33.3, 46.4, 49.8, 52.6, 59.0, 60.2, 122.0, 124.6, 136.2.

2.2.3 Grafting of ILs on silica gel

The preparation process was according to known process[15] and shown in step 4 in scheme 1. The IL-SO₃H (1.0 g) was dissolved in absolute ethanol (30 mL) and treated with silica gel (2.0 g). After heating the slurry under reflux conditions for 24 h, the solid was isolated by filtration and washed with ethanol (5 * 10 mL), then was dried under 100°C. The resulting solid is denoted as IL-SO₃H/SiO₂ (powder, 84% yield).

In the next step (see step 5 in Scheme 1), conc. H₂SO₄ (0.54 mL, 10 mmol) was added dropwise into the suspension solution of the above silica supported IL in ethanol (30 mL) according to previous method.[15] The final mixture was stirred at 85°C for 24 h and by filtration, washed and dried to get supported dual acidic ionic liquid **IL-SO₃H-HSO₄/SiO₂** (57% yield).

The immobilization processes of N-(3-propyltriethoxysilane) imidazolium chloride and N-(3-propyltriethoxysilane) imidazolium hydrogen sulfate on silica gel were according to above process, shown in step 6, 7 in scheme 1 and the products were donated as **IL/SiO₂**, **IL-HSO₄/SiO₂**.

2.3 Characterization of catalysts

Element analysis (C, H, N, S) was measured by an Elementar Analysensysteme (GmbH VarioEL cube V1.2.1) to determine the chemical composition of catalysts. The thermogravimetric-differential scanning calorimetry (TG-DSC) curves were obtained from a NETZSCH STA 449F3 thermogravimetric analyzer over the temperature range of 20 to 1000°C at a heating rate of 10°C/min. N₂ adsorption–desorption measurements was carried out using an Autosorb-iQ analyzer (U.S.). Pore size distributions and the specific surface areas were calculated via the

BJH method and BET method respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet (iS10) IR spectrometer. Solid ¹³C Nuclear Magnetic Resonance (NMR) experiments were performed using a Bruker Avance II WB 400 MHz NMR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AX (300 MHz) spectrometer using CDCl₃ or DMSO-d₆ as solvent and reference. ²⁹Si MAS-NMR spectra were recorded on a Varian-Infinity Plus Spectrometer at 400 MHz. Determination of acidic sites: The amounts of acidic site after synthesis of ILs/SiO₂ were measured by means of acid–base titration. In a typical experiment 0.2 g of acidic ionic liquid modified silica catalyst was added to 5 g aqueous solution. The resulting suspension was allowed to equilibrate for 6 h and then titrated with 5.05×10^{-2} M (aq.) NaOH using phenolphthalein as the indicator.[16]

2.4 Catalytic activity

2.4.1 Conversion of carbohydrates

All the dehydration reaction experiments were performed in a 5 mL round bottom flask under magnetic stirring and equipped with a condenser. In a typical procedure, specific amount of substrates and powdered catalyst (ILs/SiO₂) were charged into the DMSO (1.8g). The reactor was raised to a certain temperature and held at this temperature for a given period of time. After reaction, the solid catalyst was centrifuged and washed with ethanol; the supernatant liquid were diluted and then analyzed by HPLC based on the external standard method. The amount of catalyst was decided as 0.05 g and the substrates as 0.2 g after optimization in advance.

2.4. 2 Conversion of cellulose

For the conversion process for cellulose, it was the same as that for cellobiose, glucose, xylose except exclusion of the pre-treatment step. For pre-treatment, cellulose (0.2 g) was added into [BMIM]Cl (2 g), and the whole mixture was heated at 160°C for 0.5 h with stirring for dissolution of cellulose.

2.5 Analysis of substrates and products

2.5.1 Analysis of sugars, 5-HMF and furfural.

After reaction, the mixture was centrifuged and the supernatant liquid was analyzed by high-pressure liquid chromatography (HPLC). Substrates were analyzed using an Agilent 1100 Series HPLC equipped with a PHENOMENEX REZEX RHM-Monosaccharide H⁺ (8%) (300 mm ×7.8 mm, 5 μ m) column and a refractive index detector (RID). The column temperature was maintained at 70.0°C and water was used as mobile phase (flow rate: 0.60 ml/min). 5-HMF was quantified using a reversed-phase C18 column and a multi-wavelength detector at 280 nm connected to HP1090 HPLC. The mobile phase was 50.0% (v/v) acetonitrile aqueous solution at a flow rate of 0.5 ml/min. To ensure the reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. The obtained results including conversion and yield data were found to be reproducible in the range of \pm 5.0% variation.

Conversion of substrates and the yield of products were calculated according to the following equations:

The conversion of substrates (mol%) = the molar of substrates converted *100 / the molar of initial substrates.

The yield of products (mol%) = the molar of products produced *100 / the molar

of initial substrates \times n. (n is 1 for monosaccharide and n is 2 for disaccharide)

The selectivity of products (%) = the molar of products produced *100/the molar of substrates converted \times n. (n is 1 for monosaccharide and n is 2 for disaccharide)

In the cases using DMSO as a solvent, the products were extracted with diethyl ether prior to gas chromatography–mass spectrometry (GC) analysis. Qualitative analysis of 5-HMF was performed by Agilent 7890A equipped with HP-5 capillary column and Triple-Axis detector.

To obtain the reliable data of the reaction, repeated experiments were carried out under identical reaction conditions. The obtained results including conversion of substrates and yield of products were found to be reproducible in the range of \pm 5.0% variation. The experimental error in injection was below 2%.

2.5.2. Total reducing sugar (TRS) assay for cellulose dehydration

2.50 mL of the clear solution from the centrifuge tube was transferred to a vial and 0.50 mL of DNS reagent was added.[17] The resulting solution was heated at 100 °C for 5.0 min to develop the red-orange color. Then the absorbance was measured at 484 nm using 1 cm quartz cells and Carey 8753 UV–Vis spectrophotometer. TRS concentration in the solution was calculated by employing a standard curve prepared using glucose.

The yield of TRS (wt%) = the weight of TRS produced *100 / the weight of initial cellulose.

2.6 Recyclability and stability study of catalyst

Reused experiments were carried out by triplicating reagent and catalyst quantities (to ensure enough catalyst was present for each reuse) under otherwise identical conditions in typical reaction runs. Upon reaction completion, catalysts were filtered off, washed thoroughly with ethanol and dried under 150 °C for 2 h prior to their next use with fresh reagents.

3 Results and discussion

3.1 Characteristics

3.1.1 Nuclear Magnetic Resonance

In our experiments, the dual acidic ionic liquid modified silica gel was characterized by ²⁹Si MAS NMR as well as ¹³C NMR spectra (Fig. 1). The ²⁹Si MAS NMR spectrum signals center for silica after the immobilization of the ionic liquid (IL-SO₃H-HSO₄/SiO₂) is at -92, -101 and -109 ppm, which are assigned to Q² and Q³ and Q⁴ groups [Qⁿ = Si(OSi)_n(OH)_{4-n}], respectively, indicating the presence of residual silanol groups. These results were consistent with literature.[18]

A chemical shift (at $\delta = -59$ and -67 ppm) indicates the formation of Si–O–Si linkage of 3-chloropropyltriethoxysilane (CPTES) to the silicon atoms of the silica via one and two siloxane bonds, i.e. Si–O–SiR–(OEt)₂ and(Si–O)₂SiR–OEt, assigned to T¹ and T² groups [T^m = R-Si(OSi)m(OR/OH)(3-m)], respectively. The absence of T^m shifts in the silica anchored triethoxysilane derivatives of functional ionic liquid spectrum indicates the successful incorporation of CPTES on silica via covalent bonding. [19] In addition, the solid-state ¹³C CP-MAS NMR spectrum (Fig. 1) of IL-SO₃H-HSO₄/SiO₂ which is consistent with the ¹³C NMR of IL-SO₃H-HSO₄ confirmed the presence of the ionic liquid on the silica surface and further supported our above conclusion.

3.1.2 Elemental analysis

The loading amount of ionic liquids on silica gel was determined by element analysis.

The amount of attached molecules onto the silica surface (Lo) calculated by elemental analysis, using the following expression: Lo= the percentage of nitrogen or sulfur*1g / nitrogen or sulfur atomic weight.

Comparing the amount of attached molecules on the silica surface (Table 1), it can be concluded that the degree of functionalization of different catalysts were different. The nitrogen analysis of ILs/SiO₂ (N, 3.6, 4.2, 3.0 and 3.6 mmol/g) indicated that 1.8, 2.1, 1.5 and 1.8 mmol/g of imidazoles were, respectively, grafted on the surface of silica gel. However, as it can be observed, the N/S ratio was higher than expected value ((1/2N) : S was 0.5 for IL-SO₃H-HSO₄/SiO₂ and 1 for other catalysts) except IL-HSO₄/SiO₂ due to the presence of imidazole which was not bonded with -SO₃H. So we can conclude the anion displacement of HSO₄⁻ and Cl⁻ was sufficient but the reaction of imidazole with 1, 4-butane sulfonic acid lactone was not completed.

3.1.3 Fourier transforms infrared spectra

As can be seen from Fig. 2, there were the stretching vibration peaks of Si–O-Si (v: 1100 cm⁻¹), O–H (1638 cm⁻¹) and the stretching vibration Si–OH (v: 3450 cm⁻¹) clearly observed on curve 1. However, the FTIR spectrum of ILs/SiO₂ (Curve 2-5) exhibit two characteristic peaks at the positions of 1570 and 1460 cm⁻¹, which were attributed to the imidazole ring, indicating that imidazole was successfully grafted on the surface of silica gel both in ILs/SiO₂. Both a very weak band at 1208 cm⁻¹ totally appeared on curves 4 and 5 assigned to the S=O stretching vibration in the silica, which convinced us that the HSO₄⁻ was successfully grafted on imidazole.[20]

3.1.4 N₂ adsorption-desorption

N₂ adsorption–desorption isotherms at 77 K of SiO₂ and ILs/SiO₂ were depicted in Fig. 3. And BJH pore-size distributions of the samples were shown in the inset of Fig. 3.

The samples showed a type IV isotherm with H1 hysteresis, characteristic of highly mesoporous materials. Immobilization of ionic liquid significantly affected the surface area and pore size distribution of the modified samples. The SiO₂ sample possessed the pore volume of 0.97 cm³/g and the BET surface area of 361 m²/g, as shown in Table 1. Immobilization of ILs decreased the surface area and shifts the pore to smaller volume. The both introduction of HSO₄⁻ and R-SO₃H on the IL-SO₃H-HSO₄ /SiO₂ further decreased surface area to only 155 m²/g. Similar reduction after immobilization of other ILs in the BET surface area, pore volumes and pore diameters was also observed in Table 1.

3.1.5 Thermogravimetric Analysis

The thermogravimetric analysis (TG) curve showed (Fig. 4) an initial weight loss under 100°C for both catalysts due to surface silanol groups and the adsorbed water in silica.

Complete loss of all the covalently attached organic structure was seen in the 163-579°C temperature range, and the organic fraction corresponded to 28%, 33%, 41%, 43% weight of the acidic ionic liquid modified silica for IL/SiO₂, IL-HSO₄/SiO₂, IL-SO₃H/SiO₂, IL-SO₃H-HSO₄/SiO₂. However, for the acid functional IL, this decomposition of the organic structure occured in three steps. And the three peaks (in the DTG curve at 163, 367 and 487°C) were related to 6.8, 19.6 and 15.9% weight losses. From TG analysis data, the SO₃H and HSO₄ group loading of the catalyst can be calculated as 0.4 and 1.5 mmol/g (total S loading amount is 1.9 mmol/g), which was agree with the result of element analysis (1.9 mmol/g).

3.1.6 Acidity determination

Titration of acidic ionic liquid modified silica catalyst with 5.05×10^{-2} M NaOH (aq), using phenolphthalein as the indicator gave H⁺/g of ILs/SiO₂ and the results were summarized in Table 1. The acidic site loading in IL-SO₃H-HSO₄/SiO₂ and IL-HSO₄/SiO₂ was found to be 2.0 and 1.5 mmol/g, which indicates 2.0 mmol/g and 1.5 mmol/g sulfonic acid groups was respectivly grafted on to the surface of the silica support. The agreement between the acid–base titration as well as with the organic group loading determined by TGA (1.5, 1.9 mmol/g) and element analysis (1.5, 1.9 mmol/g), is a clear evidence that the sulfonic groups are principally located on the porous surfaces of the silica, where they are accessible for adsorption and catalytic reaction processes. On the other hand, the acidic site loading in SiO₂/IL is more than the sulfur loading measured with element analysis, which is due to the presence of H⁺ on imidazole as shown in scheme 1. However, the fact that the acidity of IL-SO₃H/SiO₂ (1.0 mmol/g) is higher than the SO₃H group loading amount (0.4 mmol/g) proved again that the reaction of imidazole with 1, 4-butane sulfonic acid lactone is not completed.

3.2 Reactions

3.2.1 Conversion of fructose into 5-HMF

In order to demonstrate the best performance of ILs/SiO₂ on the fructose-to-HMF conversion, IL-SO₃H-HSO₄/SiO₂ was selected as a representative catalyst for discussing the effects of reaction time and temperature on fructose dehydration (shown in Supplementary Fig. S1 and the optimized conditions were got (i.e., substrate concentration of 10 wt% (the mass of fructose of 0.2 g and the mass of solvent of 1.8 g), the mass ratio of substrate to catalyst of 4:1, 110°C, 120 min)). And

parallel control reactions of fructose conversion employing ILs/SiO₂ together with neat ionic liquids (IL-SO₃H-HSO₄) and SiO₂ as the catalysts were carried out at optimized conditions (Table 2 and entries 1-6). All these four SFILCs showed excellent fructose conversion, as well as 5-HMF yield. The yield of 5-HMF ranged slightly (from 93.8% to 97.5%) depending on the sort of supported ionic liquids, however when the reaction was carried out using silica as catalyst, only with 31.3% product detected by HPLC analysis, which could be reasonably attributed to the enough acid sites of all immobilized ionic liquids for fructose conversion. In our experiments, it was found that the catalytic activity of immobilized ionic liquid (IL-SO₃H-HSO₄/SiO₂) was similar with the neat ionic liquid (IL-SO₃H-HSO₄), revealing that SFILCs, with important features of heterogeneous catalysts, (i.e. high interfacial surface area, high structure stability, reusability), also have attractive features of homogeneous catalyst such as high catalysis selectivity.

3.2.2 Catalytic conversion of other carbohydrates into 5-HMF or furfural

Apart from fructose, other carbohydrates (glucose, xylose, sucrose, cellobiose) were also tested. We have tabulated the results of the carbohydrate dehydration reaction in Table 2 (entries 8-23).

Glucose is a monomer unit of cellulose, which has great potential and promising application prospect; however, dehydration of glucose to 5-HMF is much more challenging in comparison with fructose dehydration. The four FPILCs were thus utilized to catalytic conversion of glucose for the production of 5-HMF, where the reaction time and temperature required were significantly longer and higher respectively, due to its relatively stable structure. Treatment of glucose with IL/SiO₂, IL-HSO₄/SiO₂ and IL-SO₃H/SiO₂ in DMSO at 160 °C for 180 min gave relatively low

yield of 5-HMF (18.7%, 19.2% and 23.5% respectively); while moderated result on glucose-to-HMF (i.e. 43.3% of 5-HMF yield and 96.1% conversion) were achieved, using IL-SO₃H-HSO₄/SiO₂ as the catalyst (Table 2 and entries 12-15). These data indicated that the catalytic efficiency of supported ionic liquids in term of 5-HMF

Reaction conditions: the mole of catalyst is 1.1 mmol, the mass ratio of substrate to catalyst is 4:1, the substrate concentration is 10 wt% (=the mass of substrate/(the mass of substrate + the mass of solvent)), the reaction temperature is 110 °C, reaction time is 120 min; The product is 5-HMF. ^a IL-SO₃H-HSO₄/SiO₂ was recycled (the fifth cycle) by washing with ethanol and drying at 150°C. ^b Reaction conditions: reaction temperature is 160 °C, reaction time is 180 min; ^c Yield: furfural. ^dThe catalytic test was performed in the presence of [BMIM]Cl. 5-HMF: 5-hydroxymethylfurfural, TRS: Reducing sugar.

yield or selectivity is closely related to the acidity and the functional groups in the catalysts. This is in agreement with the work of Ronen Weingarten and George W. Huber,[21] where they find that higher 5-HMF selectivity was observed with relatively high Brønsted acid sites.

Observed in an order as IL/SiO₂ < IL-SO₃H/SiO₂ < IL-HSO₄/SiO₂ < IL-HSO₄/SiO₂ < IL-SO₃H-HSO₄/SiO₂, reaction activity expressed in terms of furfural yield (Table 2 and entries 16-19) increased considerably from 31.0 to 49.7% because the presence of Brønsted acid sites is particularly important to the selective conversion of xylose into furfural,[22] whereas the conversion of xylose was fluctuant between 93.8% and 95.6%. It should be also noted that IL/SiO₂ with lowest acid sites afforded the furfural yield of 31.0% and xylose conversion of 94.2%, the reason was very possibly related to the fact chlorine anion in SiO₂/IL positively affected xylose conversion, although Brønsted acids could strongly favor furfural formation.[23]

Ionic liquids modified silica, similarly, were both highly effective catalysts for sucrose (Table 2 and entries 8-11), consisting of one glucose molecule and one fructose molecule, dehydration reaction in the solution of DMSO. It took IL-SO₃H-HSO₄/SiO₂ only 120 min to finish the reaction at 110°C with 75.6% of sucrose conversion, offering the value of 5-HMF selectivity as high as 82.4%. Under the same reaction condition, IL-HSO₄/SiO₂ was also very active catalysts, yield of 5-HMF as 61.6% was achieved, which was 5% much more in comparison with that of SiO₂/IL and IL-SO₃H/SiO₂. Principally, this remarkable improvement could be attributed to the significantly high Brønsted acid sites after HSO₄⁻⁻ substituting Cl⁻⁻, which lead to a greatly enhancement of the interact of substrate and H⁺ over the surface of silica nanoparticles.[24] It should be noted that the conversion of sucrose to 5-HMF is very attractive, but lower than that of fructose. The decrease in the 5-HMF yield in the case of sucrose compared to the fructose is presumably the result of a slower conversion of glucose compared with fructose.[25] In other words, sucrose behaved similarly to the 1:1 mixture of fructose and glucose.

Cellobiose, a kind of disaccharide consisting of two glucose molecules, was employed as substrates. As it is shown in Table 2 (entries 20-23), IL-HSO4/SiO₂ and IL-SO₃H-HSO₄/SiO₂ remarkably improved the 5-HMF yield. The activity order in term of 5-HMF yield and substrate conversion coincides with the trend that was observed for sucrose dehydration reaction, indicating that acidity of ionic liquids still play a role in the process of sugars hydrolysis. The cellobiose-to-HMF conversion contains three steps: hydrolysis of cellobiose-to-glucose, isomerization of glucose-to-fructose and dehydration of fructose-to-HMF. Because acid catalysts can facilitate the first step, we suggest that it is the reason why the highest yield of glucose appeared in the case of IL-HSO₄/SiO₂ and IL-SO₃H-HSO₄/SiO₂. In addition,

it can also be proposed that the cellobiose-to-glucose is the rate-determining step among the three reactions. Therefore, catalysts with stronger acidity would favor the production of glucose that was then converted to 5-HMF, resulting in high yields of 5-HMF.[26]

To sum up, there is a direct correlation between 5-HMF or furfural yields, as well as carbohydrates conversions and the fraction of Brønsted sites. The strong acid sites of SO₃H groups together with HSO₄⁻ in the IL-SO₃H-HSO₄/SiO₂ must have fully played the roles as active centers for the a variety of carbohydrates dehydration reaction.

3.2.3 Conversion of cellulose

To gain insight into the catalyst activity for biomass conversion, we utilized all these four catalysts for further study of dehydration of microcrystalline cellulose in the presence of [BMIM]Cl (Table 2 and entries 24-27). On the basis of above discussions, both solid dual acid functional ILs produced good 5-HMF yields in the dehydration of fructose and glucose, herein, their effectiveness in the cellulose-to-HMF conversion via a single step proceeding in [BMIM]Cl (1-butyl-3-methylimidazolium chloride) with DMSO as co-solvent at 160 °C for 3 h were also examined. Satisfactorily, IL-SO₃H-HSO₄/SiO₂ remained effective for the one-pot cellulose-to-HMF conversion, achieving an glucose yield of 20.4% and TRS yield of 77.1%. In comparison, the use of IL/SiO₂ for the same catalytic process gave a lower TRS yield of 57.4% under otherwise identical conditions. These results well indicated the synergistic effect of HSO₄⁻ and -SO₃H group in the bifunctional catalysts on the selective conversion of cellulose into glucose. In fact, several groups have also synthesized -SO₃H and HSO₄⁻ bi-functionalized ionic liquids for effective cellulosic conversion.[27]

3.3 Recyclability and stability study of catalyst

The reusability of the ILs/SiO₂ was also investigated for dehydration of fructose with IL-SO₃H-HSO₄/SiO₂ at the optimized conditions (Supplementary Fig. S2). In this regard, after the first run of reaction, the catalyst was filtered and then washed with ethanol and dried at 150°C for 2 h. The recycled catalyst was again used for the fructose conversion with identical conditions. The results showed the conversions of fructose maintained at around 99% (unshown here) till the fifth run. Additionally, no significant loss of 5-HMF yield was observed till the fifth run (Table 2 and entries 7). It meant that the immobilized functional groups (i.e., SO₃H and HSO₄) did not leach largely during the complicated and repeated process. And the element analysis of the used catalyst confirmed that less than 0.3% of total S leached into DMSO in five cycle (shown in Table 1). Meanwhile, the FT-IR spectrum of the recovered IL-SO₃H-HSO₄/SiO₂ was well consistent with that of the fresh one (Supplementary Fig. S3), revealing a durable structure of the catalyst.

4. Conclusions

In conclusion, a series of new ILs/SiO₂ have been developed in a green route and were systematically used in conversion of various carbohydrates into furan derivatives for the first time, displaying good catalytic activity. Moreover, supported dual acid functionalized ionic liquids (IL-SO₃H-HSO₄/SiO₂) with higher acidity showed more efficient catalytic activity in comparison with other SFILCs. The catalyst also showed high recyclability with a minor loss of performance. SFILCS, with grant greater variety and regulate the physicochemical properties, generated an appealing catalyst which changed the limitations of ILs associated to the viscosity, separation, cost and toxicity. The novel catalysts integrating the benefits of ionic liquid with the common advantages of immobilizations open up a wide avenue of green biomass refinery processes toward the production of 5-HMF.

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Fig. 1 ²⁹Si CP-MAS NMR and ¹³C CP-MAS NMR spectrum of silica after immobilization of the ionic liquid (IL-SO₃H-HSO₄/SiO₂ sample)



Fig. 2 FT-IR spectra: (1) SiO₂ (2) IL/SiO₂; (3) IL-SO₃H/SiO₂; (4) IL-HSO₄/SiO₂; (5) IL-SO₃H-HSO₄/SiO₂



Fig. 3 N₂ adsorption–desorption isotherms: (1) SiO₂; (2) IL/SiO₂; (3) IL-SO₃H/SiO₂; (4) IL-HSO₄/SiO₂; (5) IL-SO₃H-HSO₄/SiO₂



Fig. 4 TG curves of ILs/SiO $_2$



Scheme 1 Synthesis of ionic liquids and the silica supported ionic liquids catalysts

sample	S _{BET}	Vp	Pore diameter	Loading amoun [mmol/g]		t Acidic sites [mmol/g]
	[m ² /g]	[cm ³ /g]	[nm]	1/2 N	S	
SiO_2	361	0.97	9.6	0	0	-
IL/SiO ₂	220	0.59	9.6	1.8	0	0.9
IL-SO ₃ H/SiO ₂	168	0.46	9.5	2.1	0.4	1.0
IL-HSO4/SiO2	172	0.45	9.6	1.5	1.5	1.5
IL-SO3H-HSO4/SiO2	155	0.38	7.8	1.8	1.9	2.0
IL-SO3H-HSO4/SiO2-us ed	-	-	-	1.8	1.6	-

Table 1 The physical parameters obtained for SiO2 and ILs/SiO2.

Entry Substrate			Conv.(%)	Yield (%)			
	Substrate	Catalyst		TRS	Glucose	5-HMF/ Frufrual	
1	fructose	SiO ₂	66.7	-	-	31.3	
2	fructose	IL/SiO ₂	98.0	-	-	97.1	
3	fructose	IL-SO ₃ H/SiO ₂	> 99	-	-	96.5	
4	fructose	IL-HSO ₄ /SiO ₂	> 99	-	-	93.8	
5	fructose	IL-SO ₃ H-HSO ₄ /SiO ₂	> 99	-	-	97.5	
6	fructose	IL-SO ₃ H-HSO ₄	> 99	-	-	> 99	
7 ^a	fructose	IL-SO ₃ H-HSO ₄ /SiO ₂	> 99	-	-	92.7	
8	Sucrose	IL/SiO ₂	72.6	-	-	54.3	
9	Sucrose	IL-SO ₃ H/SiO ₂	76.6	-	-	57.6	
10	Sucrose	IL-HSO ₄ /SiO ₂	76.3	-	-	61.6	
11	Sucrose	IL-SO ₃ H-HSO ₄ /SiO ₂	75.6	-	-	62.3	
12 ^b	glucose	IL/SiO ₂	89.1	-	-	18.7	
13 ^b	glucose	IL-SO ₃ H/SiO ₂	91.9	-	-	19.2	
14 ^b	glucose	IL-HSO ₄ /SiO ₂	92.8	-	-	23.5	
15 ^b	glucose	IL-SO ₃ H-HSO ₄ /SiO ₂	96.1	-	-	43.3	
16 ^{b, c}	xylose	IL/SiO ₂	94.2	-	-	31.0	
17 ^{b, c}	xylose	IL-SO ₃ H/SiO ₂	93.8	-	-	34.4	
18 ^{b, c}	xylose	IL-HSO ₄ /SiO ₂	95.6	-	-	44.5	
19 ^{b, c}	xylose	IL-SO ₃ H-HSO ₄ /SiO ₂	94.0	-	-	49.7	
20 ^b	cellobiose	IL/SiO ₂	> 99	-	6.1	14.7	
21 ^b	cellobiose	IL-SO ₃ H/SiO ₂	> 99	-	6.3	15.0	
22 ^b	cellobiose	IL-HSO ₄ /SiO ₂	> 99	-	4.0	28.6	
23 ^b	cellobiose	IL-SO ₃ H-HSO ₄ /SiO ₂	> 99	-	4.5	31.4	
24 ^{b, d}	cellulose	IL/SiO ₂	-	57.4	11.4	2.8	
25 ^{b, d}	cellulose	IL-SO ₃ H/SiO ₂	-	39.6	9.9	5.1	
26 ^{b, d}	cellulose	IL-HSO ₄ /SiO ₂	-	62.0	22.4	2.9	
27 ^{b, d}	cellulose	IL-SO ₃ H-HSO ₄ /SiO ₂	-	77.1	20.4	5.9	

Table 2 Results for conversion of various carbohydrates catalyzed by ILs/SiO₂.