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Brønsted acid ionic liquid catalyzed formation of pyruvaldehyde dimethylacetal from triose sugars

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ABSTRACT

A series of sulfonic acid functionalized ionic liquids (SO_3H-ILs) have been synthesized, characterized and investigated as catalysts for the conversion of the triose sugars, 1,3-dihydroxyacetone (DHA) and glyceraldehyde (GLA), to pyruvaldehyde dimethylacetal (PADA) in methanol. Depending on the reaction conditions and the applied SO_3H-ILs a good yield of up to 52% of PADA was obtained. Under identical reaction conditions the derivative of PADA, 1,1,2,2-tetramethoxy propane (TMP), could be obtained in yields up to 49% using another SO_3H-IL.

1. Introduction

Carbohydrates contained in biomass have in the last decade been established as important renewable feedstocks to make carbonaceous chemicals and fuels. Glucose is the most important compound in carbohydrates and it is readily available in abundance as cellulose polymer. Hence, transformations of glucose into bio-platform chemicals have in particular been extensively investigated. Isomerization of glucose to fructose is a key reaction in the industrial process to produce high-fructose corn syrup as sweetener and pave also a way to make a wide range of chemicals and fuels directly [1–4]. The direct conversion of glucose/fructose to lactic acid and 5-hydroxymethyl furfural (HMF) are important transformations because these bio-platform chemicals have a variety of applications. For example, HMF can be selectively oxidized into furan-2,5-dicarboxylic acid, which is an alternative chemical to terephthalic acid [5]. Similarly, transformation of C5 sugars to fuels and chemicals are also important, for example, dehydration of xylose to furfural and subsequent conversion into the value-added chemical tetrahydrofuran [1,6].

Another important transformation in carbohydrate chemistry is the conversion of triose sugars to pyruvic acid (in water) or pyruvaldehyde acetal (in alcohol). Acetals are generally important in organic synthesis where they are used as protecting groups for carbonyl compounds, since they are stable under basic conditions and in the presence of oxidizing and reducing agents [7–9]. They may also be important chemicals themselves like, for example, acetaldehyde diethylacetal which is used as a flavoring compound in distilled beverages. The typical synthetic route to acetals involves reaction of an oxo-containing compound with a dissolved acid catalyst in alcohol or the orthoformate compound [10]. However, recently it has been shown that ordinary solid acid zeolites are active catalysts for the dehydration of the trioses 1,3-dihydroxyacetone (DHA) and glyceraldehyde (GLA) to form pyruvaldehyde (PA), which reacted further – depending on the nature of the acid sites on the catalyst – to form lactic acid in water or methyl lactate and pyruvaldehyde dimethylacetal (PADA) in methanol [11].

Ionic liquids (ILs) are low-melting organic salts that can be attractive alternatives to common organic solvents due to their non-measurable vapor pressure, relatively high thermal stability, tunable acidity or basicity as well as combined catalyst-solvent properties [12–15]. Importantly, the solubility of the polysaccharide cellulose can also be much higher in ILs than in common organic solvents – a feature that has intensively increased the use of IL catalyst-solvent systems for making bio-platform chemicals from carbohydrates [16–19]. Since classical ILs lack chemical functionality, new concepts have emerged where functional groups are integrated in the IL ions. In this context, Davis and coworkers reported in 2002 the first amine functionalized imidazolium-based ILs (task-specific) for CO_2 capture [20]. Subsequently, sulfonic acid functionalized imidazolium-based ILs were also reported and investigated for Fischer esterification and pinacol rearrangement reactions with excellent reusability [21]. Since this pioneer work several other reports on the synthesis and application of new acid and base functionalized ILs have followed [22–25]. In our

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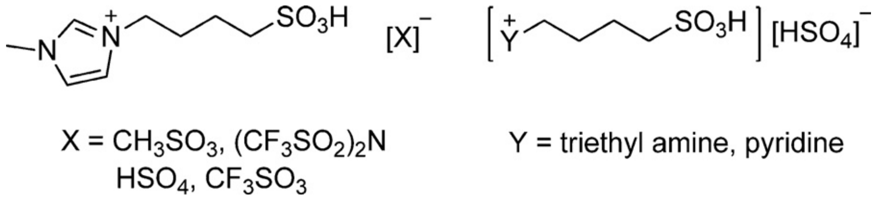

Scheme 1. The structures of the SO_3H-ILs.

previous reports, we have shown that sulfonic acid functionalized ILs were promising catalyst for the dehydration of fructose and glucose to make ethyl levulinate and ethyl-D-glucopyranoside in ethanol, respectively [3].

In the present study, we report the synthesis of a series of sulfonic acid functionalized imidazolium-, pyridinium- and ammonium-based ILs (SO_3H-ILs) with the cations: 1-methyl-3-(4-sulfobutyl)-imidazolium ([BMIm-SO_3H][X], X = HSO_4, NTf_2, OMs and TfO), 1-(4-sulfobutyl)pyridinium ([BPyr-SO_3H][HSO_4]) and *N,N,N*-triethyl-4-sulfobutanaminium ([NEt_3B-SO_3H][HSO_4]). The structures of the SO_3H-ILs are depicted in Scheme 1. The SO_3H-ILs were tested as catalysts in the conversion of the trioses DHA and GLA into PADA using methanol as solvent under autogenic pressure. The influence of reaction parameters such as reaction time, temperature and concentration of DHA was optimized.

2. Experimental

2.1. Synthesis and characterization of SO_3H-ILs

1-methylimidazol (99%, Sigma–Aldrich) or pyridine (>99%, Sigma–Aldrich) or triethylamine (>99.5%, Fluka) (0.2 mol) and 1,4-butanesultone (99%, Aldrich, 0.2 mol) were charged in a 100 ml round bottomed flask. The mixture was then stirred at 40–80 °C for 10 h. The solid zwitterion formed was recovered by filtration, washed repetitively with diethyl ether until all unreacted reactants were completely removed (confirmed by NMR) and then dried under reduced pressure (15 mbar, 50 °C) overnight. A stoichiometric amount of acid (98% H_2SO_4, >98% TfOH, 95% $HNTf_2$ or >99.5% MsOH, Sigma–Aldrich) was subsequently added drop wise to the respective zwitterion and the mixture stirred at 80 °C for 6 h. The obtained viscous ionic liquids were finally purified by extractive washing with diethyl ether and finally dried under reduced pressure (15 mbar, 50 °C) overnight. Yields were above 95% for all ILs.

The identity of the synthesized sulfonic acid functionalized ionic liquids was confirmed by NMR (Bruker AM360 NMR spectrometer, 25 °C). The thermal decomposition temperature (T_d) of the SO_3H-ILs were measured by TGA analysis (TGA/DSC 1 apparatus, Mettler Toledo) by heating the ionic liquid (9–18 mg) in an aluminum sample holder from 40 °C to 800 °C with a heating ramp of 20 °C/min under nitrogen atmosphere.

1-Methyl-3-(4-sulfobutyl)imidazolium trifluoromethanesulfonate ([BMIm-SO_3H][OTf]): ^{1}H NMR (300 MHz, D_2O): δ/ppm = 1.5–1.6 (m, 2H; CH_2), 1.8–1.9 (m, 2H; CH_2), 2.7–2.8 (t, 2H; CH_2-SO_3H), 3.7 (s, 3H; N—CH_3), 7.25 (s, 1H; CH), 7.35 (s, 1H; CH), 8.6 (s, 1H; N—CH—N); ^{13}C NMR (75.5 MHz, D_2O): δ/ppm = 20.5, 27.9, 35.5, 49.0, 50.0, 121.9, 123.4, 131.0, 135.5; T_d > 200 °C.

1-Methyl-3-(4-sulfobutyl)imidazolium hydrogensulfate ([BMIm-SO_3H][HSO_4]): ^{1}H NMR (300 MHz, D_2O) δ/ppm = 1.5–1.6 (m, 2H; CH_2), 1.8–1.9 (m, 2H; CH_2), 2.7–2.8 (t, 2H; CH_2-SO_3H), 3.7 (s, 3H; N—CH_3), 7.25 (s, 1H; CH), 7.35 (s, 1H; CH), 8.6 (s, 1H; N—CH—N); ^{13}C NMR (75.5 MHz, D_2O): δ/ppm = 20.5, 27.9, 35.5, 49.0, 50.0, 121.9, 123.4, 135.5; T_d > 300 °C.

1-Methyl-3-(4-sulfobutyl)imidazolium methanesulfonate ([BMIm-SO_3H][OMs]): ^{1}H NMR (300 MHz, D_2O): δ/ppm = 1.5–1.6 (m, 2H; CH_2), 1.8–1.9 (m, 2H; CH_2), 2.7–2.8 (t, 2H; CH_2-SO_3H), 3.7 (s, 3H; N—CH_3), 7.25 (s, 1H; CH), 7.35 (s, 1H; CH), 8.6 (s, 1H; N—CH—N); ^{13}C NMR (75.5 MHz, D_2O): δ/ppm = 20.7, 27.9, 35.5, 38.3, 48.6, 49.9, 121.9, 123.4, 135.7; T_d > 300 °C.

1-Methyl-3-(4-sulfobutyl)imidazolium bis((trifluoromethyl)sulfonyl)amide ([BMIm-SO_3H][NTf_2]): ^{1}H NMR (300 MHz, D_2O): δ/ppm = 1.5–1.6 (m, 2H; CH_2), 1.8–1.9 (m, 2H; CH_2), 2.7–2.8 (t, 2H; CH_2-SO_3H), 3.7 (s, 3H, N—CH_3), 7.25 (s, 1H; CH), 7.35 (s, 1H; CH), 8.6 (s, 1H; N—CH—N); ^{13}C NMR (75.5 MHz, D_2O): δ/ppm = 20.7, 27.9, 35.2, 48.6, 49.8, 117.0, 121.9, 123.3, 135.3; T_d > 200 °C.

N,N,N-triethyl-4-sulfobutaneammonium hydrogensulfate ([NEt_3B-SO_3H][HSO_4]): ^{1}H NMR (300 MHz, D_2O): δ/ppm = 1.0–1.2 (t, 9H; 3CH_3), 1.5–1.8 (m, 4H; 2CH_2), 2.7–2.8 (t, 2H; CH_2-SO_3H), 3.0–3.2 (m, 8H; 4CH_2—N); ^{13}C NMR (75.5 MHz, D_2O): δ/ppm = 6.5, 19.9, 21.0, 49.9, 52.3, 55.9; T_d > 300 °C.

1-(4-Sulfobutyl)pyridinium hydrogensulfate ([BPyr-SO_3H][HSO_4]): ^{1}H NMR (300 MHz, D_2O): δ/ppm = 1.5–1.7 (m, 2H; CH_2), 1.9–2.1 (m, 2H; CH_2), 2.7–2.8 (t, 2H; CH_2-SO_3H), 4.4–4.6 (t, 3H; N—CH_2), 7.8–8.0 (t, 2H; 2CH), 8.4 (t, 2H; 2CH), 8.7 (d, 1H; CH); ^{13}C NMR (75.5 MHz, D_2O): δ/ppm = 20.5, 28.9, 49.6, 60.7, 127.9, 143.8, 145.3; T_d > 300 °C.

2.2. Catalytic testing

The catalytic reactions were carried out in 15 ml ace pressure tubes. 139.3 mg (1.5 mmol) of DHA (97%, Sigma–Aldrich) or 142.2 mg (1.5 mmol) of GLA (95%, Sigma–Aldrich), 0.11 mmol of SO_3H-IL, 30 mg of naphthalene (internal reference) and 4 g of methanol (>99.9%, Sigma–Aldrich) were charged into the ace pressure tube and heated under stirring at 120 °C (oil bath temperature) for 24 h.

2.3. Reactant and product analysis

The reaction mixtures were subjected to GC-FID analysis (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 μm × 0.25 μm) as well as HPLC-RI analysis (Agilent 1200 series, 30 cm Aminex© HPX-87H column, 0.005 M H_2SO_4 eluent, flow rate 0.6 ml/min). A GC–MS system (Agilent 6850 GC coupled with Agilent 5975C mass detector) was used for qualitative analysis.

Conversion of the triose sugars DHA and GLA as well as yields of PA were determined by HPLC using standards made from commercial samples. The yield of pyruvaldehyde dimethylacetal (PADA) and 1,1,2,2 tetramethoxypropane (TMP) were calculated from GC results on series of PADA and TMP standards with naphthalene as internal standard.

3. Results and discussion

The conversion of DHA and GLA to PADA was carried out with SO_3H-ILs as catalysts in methanol at 120 °C and the results are presented in Table 1. Reaction of DHA with [BMIm-SO_3H][OMs] (Table 1, entry 1) yielded 41% of PADA and 45% of TMP along with more than 99% conversion of DHA with PA being observed as intermediate by HPLC. The yields of PADA and TMP were equally good or