



Immobilizing Cr³⁺ with SO₃H-functionalized solid polymeric ionic liquids as efficient and reusable catalysts for selective transformation of carbohydrates into 5-hydroxymethylfurfural



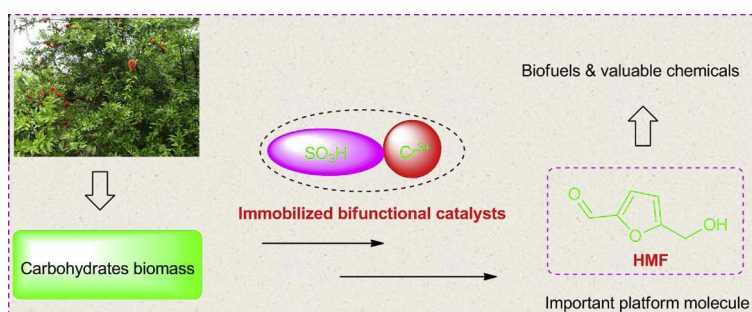
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HIGHLIGHTS

- Bi-functional solid ILs were more effective than other solid acids for HMF production.
- Fructose and glucose, as well as cellulose can be selectively converted into HMF.
- A kinetic analysis was carried out to illustrate the formation of HMF.
- Bi-functional polymeric ILs can be reused without significant loss of activity.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of functional polymeric ionic liquids (FPILs) were prepared by coupling of SO₃H-functionalized polymeric ionic liquids with different counterpart anions containing or excluding CrCl₃·6H₂O, and characterized by SEM, FT-IR, XRD, NH₃-TPD, TG, melting point, ICP-AES, and TEM. The catalytic activity of the prepared solid FPILs was investigated for the conversion of biomass including fructose, glucose and cellulose into 5-hydroxymethylfurfural (HMF) with the presence of DMSO-mediated solvents, successively producing moderate to excellent yields of HMF under atmospheric pressure. The FPILs catalysts developed in this study present improved performance on fructose-to-HMF conversion over other solid catalysts, such as functional ionic liquids supported by silica, metal oxides and strong acid ion exchange resin catalysts, and can be very easily recycled at least five times without significant loss of activity. In addition, a kinetic analysis was carried out to illustrate the formation of HMF.

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1. Introduction

Currently, 5-hydroxymethylfurfural (HMF), serving as a precursor molecule, is very useful for the production of not only the biofuel 2,5-dimethylfuran but also of important molecules including maleic anhydride, 2,5-bis(ethoxymethyl)furan, levulinic acid, 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-dihydroxymethylfu-

ran, and 5-hydroxy-4-keto-2-pentenoic acid, with a wide range of applications, such as in the production of monomers for plastics and solvents (Román-Leshkov et al., 2007; Seri et al., 2000). Renewable biomass resources, especially cellulose, glucose and fructose considered as the most important biomass sources are promising alternatives for the sustainable production of HMF. Over the last few years, various acid catalysts were used to transform carbohydrates into HMF, such as mineral acids, ion exchange resins, zeolites and metal ions (Asghari and Yoshida, 2007; Qi et al., 2008; Moreau et al., 1996; Zhao et al., 2007). In addition, a

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variety of reaction media including pure water, organic solvents and a number of biphasic water/organic systems were usually involved (Carlini et al., 2004; Bicker et al., 2003).

Ionic liquids (ILs), viewed by some as a sort of novel reaction medium, have gained a variety of applications in synthetic chemistry over the past few years (Dupont et al., 2002). Studies involving the utilization of ionic liquids as reaction media or as catalysts for the dehydration reaction of hexose to HMF have also been reported. Lansalot-Matras and Moreau (2003) found that 1-butyl-3-methylimidazol-3-ium hexafluorophosphate ([Bmim]PF₆) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) were suitable reaction media for the dehydration of D-fructose to HMF with up to 50% yield in the presence of Amberlyst-15 at 80 °C for around 3 h. Bao et al. (2008) reported that the Lewis acidic 3-allyl-1-(4-sulfurylchloride butyl)-imidazolium trifluoromethanesulfonate ([ASCBI][Tf]) could effectively catalyze the dehydration of D-fructose under microwave irradiation. On the other hand, a Brønsted acidic ionic liquid, 1-H-3-methyl imidazolium chloride, was also used as both solvent and catalyst for the dehydration of fructose and sucrose to give HMF in relatively high yield and selectivity (Moreau et al., 2006). Similarly, Tong and Li (2010) synthesized a series of Brønsted-acidic ionic liquids, in which N-methyl-2-pyrroli-donium methyl sulfonate ([NMP]⁺[CH₃SO₃]⁻) showed very high catalytic activity and selectivity in the dehydration of D-fructose, and a 72.3% HMF yield and 87.2% selectivity were obtained at 90 °C after 2 h. From an economical point of view, it is more desirable to convert cellulose directly into HMF. Tao et al. (2010, 2011) investigated the hydrolysis of cellulose in the presence of catalytic amounts of FeCl₂ (or MnCl₂) in ILs functionalized with SO₃H, simultaneously using MIBK as the extracting solvent, and an HMF yield of 34% (or 37%) was achieved.

Homogeneous acid catalyzed processes with ionic liquids as solvents or catalysts are effective as shown in above context, however, relatively lower HMF yields or selectivities were usually obtained for glucose and cellulose conversion by using Brønsted and Lewis acid catalysts, which are effective for fructose dehydration (Zhao et al., 2007), and it exists severe drawbacks in terms of equipment corrosion, separation and recycling. Solid acid catalysts with reusable property seem more promising for practical applications, such as H-form zeolites and metal phosphates can be recycled and have high (60–90.0%) HMF selectivity, but very low carbohydrate conversion (30–60.0%) even after a long (2 h) reaction time (Dupont et al., 2002; Carlini et al., 1999). In order to develop a way of producing HMF from fructose, glucose and cellulose with an efficient IL catalyst system in a green route under mild conditions (Sidhpuria et al., 2011; Neto and Spencer, 2012; Yuan and Antonietti, 2011), supported ionic liquid catalysts (SILCs) were thus utilized. Sidhpuria et al. (2011) presented an ionic liquid covalently bound to nano-sized amorphous silicas to produce supported ionic liquid nanoparticles (SILnP), and better results (99.9% fructose conversion and 63.0% HMF yield) were achieved for the dehydration reaction in terms of activity and reusability, compared with mineral acids and most other homogeneous catalytic systems. Similarly, mesoporous silica nanoparticles functionalized with both sulfonic acid (SO₃H) and ILs were synthesized and applied as effective and recyclable catalysts for generating 5-hydroxymethylfurfural (HMF) from fructose, and a high HMF yield of 72.5% was achieved in DMSO systems under mild conditions (Lee and Wu, 2012). Recently, Degirmenci et al. (2011) covalently bonded ionic liquid fragments containing CrCl₂ to mesoporous SBA-15 silica, and the introduction of CrCl₂ into [PMIm]Cl immobilized on the surface of SBA-15 led to the formation of loosely bound, catalytically active Cr²⁺ species. With the prepared catalyst, an HMF selectivity of 70% at a glucose conversion of 50% was achieved, and the promising activity may be attributed to the specific reaction environment on the surface that locally resembles the

characteristics of the bulk ionic liquid and isolates the catalytic species from excessive interaction with the solvent, but the stability of the catalysts needs to be improved because of IL and Cr²⁺ leaching during the reactions.

Ionic polymers containing IL units are potentially capable of acting the bifunctions of IL and polymer, such as high thermal stability, easily shaping, corrosion resistance, and variety of available structures (Yuan and Antonietti, 2011). In present study, a series of functional polymeric ionic liquids (FPILs) were prepared and used as efficient and recyclable catalysts for fructose/glucose/cellulose-to-HMF conversion under mild reaction conditions, being able to produce 90.6%, 48.7% and 30.8% yield of HMF, respectively. The FPILs catalysts are cheaper, selective, and more easily operated under atmospheric conditions; and the SO₃H-functionalized IL polymer was first synthesized from coupling task-specifically designed SO₃H-functionalized polymeric IL with PW₁₂O₄₀³⁻ and Cl⁻, giving the monofunctional catalysts FPIL **1a** and **1b**, respectively; Then, CrCl₃·6H₂O was introduced into the polymeric ILs to afford the corresponding bifunctional catalysts FPIL **2a** and **2b** (Supplementary Scheme S1).

Recently, our group has successfully employed the Brønsted acidic heteropolyanion-based polymeric hybrid catalyst (FPIL **1a**) for the dehydration of fructose, and found that this mono-functional polymeric IL with a very low specific surface area 1 m² g⁻¹ and a negligible pore volume showed efficient performance for the dehydration reaction, producing good yields of HMF (up to 83%); however, low yields of HMF were obtained when glucose was used as the substrate (Li et al., 2013). An improved approach is based on the insight that a specific coordination environment of the chromium species is necessary for selective glucose and cellulose transformations. Herein, two polymeric ILs (FPIL **2a** and **2b**) simultaneously functionalized with Brønsted/Lewis acidic groups were thus synthesized.

2. Methods

2.1. Materials

1-Vinylimidazole, 1,3-propanesultone, azobisisobutyronitrile (AIBN), H₃PW₁₂O₄₀ (PW), fructose, glucose and HMF, were purchased from Shanghai Aladdin Industrial Inc.; methanol, acetone, ether, ethanol, CrCl₃·6H₂O, HCl, dichloromethane (CH₂Cl₂), H₂SO₄, and dimethylsulfoxide (DMSO) were purchased from Chongqing Chuandong Chemical Reagent Company. All chemicals were of analytical grade and used as received, unless otherwise noted.

2.2. Preparation of Poly(VMPS)

Poly(VMPS) was synthesized as reported in the previous literature (Leng et al., 2012) with a slight modification. To a 50 mL round-bottomed flask containing 1,3-propane-sultone (30 mmol, 4.07 g) cooled in ice bath, 1-vinylimidazole (30 mmol, 3.00 g) was slowly added, followed by stirring of the mixture at room temperature for about 8 h until it turned into solid, which was washed with ether and dried in vacuum at room temperature to afford pure 1-vinyl-3-propane sulfonate imidazolium (VMPS). ¹H NMR (500 MHz, D₂O) δ (ppm) = 2.23–2.28 (m, 2 H, –CH₂), 2.82–2.87 (m, 2H, –CH₂), 4.39–4.44 (t, 2H, –CH₂), 5.31–5.33 (d, 1H, –CH), 5.64–5.65 (d, 1H, –CH), 7.11–7.14 (m, 1H, –CH), 7.53–7.55 (d, 2H, –CH₂), 9.08 (s, 1H, –CH). The obtained VMPS (2.50 g) and azobisisobutyronitrile (AIBN) (0.05 g) were dissolved in methanol (10 mL), and the mixture was refluxed at 60 °C for 24 h with stirring. Then the solvent was removed under reduced pressure, and the residue was washed with ethanol to give a white solid, abbreviated as Poly(VMPS).

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