



Note

Catalytic conversion of glucose to 5-hydroxymethyl furfural using inexpensive co-catalysts and solvents

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ABSTRACT

Efficient conversion of glucose to 5-hydroxymethyl furfural (5-HMF), a platform chemical for fuels and materials, was achieved using CrCl_2 or CrCl_3 as the catalysts with inexpensive co-catalysts and solvents including halide salts in dimethyl sulfoxide (DMSO) and several ionic liquids. 5-HMF (54.8%) yield was achieved with the CrCl_2 /tetraethyl ammonium chloride system at mild reaction conditions (120 °C and 1 h). The 5-HMF formation reaction was found to be faster in ionic liquids than in the DMSO system. Effects of water in the reaction system, chromium valence and reaction temperature on the conversion of glucose into 5-HMF were discussed in this work.

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In the past 150 years, fossil fuels (petroleum, coal, and natural gas) have been the dominant sources for energy and chemicals.¹ However, due to the rapid economic development and population growth, fast consumption of these resources has accelerated their depletion. The global concerns over energy security, the environmental issues related to the use of fossil fuels, as well as the sustainability of the economic development have intensified the efforts in seeking alternative resources for energy and chemical production. Biomass, with a total annual production of 2.74×10^{19} Btu equivalent of about eight times of the energy consumed each year in the world, offers an immense, renewable, and carbon-neutral source for fuels and chemicals.

Glucose is the main building block of biomass, for example, cellulose and starch. Although it has been successful in bio-conversion of cellulose and starch to ethanol fuel, the process to convert a 6-C glucose molecule into two molecules of ethanol (plus two molecules of CO_2) has an inherently lower efficiency with respect to energy and carbon utilization efficiency. Moreover, ethanol is not an ideal transportation fuel because of its low energy density (23 MJ/L),² high volatility, and its readiness in water absorption from air. The ethanol-fueled vehicles have only about 66% of efficiency compared with those fueled with gasoline. In this regard, it is urgently needed to explore conversion technologies to convert plentiful biomass resources into bio-fuels with higher

energy contents. 5-Hydroxymethyl furfural (5-HMF), is a dehydration intermediate product in glucose fermentation processes.³ 5-HMF can be easily converted to dimethylfuran (DMF) with further improved energy content through hydrogenation.⁴ The energy content of DMF (31.5 MJ/L) is comparable to that of gasoline (35 MJ/L) and 40% greater than that of ethanol.² Furthermore, DMF (bp = 92–94 °C) is less volatile than ethanol (bp = 78 °C) and is immiscible with water, making it a better candidate for alternative liquid transportation fuels. 5-HMF can also be a platform chemical for a variety of synthetic materials.⁵

The conversion of fructose to 5-HMF is a readily straightforward process that has been demonstrated in water and organic solvents,⁶ in multiphase systems,^{7,8} and in ionic liquids.^{9,10} However, fructose is not an abundant building block in cellulose and starch, although fructose can be produced from glucose via some expensive isomerization processes. Obviously, direct conversion of glucose into 5-HMF offers a better economic value. Zhao et al.¹⁰ have successfully produced 5-HMF from glucose at a high yield (69%) with chromium chlorides as the main catalysts combined with expensive alkylimidazolium chloride ionic liquids, such as 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), as the co-catalyst. Separation of 5-HMF product from the ionic liquids may be achieved by solvent extraction with low boiling point organic solvents followed by evaporation and purification. Li et al.¹¹ obtained a surprisingly high yield (91%) of 5-HMF from glucose using the same catalyst/co-catalyst system as was used by Zhao et al.,¹⁰ but under the microwave irradiation conditions. While promising, this catalytic method has

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limitation in the process economics due to the use of a large amount of expensive ionic liquid solvents. Binder and Raines⁵ demonstrated that with chromium chlorides as the main catalyst, polar aprotic organic solvent combined with some halide (Cl, Br) salts could replace ionic liquid as a co-catalyst to convert glucose to 5-HMF at a high yield up to 80%. The drawbacks of this approach may be the difficulty in separation of the 5-HMF product from the high boiling point solvents and recovery of large amount of halide salts used in the process (the addition amount of these salts was over 10% of solvent in weight).

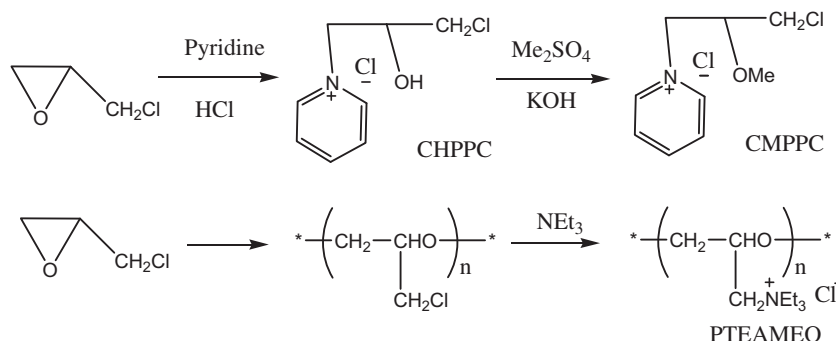
The main objective of the present research was to produce 5-HMF from glucose using CrCl₂ or CrCl₃ as the main catalysts with different inexpensive co-catalysts and solvents including halide salts in dimethyl sulfoxide (DMSO) and several new ionic liquids synthesized by ourselves.

1. Experimental

1.1. Materials

The raw materials and chemicals used in this research mainly include: glucose, fructose, dimethyl sulfoxide (DMSO), chromium dichloride (CrCl₂), chromium trichloride (CrCl₃), tetraethyl ammonium chloride (TEAC), epichlorohydrin, pyridine, dimethyl sulfate, lithium chloride, potassium bromide, zinc chloride, H₂SO₄-pretreated zeolite as a solid ultra acid, 5-HMF standard, and 0.005 M H₂SO₄ HPLC-grade water. All the raw materials and chemicals as listed above were ACS reagent-grade chemicals from Sigma–Aldrich and were used as received without further treatment.

Several new ionic liquids were synthesized and tested as the reaction co-catalysts and solvents. (3-chloro-2-hydroxypropyl) pyridinium chloride (CHPPC) was synthesized following Zhao's procedure.¹² That is, to a stirred solution of pyridine in ethanol at room temperature was added concentrated hydrochloric acid. After addition of the acid, the mixture was cooled to room temperature, and epichlorohydrin was added dropwise with stirring. Then the reactor flask was irradiated in the water bath of a laboratory ultrasonic cleaner at 25 °C for 2 h. Upon completion, the solvent was removed by evaporation under reduced pressure with heating at 60 °C, followed by vacuum drying to yield a colorless liquid of CHPPC. (3-chloro-2-methoxypropyl) pyridinium chloride (CMPPC) was synthesized by reacting CHPPC with dimethyl sulfate in the presence of barium hydroxide at room temperature for 8 h.¹³ Poly(triethylammonium methylene ethylene oxide) (PTEAMEO) salt was synthesized by first cationic polymerization of epichlorohydrin with BF₃ plus ethanol as the initiator at 0 °C,¹⁴ then reacting polyepichlorohydrin with triethylamine in ethanol under reflux for 10 h.¹⁵ The synthetic procedures for these ILs are depicted schematically in the following Scheme 1.



Scheme 1. Synthesis of ionic liquids of CHPPC, CMPPC, and PTEAMEO.

1.2. Experimental methods for conversion of glucose to 5-HMF

In a typical run for the synthesis of 5-HMF in DMSO, a 100 mL three-neck reactor was equipped with Dean-stark trap, a condenser, a purge gas (nitrogen) inlet, nitrogen outlet and a thermometer in the three necks, respectively. The reactor was first evacuated and purged with nitrogen, then 25.00 g DMSO, 5.00 g glucose, and 0.110 g CrCl₂ (0.03 M), 0.150 g (0.03 M) tetraethyl ammonium chloride, and 3.0 mL of benzene (as a stripping reagent for water removal via azeotropic evaporation) were added to the reactor. The Dean-stark was filled with benzene. The reactor was put into an oil bath preheated at 130 °C. The reaction mixture was stirred with a magnetic stirrer under nitrogen protection for 2 h. The reaction mixture was analyzed with HPLC to determine the contents of remaining glucose and 5-HMF in the product.

Synthesis of 5-HMF from glucose in ionic liquid solvents was conducted following the similar procedure as above in a 50 mL three-neck reactor with nitrogen purge or a 15 mL sealed reactor with nitrogen protection. In a typical run, 1.00 g glucose and 5.00 g ionic liquid and 0.03 M chromium chloride (CrCl₂ or CrCl₃) were reacted at 120 °C for 1 h. The reported yield of 5-HMF was calculated to be % of the moles of 5-HMF actually produced in each test to the theoretical maximum moles of 5-HMF if assuming 100% conversion. Duplicate tests were performed for most reaction conditions, and the maximum relative errors were ensured within 10%, as demonstrated in Figure 1.

The reaction products were analyzed by HPLC and quantified with calibration curves generated from commercially available standards. As the typical measurement procedure, the product mixture was first diluted with HPLC grade 0.005 M H₂SO₄ water, filtered with 0.45 μm filters, and analyzed using a Waters Breeze GPC–HPLC (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump with refractive index (RI) and UV detector). The analysis was conducted with Bio-Rad HPX-87H column (300 × 7.8 mm) using HPLC grade 0.005 M H₂SO₄ water solution as the eluent at a column temperature of 65 °C and a flow rate of 0.8 mL/min. Glucose and 5-HMF were detected with an RI detector and a UV detector, respectively. The reaction mixtures (diluted with methanol) were also analyzed by GC–MS (Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC) using a silicon column with temperature programming from an initial temperature of 65 °C to a final temperature of 280 °C at 10 °C/min with 2 min of initial and final time, to verify the formation of 5-HMF.

2. Results and discussion

2.1. Catalytic conversion of glucose to 5-HMF in DMSO

Zhao et al.¹⁰ reported that CrCl₂ combined with an expensive ionic liquid ([EMIM]Cl) as a co-catalyst or solvent could effectively

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