

'Single-step' Catalytic Cellulose Conversion in Ionic Liquids

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Introduction

Most of natural resources (e.g. petroleum and coal, etc) have a limited reserve and their use continues to increase CO₂ emission to the atmosphere, which is recognized as the major factor for climate change (CO₂-induced global warming). Biomass, as a renewable resource, falls in the natural carbon cycle, thus will not lead to a net increase in CO₂ emissions to the atmosphere.

Among the various biomass resources, cellulosic sources are favored because of their abundance in nature and the fact that they do not fall in the food chain for animals or humans.¹ Cellulose consists of polydisperse linear glucose polymer chains, which form hydrogen-bonded super-molecular structures. An extensive network of hydrogen-bonding and Van der Waals forces makes cellulose polymer chains in an ordered alignment that, depending on the type of biomass, results in a supra-molecular cellulose structure of various size, crystallinity, and complexity, which make cellulose completely insoluble in normal aqueous solutions and most common organic solvents. Dissolving cellulose in ionic liquids based on imidazolium salts was recently reported in the literatures.² One promising platform chemical from cellulosic biomass is 5-hydroxymethylfurfural (HMF), which is suitable for use in polymer synthesis or production of liquid biofuels. The catalytic formation of HMF from glucose, the unit of cellulose, in ionic liquids has been reported in the literature.³

For the first time, we present a unique "single-step" catalysis pathway that depolymerizes cellulose rapidly under mild conditions and converts the resulting glucose to HMF. Transition metal chlorides dissolved in imidazolium-based ionic liquid (1-ethyl-3-methylimidazolium chloride) were used as the catalysts at temperatures of 80-120°C to perform cellulose depolymerization and the subsequent production of HMF with high selectivity.

Materials and Methods

A Symyx high-throughput batch reactor was used to run multiple ionic liquid samples under programmed temperatures and duration. Cellulose (fibrous, long) in this work was purchased from Sigma-Aldrich. 1-Ethyl-3-methylimidazolium chloride ([EMIM]Cl, 99%) was supplied by Solvent-Innovation (Lot No. 99/972). CuCl₂ (99.9%) and CrCl₂ (99.9%), and PdCl₂ (99.9%) were ordered from Sigma-Aldrich. All chemicals were used without further purification. Product analysis was performed by use of HPLC (Agilent, ion exclusion column).

Results and Discussion

A series of depolymerization experiments were carried out with two metal chlorides, CuCl₂ and CrCl₂, (total metal loading 35 mM) while the relative proportions of the two metals varied from a Cu mole fraction (χ_{CuCl_2}) of 0 to 1. After 1 h of reaction, very low activity (total product yield <10%) for cellulose hydrolysis was seen for the solutions containing a single metal chloride (i.e., χ_{CuCl_2} = 0 or 1, Fig. 1). In strong contrast, mixtures of the two metal chlorides resulted in total product yields as high as 65% (χ_{CuCl_2} = 0.95) with the

most active range being χ_{CuCl_2} of 0.83-0.95. Various spectroscopy methods (EXAFS, EPR, and UV-Vis, etc) were used to study reaction mechanism for catalytic cellulose conversion in ionic liquids. For example, the results of EXAFS indicate that that Cu(II) in [EMIM]Cl is tetrahedral coordinated by Cl⁻ ions with a Cu-Cl bond distance of 2.258 Å, and a bond angle of 108°. The signal broadening of EPR with Pd addition suggests greater interaction of Cu(II) with solvent and other metal ions, whereas the isotropic nature of the signal implies enhanced mobility of the Cu(II) ions in the solvent as a result of PdCl₂ in the ionic liquid. While a detailed mechanism for the intensified cellulose hydrolysis activity by the paired metal chlorides remains to be unveiled, the experimental evidence presented above offers some clues about the unique character of the paired metal chlorides in [EMIM]Cl solvent.

Significance

We demonstrated high yields of HMF formation in a single-step process starting with cellulose. The lower reaction temperature, the ability to tune the catalyst properties to adjust yields, and the ability to recycle the solvent and catalyst, all suggest that our catalytic production of HMF directly from crystalline cellulose offers a potentially new route to allow for the first time, effective and sustainable use of cellulosic biomass for liquid fuel or chemical production.

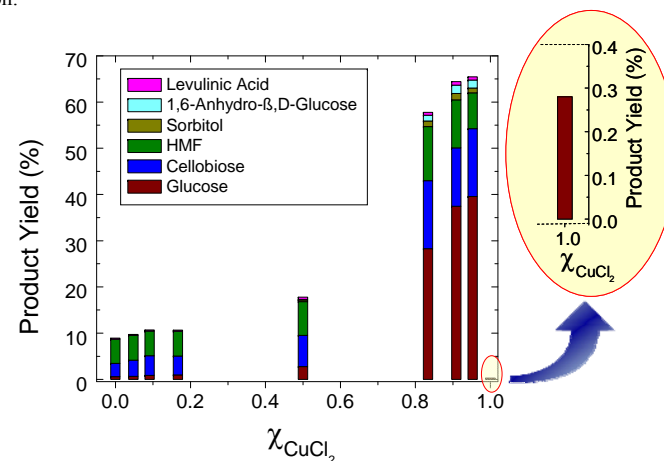


Figure 1. Product yields of cellulose conversion using single and paired CuCl₂ /CrCl₂ catalysts having χ_{CuCl_2} ranging from 0 to 1 at 120°C.

References

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