ARTIFICIAL CELLULASE TYPE IONIC LIQUID CATALYSTS FOR CELLULOSE HYDROLYSIS

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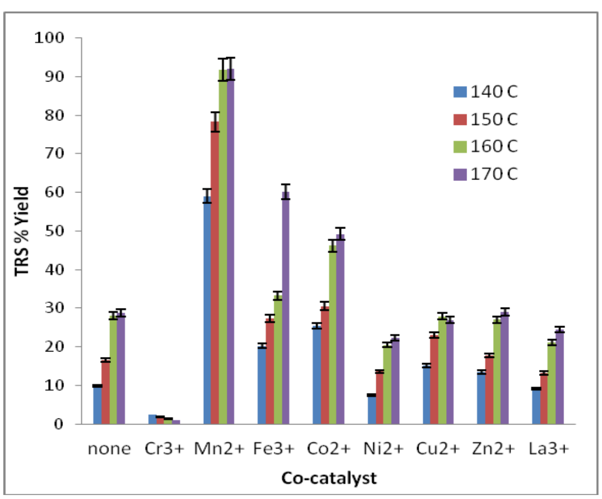
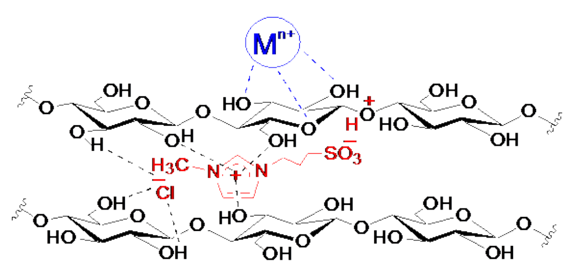
Efficient hydrolysis of lignocellulosic biomass to fermentable sugars is a challenging step and the primary obstacle for the large scale production of cellulosic ethanol. Ionic liquids are well known for their ability to dissolve cellulose and our interest in the search for efficient catalytic methods for saccharification of polysaccharides has led us to develop -SO_3H group functionalized Brönsted acidic ionic liquids (BAILs) as solvents as well as catalysts. Later we found that these sulfuric acid derivatives can be used as catalysts in aqueous phase as well. For example, BAIL 1-(1-propylsulfonic)-3-methylimidazolium chloride aqueous solution was shown to be a better catalyst than H_2SO_4 of the same [H^+] for the degradation of cellulose. This observation is an important lead for the development of a BAIL based cellulase mimic type catalyst for depolymerization of cellulose. In an attempt to develop a recyclable, simple enzyme mimic type catalysts we have studied quantitative structure activity relationships of a series of BAILs and found that activity decreases in the order: imidazolium > pyridinium > triethanol ammonium. Furthermore, we have investigated the effects of selected metal ions on 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed hydrolysis of cellulose in water at 140-170 °C. The total reducing sugar (TRS) yields produced during the hydrolysis of cellulose in aq. BAIL solution using Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} Ni^{2+}, Cu^{2+}, Zn^{2+}, and La^{3+} chlorides as co-catalysts as well as interactions of catalysts with cellulose are shown in the figure below. These results show that cellulose samples with Mn^{2+}, Fe^{3+}, Co^{2+} as co-catalysts produce significantly higher TRS yields compared to the sample without the metal ions. The highest enhancement was observed with Mn^{2+} and produced TRS yields of 59.1, 78.4, 91.8, and 91.9 % at 140, 150, 160, and 170 °C respectively; whereas cellulose hydrolyzed without Mn^{2+} produced TRS yields of 9.8, 16.5, 28.0, and 28.7 % at the same four temperatures. This paper will present the development of BAIL based artificial cellulase type catalysts, QSAR studies, catalyst immobilizations, applications on lignocellulosic biomass materials (corn stover, switchgrass, poplar) and recycling studies.





The TRS % yields produced during the hydrolysis of cellulose in aq. 1-(1-propylsulfonic)-3-methylimidazolium chloride (0.0321 mol H^+/L), at 140-170 °C, 3h, using metal chlorides ([M^{n+}] = 20 mol% of glucose eqv.) as co-catalysts and possible interactions of catalysts with cellulose