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Ionic liquid based artificial cellulase type catalysts for cellulosic ethanol process

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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 Brønsted 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 (QSAR) of a series of BAIL catalysts and found that activity with different cation types 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 BAIL catalyzed hydrolysis of cellulose in water at 140-170°C. The total reducing sugar (TRS) yields produced during the hydrolysis of cellulose (DP~450) in aq. 1-(1-propylsulfonic)-3-methylimidazolium chloride solution at 140-170°C 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. These results show that cellulose samples heated with Mn^{2+} , Fe^{3+} , Co^{2+} as co-catalysts produce significantly higher TRS yields compared to the sample heated without the metal ions. The highest catalytic effect enhancement is 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 is a 503, 375, 228, and 220% enhancement in TRS yield due to the addition of Mn^{2+} as a co-catalyst to BAIL catalyzed cellulose hydrolysis at 140, 150, 160 and 170°C respectively. 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 total reducing sugar (TRS) % yields produced during the hydrolysis of cellulose (DP~450) 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.

Biography

Ananda S Amarasekara is a Professor in the Department of Chemistry at Prairie View A&M University in Texas. He received his PhD in Organic Chemistry from the City University of New York in 1985. His research interests include cellulosic ethanol, renewable fuels, and catalysis in biomass processing. He has published ~100 research publications in peer-reviewed journals.

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