Acidic imidazolium salts: catalysts for biomass transformation

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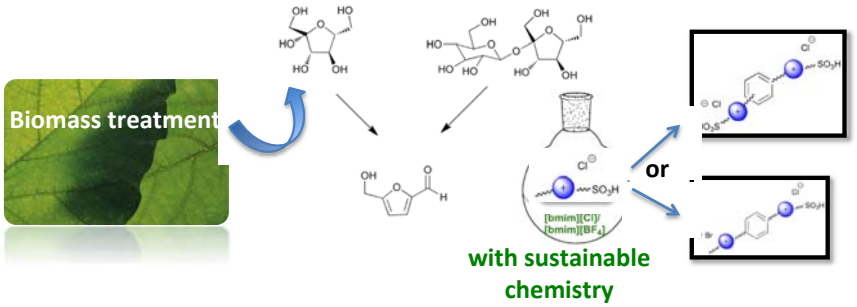
The research of energetic sources, alternative to fossil fuels, is a hot topic that encompasses various disciplines. In this field, the treatment of biomass and their subsequent transformation in products of industrial value is continuously emerging.[1] For example, carbohydrates derived from biomass can be efficiently converted in 5-hydroxymethylfurfural (5-HMF), which represents an important chemical platform for the obtainment of solvents, biofuels and polymers.[2]

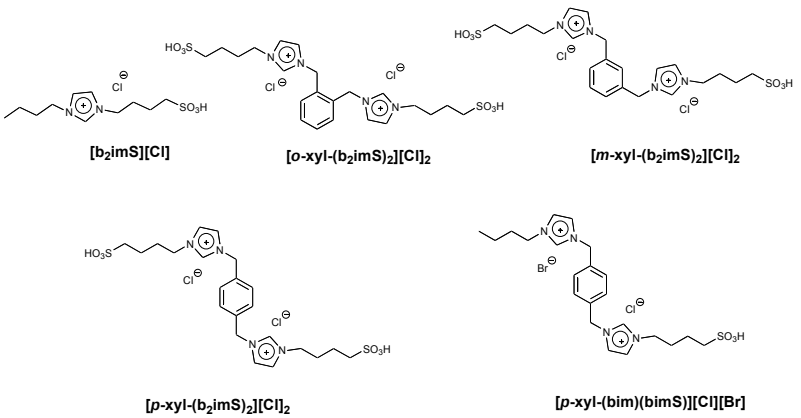
In particular, the conversion of mono- and disaccharides has been extensively studied in different media – water, organic solvents, ionic liquids- and with a wide range of catalysts, spanning from strong acids to metal complexes.[3] However, in most processes of biomass conversion, catalysts and high operational temperatures do not fit green chemistry principles, turning the whole transformation into a less eco-friendly process. For this reason, we have synthesized some novel mono- and diimidazolium functionalised organic salts and we have tested their catalytic ability for fructose and sucrose conversion in 5-HMF. These novel catalysts can be used as homogeneous catalysts. In addition, the dicationic salts are usually less soluble in the extraction solvent than monocationic ones, so they can be recovered and reused several times. We performed the reactions in ILs binary mixtures as it has been demonstrated that good yields in 5-HMF have been obtained in this media.[4] In particular, we decided to test the catalytic ability of the novel salts in the most efficient mixture among the ones previously studied, the 1-butyl-3-methylimidazolium chloride/tetrafluoroborate -[bmim][Cl]/[bmim][BF_4]- at $X_{Cl} \approx 0.5$ (Scheme 1).



Scheme 1: representation of carbohydrate transformation in ILs mixture and functionalised salts as catalysts.

Catalysts properties

Chloride based mono- and diimidazolium salts with 1-butyl(4-sulfonic acid) as alkyl chains have been synthesized (Scheme 2). Diimidazolium catalysts differ for substitution on central xylene spacer, in addition one of them is non-symmetric as it presents only one acidic alkyl chain. These structural differences influence thermal properties and acidity of salts, evaluated by DSC-measurements and Hammett method, respectively.



Scheme 2: chemical structure of novel imidazolium salts used as catalysts for carbohydrates conversion in 5-HMF.

Fructose and sucrose conversions

Reactions for both carbohydrates have been performed at 60 °C. First of all, for each salt a study as function of different amounts of catalyst has been carried out at fixed times; in all cases the 20% of catalyst brought to a good 5-HMF yield. So, with this quantity of catalyst, kinetic studies of carbohydrates conversion have been carried out using **[b$_2$imS][Cl]**, **[*o*-xyl-(b$_2$imS)$_2$)][Cl]$_2$** and **[*m*-xyl-(b$_2$imS)$_2$)][Cl]$_2$** as catalysts. Indeed, these salts presented the highest percentage yields in the preliminary study and assure a homogeneous catalysis differently from *para*-salts.

Fructose conversion brought to ≈ 60% yield in 90 min in some cases, while sucrose in the same time gave ≈ 30% yield. These represent competitive results compared to the ones reported in literature, also in terms of time and temperature of reaction.

References

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