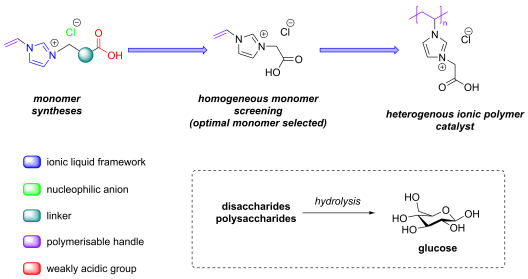
Catalytic polysaccharide hydrolysis using separable Brønsted acidic imidazolium salts and ionic polymers in water

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Catalytic polysaccharide hydrolysis is a key step in the valorisation of cellulosic and starchy biomass, as glucose is a key intermediate in potential biorefineries[1] for the production of fuels and platform chemicals (e.g. dimethylfuran, levulinic acid, γ-valerolactone)[2]. Carrying out this hydrolysis with heterogeneous catalysts in water is desirable as it improves catalyst separation and avoids organic solvents. We report the systematic design of imidazolium salts containing pendant carboxylic acid groups and their use in cellulose and starch depolymerisation in water as well as the design and preparation of a cross-linked weakly acidic polymer network that heterogeneously catalyses starch depolymerisation to glucose in water.



Acidic imidazolium compounds were screened in the hydrolysis of the model compounds cellobiose and maltose (as homogeneous models of cellulose and starch, respectively). A vinylimidazolium salt containing a pendant carboxylic acid group was found to be effective in the depolymerisation of cellulose and starch. This monomer was then polymerised to create a cross-linked insoluble acidic polymer network for the heterogeneous cleavage of saccharides. The heterogeneity of the polymer catalyst and the hydrothermal stability of the polymer was investigated and humins deposition onto the polymer surface is proposed as a possible catalyst poisoning pathway.

With the most active vinylimidazolium monomer, good yields of glucose were obtained from model saccharides, cellulose, and potato starch. Subsequent polymerisation yielded a heterogeneous ionic polymer catalyst which was active for the conversion of model saccharides and potato starch to glucose in water. Gratifyingly, the yields obtained with the polymer catalyst are similar to those obtained with the monomer catalyst and are obtained in water at relatively mild temperatures (120 –140 °C). Catalysis with the polymer network was tested for its heterogeneity and the catalyst remains active even at low (1:10 catalyst:potato starch, by mass) loadings.

1] Cherubini F., *Energy Convers. Manag.*, **2010**, *51*, 1412–1421.
[2] Melero J. A.; Iglesias J.; A. Garcia A. *Energy Environ. Sci.*, **2012**, *5*, 7393–7420.