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Acid-modified clays as green catalysts for the hydrolysis of hemicellulosic oligosaccharides†

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The hydrolysis of hemicellulosic oligosaccharides (OS) was investigated using acid-activated clays (prepared from natural Porto Santo montmorillonite clay) as catalysts. Acid activation was performed in HCl solution or with aluminium exchange. The clay catalysts were characterized by XRD, N₂ adsorption isotherms, CEC, FTIR, titration of acid sites in water and adsorption of sugars and disaccharides. They were tested for the hydrolysis of a model compound, maltose, and of OS-rich liquor from rice straw fractionation. The HCl-activated clays were the most efficient catalysts for maltose hydrolysis. It was demonstrated that the hydrolysis of OS into monomer sugars over a clay catalyst is technically feasible and that this reaction leads to the selective removal of glucose, arabinose and acetic acid side groups from the OS structure, thus yielding simpler xylo-oligosaccharide chains. Furthermore, no significant conversion of monomer sugars into furans was observed.

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1. Introduction

Hemicellulose is one of the three main components of lignocellulosic biomass, together with cellulose and lignin, representing 15 to 35 wt% of biomass dry weight, and its upgrade is considered today as an essential element of cost-effectiveness for biorefinery processes.¹ It contains several sugars, namely pentoses (such as xylose and arabinose), and hexoses (such as glucose, galactose and mannose).² The most abundant hemicelluloses, especially in angiosperms, are xylans, where the xylose units constitute the skeleton of the hemicellulose chain, with glucose, arabinose, galactose and/or mannose as side units. Acetyl groups and uronic acids are also typically present.

To upgrade hemicelluloses, their separation from cellulose and lignin is required and various pre-treatment methods, such as dilute acid hydrolysis, autohydrolysis or steam explosion, have been developed.^{3,4} These processes lead to the

deconstruction of lignocellulose into a solid fraction, containing mainly cellulose and lignin, and an aqueous liquid fraction, containing ex-hemicellulose sugars, acetic acid and some impurities. Depending on the operating conditions, a large amount of these sugars is usually in the oligomeric form. Although these oligosaccharides (OS) can be marketable by themselves, their low market volume imposes the use of other alternatives. As such, further hydrolysis into monomeric sugars, mainly xylose, arabinose and glucose will enable their final transformation by fermentation or chemical catalysis into biofuels (e.g. bioethanol or biobutanol) or bioproducts (e.g. xylitol, furfural, etc.).^{2,5–7} Hemicellulosic OS are currently hydrolysed using mineral acids such as sulphuric acid,⁴ leading to the dehydration of a fraction of the produced sugars into furfural and 5-hydroxymethylfurfural (HMF) and to safety and corrosion issues. OS can also be hydrolyzed by enzymes, but the process is more expensive, requires long reaction times and the action of several accessory enzymes, and the yields are rather low when compared with those obtained by acid hydrolysis. A green alternative is the replacement of mineral acids with solid acid catalysts during OS hydrolysis, with increased sugar selectivity.

Hemicellulose or hemicellulosic OS hydrolysis using solid acid catalysts aroused less interest than cellulose hydrolysis in the literature (for a review see ref. 8). Sulfonated resins⁹ and sulfonated silica¹⁰ have been used for this purpose. Zeolites, resins, activated carbons and functionalized oxides are also able to hydrolyse model disaccharide compounds (sucrose and cellobiose).¹¹ Among these catalysts, those with a high hydrophilic surface (e.g. carbon materials) with a good

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