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Hydrolysis of disaccharides over solid acid catalysts under green conditions

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ABSTRACT

The hydrolysis of the three most important disaccharides: sucrose, maltose and cellobiose, has been comparatively studied in mild conditions (50–80 °C) in water over several solid acid catalysts. Strong acidic resins (Amberlite A120 and A200), mixed oxides (silica-alumina and silica-zirconia), and niobium-containing solids (niobic acid, silica-niobia, and niobium phosphate) have been chosen as acid catalysts. The hydrolysis activity was studied in a continuous reactor with fixed catalytic bed working in total recirculation mode. Rate constants and activation parameters of the hydrolysis reactions have been obtained and discussed comparing the reactivity of the α-1,β-2-, α-1,4-, and β-1,4-glycosidic bonds of the employed disaccharides. The following order of reactivity was found: sucrose >> maltose > cellobiose. The sulfonic acidic resins, as expected, gave complete sucrose conversion at 80 °C and good conversions for cellobiose and maltose. Among the other catalysts, niobium phosphate provided the most interesting results toward the disaccharide hydrolysis, which are here presented for the first time. Relations between activity and surface acid properties are discussed.

1. Introduction

The hydrolysis of polysaccharides is currently attracting great attention, because high amount of low cost C6 sugars has the potentiality to replace intermediates, now obtained from fossil resources, for forming important chemicals and fuels. Polysaccharides such as starch, cellulose, and inulin can be converted to monosaccharides, in particular, glucose and fructose. Monosaccharides represent the starting point for the synthesis of a variety of chemicals by enzyme- and acid-catalyzed reactions,[1,2] among which very old or more recent reactions are included: for example, ethanol can be obtained from monosaccharide fermentation, 5-hydroxy-methylfurfural (HMF) from monosaccharide dehydration, etc. Particular importance is currently devoted to HMF which is considered one of the three most promising building blocks for the development of a carbohydrate economy.[2–4]

The hydrolysis of polysaccharides can be performed employing specific enzymes, but also by means of solutions containing mineral acids or by solid acids. The enzymatic conversion of poly- and oligosaccharides to monosaccharides was already studied in our research group starting from cellulosic materials, malto-oligosaccharides, and inulin.[5] The hydrolysis is several times faster with enzymes than with mineral acids. However, enzyme catalyzed processes have usually problems of narrow operating ranges, enzyme stability, enzyme recovery from the products, etc. The homogeneous-acid catalyzed processes often run with not sufficiently high efficiency. Formation of large amounts of acid waste, considerable energy consumption in the separation process, and problems of corrosion are the main drawbacks. The development of easily separable and reusable solid acid catalysts for the hydrolysis of poly- and oligosaccharides is therefore considered essential to convert biomass into useful chemicals with a lowest environmental impact.

The most suitable and friendly solvent for hydrolysis is, obviously, water. To obtain high catalytic conversion of saccharides in water, solid acids must have water-tolerant properties.[6–8] Moreover, the presence of a strong protonic acidity and an easy accessibility of saccharides to the active sites of the catalyst surface allow satisfactory reaction rates to be obtained. Strong acidic ion exchange resins (like sulfonic acidic resins) and super-acidic resins (like Nafion), organic–inorganic hybrid sulfonic mesoporous silicas, H-type zeolites, cesium-heteroplyacids, and layered transition-metal oxides are presented in the literatures[9–17] as efficient catalytic systems for the hydrolysis of disaccharides, starch, and cellulose. In general, severe conditions in terms of temperature (up to 120 °C in water and also in supercritical conditions[18]) and high saccharide concentration (up to 100 g L^{-1}) were used to push the catalyst activity toward the achievement of high conversions. Layered transition metal oxides containing niobium demonstrated to be particularly active in the disaccharide hydrolysis,[15] suggesting the importance to investigate niobium-containing catalysts for these reactions.

In this work, the hydrolysis of three different disaccharides, sucrose, maltose, and cellobiose, over different types of solid acid catalysts commercially available and less costly has been studied, choosing green and mild conditions for their accomplishment.

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Within the chosen solids, niobium phosphate has been here studied for the first time, as far as the authors known, beside the more conventional niobium oxide and a mixed silica-niobia sample, due to the importance of niobium containing solids as water-tolerant acids. The disaccharide hydrolysis reactions were carried out in water and at low temperatures (between 50 and 80 °C) to avoid formation of by-products which could prevent using the obtained monosaccharide solutions for further transformation, for example, for enzymatic treatment that requires pure solutions.

The three different disaccharides, whose chemical structures in water are reported in Fig. 1, have been chosen both for their importance as products deriving from biomasses and because different reactivity with acidic catalyst is expected due to their different molecular structure. Sucrose molecule is constituted by glucosidic and fructosidic units linked by α-1,β-2 glycosidic bond; it has no reducing end. Maltose and cellobiose molecules are constituted by glucosidic units linked by of α-1,4- and β-1,4-glycosidic bonds, respectively. Both these two disaccharides have reducing ends. The α-1,4- and β-1,4-glycosidic linkages present in maltose and cellobiose are also present in the starch and cellulose, respectively. The results obtained studying the activity of acidic catalysts in the hydrolysis of these two disaccharides can give useful indications for the hydrolysis of the relative polysaccharides. Certainly, maltose and cellobiose are much more difficult to hydrolyze than

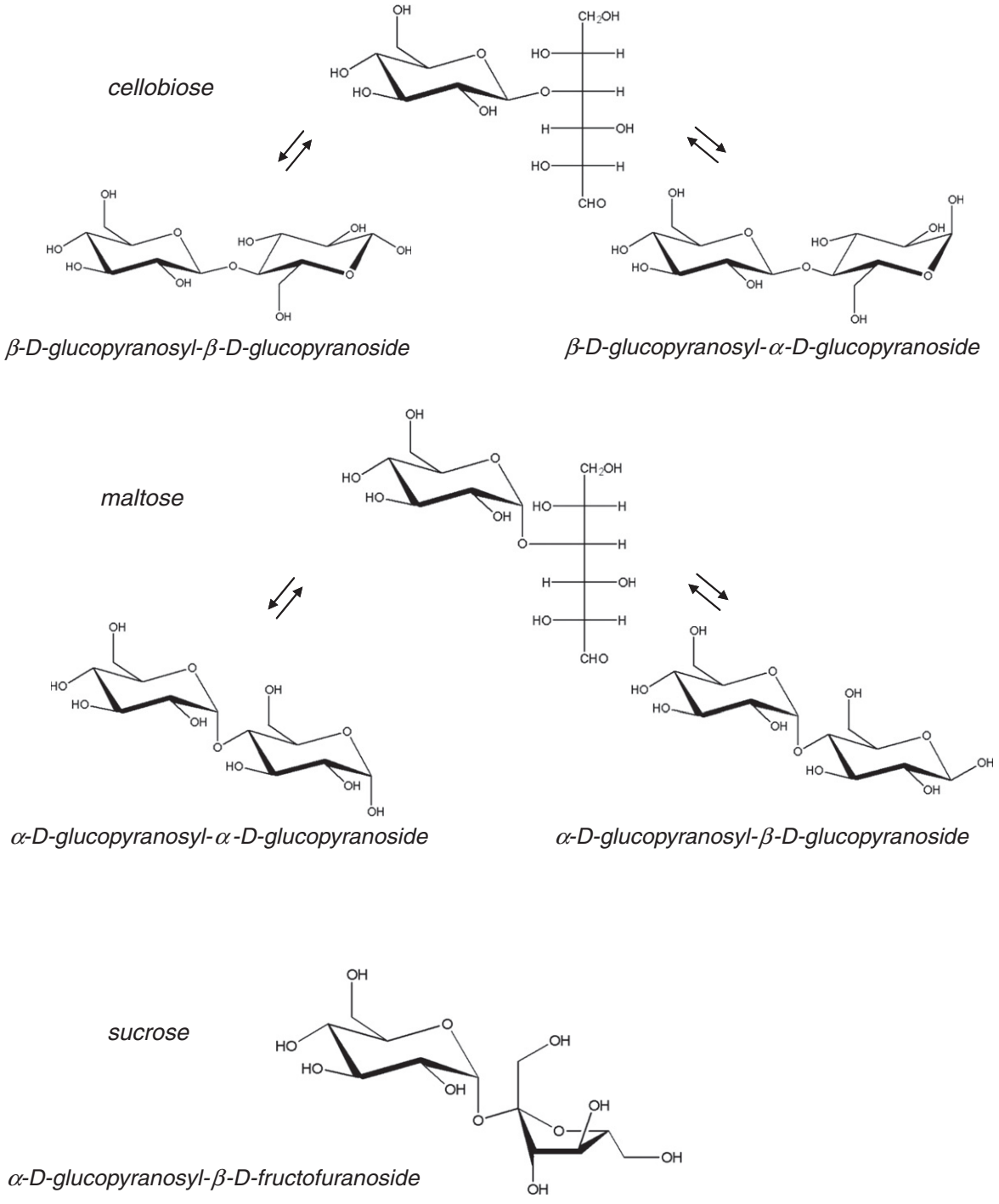

Fig. 1. Chain and ring forms of the three studied disaccharides (sucrose, maltose, and cellobiose) in water.