Hemicellulose arabinogalactan hydrolytic hydrogenation over Ru-modified H-USY zeolites

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ARTICLE INFO

ABSTRACT

The hydrolytic hydrogenation of hemicellulose arabinogalactan was investigated in the presence of protonic and Ru (1–5 wt.%)-modified USY zeolites (Si/Al ratio = 15 and 30). The use of the purely acidic materials was effective in depolymerizing the macromolecule into free sugars. While the latter partly dehydrated into 5-hydroxymethylfurfural and furfural, the generation of high molecular-weight compounds (aggregates of sugars and humins) was not favored, in contrast to previous evidences over beta zeolites. Application of the bifunctional Ru/USY catalyst, comprising well-dispersed metallic nanoparticles on the aluminosilicate support, resulted in the formation of galactitol and arabitol, in the suppression of dehydration side products, and further inhibition of polymerization reactions, which only yielded low molecular-weight oligomers. Detailed analysis of the reaction pathways as well as kinetic modeling of hydrolytic hydrogenation was performed with an advanced reaction mechanism.

1. Introduction

In view of enabling a transition toward a biobased economy, the depolymerization of the main chemical components of lignocellulosic biomass [1,2], i.e., cellulose and hemicellulose, to their sugars components by hydrolysis is an essential step which lies at the very beginning of multiple value chains for the sustainable production of fuels and chemicals. Due to the recalcitrant nature of the macromolecules, in particular the crystalline cellulose, this process is conducted under harsh conditions. Therefore, the C_6 and C_5 monosaccharides formed can easily further convert into hydroxymethylfurfural (HMF) or furfural and oligomerization reactions leading to various humins are favored. A promising way of avoiding these undesired transformations of thermally-unstable sugars is to hydrogenate them into the corresponding more robust polyols. This methodology is an attractive means to boost the selectivity of the hydrolysis process and generate valuable chemicals in one pot.

Balandin et al. [4] firstly demonstrated the hydrolytic hydrolysis of cellulose to sorbitol, health care, food, and cosmetic additive,

over a Ru/C catalyst in the presence of low-concentrated mineral acids. A revival of the interest in this reaction came only after a work of Fukuoka and Dhepe [5] who reported the use of an alumina-supported platinum catalyst for the production of sorbitol and mannitol with 25% and 6% yields, respectively. Later a range of carbon materials used as such or functionalized with sulfonic groups [3,6] and other solid acids including heteropolyacids, metal oxides, and zeolites [7] have been evaluated. The latter class of catalysts has received particular attention. Thus, the hydrolytic hydrogenation of unspecified cellulose [8], microcrystalline cellulose in the presence of mineral acid traces [9] and birch pulp mill cellulose with lower molecular weight and presence of xylan [10,11] have been performed with various metal-modified zeolites, including Ru-containing beta [8] and USY [9].

In contrast to cellulose, which requires extensive pre-treatment (e.g., ball milling) to reduce its crystallinity and thus enhance its reactivity, hemicelluloses, comprising amorphous branched hetero-polymers with shorter chains than cellulose, have been more readily solubilized and processed. Hemicelluloses comprise a number of polysaccharides, e.g., xylan, glucuronoxylan, arabinoxylan, arabinogalactan, galactoglucomannan, etc., which differ from each other in terms of nature and relative amount of their building blocks (hexoses and pentoses) and degree of

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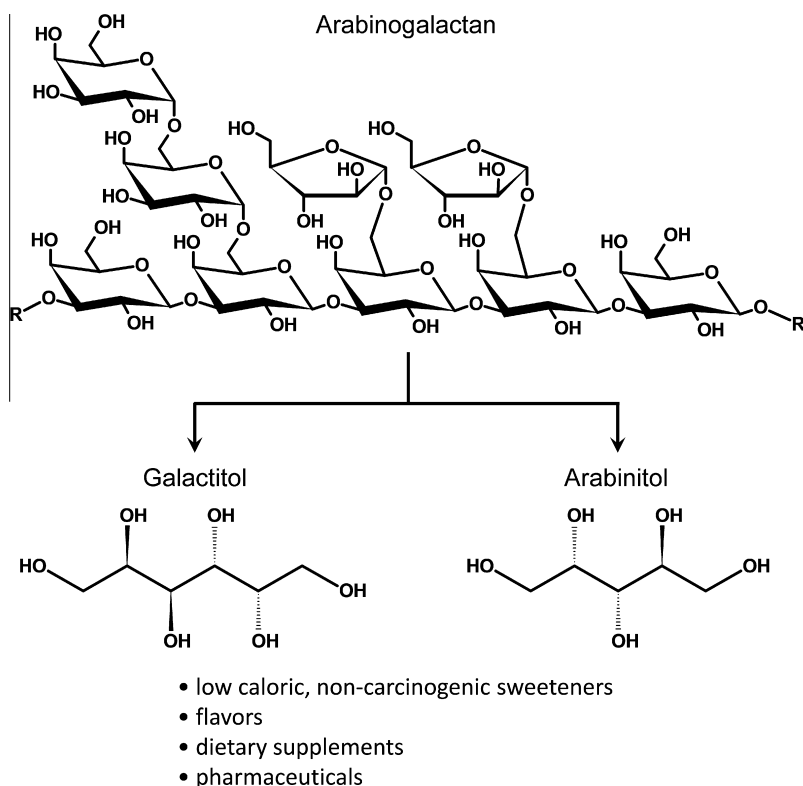
Scheme 1. Applications of the sugar polyols obtained by hydrolytic hydrogenation of arabinogalactan.

polymerization. For instance, arabinogalactans (AG), appearing in large quantities in larch species such as *Larix sibirica*, consist of β-D-galactopyranose as a backbone with D-galactopyranose and L-arabinofuranose side chains (Scheme 1). The average molar ratio of galactose to arabinose in AG is about 6:1 and the molar mass is 20,000–100,000 g mol^{-1} [12].

The preparation of the free sugars arabinose and galactose has been first attempted using sulfonic acid-functionalized polymers [13]. In comparison with such catalysis better results in terms of catalyst activity and stability were obtained with zeolites in their protonic form in the case of xylan hydrolysis [14]. In view of this result and due to the superior performance of Ru-containing materials for the hydrogenation of arabinose and galactose to their corresponding polyols (arabinitol and galactitol) [15–17], which find application as low caloric, non-carcinogenic sweeteners, flavors, dietary supplements, and pharmaceuticals, it was natural to apply bifunctional Ru-beta zeolites catalyst in hydrolytic hydrogenation of arabinogalactan [18,19]. While the side reactions to HMF and furfural were minimized, only limited yields to the corresponding polyols have been achieved over these bifunctional catalysts. Furthermore, substantial formation of high molecular weight compounds, that is, aggregates of sugars and humins (polydispersed heterogeneous carbonaceous materials), occurred. Mechanistic aspects of humins formation have recently been addressed [20–25]. Their formation mechanism has been related to polycondensation reactions giving a network of furan rings linked by ether or acetal bonds [20]. At the same time infrared spectroscopy studies [23] did not support the concept of acetal bonds formation advanced by Sumerski et al. [20]. Patil et al. [21,22] pointed out the involvement of a 2,5-dioxo-6-hydroxyhexenal intermediate formed by rehydration of HMF in the condensation process. In particular, it has been highlighted that this intermediate undergoes aldol condensation with HMF leading to humins, which cannot be formed directly from hexoses.

In the present work, hydrolysis and hydrolytic hydrogenation of AG were alternatively studied over ultra-stable Y (USY) and Ru/USY zeolites, respectively. Materials featuring distinct acidity and metal loading were compared and a range of methods were applied to investigate the formation of humins in terms of both structural properties and chemical nature of the precursor(s). Based on the experimental observations, an advanced reaction network was proposed which was used as the basis for kinetic modeling of the hydrolytic hydrogenation.

2. Experimental section

2.1. Catalyst preparation

USY-15 (CBV720, molar Si/Al = 15, protonic form) and USY-30 (CBV760, molar Si/Al = 30, protonic form) zeolites were purchased from Zeolyst International and used as received. The incorporation of ruthenium (nominal loading 1–5 wt.%) into the zeolites was performed by spray deposition using RuCl$_3 \cdot x$H$_2$O (Sigma–Aldrich, 99.9%) as the metal precursor. This technique, pioneered by Yara International [26] enabled the deposition of metal (oxide) particles onto a zeolite support with a high degree of dispersion [27]. The preparation was carried out using a benchtop Büchi Mini Spray Dryer B 290 equipped with a two-fluid nozzle (diameter = 1.5 mm) and a spray chamber of 10 dm^3. Prior to the synthesis, deionized water was passed through the system for 45 min in order to reach thermal equilibrium. RuCl$_3 \cdot x$H$_2$O was dissolved in deionized water (5 cm^3) under magnetic stirring. Thereafter, the zeolite powder (1.0 g) was added. The obtained slurry, continuously stirred, was pumped to the nozzle of the spray dryer at a rate of 2 cm^3 min^{-1} together with a constant spray air flow of 0.4 m^3 h^{-1}, resulting in the formation of fine droplets of 5–20 μm size. The aspiration rate was set at 35 m^3 h^{-1} and the inlet and outlet temperatures of the spray chamber were kept at 493 and 373 K, respectively. The hot drying gas flowed co-currently with the sprayed slurry and its