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RESEARCH

Highly selective valorisation of D-xylose from corncobs hydrolysates catalysed by C-scorpionate gold(III) complexes

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Abstract

D-xylonic acid is a multifunctional, environmentally friendly, and versatile platform chemical, and one of the most promising conversion products of D-xylose for replacing several petrochemicals that is still not produced commercially. Although microbial conversion is the most widely studied process, the low efficiency and cost of these methods create opportunities for the development of chemical routes. In this work, we report for the first time the direct chemical conversion of real hemicellulose-derived pentose-rich hydrolysates into D-xylonic acid. Furthermore, a novel chemical oxidation route based on C-scorpionate gold(III) complexes was explored. Two specific complexes are used as model catalysts, the cationic $[AuCl_2(\kappa^2\text{-Tpm})]Cl$ (*1*, Tpm = hydrotris(pyrazol-1-yl)methane, $HC(C_3N_2H_3)_3$) or the neutral $[AuCl_2(\kappa^2\text{-Tpms})]$ complex (*2*, Tpms = tris(1*H*-pyrazol-1-yl)methane sulfonate, $[SO_3C(C_3H_3N_2)_3]^-$). The catalytic operational conditions (*i.e.*, reaction time, temperature, type and concentration of alkali and oxidant agent) were initially optimised for D-xylose solutions using cationic complex *1*. Under the best conditions (100 °C, 2 mmol NaOH and 20 mmol H_2O_2) nearly 100% conversion of D-xylose and a 94% D-xylonic acid yield were achieved, with minimal formation of secondary products, when using 6 g/L D-xylose as sole carbon substrate. The direct catalytic conversion of real hemicellulosic hydrolysate, without any previous purification was possible and up to 36 g/L of D-xylose, regardless of the presence of other sugars, aliphatic acids, furans and phenolic compounds. Comparing similar catalytic conditions among model D-xylose solutions and real hydrolysates with similar titres, the later presented better performance, even though D-xylose conversion and D-xylonic acid yield decreased slightly for higher D-xylose concentrations. The catalysis was further improved by using the neutral gold(III) C-scorpionate complex *2*, which further increased the D-xylose conversion and selectivity.

Keywords Corncobs · C-scorpionate · Gold(III) complex · D-xylonic acid · D-xylose · Catalytic oxidation

1 Introduction

D-xylonic acid, an oxidation product of D-xylose, has been ranked among the top 30 value-added chemicals derived from biomass [1, 2] and set off a wave of research as a high-value-added product since 2021 [3]. This sugar acid has gained increased interest due to its similar applications to those of other sugar acids, such as gluconic acid, which are used in the pharmaceutical and food industries.

Additionally, D-xylonic acid has the potential to be used as a platform chemical and a precursor in the manufacture of various bioproducts, including 1,2,4-butanetriol, bioplastics, and other polymers [4, 5]. In particular, D-xylonic acid has potential for the development of new materials, e.g., as a cement or concrete additive due to its potential as a concrete retarder, chelating agent, and oil dispersant [6].

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