N°608 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Catalytic evaluation of Sn-containing zeolites for the transformation of complex sugar mixtures into methyl lactate: an approach to hemicellulose valorization

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PURPOSE OF THE ABSTRACT

Lignocellulosic biomass is a complex feedstock whose main components (cellulose, hemicellulose and lignin) must be separated for an efficient chemical valorization. Unlike cellulose and lignin which find interesting applications in different fields (materials synthesis, chemicals, biofuels,?) the valorization of hemicellulose is scarcely tackled, far from furfural synthesis, probably because of a complex composition. Tin containing zeolites have demonstrated good performance on the transformation of a wide variety of monosaccharides to value-added products, although their suitability in the transformation of complex mixtures, such as those coming from hemicelluloses, has not received adequate attention. This contribution deals with the use of tin containing zeolites with different topologies in the transformation of C5 & C6 and disaccharides, emulating several hemicellulose hydrolysates to assess the versatility of the catalysts.

Commercial zeolites (ZSM5; ?; USY) were subjected to a two-step dealumination stage using aqueous HNO3 solution (10 mol·L-1; 20 mL·g-1zeo; 1h). Tin was incorporated by grafting SnCl4 onto the hydroxyl nests created at the aluminum vacancies. The materials were calcinated at 550°C and ion exchanged with KCl aqueous solutions (0.5 M, 100 mL·g-1zeo, 50 °C) to boost their activity in retroaldol condensation reactions [1]. Catalytic tests were carried out in Teflon lined batch reactors loaded with 10 mL of methanolic solutions of the corresponding monosaccharide (0.26 mol·L-1) together with 0.1 g of catalyst. Reactions were conducted at 150 °C for 6 h under magnetic stirring. The reaction media was analyzed with a gas chromatograph fitted with a CP-WAX 52CB column.

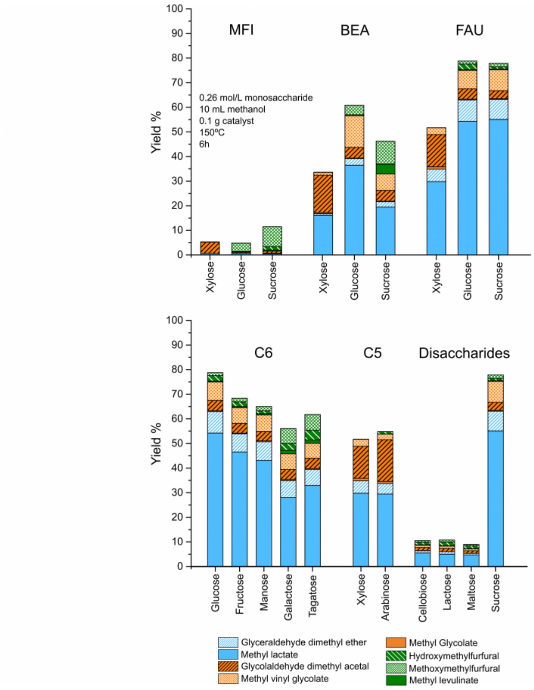
Fig. 1 (up) presents the products distribution obtained with ZSM5 (MFI), beta (BEA) and USY (FAU) zeolites in the transformation of xylose (C5), glucose (C6) and sucrose (C6 disaccharide). MFI structure was nearly unactive, suggesting that sugars transformation cannot be promoted inside the pores of the MFI structure, even with the smaller C5-monosaccharides. As for the BEA framework geometry, xylose was readily converted into methyl lactate and glycolaldehyde dimethyl acetal (GADMA) as main products, while glucose provided the largest yield towards methyl lactate. On the contrary, sucrose was transformed in a lower proportion towards hydroxyesters, probably as a result of its bulkier size. Finally, large pore Sn-USY zeolite promoted the transformation of xylose, glucose and sucrose in every efficient manner and no differences were observed between glucose and sucrose product distributions. Considering these data, Sn-USY was selected to be tested in the transformation of a wider range of sugar monosaccharides (Fig. 1-down). All the tested C6 monosaccharides yielded similar products distribution, but distinct substrate conversion, where glucose stands out. Nearly the same occurred when testing xylose and arabinose (C5 sugars). On the other hand, sucrose was the only disaccharide, among the studied, converted with this catalyst, suggesting an easier hydrolysis/alcoholysis of the glycosidic bond in this disaccharide.

Three different synthetic sugar mixtures, emulating several hemicellulose hydrolysates were studied as substrates (eucalyptus, pine & sugarcane bagasse, Fig.2). The presence of different sugars seemingly did not exert any

positive or negative influence, yielding identical products distributions to those calculated from the catalytic tests with individual substrates. Predominance of C5 sugars in hemicellulose (eucalyptus, sugarcane) yielded higher amounts of GADMA, nevertheless, transformation of all the emulated hemicellulose hydrolysates provided methyl lactate yields above 30%.

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union´s Horizon 2020 research and innovation program under grant agreement No 101023202

FIGURES



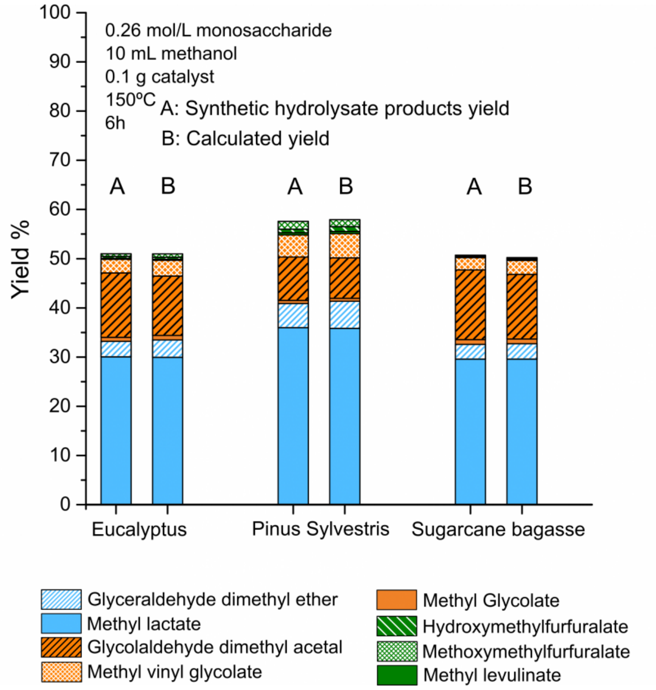


FIGURE 1

Transformation of sugar monosaccharides & disaccharides into methyl lactate with Sn-zeolites.

Influence of zeolite topology (up) and activity of Sn-USY zeolite with different substrates (down)

FIGURE 2

Products distribution obained in the transformation of emulated hemicellulose hydrolysates in the presence of Sn-USY zeolite.

A - Products distribution achieved in catalytic tests; B - Theoretical products distribution calculated from results for single monosaccharides

KEYWORDS

Methyl lactate | Sn-USY | hemicellulose | retroaldol condensation

BIBLIOGRAPHY

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