Depolymerization of hemicelluloses with solid acid catalysts: experimental and kinetic studies

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Abstract: Hydrolysis of hemicelluloses is a key step in biorefineries. In this work, TiO_2-based catalysts were prepared and applied to the hydrolysis of a model oligosaccharide, cellobiose, and then to a real hemicellulose, xylan from corncob. The experimental study showed that xylan reacted much faster than cellobiose and yielded xylose and furfural with low humins production. A kinetic model was built to elucidate the formation of humins and showed that the direct pathway "oligosaccharides to humins" is predominant in our reaction conditions.

Keywords: Hemicellulose, Acid catalyst, Hydrolysis.

1. Introduction

Hemicelluloses are non-crystalline polysaccharides present in lignocellulose in significant amount, from 20 to 40 wt.%.[1] Their valorization into high added value sugars or platform chemicals is a major stake for biorefineries.[2,3] However, depolymerization of hemicelluloses by catalytic processes was underinvestigated in the past decades.[4] Here, we present recent results on catalytic hydrolysis of a model compound, cellobiose, and of real hemicelluloses using robust mixed oxide acid catalysts.

2. Experimental

Tungstated titania (Ti-W) was prepared by wet impregnation of a commercial TiO_2 support with H_2WO_4 solution. Titania-zirconia was prepared by coprecipitation-hydrolysis of $TiCl_4$ and $ZrOCl_2$. Catalytic hydrolysis was performed in a 150 mL stainless steel autoclave. A 50 g.L^{-1} solution of commercial oligosaccharides (cellobiose from Alfa Aesar or xylan from Carbosynth) was introduced in the reactor with the powder catalyst (25 g.L^{-1}). The reaction mixture was purged with nitrogen, heated and stirred mechanically. Samples were taken regularly, filtrated and diluted before analysis. Samples were analyzed by HPLC-RID-DAD equipped with a Phenomenex Rezex-ROA column. The absence of mass transfer limitations was checked.

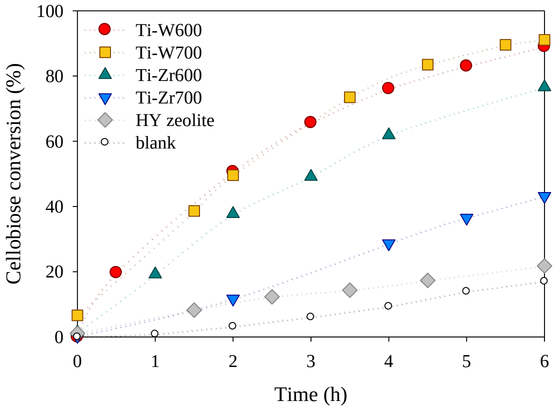

Figure 1. Cellobiose hydrolysis over solid acid catalysts.
Reaction conditions: 140°C, 50 g.L^{-1} cellobiose initial concentration, ratio catalyst:cellobiose 1:2. Lines are only for eye guide.

3. Results and discussion

Cellobiose was hydrolyzed over different TiO_2-based catalysts (**Figure 1**). The nature of dopant (W or Zr) and the temperature of calcination (600 or 700°C) had an impact on the catalytic activity. This effect was rationalized by the number and strength of acid sites (data not shown). The most active catalyst, Ti-W600, was also selective for glucose production and recyclable over 3 runs. As a comparison, HY zeolite, a commercial acid catalyst used in literature of hemicellulose hydrolysis,[56] was poorly active in our reaction conditions.

Xylan was a commercial polysaccharide containing xylose units (80 %) and glucose units (10 %) with a low degree of acetylation (2 %).For xylan

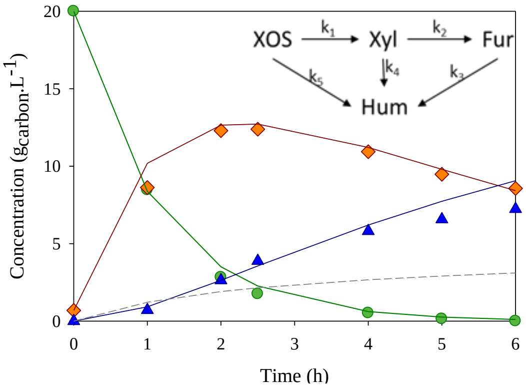

Figure 2. Concentration profiles for xylo-oligosaccharides and related products over Ti-W600. *Dots correspond to experimental data and lines correspond to kinetic modelling. XOS (●), Xylose (Xyl) (♦), Furfural (Fur) (▲). Dotted lines: humins.*

hydrolysis, the composition of the reaction medium was followed over time (**Figure 2**) and led to the design of a reaction network including the formation of humins (degraded products). Particularly, at 140°C, the hydrolysis of xylo-oligosasccharides (XOS) was complete after 4 h whereas the conversion of gluco-oligosaccharides (GOS) was slower (**Table 1**), showing that the mechanisms involved in the hydrolysis of pentosan and glucosan are rather different.

A kinetic model was designed based on the mechanism proposed on **Figure 2** (insert). Kinetic modelling was based on the following hypothesis: i) the system is a batch reactor with a constant volume of liquid; ii) all reactions follow pseudo-homogeneous, first order kinetics; iii) the water content changes are negligible; iv) kinetic constants k_i are apparent pseudo-rate constants including a factor corresponding to the catalyst concentration. The model fitted experimental values and first order pseudo-apparent kinetic constants were determined (**Table 1**).

It is interesting to note that xylo-oligosaccharides and gluco-oligosaccharides (including cellobiose) react differently over the same solid acid catalyst, Ti-W600, and under similar reaction conditions. When compared with the kinetic study of cellobiose hydrolysis, XOS gave unexpected high hydrolysis reaction rates. Indeed, the cleavage of β-1,4-osidic bond between two xylose units seems to be favored when compared with the same cleavage between two glucose units. Moreover, the degradation of reactants and products in humins follows different pathways for xylan and for cellobiose. HMF is a source of humins during cellobiose hydrolysis whereas degradation of furfural is slower during xylan hydrolysis, where humins are formed mainly from xylan. Gluco-oligosaccharides seem to be closer to cellobiose reactivity since their rate of hydrolysis is comparable.

Table 1. First order pseudo-apparent kinetic constants values for xylan

Starting material	**Kinetic constant value at 140°C (h^{-1})**					**α**
	k_1	**k_2**	**k_3**	**k_4**	**k_5**	**k_1/k_1+k_2**
Cellobiose	0.259	0.043	0.291	0	0.065	0.858
XOS	0.791	0.159	0.088	0	0.05	0.832
GOS	0.217	0.041	-	-	-	0.841

4. Conclusions

Kinetic modelling of cellobiose and xylan hydrolysis, including degradation pathways, allowed us to determine the origin of humins. The direct degradation of cellobiose and oligosaccharides to humins is a major pathway in degradation mechanisms. In a near future, further studies of complex hemicelluloses depolymerization, including in-depth analysis of reaction products and elaborated kinetic modelling, will be performed to improve the understanding of biomass deconstruction reactions.

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