Adsorption and Depolymerization of Cellulose-Derived Long-Chain β-Glucans by Post-Synthetically Functionalized Zeolite-Templated Carbon Catalysts

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Abstract: We report adsorption and subsequent depolymerization of cellulose-derived long-chain β-glucans with their average molecular weight of 3600 g mol^{-1} in zeolite-templated carbon (ZTC) material. In the former step, the 1.1 nm micropores of ZTC behave as the fittest hosts to take in such large β-glucan guests, based on the principles of supramolecular chemistry. The post-synthetic modification with H_2O_2 within 60 min successfully introduces weak-acidic functionalities to ZTC with preserving its unique microporous structure and β-glucan-adsorption performance. This leads to an increase on its catalytic activity for depolymerization of adsorbed β-glucans to produce glucose in up to 87% yield.

Keywords: Adsorption, Cellulose Depolymerization, Weak-acidic carbons.

1. Introduction

Depolymerization of cellulose—the most abundant biomass-derived polymer on earth—has been placed over the central of biorefinery, since this upstream reaction should pave the way toward the production of various value-added chemicals via further downstream transformation of glucose. Cellulase enzymes are known to accelerate this reaction due to their bifunctionality consisting of aromatic domains present in microporous cavities that adsorb substrates as well as a pair of carboxylate/carboxylic acid that activate and break β-1,4-glycosidic bonds.[1] Solid materials mimicking these two functions of enzymes are expected to exhibit excellent catalytic activity for cellulose hydrolysis, yet such materials have not been devised so far. In this presentation, we demonstrate that such a bifunctional material is now possible to be synthesized via post-synthetic functionalization of microporous ZTC,[2] where a precise control of functionalization is required to achieve high performance of ZTC in both adsorption and hydrolysis steps.

2. Experimental

ZTC was synthesized by following the previously reported procedure.[2] The weak-acid sites were then introduced to 50 mg of ZTC by post-synthetic modification conducted in 5 mL of aqueous solution containing either H_2O_2, HNO_3, or NaClO. The suspension was stirred at room temperature for typically 30 min and then was filtered. The solid was washed with water repeatedly, followed by drying under vacuum. The resulting samples thus prepared in H_2O_2, HNO_3, and NaClO are denoted as Z-H(t), Z-N(t), and Z-S(t), respectively, where t represents the treatment time in minutes.

For adsorption and depolymerization of β-glucans on the ZTC samples, a stock solution containing dissolved β-glucans (2 g L^{-1}), which have 3600 g mol^{-1} of average molecular weight determined by GPC, in concentrated HCl was initially prepared by following the reported method.[3,4] Then, 20 mg of ZTC was dispersed in 40 mL of the stock solution. The suspension was vortexed at 277 K for 10 min, followed by filtration to separate liquid and solid fractions. The adsorption uptake was estimated from a difference between the amount of β-glucans in the stock solution and that in the liquid filtrate, both of which were determined by HPLC after complete depolymerization of β-glucans to glucose. The solid phase was washed with 1 mL of water three times and was dried under vacuum overnight. The dried residue was subsequently used for depolymerization in 1 mL of water at 453 K for 3 h. The product mixture was analyzed by HPLC.

3. Results and discussion

We initially investigated adsorption performance of parent and modified ZTCs. The β-glucan uptakes for all Z-H materials were 315–390 mg g^{-1} (see Table 1), identical to the parent ZTC (306 mg g^{-1}), since the microporous network of ZTC was maintained even after the modification by H_2O_2; while the degree of functionalization can be varied upon prolonging the treatment time. According to the principles of supramolecular chemistry reported by Rebek *et al.*,[5] where 55% of the ratio of guest volume to host's vacancy volume offers the most stabilized state of host-guest complex, the 1.1 nm micropores of parent ZTC and Z-H hosts are optimal for the β-glucan guests. In stark contrast, the modification in HNO_3 and NaClO collapsed such micropores, which resulted in a significant decrease on adsorption performance (≤ 138 mg g^{-1}).

Table 1. Properties of parent and modified ZTC materials and their performance in adsorption and hydrolysis of β-glucans.

Material	Acid site[a] /mmol g^{-1}	Micropore area /m^2 g^{-1}	Pore size[b] /nm	β-Glucan uptake[c] /$mg_{\text{Glu eq}}$ g^{-1}	Glc yield[d] /%
ZTC	1.05	3480	1.14	306	66
Z-H(5)	1.81	3700	1.09	390	72
Z-H(15)	2.10	3360	1.09	315	78
Z-H(30)	2.32	3400	1.09	328	85
Z-H(60)	2.48	3050	1.09	315	84
Z-N(30)	3.84	1550	0.53	138	24
Z-S(30)	5.14	1510	0.53	0	n.d.[e]

[a]Quantified by acid-base back titration. [b]Pore diameter was estimated by NLDFT calculation. [c]Based on mass of glucose unit in β-glucans per mass of adsorbent. [d]Glucose yield was in hydrolysis of β-glucans adsorbed on ZTC materials. [e]Not determined.

We then turned to examine catalytic activity of these ZTC materials for depolymerization of adsorbed β-glucans to a monomer, glucose, in water at 453 K for 3 h. The parent ZTC produced glucose in 66% yield, and this value increased up to 84–85% upon increasing the H_2O_2-treatment time (see Z-H materials in Table 1). The fact that the microporous structure of parent ZTC is preserved after the H_2O_2-modification offers us a unique opportunity to fairly investigate how weak-acid site amount impacts on hydrolytic activity, with excluding other textural effects. The direct relationship between catalytic activity based on glucose yield and acid site density demonstrates weak-acid sites of ZTCs to activate and cleave β-1,4-glycosidic bonds (Figure 1). Although the modification by HNO_3 and NaClO provided 3.84–5.14 mmol g^{-1} of acid sites, which are at least 1.5-fold higher than the cases of Z-H series, Z-N(30) and Z-S(30) were poor catalysts for β-glucan depolymerization, possibly due to limited accessibility of surface sites as a result of pore collapse.

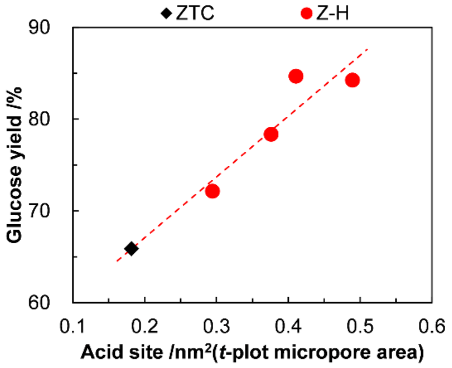

Figure 1. Glucose yield as a function of acid site density.

4. Conclusions

The post-synthetically modified ZTC materials exhibit bifunctionality for adsorption and depolymerization of long-chain β-glucans, similar to cellulase enzymes. The 1.1 nm micropores of ZTCs work as the optimal hosts to take in such large β-glucan guests, and subsequently, weak-acid functionalities introduced via precisely-controlled H_2O_2-modification activate and cleave β-1,4-glycosidic bonds.

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