A3-11 Biomass conversion by heterogeneous catalysis

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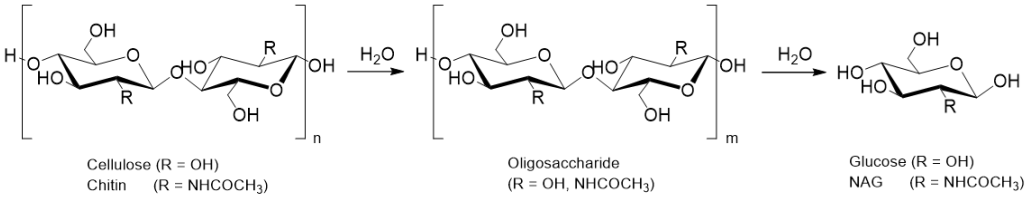
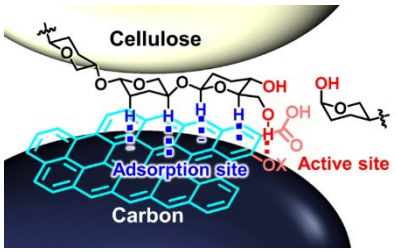
Conversion of biomass offers a promising route for the synthesis of valuable compounds. Cellulose and chitin are the most abundant biomass components having renewable carbon, and nitrogen is also renewable with chitin. They are polymers of glucose and *N*-acetylglucosamine (NAG) linked by β-1,4-glycosidic bonds. Hydrolysis of cellulose and chitin gives oligosaccharides and monomers (Scheme), which are important building blocks to produce bulk and fine chemicals. However, efficient practical processes for the hydrolysis have not yet been established due to the recalcitrance of the polymers. Heterogeneous catalysis is a strong candidate for the valorization of biomass, as they may be easily separated form reaction mixtures and show unique product selectivity [1]. Here we report our work on valorization of cellulose and chitin by heterogeneous catalysts. The structure-activity relationship is discussed for the carbon-catalyzed hydrolysis.



In the mix-milling of air-oxidized carbon (AC-Air) and cellulose, crystalline cellulose turned amorphous and formed good solid-solid contact with the carbon surface (Figure). Then the adsorbed cellulose was hydrolyzed by the weak acids [2]. AC-Air showed excellent activity for selective synthesis of oligomers (cellotriose, -tetraose, -pentaose and -hexaose) upon hydrolysis of cellulose in a semi-flow reactor [3].



Chitin has a more robust crystal structure than cellulose, and selective depolymerization of chitin is extremely difficult. Eventually, we found mechanocatalysis is effective; chitin was mixed with AC-Air and ball-milling of the sample transformed chitin into NAG-oligomers [4]. Cello- and chitin-oligosaccharides work as elicitors for plants.

1) A. Fukuoka, P. L. Dhepe, *Angew. Chem. Int. Ed.* **2006**, *45*, 5161.
2) H. Kobayashi, M. Yabushita, A. Fukuoka et al., *ACS Catal.* **2013**, *3*, 581.
3) P. Chen, A. Shrotri, A. Fukuoka, *ChemSusChem* **2019**, *12*, 2576.
4) H. Kobayashi, Y. Suzuki, A. Fukuoka et al., *Angew. Chem. Int. Ed.* **2023**, *62*, e202214229.

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[2] Heterogeneous Catalysis, Green Chemistry

[3] 2015 The Catalysis Society of Japan Award, 2015 GSC Award, 2020 Inoue Harushige Award, 2022 The Japan Petroleum Institute Award, 2023 The Chemical Society of Japan Award, 2024 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology.

[4] P. Hawken, Drawdown: The Most Comprehensive Plan Ever Proposed to Reverse Global Warming

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