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Development of Solid Catalysts for Depolymerization of Cellulosic Biomass and Preservation of Fruits and Vegetables

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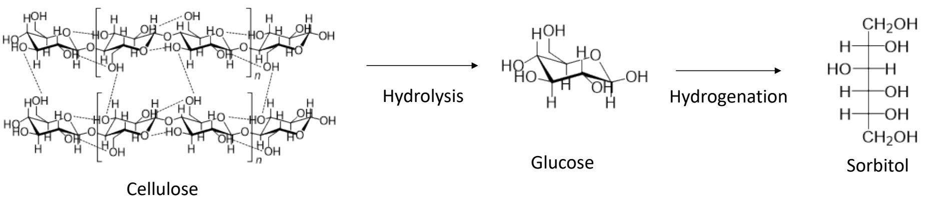
We have studied heterogeneous solid catalysis for valorization of cellulose and chitin, which are abundant plant and marine biomass. In cellulose depolymerization, we discovered that supported Pt catalyzes hydrolytic hydrogenation of cellulose to sorbitol via glucose (Figure).[1] Pt/C is a bifunctional catalyst with high durability, and carbon works as solid acid for hydrolysis. This finding led us to develop weakly acidic carbons for cellulose hydrolysis, and ball-milling of mixed cellulose and the carbon catalyst is imperative to increase physical contact between the solid substrate and the solid catalyst.[2] In the mechanistic study, we found that aromatic surface of carbon adsorbs cellulose through CH-π bonding,[3] and that weakly acidic sites on carbon attack glycosidic bonds in cellulose. We have extended this chemistry to the depolymerization of chitin to chitin-oligomers and monomer *N*-acetylglucosamine (NAG). Hydrolysis of chitin was promoted by ball-milling with weakly acidic carbon to form chitin oligomers and NAG with high selectivity.[4] NAG can be further converted to various organonitrogen compounds.



We also studied low-temperature oxidation of ethylene by solid catalysts. Even a trace amount of ethylene accelerates the aging and ripening of fruits and vegetables, and thus continuous removal of ethylene is a key to minimizing the food waste. We found high activity of silica-supported Pt catalyst for low-temperature oxidation of ethylene.[5] This excellent ability have made the catalyst commercialized in refrigerators and in storage houses since 2015. The structure-activity correlations were studied, in which the combination of hydrophobic silica and Pt is important in activation of adsorbed ethylene and oxidation to CO_2.[6]

1) A. Fukuoka, P.L. Dhepe, *Angew. Chem. Int. Ed.*, **2006**, *45*, 5161. 2) H. Kobayashi, A. Fukuoka et al., *ACS Catal.*, **2013**, *3*, 581. 3) M. Yabushita, H. Kobayashi, A. Fukuoka et al., *ChemSusChem*, **2015**, *8*, 3760. 4) H. Kobayashi, A. Fukuoka et al., *Angew. Chem. Int. Ed.*, **2022**, e202214229. 5) C. Jiang, K. Hara, A. Fukuoka, *Angew. Chem. Int. Ed.*, **2013**, 52, 6265. 6) S.S. Satter, K. Nakajima, A. Fukuoka et al., *ACS Catal.*, **2020**, *10*, 13257.