Conversion of Cellulosic Biomass into Chemicals by Heterogeneous Catalysts
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Introduction
The production of renewable chemicals and fuels from biomass has attracted worldwide interest for nurturing sustainable societies. Cellulose, a polymer composed of glucose units, is the most abundant and non-food biomass resource, and glucose is a versatile precursor to biodegradable plastics and fuels. The selective conversion of cellulose to glucose (Figure 1) typically requires large amounts of mineral acids, expensive enzymes, or ionic liquid solvents because of the persistent and water-insoluble properties of cellulose and the chemical instability of glucose. Solid catalysts are expected to overcome these drawbacks [1-5]. Recently, we demonstrated that a mesoporous carbon CMK-3 catalyzes the hydrolysis of cellulose [6]. Simple weakly acidic and water-tolerant carbons might be useful for this reaction, which motivated us to study the catalysis of various carbons. In this work, various carbon materials have been tested as a catalyst for hydrolysis of cellulose and cellulosic biomass [7].

Materials and Methods
The coke powder was activated using KOH under N₂ at 973 K. The resulting black powder was washed with water, 1 M HCl aq., and boiling water. Finally, the purified carbon was dried at 353 K to be K26. Microcrystalline cellulose and K26 were milled together in a ceramic pot with alumina balls at 60 rpm for 2 days. The mill-milled sample [374 mg, containing cellulose (324 mg) and K26 (50 mg)] and 0.012% HCl aq. (or distilled water) (40 mL) were charged in a hastelloy C22 high-pressure reactor (100 mL). The mixture was heated to 453 K in 11 min, maintained at that temperature for 20 min, and cooled down for 20 min by blowing air. The aqueous phase was analyzed by high-performance liquid chromatography (columns: Shodex Sugar SH-1011, Phenomenex Rezex RPM-Monosaccharide Pb+1). Yield of products were determined by the absolute calibration method, whose error was ±1%. The identification of products was checked by a LC/MS (APCI). Conversion of cellulose was determined based on the weight difference of the solid part before and after reaction.

Results and Discussion
The hydrolysis of cellulose by carbon catalysts occurs at the solid-solid interface, and their limited collision is a major obstacle in this type of reaction. Therefore, cellulose and K26 were ball-milled together, denoted as mix-mill hereafter, as a pretreatment to improve their contact. The mixed state can continue in the subsequent hydrolysis reaction thanks to the insoluble properties of the catalyst and the substrate. The mix-milled sample afforded 91% yield of sugars [glucose (20%), fructose (0.6%), mannose (0.7%), and oligomers (70%)] with 98% selectivity (Figure 2), whereas the separately milled K26 and cellulose provided only 13% yield of the products, indicating that the mix-milling pretreatment drastically and selectively accelerated the hydrolysis of cellulose. The polymerization degree of our mix-milled cellulose (690) and singularly-milled one (640) were almost the same due to the mild conditions (simple ball-milling at 60 rpm). The mix-milled sample and the separately-milled one showed almost the same distribution of particle sizes and the amorphous structure of cellulose, determined by laser diffraction, XRD, and 13C NMR. Hence, a possible role of the mix-milling pretreatment is making better physical contact between the cellulose and the carbon.

The hydrolysis of mix-milled cellulose mainly produces soluble oligomers as described above. The oligomers were easily hydrolyzed to glucose by only 0.012% HCl, which neither corrodes common stainless steel reactors nor has a negative economic effect. Accordingly, the hydrolysis of mix-milled cellulose in trace HCl afforded as high as 88% yield of glucose with 90% selectivity based on the conversion of cellulose (98%) (Figure 2), whereas the hydrolysis of separately-milled cellulose and K26 in the HCl solution gave only 30% yield of glucose owing to the lower conversion (40%). Clearly, the mix-milling treatment is essential. We also studied the saccharification of bagasse pulp as a real biomass substrate by an inexpensive steam-activated carbon BA (Ajinomoto). Hemicellulose was converted to xylose and arabinose in 92% yield and cellulose was converted to glucose, fructose, and mannose in 80% yield. This separate production of sugars is advantageous for further use.

Significance
High-yielding one-pot synthesis of glucose from cellulose and pentoses/hexoses from real biomass is achieved by using simple activated carbons in only 0.012% HCl aqueous solution.

References