Selective Production of Xylose and Xylo-oligosaccharides from Bamboo Biomass by Sulfonated Allophane Solid Acid Catalyst

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Bamboo biomass was hydrolyzed by using sulfonated allophane catalyst and hemicellulose in bamboo was preferentially decomposed to xylose and xylo-oligosaccharides in the range from 130 to 160 °C.

Currently, environmental problems such as global warming and dwindling energy resources are becoming increasingly critical issues. Utilization of biomass, especially inedible lignocellulosic biomass is highly desirable for the construction of sustainable society.[1]

Saccharification is a valuable process for obtaining valuable platform chemicals from lignocellulosic biomass. Though hydrolysis using mineral acids, enzymes, or high temperature compressed water has been widely investigated, these processes have some drawbacks. For example, acid hydrolysis requires highly corrosive mineral acid such as sulfuric acid which then creates waste disposal problems. Enzymatic hydrolysis requires long conversion time as well as costly enzymes. Hydrolysis in high temperature compressed water requires severe conditions where the reaction control is often burdensome because of the very short reaction time.

Recently, utilizations of solid catalysts for biomass conversion have been eagerly investigated.[2,3] Solid catalysts are thought to be more beneficial than homogeneous catalysts such as mineral acids because of facile catalyst separation.

Mesoporous silicas have hydroxy groups on their surfaces and they can be chemically bonded to sulfone groups and be used as solid acid catalysts.[4] They are used as catalysts for saccharide hydrolysis such as sucrose and starch.[5]

Allophane, an amorphous aluminosilicate, has high surface area with a high ability to adsorb ionic or polar substances due to amphoteric ion-exchange activity.[6,7] Therefore, it is very suitable material for chemical bonding.

Most saccharification research using solid catalysts simply use cellulose as substrate.[3] When whole biomass is used as starting material, it is also necessary to separate hemicellulose and lignin.

Herein, we report the selective production of xylose and xylo-oligosaccharides from hydrolysis of bamboo, a typical lignocellulosic resource in Japan, using sulfonated allophane as a solid acid catalyst. We found that hemicellulose in bamboo is mainly decomposed at specific temperatures and xylose as well as xylo-oligosaccharide were selectively produced from bamboo. Bamboo was selected as biomass sample in this study because it is very abundant in Japan and many other Asian countries. It is also one of the fastest-growing in plant species so it is a very promising biomass resources.

The bamboo used was "moso bamboo" (*Phyllostachys pubescens*) obtained from lumber manufacturer in Chiba prefecture, Japan. The bamboo is ground with a centrifugal mill (Retsch ZM-1) and screened with a 0.177 mm sieve and dried at 105 °C for 3.0 h. Allophane is obtained from Shinagawa Chemicals Co., Ltd. Sulfated zirconia (JRC-SZ-1) and H-form zeolite H-ZSM-5 (JRC-Z5-90H) obtained from Catalysis Society of Japan are also used as reference catalysts.

Table 1. Components of bamboo biomass (dry base)

Component	wt %
Cellulose	43.5
Hemicellulose	26.6
Lignin	26.4
Other extractives	0.9
Ash	2.6

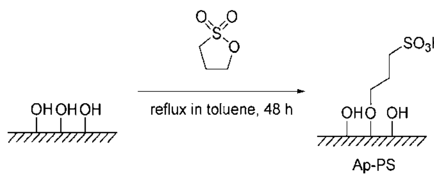

Figure 1. Synthesis of sulfonated allophane (Ap–PS).

Chemical analyses of bamboo biomass components were carried out according to methods literature.[8] Chemical components of bamboo biomass are shown in Table 1.

Preparation of sulfonated allophane (Ap–PS) was carried out as follows. Propane-1,3-sultone (0.31 g, 2.5 mmol) and allophane (1.0 g) were refluxed in toluene for 48 h. The obtained powder was dried to remove toluene. The synthetic scheme of Ap–PS is shown in Figure 1. Characterization data of allophane and Ap–PS are shown in Table S1.[9]

Hydrothermal decomposition of bamboo powder was carried out as follows. Bamboo powder (0.1 g), catalyst (0.05 g), and water (5.0 mL) in a high-pressure glass tube (volume 20 mL) with PTFE screw cap in an oil bath were stirred by magnetic stirrer for a specific time at a specific temperature. At certain intervals, the glass tube was cooled at room temperature and about 200 μL was sampled for analyses.

The analyses of saccharides in bamboo extracts were carried out by high-performance liquid chromatography (HPLC) with refractive index detection (RI). Details of HPLC instruments and analytical conditions are shown in Figure S1.[9]

Table 2 shows the decomposition of bamboo powder and the yields of xylose and glucose during the reaction at 150 °C for 4.0 h using Ap–PS catalyst, allophane (without sulfo group), blank (without catalyst), and reference catalysts. When Ap–PS was used, 40.0 wt % of the bamboo powder was decomposed

Table 2. Decomposition of bamboo powder[a)]

Catalyst	Decomposition/wt %	Xylose yield/wt %[b)]	Glucose yield/wt %[b)]
Ap–PS	40.0	40.9	0.6
Allophane	27.0	Trace	Trace
Blank	21.7	Trace	Trace
JRC-SZ-1	35.9	36.8	0.9
JRC-Z5-90H	55.6	5.3	Trace

[a)]Bamboo powder (0.1 g), catalyst (0.05 g), water (5 mL), 4.0 h, 150 °C. [b)]Percentages of xylose and glucose yield are shown on the bases of hemicellulose and cellulose in the original bamboo biomass respectively.

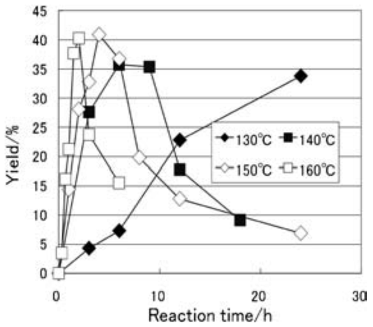

Figure 2. Changes of xylose during the reaction at various temperature using Ap–PS (130–160 °C).

and 40.9 wt % of hemicellulose in the bamboo powder was liberated in the water phase as xylose, whereas very little glucose was detected (0.6 wt %). This result indicates that xylan in bamboo hemicellulose was selectively hydrolyzed and very little cellulose was decomposed. From the decomposition amount (40.0 wt %) and the components of bamboo biomass, part of lignin in the bamboo powder was also thought to be decomposed. Traces of xylose and glucose were produced during the reaction using allophane and in blank. This result indicates that the sulfo groups on catalyst surface are effective for the decomposition of hemicellulose.[10]

Sulfated zirconia (JRC-SZ-1) also showed high activity; however, the pH of the supernatant solution in the reactor became from 4.30 to 2.40 after the reaction. This result indicates that significant leaching of sulfate groups occurred. As for Ap–PS, the leaching of sulfo groups hardly occurred.[10] From these results, the decomposition of hemicellulose can be proceeded under relatively high pH condition in the case of Ap–PS.

JRC-Z5-90H showed the highest decomposition rate (55.6 wt %) with low xylose yield in the hydrolysis. It is thought the decomposition to small molecules other than sugars was predominant in the case of JRC-Z5-90H.

Figure 2 shows the xylose yield based on hemicellulose in the original bamboo powder during the reaction at 130–160 °C. Reaction rate increased as the reaction temperature increased and at 150 °C the yield of xylose peaked (40.9 wt %) after 4.0 h. This suggests that produced xylose was subsequently converted to other compounds such as furfural. On the other hand, the glucose yields were about 1.3 wt % at 150 °C even after 24 h and 1.3 wt % at 160 °C after 6.0 h. Thus, the decomposition of cellulose in bamboo powder hardly occurred under these experimental conditions.

HPLC chromatograms for extracts of bamboo powder at 150 °C for 1.0–6.0 h are shown in Figure S1.[9] Though peaks derived from xylo-oligosaccharides are shown in chromatograms of 1.0 and 3.0 h, these peaks almost disappeared after 6.0 h. Xylo-oligosaccharides are thought to be completely decomposed to xylose or other compounds at more than 6.0 h. Therefore, the careful optimization of reaction time and temperature is necessary to increase xylo-oligosaccharide yield.

In these experiments, we have shown that the xylose and xylo-oligosaccharide can be selectively produced from the hemicellulose in bamboo biomass by using Ap–PS with less leaching of acid groups. From these results, we believe that our solid acid catalyst process has promising potential to separate beneficial chemicals from biomass without harmful acidic liquid medium.

References and Notes

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9 Supporting Information is available electronically on the CSJ Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
10 To examine the stability of Ap–PS during the reaction, Ap–PS in water was thermochemically treated without a substrate in the same conditions as the catalytic reaction. The pH of water has hardly changed (pH 4.30 before heating and pH 3.88 after heating at 150 °C for 4.0 h). Therefore, it can be considered that the leaching of the sulfo group is negligible.

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