Selective Hydrolysis of Cellulose and Polysaccharides into Sugars by Catalytic Hydrothermal Method Using Sulfonated Activated-carbon

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Mildly hydrothermal reaction using solid acid catalysts for cellulose hydrolysis into glucose has potential abilities to be one of the key technologies for a future sustainable society using cellulose biomass. Among the solid acid catalysts tested, such as H-form zeolite catalysts and sulfated and sulfonated catalysts, sulfonated activated-carbon (AC-SO3H) catalyst showed remarkably high yield of glucose in the hydrolysis of cellulose with β-1,4-glycosidic bonds under hydrothermal conditions at temperatures around 423 K. The AC-SO3H catalyst with hydrothermal pre-treatment had excellent catalytic properties attributed to the high hydrothermal stability and the strong acid sites of the sulfon functional groups and the activated carbon surfaces for polysaccharide adsorption. A bifunctional sulfonated activated-carbon supported platinum (Pt/AC-SO3H) was prepared by impregnation of platinum on activated carbon (AC) and sulfonation of the prepared Pt/AC. Gluconic acid was produced from polysaccharides, such as starch and cellulbiose, in water at 393 K under air by a one-pot process using the Pt/AC-SO3H catalyst.

Keywords
Cellulose, Glucose, Catalytic hydrothermal hydrolysis, Gluconic acid, Sulfonated activated carbon

1. Introduction

Biomass resources are promising as sustainable chemical resources1,2. Cellulose is a polysaccharide consisting of a linear chain of β-1,4-glycosidic bonded D-glucose units. Cellulose is the most abundant source of biomass, and could become an alternative to fossil resources for sustainable production of chemicals and fuels, thus preventing global warming by decreasing atmospheric CO2 generated from the consumption of fossil fuels3,4. Uses of cellulose have been limited to timber, paper, wood fuel, and so on, because of its robust structure with hydrogen bonds within and between cellulose molecules formed by the β-1,4-glycosidic bonds of D-glucose5. Glucose has been investigated as a renewable feedstock molecule, which can be efficiently converted into various chemicals, fuels, foods, and medicines5,6,7. Therefore, cellulose hydrolysis into glucose is a key process for the wider use of cellulose.

Previous research has concentrated on the degradation of cellulose with enzymes5,6, mineral acids (H2SO4,7,8,9,10), HCl11,12, and HF13) and hydrothermal methods14,15. Enzymatic processes and sulfuric acid processes have significant drawbacks such as high enzyme cost, long residence times associated with the necessary low reaction temperature, and severe controls on enzymes and waste fluids. Sulfuric acid methods are inexpensive and fast, but the large-scale use of sulfuric acid generally suffers from energy inefficiency, catalyst recovery, and reactor corrosion, and requires thorough separation and neutralization of the sulfuric acid residue, resulting in high amounts of waste. Recently, cellulose hydrolysis methods using ionic liquid, such as 1-butyl-3-methylimidazolium chloride (BMImCl), have been reported16,17. Ionic liquid methods are fast and cause less reactor corrosion, but also have problems with high cost and separation. On the other hand, hydrothermal reactions are environmentally friendly methods. Severe hydrothermal conditions, such as supercritical water, result in the saccharification of cellulose within extremely short residence times of some seconds, so avoid further degradation and dehydration of produced oligo-saccharides and glucose18. However, control of reactions and effective heat recovery are difficult to achieve in such short residence times. Therefore, saccharification of ligno-cellulosic materials has never been commercially implemented19.

Mildly hydrothermal conditions and less short reaction times are desirable for industrial applications of the hydrolysis of cellulose into glucose. Mildly hydrothermal conditions will greatly decrease the reaction
rates of cellulose hydrolysis. One possible solution is to decrease the crystallinity of cellulose before the hydrolysis, which is expected to accelerate the hydrolysis of cellulose as in the digestive system of ruminants. Ball-milling treatment of microcrystalline cellulose resulted in an insoluble material with $\beta$-1,4-glycosidic bonds but containing large noncrystalline regions as confirmed by XRD and CP/MAS $^{13}$C NMR\(^2\). The reaction rate of cellulose hydrolysis using dilute sulfuric acid at 448 K increased with decreasing cellulose crystallinity\(^2\).

To reduce the effects on the environment, sulfuric acid should be replaced by solid catalysts. Recent advances in the catalytic conversion of cellulose were summarized in a review paper\(^2\). Heterogeneously catalytic processes for microcrystalline cellulose conversion into sugar-alcohols have been described\(^2\)~\(^5\), which are expected to provide a renewable efficient hydrogen source\(^2\)~\(^7\), by combination of hydrolysis with instantaneous hydrogenation on supported noble metal catalysts, such as Pt/Al$_2$O$_3$ and Ru/C, in hot water with compressed hydrogen gas. The disadvantages of these heterogeneously catalytic processes are the requirement for hydrogen gas and noble metals and the uses of the product sugar-alcohols are limited, compared with glucose. Glucose production from soluble starch and polysaccharides over solid catalysts has been reported\(^8\)~\(^9\), but production of glucose from insoluble cellulose using solid acid catalysts without hydrogen gas is less well understood. Therefore, a new heterogeneous catalytic process is a challenge for glucose formation from cellulose by the combination of mildly hydrothermal reactions and solid acid catalysis without hydrogen gas. Solid acid catalyst called sugar catalyst has been prepared by the carbonization and sulfonation of saccharides\(^10\)~\(^13\). This catalyst has the high activity in water for the hydration of 2,3-dimethyl-2-butene at 343 K\(^14\), and the esterification of higher fatty acids at 353 K\(^15\).

Here, we introduce an efficient green process to combine mildly hydrothermal reactions and solid acid catalysis for the selective hydrolysis of cellulose into glucose at 373-450 K with autogenous pressures\(^16\)~\(^18\). A sulfonated activated-carbon (AC-\textSO$_3$H) was used as an effective solid acid catalyst below 450 K (Scheme 1). Activated carbon, which is common carbon substance for catalysts, is used as the precursor because of its high hydrothermal stability and high surface area. We also describe the hydrothermal stability of the AC-\textSO$_3$H catalyst and the negative effects of free sulfuric acid ions on the glucose production from cellulose. In addition, we prepared a sulfonated activated-carbon supported platinum (Pt/AC-\textSO$_3$H) catalyst and demonstrated one-pot production of gluconic acid from polysaccharides in hot water under air using this Pt/AC-\textSO$_3$H catalyst without pH adjustment agents (Scheme 2)\(^19\).

2. Experimental

2.1. Materials

The H-form zeolite materials, H-beta (12) (Si/Al = 12), H-beta (75) (Si/Al = 75), H-mordenite (10) (Si/Al = 10), and H-ZSM5 (45) (Si/Al = 45), sulfonated zirconia (JRC-SZ-1), and $\gamma$-alumina (JRC-ALO-2), were supplied by the Catalysis Society of Japan. Commercial silica (Caract Q-6, Fuji Silysia), activated carbon (powder, Wako Pure Chemical Ind.), and ion-exchange resin (Amberlyst 15, Organo) were also used as catalysts. The other chemicals used in this article were reagent grade.
2. Catalyst Preparation Procedures

The sulfonated activated-carbon (AC-SO$_3$H) was prepared by the following method based on a previous report. Typically, activated carbon (Wako Pure Chemical Ind., powder, 1.0 g) was added concentrated H$_2$SO$_4$ (18 mol·L$^{-1}$, 20 mL) and heated under argon flow (40 mL·min$^{-1}$) at 423 K (5 K·min$^{-1}$) for 16 h. The resultant sulfonated-activated carbon was washed repeatedly with hot distilled water (3 L, 353 K). To prevent elution of SO$_4^{2-}$ ions during reactions under hydrothermal conditions at 403-453 K, the black powder was hydrothermally treated at 473 K for 3 h, and then washed again with hot distilled water until sulfate ions were no longer detected in the wash water.

Pt/AC-SO$_3$H catalyst was prepared by the impregnation and sulfonation method. About 4 wt% Pt/AC was prepared by the impregnation method using a commercial activated carbon (AC) powder (Wako Pure Chemical Ind.) and H$_2$PtCl$_6$·6H$_2$O (Soekawa Chemical), with heating under hydrogen flow at 573 K for 6 h to form fine Pt particles on the AC. To confirm the metallic state of platinum by X-ray diffraction (XRD), the platinum loading was 4 wt%. Pt/AC-SO$_3$H catalysts were prepared by sulfonation of the Pt/AC (1.0 g) with concentrated (96 %) sulfuric acid (20 mL; Wako Pure Chemical Ind.) at 423 K under flowing Ar (20 mL·min$^{-1}$), as well as sulfonation of AC into AC-SO$_3$H. After washing repeatedly with 3 L of distilled water at 353 K, the obtained powder was hydrothermally pre-treated at 473 K using two autoclaves lined with Teflon (70 mL) to prevent elution of SO$_4^{2-}$ ions during reaction under hydrothermal conditions at 373-453 K. The product was washed again until sulfate ions were no longer detected in the wash water.

The S content was determined with a CHNS analyzer (Thermo Finnigan, Flash EA1112). The Pt content was determined with an inductively coupled plasma (ICP, SII, SPS7000A). A gas sorption analyzer (Quantachrome, NOVA1000) was used for N$_2$ physisorption to determine the surface areas of solid catalysts. The acid sites in the catalysts were determined by the titration method as follows. Sodium hydroxide aqueous solution (0.01 mol·L$^{-1}$, 20 mL) was added to the catalyst (0.040 g). The mixture was stirred for 2 h at room temperature. After centrifugal separation, the supernatant solution was titrated with hydrochloric acid (0.01 mol·L$^{-1}$) aqueous solution using phenolphthalein.

2.3. Catalytic Reactions

A typical catalytic reaction procedure was as follows. Catalyst (50 mg) and water (5.0 mL) were introduced into a steel autoclave lined with Teflon (25 mL) under...
White cellulose powders treated by ball-milling, soluble starch, pullulan, cellobiose, maltose, and glucose were used as reactants (45 mg). Ball-milling experiments were performed using ZrO₂ balls (mass of 1.8 kg and diameter of 2 cm). The balls were loaded with 20 g of cellulose (Fluka, Avicel® PH-101, microcrystalline) into a ZrO₂ bottle (2000 mL). The closed autoclave was heated at 393 K in an electric oven with an axis to rotate the autoclaves which were vertically rotated (22 rpm) to stir the reaction media.

After the reaction, the reaction mixture was separated by using normal filter paper. The filtrate solution was analyzed with two HPLC systems (Hitachi, L-7490 RI detector, Shodex Sugar KS-802 column; Hitachi, L-2035 UV-vis detector, Shodex RSpak KC-811 double columns) for saccharides and organic acids, and TOC analyzer (Shimadzu, TOC 5000 A) for total amounts of water soluble organic compounds. The dissolved SO₄²⁻ ions in the filtrate solution were determined by ion chromatography (Dionex, DX-120, IonPac AS14A column). The yields of products and total water soluble organic compounds (WSOCs) were measured as carbon % based on moles of carbon included in the charged saccharides as determined by CHNS analyzer. For example, the yield of glucose was calculated as follows:

\[
\text{Glucose yield (\%)} = \left( \frac{\text{mol of glucose} \times 6}{\text{mol of carbon included charged saccharides determined by CHNS analyzer}} \right) \times 100
\]

The yields of total WSOCs were determined by a TOC analyzer. The yields of total WSOCs and water soluble by-products and the selectively of glucose were calculated as follows:

\[
\text{Total WSOCs yield (C-%)} = \left( \frac{\text{mol of water soluble organic carbon}}{\text{mol of carbon included charged cellulose}} \right) \times 100
\]

\[
\text{Water soluble by-products yield (C-%)} = \text{yield of total WSOCs} - \text{yield of glucose}
\]

The product yield at each reaction time was determined by high performance liquid chromatography (HPLC), TOC, and IC analyzers for the filtrate solution of each reaction batch. The error of experimental data in this study, such as the amounts of sulfo groups, Pt loading, surface area, and product yields, was within 10 %.

3. Catalytic Hydrothermal Hydrolysis of Cellulose into Glucose

3.1. Reaction Behaviors of Glucose under Hydrothermal Conditions

The hydrothermal reactions of cellulose in supercritical water resulted in easy saccharization into mixtures of oligo-saccharides and glucose within extremely short residence times which avoided further degradation and dehydration of the products. However, control of reactions is difficult in such short residence times. Mildly hydrothermal conditions and less short reaction times are desirable for industrial applications of the hydrolysis of cellulose into glucose.

To assess the range of the reaction temperature for high glucose yields from cellulose, the hydrothermal stability of glucose was examined. The hydrothermal reactions of glucose were carried out without catalysts for 30 min (Fig. 1). The concentrations of glucose were constant at temperatures below 450 K, but drastically decreased under hydrothermal conditions at temperatures over 470 K. If the hydrolysis of cellulose is carried out at over 470 K, the produced glucose may be not stable and will react further. Consequently, glucose is stable under hydrothermal conditions below 450 K during less short residence times of products. Therefore, cellulose hydrolysis was investigated using solid acid catalysts under mildly hydrothermal conditions at temperatures below 450 K.

3.2. Effects of Ball-milling Treatments on the Selective Hydrolysis of Cellulose

The crystallinity of cellulose was characterized by XRD. Figure 2 shows the effects of ball milling on the XRD patterns of cellulose. After ball milling for over 24 h, the diffraction peaks attributed to cellulose had almost disappeared, indicating that the crystallinity of cellulose markedly decreased with ball-milling treatment. Even after ball-milling treatment, all cellulose powders were white and insoluble in water. The degrees of polymerization of the cellulose molecular chains might also not have decreased with the ball-milling treatment, which might not promote the hydrolysis of glycoside bonds. Therefore, hydrothermal hydrolysis of each cellulose using the AC-SO₃H catalyst at 423 K was carried out. As shown in Figs. 2 and 3, the crystallinity of cellulose affected the conversion into glucose. Decreased cellulose crystallinity re-
sulted in increased glucose yield even in reactions using solid acid catalysts, as in the hydrothermal reactions of cellulose using diluted sulfuric acid\textsuperscript{21).} Cellulose powder pre-treated for 48 h was used in the following reactions.

### 3.3. Catalytic Hydrothermal Hydrolysis of Cellulose over Various Catalysts

#### 3.3.1. Characterizations

The characterization data of the catalyst materials are summarized in Table 1, in which values given in parentheses for the H-form zeolites are the Si/Al ratios. In the case of H-form zeolites, the amounts of Al atoms theoretically correspond to the amounts of Brønsted acid sites. The acid sites were determined by the titration method in aqueous solutions and were inversely proportional to the Si/Al ratios, except for H-mordenite (20). The acid sites of H-mordenite were difficult to accurately determine (20) because the powder was suspended in NaOH aqueous solution and some parts of the powder could not be separated from the aqueous solution for the titration. The specific surface areas of catalysts were measured without pre-heating treatment (Table 1). The areas of the H-form zeolites were lower than those after dehydration treatment at about 673 K. In particular, the H-form of zeolites with lower Si/Al ratios, such as H-mordenite (10) and H-beta (13), showed significantly lower specific surface area, because the micropores of such hydrophilic zeolites were filled by water molecules under air.

The activated carbon had high surface area of 1243 m\textsuperscript{2}·g\textsuperscript{-1}. The activated carbon was sulfonated and then hydrothermally pre-treated at 473 K to improve its tolerance to the hydrothermal catalytic reaction media at around 423 K. Although the sulfonation treatment of the activated carbon and the subsequent hydrothermal treatment decreased the surface area, the sulfonated activated-carbon (AC-SO\textsubscript{3}H) still had high surface area of 806 m\textsuperscript{2}·g\textsuperscript{-1}. The XRD pattern showed two broad peaks at around 24° and at around 42° attributed to amorphous carbon consisting of aromatic carbon sheets oriented in a considerably random directions\textsuperscript{37} (Fig. 4). The XRD pattern was almost same as that before the sulfonation. AC-SO\textsubscript{3}H contained 0.63 mmol·g\textsuperscript{-1} of acidic sites, which was in good agreement with the sum of acidic sites of untreated activated-carbon (0.25 mmol·g\textsuperscript{-1}) and an S content of AC-SO\textsubscript{3}H

![Figure 2](image1.png) XRD Patterns of Cellulose Samples Pre-treated by Ball Milling for 0-144 h

![Figure 3](image2.png) Hydrothermal Hydrolysis of Cellulose in Fig. 2 Using AC-SO\textsubscript{3}H Catalyst at 423 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al [molar ratio]</th>
<th>S contents [mmol·g\textsuperscript{-1}]</th>
<th>Acid sites [mmol·g\textsuperscript{-1}]</th>
<th>S. A. [m\textsuperscript{2}·g\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.095</td>
<td>407</td>
</tr>
<tr>
<td>γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.049</td>
<td>140</td>
</tr>
<tr>
<td>H-mordenite (10)</td>
<td>10</td>
<td>n.d.</td>
<td>0.7</td>
<td>15</td>
</tr>
<tr>
<td>H-beta (13)</td>
<td>13</td>
<td>n.d.</td>
<td>1.05</td>
<td>105</td>
</tr>
<tr>
<td>H-ZSM-5 (45)</td>
<td>45</td>
<td>n.d.</td>
<td>0.30</td>
<td>124</td>
</tr>
<tr>
<td>H-beta (75)</td>
<td>75</td>
<td>n.d.</td>
<td>0.18</td>
<td>315</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>n.d.</td>
<td>0.0</td>
<td>0.24</td>
<td>1243</td>
</tr>
<tr>
<td>AC-SO\textsubscript{3}H</td>
<td>n.d.</td>
<td>0.44</td>
<td>0.67</td>
<td>806</td>
</tr>
<tr>
<td>Sulfated zirconia</td>
<td>n.d.</td>
<td>1.2</td>
<td>1.60</td>
<td>52</td>
</tr>
<tr>
<td>Amberlyst 15</td>
<td>n.d.</td>
<td>1.7</td>
<td>1.8</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Amounts of acid sites on catalysts were determined by a titration method.

\textsuperscript{b} Specific surface area was measured without pre-heating treatments of catalysts.

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All S atoms in the sugar catalyst, a sulfonated carbon material, are contained in SO$_3$H groups according to X-ray photoelectron spectroscopy (XPS) spectra. The same would be true in the case of our AC$_x$SO$_3$H, and the high catalytic activity would be due to the SO$_3$H groups. The S contents of sulfated zirconia and Amberlyst 15 are 1.2 and 1.7 mmol・g$^{-1}$, which are larger than that of the AC$_x$SO$_3$H. Both AC and AC$_x$SO$_3$H particles had sizes between 5 and 100 $\mu$m, according to SEM observations. These particle sizes were almost the same as those of milled cellulose, but were larger than the particles of the H-form zeolites and the sulfated zirconia with sizes between 0.5 and 20 $\mu$m.

### 3.3.2. Catalytic Hydrothermal Hydrolysis of the Cellulose

The catalytic results are summarized in Fig. 5. The values given in parentheses for the H-form zeolites are the Si/Al ratios. $\gamma$-Alumina and silica catalysts showed almost no activity. The H-form zeolite catalysts showed significantly higher activity than the blank reaction. The zeolite catalysts with high Si/Al ratio such as H-beta (75) and H-ZSM5 (45) showed higher activity for glucose formation than the zeolite catalysts with relatively low Si/Al ratio such as H-beta (13) and H-mordenite (10). A similar relationship between Si/Al ratios and glucose yields was reported in maltose hydrolysis.

The activated carbon (AC) and AC$_x$SO$_3$H catalysts had higher hydrophobic character than zeolite catalysts. However, the AC with acidic surface functional groups, such as carboxylic groups, showed low catalytic activity for the cellulose hydrolysis. In the catalytic hydrothermal hydrolysis of cellulose at 423 K for 24 h, AC$_x$SO$_3$H catalyst formed glucose in 40.5 C-% yield, with minor water soluble by-products including C$_1$-C$_2$ carboxylic acids. The high catalytic activity was probably due to the sulfo groups. The product selectivity was about 90 C-%, estimated as the ratio of the glucose yield to the total yield of the water soluble compounds. The AC$_x$SO$_3$H catalyst showed significantly higher catalytic activity and glucose selectivity than the tested H-form zeolite catalysts, which might be due to the more hydrophobic graphene planes and strong acidic SO$_3$H surface functional groups of the AC$_x$SO$_3$H catalyst.

Among the solid catalysts tested, sulfated zirconia and Amberlyst 15 also gave relatively high yields of glucose. However, the sulfated zirconia catalyst formed a significant amount of water soluble by-products, such as carboxylic acids, oligosaccharides, and sugar derivatives. Amberlyst 15 catalyst consisting of an ion-exchange resin with SO$_3$H groups also showed considerable formation of water soluble by-products. In addition, the ion-exchange resin colored to dark brown after reaction, due to the low hydrothermal stability.

### 3.4. Catalytic Hydrothermal Hydrolysis of Cellulose over AC$_x$SO$_3$H Catalyst

Figure 6 shows the effect of reaction temperature on cellulose hydrolysis with AC$_x$SO$_3$H catalyst. The yield of glucose increased with higher temperature in the range of 403-433 K and reached 43 C-% at 433 K. However, in the range of 433-453 K, the yield of glucose markedly decreased to 3 C-% at 453 K, the yield of by-products increased, and the total yields of glucose and water soluble by-products decreased. The reaction for 3 h at 453 K resulted in a relatively high glucose yield of 44 C-%, indicating that glucose subsequently reacted to form water soluble and insoluble by-products.

After the first reaction run using AC$_x$SO$_3$H catalyst at 423 K for 24 h, the solid catalyst was filtered with the cellulose residue. The fresh cellulose was added to the filtrate solution, and then the reaction was carried out at 423 K for 24 h. As shown in Fig. 7, the reaction in
the filtrate solution without the solid catalyst resulted in a marked decrease of the glucose yield similar to those in the blank reaction (Fig. 5) and the reactions with dilute formic acid at less than 1.0 mmol·L⁻¹. However, after the 1st run, fresh cellulose was added to the resultant solution with the AC-\(\text{SO}_3\text{H}\) catalyst, and then the 2nd reaction was carried out. The reaction was repeated once again (3rd reaction). The products in the 2nd and 3rd runs were similar to the 1st run, and the glucose concentration doubled and tripled in the reactor. These results indicated that the cellulose is hydrolyzed into glucose over the solid catalyst, and the catalyst is not deactivated during the catalytic reaction.

### 3.5. Comparison of AC–SO₃H Catalyst with Diluted Sulfuric Acid Catalysts

Figure 8 shows the changes in product yields during cellulose hydrolysis using dilute acid of 0.01 mol·L⁻¹ \(\text{H}_2\text{SO}_4\) and AC–SO₃H catalyst at 423 K. The \(\text{SO}_3\text{H}\) functional groups bonded on AC–SO₃H catalyst (50 mg) in 5 mL corresponded to 0.0044 mmol·L⁻¹ which was lower than the 0.01 mol·L⁻¹ of the dilute acid. At the reaction time of 24 h, the dilute acid gave a similar glucose yield to the AC–SO₃H catalyst, but the resultant solution became brown and contained large amounts of water soluble by-products including formic, acetic, and glycolic acids. These by-products are known inhibitors for further chemical and biochemical conversions of glucose into useful chemicals. The solid acid catalysts with \(\text{SO}_4^{2-}\) elution during reaction, such as sulfated zirconia and Amberlyst 15, also showed relatively high yields of water soluble by-products which would be due to free \(\text{SO}_4^{2-}\) ions. During the reaction within 24 h, the yields of glucose increased linearly with reaction time in both reactions. Under such reaction conditions with low conversion, the AC–SO₃H catalyst always showed high selectivity for glucose, whereas the dilute acid showed high selectivity for by-products. When the reaction time was longer than 24 h, the glucose yield did not increase for either AC–SO₃H or dilute acid. Insoluble milled cellulose seemed to partly contain a robust structure resistant to hydrolysis over AC–SO₃H. The glucose yield significantly decreased in the dilute acid for reaction times longer than 24 h. Further reaction of glucose did not occur over the AC–SO₃H, compared with dilute acid. These results indicated that AC–SO₃H catalyst without \(\text{SO}_4^{2-}\) elution had excellent catalytic properties in contrast to dilute acid for cellulose hydrolysis into glucose.

### 3.6. Effects of Hydrothermal Pre-treatment of AC–SO₃H Catalyst on Selective Hydrolysis of Cellulose

To clarify the effects of pre-treatment of the AC–SO₃H catalyst (Entry 2 in Table 2) under hydrothermal conditions at 473 K on the catalytic properties, sulfonated activated-carbon without hydrothermal treatment was also examined. As shown in Entry 3, this material had \(\text{SO}_3\text{H}\) functional groups of about 0.6 mmol·g⁻¹ and surface area of 941 m²·g⁻¹, both larger than those of AC–SO₃H of Entry 2. The sulfonated activated-carbon without hydrothermal treatment (Entry 3) showed similar glucose yield to the AC–SO₃H catalyst, but also water soluble by-products yield of about 10 C-% and a significant amount of \(\text{SO}_4^{2-}\) elution after the reaction. The water soluble by-products were not oligo-saccarides, but may have been the derivatives of oligo-saccharides and glucose, such as carboxylic acids. The hydrothermal pre-treatment of the sulfonated catalyst has a
powerful effect for preventing the removal of SO$_3$H functional groups during the hydrothermal reaction. An ion-exchange resin with SO$_3$H groups (Entry 4) showed significant catalytic activity for glucose formation, but also about 8 C-% of by-products and a significant amount of SO$_4^{2-}$ elution as high as the untreated AC–SO$_3$H catalyst (Entry 3). The ion-exchange resin became dark brown after the reaction, which was due to the lower thermal stability. Sulfated zirconia (Entry 5) also showed catalytic activity for cellulose conversion into glucose. However, the resultant solution was brown and contained large amounts of water soluble by-products. Furthermore, the sulfated zirconia was decomposed during the hydrothermal reaction, which resulted in 14.1 mmol·L$^{-1}$ SO$_4^{2-}$ ions in the resultant solution.

Dilute acid of 0.01 mol·L$^{-1}$ H$_2$SO$_4$ (Entry 6) showed similar glucose yield to the AC–SO$_3$H catalyst (Entry 2), but the resultant solution was brown and contained large amounts of water soluble by-products including formic, acetic, and glycolic acids. These carboxylic acids are known inhibitors for further conversion of glucose into useful chemicals. The solid acid catalysts leading to SO$_4^{2-}$ elution during reaction, in Entries 3, 4, and 5, also had relatively high yields of water soluble by-products, which would be due to the eluted SO$_4^{2-}$ ions.

Consequently, this chemical process to combine mildly hydrothermal conditions and stable acid catalysts, such as the AC–SO$_3$H catalyst, is efficient to selectively hydrolyze cellulose into glucose. The use of solid acid catalysts without suitable pre-treatment require scrupulous attention to elution of active sites, such as sulfo groups. The bond strength between sulfo groups and activated carbon may depend on the binding location of the activated carbon. The hydrothermal pre-treatment would remove SO$_3$H groups with relatively weakly binding with the activated carbon. On the other hand, the acid strength of SO$_3$H groups also depends on the binding location.

### 3.7 Selective Hydrolysis of Starch over AC–SO$_3$H Catalyst

In reactions of cellulose using solid catalysts, the true conversion of cellulose is difficult to determine because unreacted cellulose residues cannot be completely separated from the solid catalysts and insoluble by-products. Starch contains $\alpha$-glycosidic bonds of $\alpha$-glucose, and is a soluble polysaccharide under hydrothermal condi-
The AC–SO₃H catalyst in the hydrolysis of starch showed selective glucose production of higher than 90% yield (Fig. 9). The amounts of total carbon of water soluble organic compounds was always over 96 C-% of the charged starch in the reaction-temperature region of 373–423 K for 24 h. This result suggests that most products from the hydrolysis of polysaccharides under such reaction conditions using the AC–SO₃H catalyst are present in the aqueous phase. Few products are found in the gas phases or on the solid catalysts. In this study, the conversion of cellulose was estimated to be almost equal to the yield of WSOCs. In the reaction using the AC–SO₃H catalyst at 423 K for 24 h (Entry 2 in Table 1), the cellulose conversion was estimated to be 43%. The insoluble cellulose treated by ball milling in this study probably included about a half of its structure resistant to hydrolysis over the AC–SO₃H catalyst. In addition, this result suggested that the AC–SO₃H catalyst selectively hydrolyzes soluble polysaccharides into monosaccharides.

4. Direct Production of Gluconic Acid from Polysaccharides Using a Bifunctional Pt/AC–SO₃H Catalyst

D-Gluconic acid is an important industrial product, used as an intermediate in the food industry, in pharmaceutical applications, and as a water-soluble cleansing agent. Recent developments have shown the potential of inorganic heterogeneous catalysts for oxidizing monosaccharides with oxygen or air. However, most natural saccharides are polysaccharides. Therefore, a one-pot synthesis of sugar acids from polysaccharides would be extremely important in a sustainable society. Bifunctional catalysts for the hydrolysis of polysaccharides such as starch and cellulose into monosaccharides such as glucose and for the oxidation of monosaccharides into sugar acids are likely to be developed. As is well known, polysaccharides can be converted into monosaccharides by homogeneous acid-catalyzed reactions using sulfuric acid. However, the use of sulfuric acid results in large amounts of acid waste and energy consumption in the separation process. Solid acid catalysts can also be used for the hydrolysis of polysaccharides with low environmental impact as discussed above. Although the noble metal-solids acid catalysts, such as Pt/zeolites and Pt/sulfated-zirconia, have bifunctional catalysis effects for the dehydroisomerization of butane into isobutene and the isomerization of alkanes and so on, these conventional catalysts are easily collapsed and/or dissolved in hot water with low pH values attributed to the organic acids produced. As discussed above, we achieved the selective hydrolysis of cellulose using the AC–SO₃H catalyst. Carbon materials are highly stable in hot and acidic water. AC–SO₃H is expected to be a suitable support for acid catalysis, because the activated carbon provides high surface area and high thermal stability for the impregnation method to prepare noble metal fine particles, and the AC–SO₃H provides strong acidity and water tolerance for the hydrolysis of saccharides in water.

4.1. Characterization of the Pt/AC–SO₃H Catalyst

The characterization data of the catalysts are summarized in Table 3. The platinum content of Pt/AC and Pt/AC–SO₃H were 4.2 wt% and 3.9 wt%, respectively, or about 0.2 mmol·g⁻¹. The platinum content of Pt/AC–SO₃H catalyst was almost the same as that of its precursor Pt/AC, which indicated that platinum species were little removed during the sulfonation treatment.
As shown in Fig. 10, XRD patterns of these platinum catalysts show diffraction peaks of metallic platinum which indicated that the platinum particles were mainly in the metallic state. The platinum particle sizes increased from 3.3 nm in Pt/AC to 4.7 nm in Pt/AC-\textsubscript{SO3H}, based on the XRD findings. The S content of Pt/AC-\textsubscript{SO3H} was 0.26 mmol \cdot g\textsuperscript{-1}, as determined by CHNS elemental analysis, which was comparable but less than the 0.44 mmol \cdot g\textsuperscript{-1} of AC-\textsubscript{SO3H}. The specific surface area of Pt/AC-\textsubscript{SO3H} was 226 m\textsuperscript{2} \cdot g\textsuperscript{-1}. This surface area was much higher than those of sulfonated carbon-nanotube (CNT\textsuperscript{49}), sulfonated CNT supported platinum\textsuperscript{51}, and sulfonated carbon\textsuperscript{31}, but lower than that of the Pt/AC precursor. The specific surface area of AC-\textsubscript{SO3H} was also significantly less than that of AC. The surface area was measured by the BET method without the heating pre-treatment. The sulfonation treatments resulted in decreased surface area, which might be due to the increase of adsorbed water with more acidic surface functional groups on the sulfonated catalysts and the decrease of porosity. These findings show that Pt/AC-\textsubscript{SO3H} with strong acidic sulfo groups, platinum fine particles, and high surface area was prepared by the impregnation and sulfonation method.

### 4.2. Catalytic Conversion of Starch

The reaction results at 393 K for 24 h are summarized in Fig. 11. After the reactions, all solutions were clear and colorless. A blank reaction without catalyst formed almost no glucose or oligosaccharides but formed the amounts of water soluble organic compounds (WSOCs) corresponding with the starting starch, based on carbon %. The main component of the WSOCs was unreacted starch. The AC catalyst had acidic surface functional groups, such as carboxylic acid groups, but showed low catalytic activity for the starch hydrolysis. The AC catalyst formed about 1 C-% yield of glucose and 31 C-% of other water soluble organic compounds which were mainly unreacted starch. The other 68 C-% disappeared from the water phase. As shown in Table 4, the C and H chemical compositions of the AC treated under hydrothermal conditions without starch was almost the same as that of fresh AC. In contrast, the C/H ratio of the AC catalyst after the starch reaction was lower than that of the fresh AC. The decrease in C/H ratio corresponded to the adsorption of about 75 C-% of starch on the AC. The other 68 C-% was probably adsorbed on the AC. In contrast, the AC-\textsubscript{SO3H} catalyst formed glucose in 69 C-% yield and oligosaccharides, such as maltose and maltotriose, in 29 C-% yield, but almost no water soluble by-products. As shown in Fig. 12 (a), the glucose yields increased with longer reaction time over the AC-\textsubscript{SO3H} catalyst, and the glucose yield was over 90 C-% and the yield of WSOCs was about 95 C-% after 70 h. The AC-\textsubscript{SO3H} catalyst selectively converted

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET\textsuperscript{a) (m\textsuperscript{2} \cdot g\textsuperscript{-1})}</th>
<th>Acid\textsuperscript{b) (mmol \cdot g\textsuperscript{-1})}</th>
<th>S content\textsuperscript{c) (mmol \cdot g\textsuperscript{-1})}</th>
<th>Pt content\textsuperscript{d) (wt%)}</th>
<th>Pt particle size\textsuperscript{e) (nm)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1243</td>
<td>0.24</td>
<td>0.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AC-\textsubscript{SO3H}</td>
<td>806</td>
<td>0.69</td>
<td>0.44</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pt/AC</td>
<td>1202</td>
<td>n.d.</td>
<td>0.0</td>
<td>4.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Pt/AC-\textsubscript{SO3H}</td>
<td>226</td>
<td>0.57</td>
<td>0.26</td>
<td>3.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

a) Determined by nitrogen adsorption.  
b) Determined by titration.  
c) Determined by CHNS analyzer. 
d) Determined by ICP.  
e) Estimated by powder XRD.

**Fig. 10** XRD Patterns of Activated Carbon (a), AC-\textsubscript{SO3H} (b), Pt/AC (c), and Pt/AC-\textsubscript{SO3H} (d)

**Fig. 11** Reactions of Starch at 393 K for 24 h
starch into glucose, and adsorption of glucose on the ACSO₃H catalyst was negligible. The molar ratio of produced glucose to sulfo groups in the AC.SO₃H was about 10, indicating that the sulfo groups acted as a catalyst for the hydrolysis of starch.

As shown in Fig. 11, the Pt/AC.SO₃H catalyst also gave high yields of the hydrolysis products, indicating that the Pt/AC.SO₃H catalyst had sulfo groups to hydrolyze starch, like the AC.SO₃H catalyst. However, a main product was gluconic acid in 40 C-% yield. Minor amounts of degradation products, such as acetic acid and formic acid, were also formed. We carried out the catalytic reactions with various amounts of catalysts. As shown in Fig. 13 (b), the yield of gluconic acid increased linearly with higher amount of catalysts up to 100 mg over the Pt/AC.SO₃H catalyst, like the yield of glucose over the AC.SO₃H catalyst (Fig. 13 (a)). The platinum particles were the active sites for

<table>
<thead>
<tr>
<th>C [wt%]</th>
<th>H [wt%]</th>
<th>Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>68</td>
<td>After starch reaction at 393 K for 24 h</td>
</tr>
<tr>
<td>AC</td>
<td>87</td>
<td>After hydrothermal treatment at 393 K for 24 h</td>
</tr>
<tr>
<td>AC</td>
<td>87</td>
<td>Before both treatments</td>
</tr>
</tbody>
</table>

Reaction conditions: starch 45 mg, water 5.0 mL, and catalyst 50 mg.

Fig. 12 Changes in Product Yields during Reaction of Starch at 393 K over AC.SO₃H (a) and Pt/AC.SO₃H (b) Catalysts

Fig. 13 Effects of the Amounts of AC.SO₃H (a) and Pt/AC.SO₃H (b) Catalysts on the Reactions of Starch at 393 K for 24 h
glucose oxidation into gluconic acid because the catalysts without platinum formed no gluconic acid. After reaction, the used Pt/AC-\text{SO}_3\text{H} catalyst was characterized. The amount of platinum in the used Pt/AC-\text{SO}_3\text{H} was 4.0 wt% determined by ICP, and the average platinum particle size was estimated to be 4.5 nm by XRD, which were almost the same as before the reaction. In addition, no leaching of platinum from Pt/AC-\text{SO}_3\text{H} catalysts was observed in the resultant solution by ICP. The acid properties evaluated by the titration method were also not changed by the reactions with starch. The catalytic active sites, such as Pt particles and sulfo groups, remained stable during the reaction in hot aqueous solution, because of the hydrothermal pre-treatment of the Pt/AC-\text{SO}_3\text{H} catalyst at 473 K.

Figure 12 (b) shows the changes in product yields during starch hydrolysis using the Pt/AC-\text{SO}_3\text{H} catalyst at 393 K. Although the yields of oligosaccharides, glucose, and gluconic acid increased linearly with longer reaction time within 9 h, the yield of oligosaccharides decreased with reaction time longer than 9 h, and the yield of glucose decreased with reaction time longer than 18 h. In contrast, gluconic acid was sequentially produced and became the main product at 24 h. Molar ratios of gluconic acid to total S atoms and total Pt atoms in the catalyst were about 8 and 9, respectively, indicating that the sulfo groups and platinum particles in the catalyst accelerated the hydrolysis of starch into glucose and the oxidation of glucose into gluconic acid. The catalyst was separated by filtration, and then repeatedly used. Although a small amount of the catalyst was lost in each run, gluconic acid and glucose were formed as the main products even in the third run with little slowing of formation rate (Fig. 14).

The pH values before and after starch reaction over Pt/AC-\text{SO}_3\text{H} catalyst were nearly neutral at about 6 and about 3, respectively. The decrease in pH value was mainly due to the production of gluconic acid. The filtrate solution after the reaction using the Pt/AC-\text{SO}_3\text{H} catalyst contained almost no sulfuric ion as detected by ion chromatography. In addition, fresh starch was introduced into the filtrate solution and then the reaction in the filtrate solution without catalyst was carried out at 393 K for 24 h, but the starch was not hydrolyzed. These results clarified that the gluconic acid was produced from starch by the one-pot process using the heterogeneous bifunctional Pt/AC-\text{SO}_3\text{H} catalyst.

On the other hand, the yield of gluconic acid was constant at 40 C-% over 24 h, possibly because oxygen was consumed during the oxidation reaction in the batch reactor. After reaction for 40 h, the reactor was cooled to room temperature and opened to introduce fresh air. Further reaction was carried out at 393 K for another 24 h. As shown in Fig. 3b, the yield of gluconic acid increased to about 60 C-%. These results suggest that a continuous flow of air in the reactor will increase the gluconic acid yield.

4.3. Catalytic Conversion of Various Polysaccharides

The reactions of cellobiose, maltose, and pullulan were also carried out over the Pt/AC-\text{SO}_3\text{H} catalyst at 393 K. The results are summarized in Fig. 15. The reaction products from pullulan, which is a polysaccharide of glucose with $\alpha$-glycoside bonds and is soluble in water at room temperature, were almost same as those of starch. The reaction products of maltose were glucose and gluconic acid. The yield of gluconic acid was similar to those in the reactions of starch and pullulan. The product yields from cellobiose were almost same as those from maltose, indicating that gluconic acid is also obtained directly from oligo-
saccharides with β-1,4-glycoside bonds over the Pt/AC–SO₃H catalyst. Consequently, Pt/AC–SO₃H has bifunctional catalysis for the hydrolysis and air oxidation of various polysaccharides, such as cellulose and starch, into gluconic acid.

4.4. Comparison of Pt/AC–SO₃H Catalyst and Mixed Catalyst of AC–SO₃H with Pt/AC

The Pt/AC–SO₃H catalyst (50 mg) was compared to the mixed catalyst of AC–SO₃H (50 mg) with Pt/AC (50 mg). As shown in Fig. 11, the total amount of the hydrolysis products, such as oligosaccharides, glucose, and gluconic acid, over the mixed catalyst was significantly smaller than that over the Pt/AC–SO₃H catalyst. The mixed catalyst formed glucose in 43 C-% yield, and gluconic acid in 11 C-% yield, whereas, the Pt/AC–SO₃H catalyst gave gluconic acid in 40 C-% yield. The Pt/AC–SO₃H catalyst showed higher activity than the mixed catalyst because adsorbed starch was easily desorbed after the hydrolysis of starch into sugars on the Pt/AC–SO₃H catalyst, as well as the AC–SO₃H catalyst. In contrast, adsorbed starch remained on the surface of Pt/AC in the mixed catalyst, which led to deactivation of the active platinum sites. If the conversion of starch is carried out in a two-step reaction of hydrolysis of starch over AC–SO₃H and oxidation of glucose over Pt/AC, unreacted polysaccharides and oligosaccharides might persist in the resultant solution of the first step and lead to the deactivation of Pt/AC in the second step.

5. Conclusions

This study describes our new environmentally friendly chemical process to selectively hydrolyze cellulose into glucose using sulfonated activated-carbon catalyst under hydrothermal conditions. The catalytic hydrothermal reactions using hydrothermally stable AC–SO₃H catalyst resulted in high glucose yields of about 40 C-%, significant TON values of 15 or higher, and almost no SO₄²⁻ elution, which clearly indicates the heterogeneously catalytic hydrolysis of insoluble cellulose into glucose. In addition, the eluted SO₄²⁻ ions from catalysts lead to reduced waste and catalytic deactivation, and increased water soluble by-products. This catalytic hydrothermal process using solid acid catalysts opens new opportunities for the efficient use of cellulose resources as a chemical feedstock. The new bifunctional Pt/AC–SO₃H catalyst was prepared by the impregnation and sulfonation method. The catalyst was highly water tolerant and had catalytic properties for the hydrolysis of polysaccharides and sequential air oxidation into gluconic acid in a one-pot process under hot water conditions.

Acknowledgments

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References

要 旨
スルホン化活性炭を用いた触媒水熱法によるセルロースなどの多糖類から単糖への選択的加水分解

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高知大学理学部附属水熱化学実験所. 780-8520 高知市曙町2-5-1

比較的温和な水熱反応と固体触媒反応を組み合わせる方法によりセルロースからグルコースを得るプロセスは、セルロース系バイオマスを利用する持続型社会の実現において重要な技術の一つとして期待される。著者らは、H 型ゼオライトや硫酸塩およびスルホ塩を有するものを固体触媒に用いて、β-1,4-グリコシド結合をもつセルロースに対して 150 ℃ 付近の温度で触媒水熱反応を行ったところ、スルホン化活性炭（AC-SO₃H）触媒が高いグルコース収率を示すことを見出した。この水熱前処理したスルホン化活性炭触媒が優れた触媒特性を示したのは、水熱反応場で安定であり、強酸性のスルホ塩を持ち、単糖ではなく多糖を吸着しやすい活性炭表面を有するためである。また、そのスルホン化活性炭触媒に貴金属の白金微粒子を担持した二元機能触媒（Pt/AC-SO₃H）は、活性炭に含浸法で白金微粒子を担持し、それをスルホン化することにより調製した。Pt/AC-SO₃H 触媒を用いたワンポット反応により、水浴浴中120 ℃ 空気雰囲気において、デンプンやセロリオースからグリコン酸を得た。