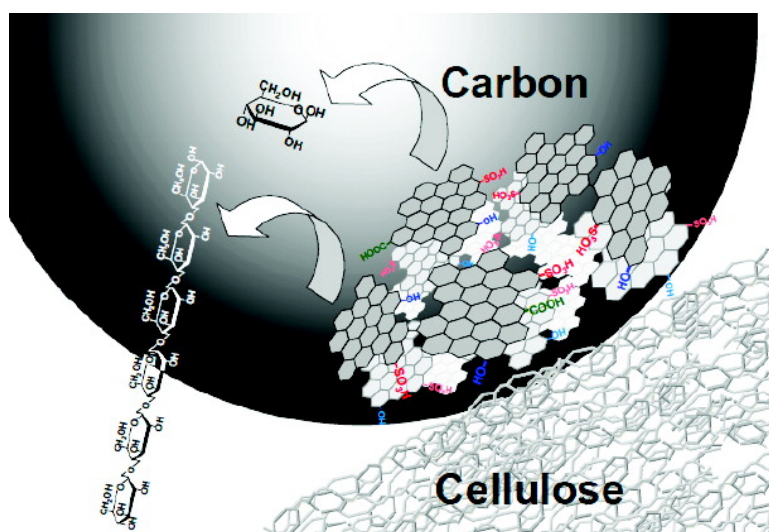


Hydrolysis of Cellulose by Amorphous Carbon Bearing SOH, COOH, and OH Groups

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Hydrolysis of Cellulose by Amorphous Carbon Bearing SO₃H, COOH, and OH Groups

Satoshi Suganuma,[†] Kiyotaka Nakajima,[†] Masaaki Kitano,[‡] Daizo Yamaguchi,[‡]
Hideki Kato,[†] Shigenobu Hayashi,[§] and Michikazu Hara^{*†‡}

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, Kanagawa Academy of Science and Technology, 3-2-1 Sakado, Takatsu-ku, Kawasaki 213-0012, Japan, and Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan

Received May 28, 2008; E-mail: mhara@msl.titech.ac.jp

Abstract: The hydrolysis of cellulose into saccharides using a range of solid catalysts is investigated for potential application in the environmentally benign saccharification of cellulose. Crystalline pure cellulose is not hydrolyzed by conventional strong solid Brønsted acid catalysts such as niobic acid, H-mordenite, Nafion and Amberlyst-15, whereas amorphous carbon bearing SO₃H, COOH, and OH function as an efficient catalyst for the reaction. The apparent activation energy for the hydrolysis of cellulose into glucose using the carbon catalyst is estimated to be 110 kJ mol⁻¹, smaller than that for sulfuric acid under optimal conditions (170 kJ mol⁻¹). The carbon catalyst can be readily separated from the saccharide solution after reaction for reuse in the reaction without loss of activity. The catalytic performance of the carbon catalyst is attributed to the ability of the material to adsorb β-1,4 glucan, which does not adsorb to other solid acids.

Introduction

A range of industrially important chemicals can be produced from sugars, including ethanol, hydrocarbons, and the starting materials for polymers.^{1,2} Among this fundamental group of biological compounds, cellulose is an abundant source of sugars in the form of saccharide polymers linked by β-1,4 glycosidic bonds. As cellulose is a key component of grasses and agricultural and wood waste, the conversion of such vegetable matter into useful sugars (saccharides) is of interest as a means of producing cellulosic ethanol fuel and a range of industrially important chemicals.¹⁻⁸ Cellulose, a water-insoluble long-chain β-1,4 glucan, is converted to saccharides by hydrolysis of the β-1,4 glycosidic bonds, and substantial effort has been devoted to the development of appropriate hydrolysis schemes, including catalysis using mineral acids,³⁻⁵ enzyme-driven reactions,⁶ the use of supercritical water,⁷ and solid catalysts for hydrogenolysis.⁸ The sulfuric acid catalyzed hydrolysis of cellulose has

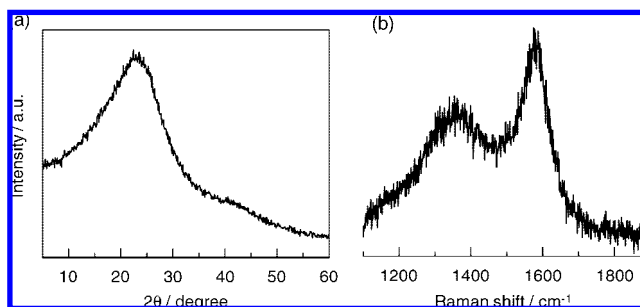


Figure 1. XRD pattern (a) and Raman spectrum (b) for the sample prepared by sulfonation of partial carbonized cellulose.

received considerable attention and has been implemented on relatively large scales.³⁻⁵ However, while sulfuric acid is inexpensive and acts as a highly active catalyst for this reaction, its use is wasteful and energy-inefficient, requiring separation, recycling, and treatment of the waste sulfuric acid.

The move toward more environmentally sustainable approaches to chemical processes has stimulated the use of recyclable solid acids as replacements for the unrecyclable liquid acid catalysts such as sulfuric acid.⁹⁻¹² Any solid Brønsted acid catalyst that is as effective as sulfuric acid in hydrolyzing cellulose is potentially applicable for the efficient conversion of cellulose, and particulate catalysts can be readily separated from the water-soluble saccharides following the reaction,

[†] Tokyo Institute of Technology.

[‡] Kanagawa Academy of Science and Technology.

[§] National Institute of Advanced Industrial Science and Technology (AIST).

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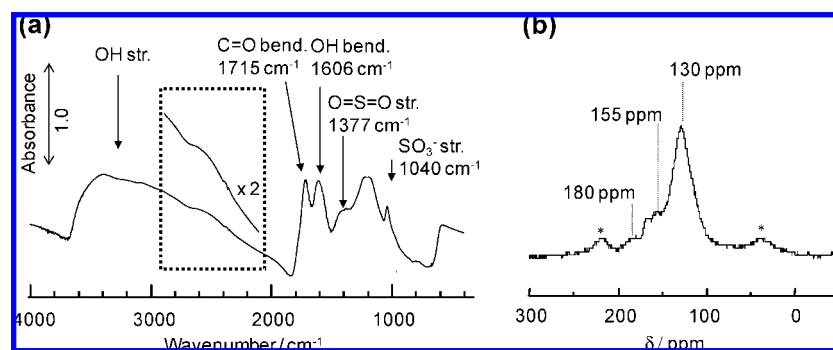


Figure 2. FTIR spectrum (a) and ^{13}C MAS NMR spectrum (b) for the carbon material prepared from cellulose.

allowing for repeated reuse of the catalyst with low energy consumption. In this study, the hydrolysis of cellulose using solid acid catalysts, including amorphous carbon with a high density of sulfonic acid groups (SO_3H), was examined for potential application in the environmentally benign saccharification of cellulose. The amorphous carbon is a solid Brønsted acid catalyst consisting of flexible polycyclic carbon sheets with SO_3H , COOH , and phenolic hydroxyl (OH) groups in a three-dimensional network that can be readily prepared by partial carbonization of natural organic compounds, such as sugar, cellulose and starch, followed by sulfonation of the resulting amorphous carbon.^{13–15} The carbon material can incorporate large amounts of hydrophilic molecules, including water, into the carbon bulk, due to the high density of the hydrophilic functional groups bound to the flexible carbon sheets. This incorporation provides good access by reactants in solution to the SO_3H groups in the carbon material, which gives rise to high catalytic performance for acid-catalyzed reactions in the presence of water such as esterification and hydration, despite the small surface area ($2\text{ m}^2\cdot\text{g}^{-1}$).¹⁴ However, the details of the carbon structure, including graphene size and functional groups other than SO_3H , and catalysis-related structure remain to be clarified.

Experimental Section

Preparation of Carbon Material Bearing SO_3H Groups. The carbon material with SO_3H groups was prepared from microcrystalline cellulose powder (Avicel, MERCK; particle size, 20–100 μm ; crystallinity, 80%; degree of polymerization, 200–300). The starting material (20 g) was heated for 5 h at 723 K under N_2 flow to produce a black solid, which was then ground to a powder. The powder (7 g) was then boiled in 150 cm^3 of fuming sulfuric acid (15 wt% SO_3) at 353 K under N_2 . After heating for 10 h and then cooling to room temperature, the suspension was filtered to yield a black precipitate, which was washed repeatedly with hot distilled water ($>353\text{ K}$, 1000 cm^3) until impurities such as sulfate ions were no longer detected in the wash water. As only a small amount of the excess fuming sulfuric acid is consumed in the reaction, the sulfuric acid recovered after filtration of the powder can be reused for repeated sulfonation of the carbon material. The densities of the functional groups in the carbon material are mainly dominated by the degree of carbonization in the carbon material before sulfonation,¹⁴ and the degree of carbonization can be controlled

with good reproducibility, resulting in the preparation of the reproducible carbon material.

Characterization. Structural information for the prepared carbon material was obtained by scanning electron microscopy (SEM, S-5200, Hitachi), powder X-ray diffraction (XRD, RINT 2100 diffractometer, RIGAKU), Raman spectroscopy (NRS-2100, JASCO), Fourier transform infrared spectroscopy (FTIR, FT/IR-6100, JASCO), ^{13}C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR), ^{31}P MAS NMR, and gas adsorption analysis. The FTIR spectrum for the carbon material was obtained by using a KBr pellet containing the prepared carbon powder. ^{13}C CP/MAS NMR spectra were measured at room temperature using a Bruker ASX-200 spectrometer at a Larmor frequency of 50.3 MHz. A Bruker MAS probehead was used with a 7 mm zirconia rotor. The spinning rate of the sample was 4.0 kHz. The frequency of the spectra is expressed with respect to neat tetramethylsilane. Experimentally, glycine was used as a second reference material, whose carbonyl signal was set at 176.48 ppm. The acid strength of the carbon material was examined by color-producing reagents and ^{31}P MAS NMR measurement, using trimethylphosphine oxide (TMPO) as a probe molecule.¹⁴ The Brunauer–Emmett–Teller (BET) surface areas and water vapor adsorption isotherms for the samples were measured by NOVA-4200e (QUANTACHROME) and AUTOSORB MP/VP (QUANTACHROME), respectively.

The amount of the functional groups bonded to the carbon material was estimated by elemental analysis (vario MICRO cube, ELEMENTAL) and cation-exchange analysis. According to X-ray photoelectron spectroscopy (XPS) analysis, all sulfur in the carbon material, which possesses SO_3H , COOH , and phenolic OH, is expected to be confined to SO_3H groups.¹⁴ The densities of SO_3H groups were thus estimated based on the sulfur content determined from sample compositions obtained by elemental analysis. The total $\text{SO}_3\text{H} + \text{COOH}$ and $\text{SO}_3\text{H} + \text{COOH} + \text{OH}$ contents were estimated from the exchange of Na^+ in aqueous NaCl and NaOH solutions, respectively, to afford the proportions of each functional group.

Hydrolysis of Cellulose. The hydrolysis of pure microcrystalline cellulose (Avicel; particle size, 20–100 μm ; crystallinity, 80%; degree of polymerization, 200–300) and eucalyptus flakes (width, 0.5–1.5 mm; thickness, 0.1–0.5 mm; length, 0.5–5.0 mm) was carried out in a Pyrex reactor (catalyst, 0.300 g; cellulose reactant, 0.025 g; distilled water, 0.700 g) at 373 K. The catalysts tested were sulfuric acid (H_2SO_4 (96%), KANTO chemical), niobic acid ($\text{Nb}_2\text{O}_5\cdot n\text{H}_2\text{O}$, CBMM), H-mordenite (reference catalyst, The Catalysis Society of Japan), Nafion NR50 (perfluorosulfonated ionomer, Aldrich), Amberlyst-15 (polystyrene-based cation-exchangeable resin with SO_3H , Aldrich), and the carbon material prepared from cellulose. In sulfuric acid reactions, 0.320 g of 96% sulfuric acid (net 0.307 g) was used as the catalyst. The Pyrex test tube reactor containing the catalyst and reactant was sealed using a Swagelok tube fitting (reactor volume, 3.5 cm^3) prior to reaction and then placed in boiling water or an oil bath. The mixture was

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stirred by a stir bar in the reactor during reaction. After the reaction, an aliquot of the supernatant solution, readily obtained by decantation, was analyzed by liquid and gel permeation chromatography (LC-2000 plus, JASCO) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MASS, AXIMA-TOF2, SHIMADU). In the sulfuric acid reactions, the reacted solution was neutralized with aqueous CaCl_2 solution, the CaSO_4 precipitate was removed by centrifugation, and the supernatant solution was analyzed.

In hydrolysis products of cellulose, the amounts of glucose and short-chain β -1,4 glucan such as cellobiose–cellotetraose can be readily estimated by liquid chromatography (LC). While water-soluble β -1,4 glucan longer than cellopentose–cellohexose can be detected by gel permeation chromatography (GPC) and MALDI-TOF-MASS, it is difficult to estimate the amount of each long-chain β -1,4 glucan solved in solution by using these methods. In this study, the yields of glucose and water-soluble β -1,4 glucan were obtained by LC and the enzymatic hydrolysis of water-soluble β -1,4 glucan using cellulase. After hydrolysis, the solid sample (catalyst and residual cellulosic reactants) was rinsed 5 times in 2 cm^3 of distilled water added directly to the reactor. During each rinse, the suspension was stirred vigorously for 30 min and then centrifuged to collect the solid and the supernatant solution. The amount of produced glucose in the collected supernatant solution was estimated by LC. 0.2 g of crude cellulase obtained from *Trichoderma viride* (Wako Pure Chemical Industries) was then added to the collected supernatant solution, and the solution was warmed in order to hydrolyze polysaccharides (water-soluble β -1,4 glucan) in the solution into monosaccharides (glucose) for 48 h at 313 K. After the enzymatic hydrolysis, glucose produced by the hydrolysis of water-soluble β -1,4 glucan was also analyzed by LC. Cellulose conversion as well as glucose and β -1,4 glucan yields were obtained by using the following equations.

$$\text{cellulose conversion (\%)} = 100(B + C)/A$$

$$\text{glucose yield (\%)} = 100B/A$$

$$\text{total } \beta\text{-1,4 glucan (\%)} = 100C/A$$

A: total amount (mol) of glucose monomer in cellulose.

B: amount (mol) of glucose produced by acid-catalyzed hydrolysis.

C: total amount (mol) of glucose monomer in water-soluble β -1,4 glucan produced by acid-catalyzed hydrolysis

Results and Discussion

Structure of the Prepared Carbon Material. The particle size and surface area of the black powder obtained by sulfonation of partial carbonized cellulose were estimated to be 10–40 μm and 2 $\text{m}^2 \text{g}^{-1}$, respectively by SEM and BET measurements. Figure 1 shows the XRD pattern and Raman spectrum for the prepared sample. The XRD pattern exhibiting two broad but weak diffraction peaks at 2θ angles of 10° – 30° and 35° – 50° is attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion.¹⁶ In the Raman spectrum, the intensity ratio of the D band (1350 cm^{-1} , A_{1g} D breathing mode) to the G band (1580 cm^{-1} , E_{2g} G mode) for the carbon material is 0.81, indicating that the average graphene size in the amorphous carbon is ca. 1 nm.¹⁷ The FTIR and ^{13}C CP/MAS NMR spectra for the carbon material are shown in Figure 2. The vibration bands at 1040 (SO_3^- stretching) and 1377 cm^{-1} ($\text{O}=\text{S}=\text{O}$ stretching in SO_3H) in the FTIR spectrum indicate that the resulting material possesses SO_3H groups. The broadband at 2300 – 2700 cm^{-1} can be assigned to an overtone (Fermi resonance) of the bending mode of

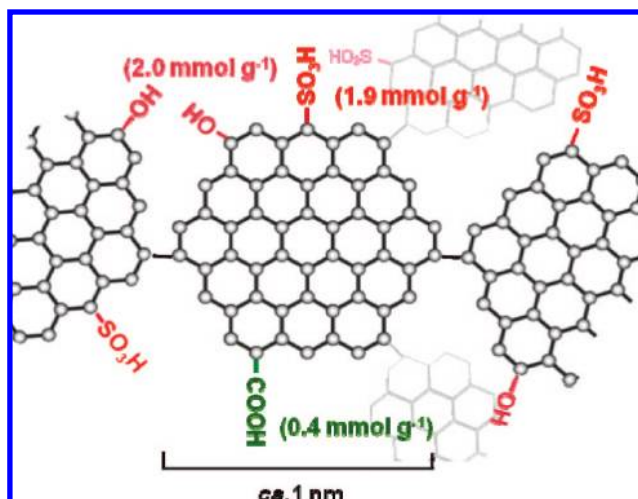


Figure 3. Proposed schematic structure of the prepared carbon material.

$-\text{OH}\cdots\text{O}=\text{}$ linked by a strong hydrogen bond, as seen in strong liquid Brønsted acids such as $\text{CF}_3\text{SO}_3\text{H}$,¹⁸ suggesting that some SO_3H groups are in close proximity. The chemical shifts at 130, 155, and 180 ppm in the NMR spectrum are attributable to polycyclic aromatic carbon atoms, phenolic OH, and COOH groups, respectively.^{16,19} The peak due to aromatic carbon with SO_3H groups ($\text{Ar}-\text{SO}_3\text{H}$, ca. 140 ppm) is not observed in the spectrum. The resonance derived from $\text{Ar}-\text{SO}_3\text{H}$ is not distinguished in the spectra of SO_3H -bearing amorphous carbon samples, because broad peaks due to aromatic carbon atoms (130 ppm) and OH groups (155 ppm) obscure the peak. Elemental analysis and cation-exchange experiment revealed that the sample composition is $\text{CH}_{0.622}\text{O}_{0.540}\text{S}_{0.048}$ and that the amounts of SO_3H , COOH, and phenolic OH groups bonded to the graphene are 1.9, 0.4, and 2.0 mmol g^{-1} , respectively.

The schematic carbon structure proposed on the basis of these results is shown in Figure 3. The prepared material is amorphous carbon consisting of SO_3H -, COOH-, and phenolic OH-bearing nanographene sheets in a considerably random fashion. If the carbon material is composed of uniform functionalized graphene sheets, each graphene sheet is expected to bind SO_3H and phenolic OH. The carbon material possesses a high density of almost neutral phenolic OH in addition to Brønsted acid sites (SO_3H and COOH). This is distinct from conventional solid acids with single functional groups.

Hydrolysis of Cellulose by Acid Catalysts. The performance of various acid catalysts was examined through the hydrolysis of pure microcrystalline cellulose powder (Avicel) at 373 K. The same amount of catalyst was used in all cases (0.3 g). The results, including acid density, maximum acidity (Hammett function; H_0), and surface area of the tested catalysts, are summarized in Table 1. The catalysts tested were sulfuric acid (H_2SO_4), niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), H-mordenite (zeolite), Nafion NR50 (perfluorosulfonated ionomer), Amberlyst-15 (polystyrene-based cation-exchangeable resin with SO_3H), and the carbon material prepared from cellulose. Niobic acid and H-mordenite are typical strong

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Table 1. Hydrolysis of Crystalline Cellulose by Various Acid Catalysts^a

catalyst	functional groups	density mmol g ⁻¹	maximum acidity H ₀	surface area m ² g ⁻¹	yields of hydrolysis products
H ₂ SO ₄		20.4	-11	—	glucose: 10% β-1,4 glucan: 38%
niobic acid	acidic OH	0.4	-5.6	90	—
H-mordenite	acidic OH	1.4	-5.6	480	—
Nafion	SO ₃ H	0.9	-11 to -13	<1	—
Amberlyst-15	SO ₃ H	4.8	-2.2	50	—
carbon material (CH _{0.62} O _{0.54} S _{0.05})	SO ₃ H	1.9	-8 to -11	2	glucose: 4%
	COOH	0.4	—		β-1,4 glucan: 64%
	phenolic OH	2.0	—		

^a Catalyst, 0.3 g; cellulose, 25 mg; water, 0.7 g; reaction time, 3 h.

inorganic solid Brønsted acids that are widely used in industrial acid-catalyzed reactions, while Nafion and Amberlyst-15 are strong polymer-based solid acids with high SO₃H density and very high activity for a range of reactions.^{9–12,20}

As shown in Table 1, neither cellulose could be hydrolyzed into glucose nor water-soluble β-1,4 glucan using conventional solid acid catalysts such as niobic acid, H-mordenite, Nafion, or Amberlyst-15, whereas the carbon material exhibited remarkable hydrolysis performance for the reaction. After reaction for 3 h, the white cellulose powder could no longer be observed in suspension, and of the 25 mg of cellulose powder (total glucose monomer; 154 μmol) added to the reaction, 68% was hydrolyzed into glucose (6 μmol, yield; 4%) and water-soluble β-1,4 glucan (total glucose monomer; 98 μmol, yield; 64%). Figure 4 shows the MALDI-TOF-MASS spectrum for the reaction solution after 3 h in the presence of the carbon material. The large signals appear at *m/z* = 162 intervals that is the mass number of glucose monomer (-(O-C₆H₁₀O₄-)_{*n*}-) in β-1,4 glucan, meaning that β-1,4 glucan as the hydrolysis products of cellulose is solved in water. The β-1,4 glucan component was estimated to be C₆H₁₁O₅-(O-C₆H₁₀O₄-)_{2–10}-O-C₆H₁₁O₅ by MALDI-TOF-MASS. Under the present reaction conditions, short β-1,4 glucans, such as cellobiose and cellotriose, 5-hydroxymethylfurfural, and levulinic acid (byproduct formed by the decomposition of glucose),²¹ were not observed in the aqueous solution after reaction. 0.3 g of H₂SO₄ (corresponding to 30 wt% H₂SO₄ solution) also has a high hydrolysis activity, and the yields of glucose and water-soluble β-1,4 glucan at 3 h reach 10 and 38%, respectively (Table 1). Dilute H₂SO₄ solution (H₂SO₄, 0.030 g; distilled water, 0.700 g (corresponding to 4.1 wt% H₂SO₄ solution); cellulose, 0.025 g; reaction temperature, 373 K), however, reduced the yields of glucose and water-soluble β-1,4 glucan to 2 and 4%, respectively. Because a dilute sulfuric acid system exhibits high catalytic performance for cellulose saccharification at temperatures above 423–453 K,²² efficient hydrolysis does not proceed in dilute sulfuric acid at 373 K. Figure 5 correlates the conversion of cellulose into water-soluble saccharides (glucose and water-soluble β-1,4 glucan) and reaction time over the carbon material with the data for H₂SO₄ under the reaction conditions indicated in Table 1. In the case

of the carbon material, all cellulose was converted into water-soluble saccharides within 6 h, and the carbon material could be readily separated from the solution containing dissolved saccharides after the reaction by simple decantation. The recovery of the carbon catalyst was 99.4–99.6%. The results for the reuse experiment of the sample are shown in Figure 6.²³ No decrease in activity was observed even after 25 reuses of the sample (total reaction time, 150 h). A total of 0.625 g of cellulose was successfully hydrolyzed in this manner. Elemental analyses of the carbon material and ion chromatography revealed that 6 μmol of SO₃H groups (*ca.* 1%) were eluted as H₂SO₄ (corresponding to 0.08 wt% sulfuric acid solution) from the carbon material at the first reaction and leaching of SO₃H groups was not detected in the subsequent reactions. The carbon material exhibited a higher hydrolysis activity for the reaction under optimal reaction conditions in a large reaction vessel. The hydrolysis of pure crystalline cellulose into glucose in the presence of the carbon material was remarkably promoted with increases in the amount of cellulose and decreases in the amount of distilled water. Figure 7 shows the hydrolysis of cellulose into water-soluble β-1,4 glucan and glucose using the carbon material at 373 K (carbon material, 1.00 g (SO₃H, 1.9 mmol g⁻¹); pure crystalline cellulose, 3.00 g; distilled water, 0.70 g). Distilled water was successively added to the reaction vessel at the rate 3 mg h⁻¹ through a microfeeder to compensate for water consumed by the hydrolysis of cellulose. The amounts of glucose and water-soluble β-1,4 glucan produced by the hydrolysis of cellulose increase in proportion to reaction time. The rate of glucose formation per weight reaches 110 μmol h⁻¹ g⁻¹ that is much larger than that of the carbon material under

- (23) The catalytic activity of the reused carbon material was evaluated by measuring the yields of glucose and β-1,4 glucan after 3 h at 373 K. The sealed Pyrex test tube reactor containing the catalyst and reactant (carbon material, 0.300 g; distilled water, 0.700 g; cellulose, 0.025 g) was placed in an oil bath at 373 K for 3 h and then cooled to room temperature. After 100 μL of the supernatant solution were withdrawn and analyzed for the estimation of the glucose and β-1,4 glucan yields (see Experimental Section), the reactor was placed in the oil bath again. After 3 h, the solid sample was rinsed 5 times in 2 cm³ of distilled water added directly to the reactor. During each rinse, the suspension was stirred vigorously for 30 min and then centrifuged to collect the solid and the supernatant solution. The solid collected in the reactor was dried overnight at 353 K and reused for the subsequent reaction. It was confirmed in each reuse reaction that all cellulose is hydrolyzed into glucose and water-soluble β-1,4 glucan by the reaction for 6 h. The collected supernatant solution was also analyzed by inductively coupled plasma atomic emission spectroscopy and ion chromatography to observe leaching of SO₃H groups.
- (24) Hydrolysis of *Eucalyptus* flakes: Chemical analyses of monosaccharides revealed that the complete hydrolysis of 25.0 mg of *Eucalyptus* flakes yielded 26.6 mg of the product, comprising glucose (66 μmol, 12.0 mg, 45.1 wt%), xylose (11 μmol, 1.6 mg, 6.0 wt%), mannose (2 μmol, 0.3 mg, 1.1 wt%), galactose (1 μmol, 0.2 mg, 0.8 wt%), lignin (8.4 mg, 31.6 wt%), and unknown water-soluble products (4.1 mg, 15.4 wt%). Cellulose, hemicellulose, and lignocellulose in *Eucalyptus* thus consist of glucose, xylose, mannose, and galactose (total saccharides; 80 μmol, 14.1 mg, 53.0 wt%). The unknown water-soluble products could be readily dissolved in ethanol and acetone, suggestive of organic compounds other than saccharides. Cellulose conversion in the hydrolysis of *Eucalyptus* flakes was obtained in a similar manner as that of the hydrolysis of pure crystalline cellulose (see above). After reaction for 3 h at 373 K, 4 μmol of glucose, 11 μmol of xylose, and water-soluble polysaccharides (total saccharide monomer: 72 μmol) were obtained from the *Eucalyptus* flakes using the carbon material, indicating that most cellulosic materials (cellulose, hemicellulose, and lignocellulose) in the flakes had been successfully hydrolyzed into monosaccharides and water-soluble polysaccharides. Under the same reaction conditions (3 h, 373 K), sulfuric acid hydrolyzed the eucalyptus flakes into 16 μmol of glucose, 8 μmol of xylose, and water-soluble polysaccharides (total saccharide monomer: 39 μmol). In both cases, the insoluble product was produced at a yield of *ca.* 30 wt% (8 mg) attributable to lignin²⁵.

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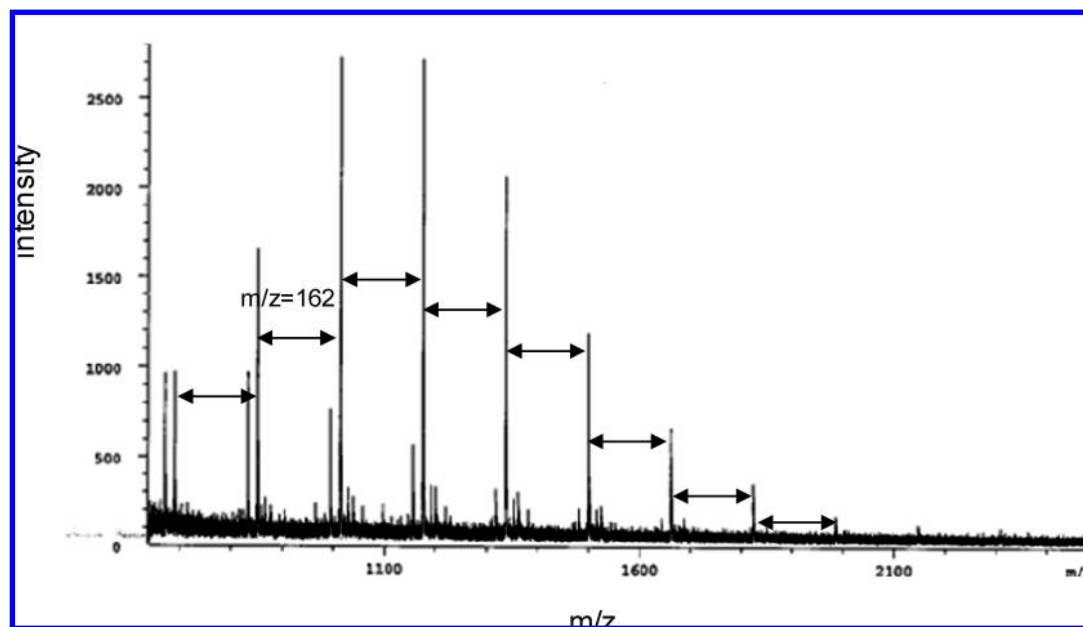


Figure 4. MALDI-TOF-MASS for the reaction solution. Carbon material, 0.300 g; cellulose, 0.025 g; water, 0.700 g; reaction temperature, 373 K; reaction time, 3 h; ion detection, positive; matrix, 2,5-dihydroxybenzoic acid–acetonitrile solution. $m/z = 162$ represents the mass number of glucose monomer ($-(\text{O}-\text{C}_6\text{H}_{10}\text{O}_4)_n-$) in β -1,4 glucan.

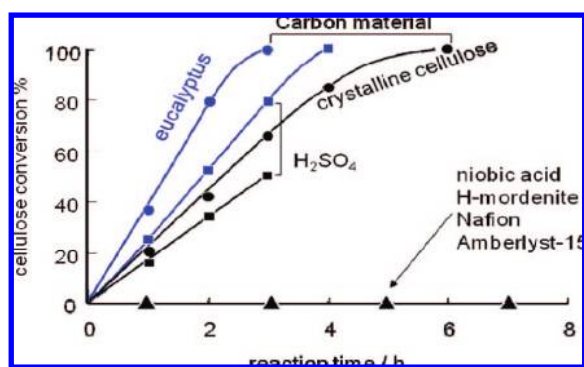


Figure 5. Time courses of cellulose conversion in hydrolysis (catalyst, 0.300 g; cellulosic reactant, 0.025 g; water, 0.700 g; reaction temperature, 373 K) of pure crystalline cellulose (black) and eucalyptus (blue) using carbon material (circles) and sulfuric acid (squares). Triangles represent the results for the hydrolysis of pure crystalline cellulose using niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), H-mordenite, Nafion, and Amberlyst-15.

the reaction conditions indicated in Table 1 (ca. $7 \mu\text{mol h}^{-1} \text{g}^{-1}$), and the turnover number of the effective acid sites (SO_3H , 1.9 mmol g^{-1}) for glucose formation is 1.6 at 27 h. In Figure 7, the glucose formation exceeds the formation of water-soluble β -1,4 glucan, in contrast to the reaction in Table 1, meaning that produced water-soluble β -1,4 glucan is efficiently hydrolyzed into glucose under the reaction conditions. This is attributable to an increase in acidity of the SO_3H groups on the carbon material with a decrease in the amount of water. The rates of glucose and water-soluble β -1,4 glucan formation in the presence of sulfuric acid were 85 and 130% those of the carbon material, respectively, under the same reaction conditions indicated in Figure 7. The apparent activation energy for the hydrolysis of cellulose into glucose in the presence of the carbon material is estimated to be 110 kJ mol^{-1} at 343–373 K (see Supporting Information Figure S1). This is smaller than that of the reaction under optimal conditions using sulfuric acid as a catalyst (170 kJ mol^{-1}).²² As expected from the Arrhenius plots in Figure S2, the formation rates of glucose and water-soluble

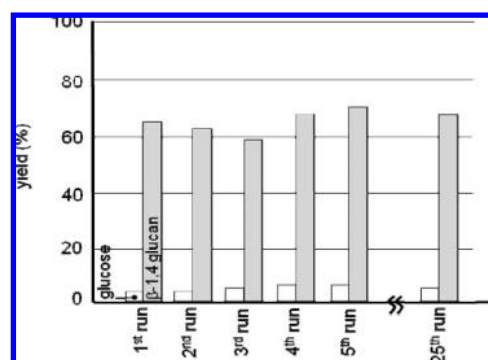


Figure 6. Catalytic activity of reused carbon material for hydrolysis of crystalline cellulose at 373 K. Catalyst, 0.300 g; water, 0.700 g; cellulose, 0.025 g. The yields were measured at 3 h after reaction. After reaction for 4–6 h, the conversion of cellulose into water-soluble saccharides reached ca. 100%; the catalyst was repeatedly rinsed with distilled water and was reused for the subsequent reaction.

β -1,4 glucan on the carbon material increased exponentially with increasing reaction temperature at 333–393 K. However, reaction temperatures above 373 K resulted in the formation of byproduct such as levoglucosan (intramolecular dehydration of glucose), maltose, cellobiose (intermolecular dehydration between glucose molecules), levulinic, and formic acids (decomposition of glucose). These results indicate that the efficient catalytic hydrolysis of cellulose appears to proceed at the interface between the carbon material and the highly crystallized cellulose in the presence of water.

The carbon material was also tested as a catalyst for the conversion of dried *Eucalyptus* flakes (country of origin; Australia) as a natural lignocellulosic substrate. The time course of conversion of cellulose and hemicellulose into water-soluble saccharides (poly- and monosaccharides) using the carbon catalyst and H_2SO_4 is shown in Figure 5.²⁴ The carbon material exhibited high catalytic performance for the decomposition of the natural substrate, and all cellulosic materials were converted into water-soluble saccharides within 3 h at 373 K. Under all

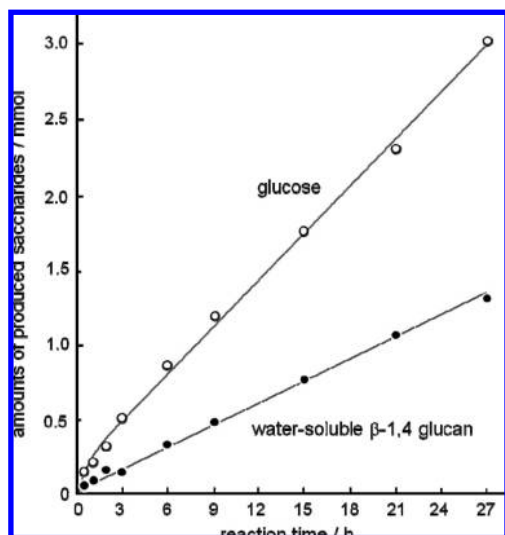


Figure 7. Time courses of the amounts of glucose (○) and water-soluble β -1,4 glucan (●) produced by the hydrolysis of pure crystalline cellulose in the presence of the carbon material at 373 K. Carbon material, 1.0 g; cellulose, 3.0 g; water, 0.7 g.

reaction conditions, the insoluble product was produced at yields of 25–33 wt% attributable to lignin.²⁵ As the sedimentation rates of thin lignin and dense carbon particles differ substantially, separation of the catalyst and lignin could be readily performed by decantation.

Catalysis and Structure of Carbon Material Bearing SO₃H, COOH, and OH. The enhanced hydrolytic catalysis of the carbon material cannot be adequately explained as being due solely to factors such as surface area or acid strength, as other acid catalysts with a similar or higher surface area and acidity do not hydrolyze cellulose (Table 1). The catalysis of amorphous carbon with SO₃H, COOH, and OH was thus further investigated by examining the adsorption of cellobiose, a short β -1,4 glucan, on each of the solid acid catalysts considered in this study. In the experiment, 0.1 g of each solid acid was added to 2 cm³ (cellobiose, 3 μ mol) of aqueous cellobiose solution (1.5 mmol dm⁻³) and then stirred at room temperature. Cellobiose was not hydrolyzed into glucose at room temperature under the experimental conditions, and the amount of adsorbed cellobiose was estimated by LC of the supernatant solution. The conventional solid acids such as H-mordenite, Nafion, and Amberlyst-15 did not adsorb cellobiose in water even after stirring for 24 h, whereas the carbon material adsorbed 24% of the cellobiose in just 3 h. The cellobiose adsorption reached a plateau at 5 h, reaching adsorption of 26% (0.8 μ mol) of the cellobiose solved in the solution. This suggests that the carbon material has a stronger affinity for β -1,4 glucan, including cellulose, than the other solid acids. It was confirmed by soaking cellulose filter papers in solid acid–water suspensions that only SO₃H-bearing carbon particles attach to the cellulose in the tested solid acids (see Figure S2, Supporting Information). The hydrolysis of cellulose into glucose using Brønsted acids involves two stages: H⁺ attack of hydrogen and β -1,4 glycosidic bonds in solid crystalline cellulose to form water-soluble β -1,4 glucan, followed by hydrolysis of the β -1,4 glycosidic bonds in the β -1,4

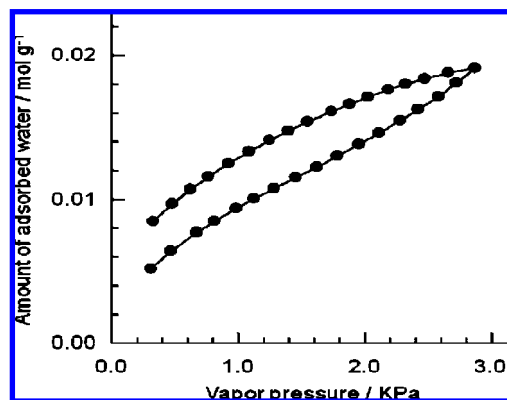


Figure 8. H₂O vapor adsorption–desorption isotherm of carbon material at 298 K.

glucan to form glucose. Efficient conversion of cellulose into glucose using a solid acid catalyst therefore requires a strong interaction between the solid acid and β -1,4 glucan (solid cellulose and water-soluble β -1,4 glucan) because the Brønsted acid sites of the solid acid cannot approach the cellulose surface without such an interaction. This is distinct from the hydrolysis in a homogeneous sulfuric acid system. The SO₃H-bearing carbon material, which is capable of adsorbing β -1,4 glucan, can thus be expected to have much higher activity for hydrolytic catalysis than the other solid acids examined in this study. It should be noted that the carbon material cannot adsorb glucose as a monomer of cellobiose at all. This suggests that the glycosidic bond in β -1,4 glucan participates in the adsorption on the carbon material. The ability to adsorb β -1,4 glucan may be attributable to phenolic OH groups bonded to the graphene sheets. In the cellobiose adsorption experiment of Amberlite IRC-50 (Ardrich), a cation-exchangeable resin with COOH, the resin did not adsorb cellobiose as well as Amberlyst-15 with SO₃H groups: these functional groups do not adsorb cellobiose. On the other hand, neutral OH groups can be linked by strong hydrogen bonds to oxygen atoms in glycosidic bonds. Cellulose is a water-insoluble β -1,4 glucan aggregate formed by the strong hydrogen bond between OH groups in glucose monomers and oxygen atoms in glycosidic bonds among β -1,4 glucan chains.

Although the carbon material has a small surface area (2 m² g⁻¹) and the effective Brønsted acid density in the carbon is only 1/10 that of sulfuric acid, the carbon is shown to be as effective as sulfuric acid in hydrolyzing cellulose. Figure 8 shows the H₂O vapor adsorption–desorption isotherm of the carbon material at 298 K. The amount of adsorbed H₂O at 1.5 kPa that is much smaller than that at saturated water vapor pressure (*ca.* 3 kPa) exceeds 0.01 mol g⁻¹. Assuming that the adsorption cross section area of H₂O is 0.125 nm², the effective surface area of the carbon material is estimated to exceed 560 m² g⁻¹ at the water vapor pressure. This means that the carbon material can incorporate large amounts of water into the carbon bulk, due to the high density of the hydrophilic functional groups bound to the flexible nanographene sheets. This incorporation provides good access by reactants in solution to the SO₃H groups in the carbon material, which gives rise to high catalytic performance, despite the small surface area.¹⁴ As a result, the effective surface area of the carbon material in the hydrolysis reaction requiring water is much larger than the BET surface area measured after dehydration. In general, large molecules with large excluded volumes such as cellobiose are not densely adsorbed on surfaces. However, if only the carbon surface is

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covered with cellobiose molecules (adsorption cross section area; *ca.* 0.9 nm^2)²⁵ without vacancy in the above cellobiose adsorption experiment, the carbon material has to have a surface area above $4 \text{ m}^2 \text{ g}^{-1}$ at least, indicating that the carbon material can incorporate even large molecules such cellobiose into the bulk in the presence of water.

One possible explanation for the high hydrolysis performance of the carbon material that has a much smaller Brønsted acid density than sulfuric acid is SO_3H groups tolerable to hydration. In the same catalyst weight, sulfuric acid always exhibits higher catalytic activity for esterification,^{14,15} an acid-catalyzed reaction in the presence of small amount of water, than the SO_3H -bearing amorphous carbon: the turnover frequency (TOF) of the effective acid sites in the carbon material is about 3 times that of sulfuric acid at most. On the other hand, the carbon material is as effective as sulfuric acid in acid-catalyzed reactions in a large quantity of water such as the hydrolysis of cyclohexyl acetate, and the TOF exceeds 10 times that of sulfuric acid.¹⁵ Sulfuric acid is subject to hydration by many H_2O molecules, resulting in a decrease in catalytic activity for the acid-catalyzed reactions in water such as hydrolysis because of a decrease in acidity by hydration. These results therefore suggest that the carbon material has SO_3H groups tolerable to hydration compared with sulfuric acid. The FTIR spectrum for the carbon material shown in Figure 2 was measured by using the carbon material exposed to the saturated water vapor at room temperature. Although the carbon sample incorporates a large quantity of water in to the carbon bulk as expected from the water adsorption–desorption isotherm in Figure 7, the broadband at $2300\text{--}2700 \text{ cm}^{-1}$ assignable to the strong hydrogen bond between SO_3H groups is nevertheless observed. This is also indicative of hydration-

tolerant SO_3H groups in the carbon material. The hydrophobic graphene sheets may prevent complete hydration of the SO_3H groups. The details of the SO_3H groups are currently under investigation.

Conclusions

Amorphous carbon bearing SO_3H , OH, and COOH groups was demonstrated to function as a highly active catalyst for the direct hydrolysis of solid cellulose, despite the small surface area and small effective acid density. The high catalytic activity for the reaction can be attributed to the ability to adsorb β -1,4 glucan, the large effective surface area in water, and SO_3H groups tolerable to hydration in the carbon material.

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Supporting Information Available: Arrhenius plots for the hydrolysis of cellulose into glucose in the presence of SO_3H -bearing carbon (Figure S1) and adsorption experiment of solid acid particles on a cellulose filter paper (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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