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High-Yielding One-Pot Synthesis of Glucose from Cellulose Using Simple Activated Carbons and Trace Hydrochloric Acid

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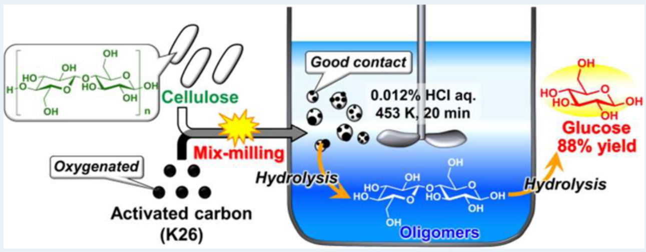
Ⓢ *Supporting Information*

ABSTRACT: High-yielding one-pot synthesis of glucose from cellulose and pentoses/hexoses from real biomass is achieved by using simple activated carbons and 0.012% HCl in water. Ball-milling cellulose and the carbon together created good physical contact between the solid substrate and solid catalyst before the reaction, selectively and drastically improving the depolymerization rate of cellulose to oligomers. Thus, our methodology overcomes a major obstacle in this type of reaction, namely, that the collision between a solid catalyst and a solid substrate is limited. Mechanistic studies have suggested that the active sites of the carbons are weakly acidic functional groups, in which vicinal carboxylic and phenolic groups synergistically work for the hydrolysis reaction.

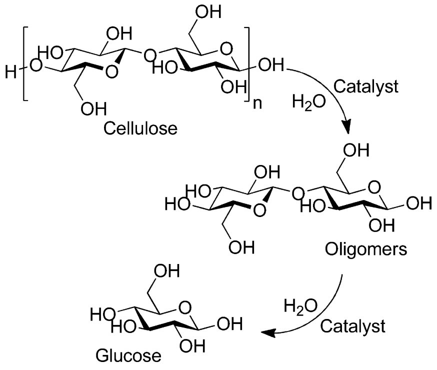


KEYWORDS: *biomass, carbon catalyst, cellulose, glucose, hydrolysis*

1. INTRODUCTION

The production of renewable chemicals and fuels from biomass has attracted worldwide interest for nurturing sustainable societies.[1−5] Cellulose, a polymer composed of glucose units, is the most abundant and nonfood biomass resource, and glucose is a versatile precursor to biodegradable plastics and fuels.[4] The selective conversion of cellulose to glucose (Scheme 1) typically requires large amounts of mineral acids, enzymes, or ionic liquid solvents because of the persistent and water-insoluble properties of cellulose and the chemical instability of glucose.[6−9] A prospective strategy to reduce the usage of soluble catalysts is the utilization of solid catalysts,[10−12] and immobilized sulfonic acids[13−16] and a silica catalyst possessing higher acidity than HZSM-5[17] have recently been developed to this end. Meanwhile, we and others demonstrated that mesoporous carbons such as CMK-3[18] catalyze the hydrolysis of cellulose.[19−21] The hydrolytic function of an oxidized carbon nanotube was also suggested in related reactions.[22] Weakly acidic and water-tolerant carbons might be potentially useful for the hydrolysis of cellulose; however, the yield of glucose needs to be improved, and the details of the catalysis have not been clarified. Hence, the purpose of this study is the high-yielding one-pot synthesis of glucose from cellulose using simple activated carbons. Mechanistic studies were also conducted to estimate the active sites on carbons.

Scheme 1. Hydrolysis of Cellulose to Glucose



2. EXPERIMENTAL SECTION

2.1. Reagents. Microcrystalline cellulose was purchased from Merck, and cellobiose was from Kanto. The carbons used in this study were a coke powder (Showa Denko), BA50 (Ajinomoto Fine-Techno), MSP20 (Kansai Netsu Kagaku), BP2000 (Black Pearls 2000, Cabot), and XC72 (Vulcan XC72, Cabot). All of the other reagents such as distilled water were the finest grade, obtained from Wako, TCI (Tokyo Chemical Industry), and Aldrich.

2.2. Preparation of K26 and K20. The coke powder was treated with KOH (3 equiv based on weight) under N_2 at 973

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Table 1. Hydrolysis of Cellulose by Carbon Catalysts[a]

					yield based on carbon (%)							
					sugar product					byproduct		
entry	catalyst	ball-milling of cellulose	T (K)	conv. (%)	glucose	fructose	mannose	oligomers	total	levoglucosan	5-HMF[b]	others[c]
1	None	single	503[h]	28	4.6	0.5	0.6	15	21	0.2	1.8	5
2	K26	single	503[h]	60	36	2.7	2.6	2.5	44	2.1	3.4	11
3	K20	single	503[h]	59	35	1.9	1.3	1.7	40	2.7	2.9	14
4	MSP20	single	503[h]	50	26	1.7	1.6	6.3	36	1.6	2.1	11
5	BA50	single	503[h]	57	17	1.0	1.0	20	39	0.9	3.5	14
6	CMK-3	single	503[h]	52	12[j]	0.9	0.8	25	39	0.7	2.5	10
7	BP2000	single	503[h]	37	6.4	0.5	0.5	12	19	0.3	1.8	16
8	XC72	single	503[h]	35	5.8	0.6	0.9	19	26	0.2	1.9	7
9	K26[d]	mix[d]	503[h]	98	57	4.3	1.4	3.7	66	3.9	12	16
10	None	single	453[i]	12	1.3	0.2	0.2	6.6	8.3	<0.1	0.2	3
11	K26[d]	mix[d]	453[i]	93	20	0.6	0.7	70	91	0.7	1.0	<1
12	K26[e]	single	453[i]	18	2.9	0.5	0.4	10	14	0.1	<0.1	4
13	K26[d], HCl[f]	mix[d]	453[i]	98	88	1.5	1.5	2.7	94	3.0	1.7	<1
14	K26[d], H_2SO_4[g]	mix[d]	453[i]	95	69	0.7	1.3	8.6	80	2.2	1.8	11
15	HCl[f]	single	453[i]	39	27	1.8	1.8	3.9	35	1.0	1.6	2
16	K26[e], HCl[f]	single	453[i]	40	30	1.3	1.3	4.3	37	1.1	0.7	1

[a] Conditions: cellulose, 324 mg; carbon, 50 mg; distilled water, 40 mL. [b] 5-Hydroxymethylfurfural. [c] (conversion) − (total yield of the shown products). [d] K26 and cellulose were ball-milled together. [e] K26 was ball-milled without cellulose. [f] 0.012 wt % HCl aq. (pH 2.5) was used instead of distilled water. [g] 0.018 wt % H_2SO_4 aq. (pH 2.5) was used instead of distilled water. [h] Rapid heating−cooling conditions (Supporting Information, Figure S1). [i] Temperature was kept for 20 min. [j] CMK-3 was synthesized several times, and the samples gave glucose in the range of 12−16% yield.[20]

K. The resulting black powder was washed with water, 1 M HCl aq., and boiling water until the washing water became neutral. Finally, the purified carbon was filtrated by a 45 μm mesh in water to remove large particles and dried at 353 K, and the resulting sample was named K26 (80% yield based on the weight of coke used). Similarly, K20 was synthesized by using KOH (2.8 equiv) with the same procedures as above. K26 was characterized by the Boehm titration,[23] diffuse reflectance infrared Fourier transform (DRIFT; Perkin-Elmer, Spectrum 100), temperature-programmed desorption (TPD; Bel, BEL-CAT-A, mass spectrometer), NH_3-TPD (Bel, BELCAT-A, mass spectrometer, $m/z = 16$), N_2 adsorption (Bel, Belsorp-mini), laser diffraction (Nikkiso, Microtrac MT3300EXII), ion chromatograph after the combustion, and energy dispersive X-ray spectroscopy (EDX; Shimadzu EDX-720). EDX analysis indicated that the concentration of residual potassium in K26 was only 120 ppm, which did not affect the catalytic activity.

2.3. Heat-Treatment of K26. K26 was charged in a quartz fixed-bed flow reactor. The temperature, monitored by a thermocouple, was elevated from 298 to 393 K in He flow (3 mL min^{-1}), and the temperature was kept at 393 K for 1 h to remove water adsorbed. Further treatment was carried out by raising the temperature to 673, 873, 1073, or 1273 K by 10 K min^{-1}, and the temperature was kept for 2 h.

2.4. Ball-Milling Treatment of Cellulose. Single ball-milling: microcrystalline cellulose (10.0 g) was milled in a ceramic pot (3.6 L) with alumina balls (1.5 cm, 2 kg) at 60 rpm for 2 days. Mix-milling: microcrystalline cellulose (10.0 g) and K26 (1.54 g) were milled together in a ceramic pot (3.6 L) with alumina balls (1.5 cm, 2 kg) at 60 rpm for 2 days. The milled cellulose was analyzed by viscometry using an Ubbelohde viscometer and 9 wt % LiCl/DMAc,[24] laser diffraction, XRD (Rigaku, MiniFlex), and ^{13}C CP/MAS NMR (Bruker, MSL-300, ^{13}C 75 MHz, MAS: 8 kHz).

2.5. Hydrolysis of Cellulose. Hydrolysis of ball-milled cellulose: the reaction was conducted in a hastelloy C22 high-pressure reactor (OM Lab-Tech, MMJ-100, 100 mL). The ball-milled 324 mg of cellulose, 50 mg of carbon, and 40 mL of distilled water (or 0.012% HCl aq.) were charged in the reactor. The temperature profiles of the reactions are shown below. Hydrolysis of mix-milled cellulose: the mix-milled sample [374 mg, containing cellulose (324 mg) and K26 (50 mg)] and 40 mL of distilled water (or 0.012% HCl) were charged in the high pressure reactor.

Two types of temperature profiles were used in the hydrolysis reactions. Rapid heating−cooling conditions: the reactor was heated to 503 K in 18 min, and then quickly cooled down to less than 323 K by blowing air for 22 min (Supporting Information, Figure S1). Reactions at T K for X min: the reactor was heated to a certain temperature (T; typically 453 K in 11 min), and the temperature was kept for X min. Then the reactor was cooled down to less than 323 K by blowing air.

The reaction mixture was separated into solid and liquid by centrifugation and decantation. The aqueous phase was analyzed by high-performance liquid chromatography (columns: Shodex Sugar SH-1011, Phenomenex Rezex RPM-Monosaccharide Pb++).[20] Yields of products were determined by the absolute calibration method with an error of ±1%. The identification of products was checked by a LC/MS (Thermo Fisher Scientific, LCQ-Fleet, APCI). Conversion of cellulose was determined based on the weight difference of the solid part before and after reaction.

2.6. Analysis of Composition of Bagasse Pulp. Bagasse pulp was obtained in Okinawa Prefecture, and the composition was analyzed by an established method (NREL, TP-510−42618).[25] The contents of cellulose, hemicellulose, and lignin were 59%, 27% (xylan 25%, arabinan 2%), and 9%, respectively, based on the dry weight.

3. RESULTS AND DISCUSSION

Several carbons were tested in the hydrolysis of ball-milled cellulose in distilled water under the rapid heating−cooling conditions (Supporting Information, Figure S1, Table 1, entries 1−8), and it was found that their catalytic activities strongly

Table 2. Control Experiments on the Hydrolysis of Cellulose[a]

			yield based on carbon (%)							
			sugar product					byproduct		
entry	reaction medium	conv. (%)	glucose	fructose	mannose	oligomers	total	levoglucosan	5-HMF[b]	others[c]
1	distilled water	28	4.6	0.5	0.6	15	21	0.2	1.8	5
17	10 μM H_2SO_4	29	4.3	0.8	0.8	17	23	0.2	1.9	4
18	50 μM acetic acid	26	3.8	0.8	0.8	17	22	0.2	2.0	1
19	filtrate of used K26[d]	22	3.1	0.5	0.6	13	17	0.1	1.4	3
20	filtrate of used K26 and cellulose[e]	39	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]

[a]Reaction conditions: ball-milled cellulose, 324 mg; solution, ca. 40 mL. Rapid heating−cooling conditions (Supporting Information, Figure S1). [b]5-Hydroxymethylfurfural. [c](conversion) − (total yield of the shown products). [d]The filtrate of K26 aqueous mixture subjected to the rapid heating−cooling conditions was used as the solvent. [e]The filtrate of the mixture of the cellulose hydrolysis by K26 (Table 1, entry 2) was used as the solvent. [f]Determination was not possible because products in the primary reaction (Table 1, entry 2) were contained, and they underwent the degradation during this reaction.

depended on their natures. The most active catalyst, alkali-activated carbon K26, afforded 60% conversion of cellulose and 36% yield of glucose (entry 2). This glucose yield was obviously higher than that in the control experiment without catalysts (4.6%, entry 1). The other products were fructose (2.7%), mannose (2.6%), water-soluble cello-oligosaccharides (2.5%), and byproducts (16%). K26 was reusable up to 4 times without loss of activity (Supporting Information, Figure S2). The production of concentrated glucose (>10 wt %) was also easily achieved (Supporting Information, Table S1), which is beneficial to avoid the energy-consuming condensation of the products. Notably, an inexpensive steam-activated carbon BA50 produced glucose in 17% yield (entry 5), which was applied to the conversion of bagasse pulp (vide infra).

We have checked if K26 functions as a solid catalyst that can hydrolyze cellulose. The pH value of an aqueous dispersion of K26 was 4.9 because of weakly acidic surface functional groups. Note that this result does not indicate the formation of soluble acids from K26 because the pH of the solution returned to 5.8 after separation of K26 using a polytetrafluoroethylene membrane. For comparison, 10 μM H_2SO_4 (pH 4.7) and 50 μM acetic acid (pH 4.6) were used in the hydrolysis of cellulose, resulting in no enhancement of conversion or yield at all (Table 2, entries 17, 18). As it is known that the hydrolysis by H_3O^+ is negligible at pH higher than 4,[26] the promotion of the hydrolysis by K26 is not ascribed to the buffering effect releasing H_3O^+ in the suspended state. Moreover, an aqueous mixture of K26 was subjected to the reaction conditions at 503 K and filtered to remove the K26. The filtrate was used for the hydrolysis of cellulose; however, the reaction was not accelerated (entry 19). In addition, soluble acidic byproducts formed from cellulose during the hydrolysis reaction degraded only 11% of the cellulose, subtracting the conversion of cellulose in the blank experiment (28%, entry 1) from that in this reaction (39%, entry 20). Therefore, soluble compounds would not be major active species in the hydrolysis of cellulose by K26.

We have also investigated whether or not cellulose is hydrolyzed as a solid substrate. The ball-milled cellulose did not contain a considerable amount of soluble oligomers (only 0.3%), verified by the extraction with boiling water, and the milled cellulose had a high enough degree of polymerization (DP = 640). The influence of the solubility of cellulose in water was also estimated. If the slightly soluble portion of cellulose (ca. 2×10^{-3} wt % at ambient temperature)[27] corresponded to the reaction performance, the hydrolysis rate should be controlled by the saturated solubility of cellulose, giving a constant concentration of dissolved cellulose. However, the rate increased almost linearly with increasing concentration of solid cellulose (Supporting Information, Table S2). Although the possibility of soluble active species or partial dissolution of the substrate is not completely eliminated, these results suggest that solid K26 hydrolyzes solid cellulose in addition to the hydrolysis by hot-compressed water[26] and small amounts of acids derived from cellulose.

Considering that the hydrolysis of cellulose by carbon catalysts also occurs at the solid−solid interface, their limited collision is a major obstacle in this type of reaction. Therefore, cellulose and K26 were ball-milled together, denoted as mix-mill hereafter, as a pretreatment to improve their contact (Supporting Information, Figure S3). The mixed state can continue in the subsequent hydrolysis reaction thanks to the insoluble properties of the catalyst and the substrate. The hydrolysis of this mix-milled sample at 503 K resulted in 98% conversion, and the products were glucose (57% yield), fructose (4.3%), mannose (1.4%), oligomers (3.7%), and byproducts (32%) (Table 1, entry 9). As the hydrolysis reaction was already completed, milder conditions (453 K, 20 min) were chosen based on the effect of temperature (Supporting Information, Figure S4) to produce sugars selectively (entries 10−16). The modified reaction afforded 91% yield of sugars [glucose (20%), fructose (0.6%), mannose (0.7%), and oligomers (70%)] with 98% selectivity (entry 11), whereas the separately milled K26 and cellulose (viz., K26 and cellulose, respectively, were singularly ball-milled) provided only 14% yield of the products (entry 12). These two results clearly indicate that the mix-milling pretreatment drastically and selectively accelerates the hydrolysis of cellulose.

An extracted solution of the mix-milled sample with boiling water was not active for the hydrolysis of singularly milled cellulose (glucose yield 1.5%, oligomers 10%), thus showing that the effect of mix-milling is not ascribed to the formation of soluble active species from K26 during its ball-milling. The DP of our mix-milled cellulose (690) and singularly milled one (640) were similar because of the mild conditions (simple ball-milling at 60 rpm). Furthermore, the extract of the mix-milled sample with boiling water contained only a small amount of soluble oligomers (2.2%). Hence, the enhancement of the reaction performance by our mix-milling is not due to the mechanocatalytic hydrolysis[28,29] during the treatment but due to the mixing. Accordingly, our pretreatment does not require such high power to dissociate the glycosidic bonds.

Physicochemical properties of the milled samples were further characterized to elucidate how the mix-milling pretreatment enhances the hydrolysis reaction. Figure 1 displays ^{13}C CP/MAS NMR spectra of the mix-milled cellulose and the singularly milled one, which are almost the identical. The broad peaks are assigned to amorphous cellulose as indicated in Figure 1,[30] and the crystallinity indexes determined from the C4 signals for both samples were less than 5%. Furthermore, these samples show almost the same XRD patterns of amorphous cellulose (Supporting Information, Figure S5) and similar distributions of particle sizes (Supporting Information, Figure S6). Thus, a possible role of the mix-milling pretreatment is making better physical contact between the cellulose and the carbon.

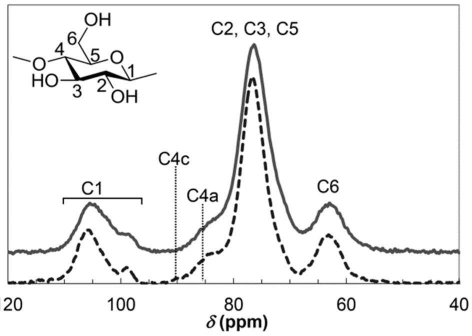

Figure 1. ^{13}C CP/MAS NMR spectra of the mix-milled K26 and cellulose (solid line) and singularly milled cellulose (dashed line). C4c shows the chemical shift of C4 in crystalline cellulose and C4a does that in the amorphous one.

The hydrolysis of mix-milled cellulose mainly produces soluble oligomers as described above (Table 1, entry 11). For further converting the formed oligomers to glucose in a one-pot reaction, we have utilized 0.012% HCl, which neither corrodes common stainless steel reactors nor has a negative economic impact because of the very low concentration and the low price.[31] The hydrolysis of mix-milled cellulose by K26 with trace HCl afforded as high as 88% yield of glucose with 90% selectivity based on the conversion of cellulose (98%) (entry 13). The yield of humins was at most 2% in this case as the recovered solid after the reaction was only 2%. Time course of this experiment indicated that oligomers were produced prior to the formation of glucose in 2 min after reaching 453 K (Supporting Information, Figure S7). Subsequently, the yield of glucose increased to 88% in 20 min and then decreased because of the degradation. H_2SO_4 was also used for the cellulose hydrolysis, but it was not as effective as HCl at the same pH (entry 14), which was due to the negative effect of SO_4^{2-} on the hydrolysis reaction (Supporting Information, Table S3). Thus, we focused on HCl, and control experiments were conducted to evaluate the contributions of HCl and K26. Hydrolysis of singularly milled cellulose by HCl provided 27% yield of glucose and 39% conversion (entry 15). The yield of oligomers was only 3.9%, showing the quick transformation of oligomers to glucose by HCl. Accordingly, HCl works for the hydrolysis of cellulose and oligomers, and the further improvement from entry 15 to 13 is accounted for the hydrolysis by K26. Besides, the hydrolysis of separately milled cellulose and K26 in the trace HCl gave a similar yield of glucose (30%) and a conversion (40%, entry 16) to those of entry 15 (yield 27%, conversion 39%), indicating that the hydrolysis by K26 without the mix-milling pretreatment was almost negligible owing to the limited collision. Clearly, the mix-milling treatment is essential.

For evaluating the durability of K26 in this system, a high concentration of the mix-milled sample (cellulose: 200 g L^{-1}, K26: 31 g L^{-1}) was used in the hydrolysis. The used K26 and unreacted cellulose were recovered, milled again with fresh cellulose, used for the hydrolysis reactions in 0.012% HCl, and the reuse experiments were repeated for 3 times (total 4 runs). The additive amount of fresh cellulose was just equivalent to that consumed in the previous run, keeping a constant amount of cellulose in each run. Conversion of cellulose was 88−91%, and glucose was obtained in 71%, 72%, 70%, and 67% yields, respectively, in the reuse experiments with the concentrations of 13 to 14 wt % (Figure 2). In addition, the degradation rate of cellulose did not decrease in another series of reuse experiments at lower cellulose conversions (Supporting Information, Figure S8A). Particle size of the mix-milled sample slightly increased in the first run because of aggregation during the recovery process, and smaller particles were not formed (Supporting Information, Figure S8B). Hence, K26 is fairly stable in the mix-milling as well as in the presence of HCl and high concentrations of products. The yields of glucose in Figure 2 were lower than that in the standard conditions (88%, Table 1 entry 13), which will be improved by the optimization for the high-concentration reactions in our future work.

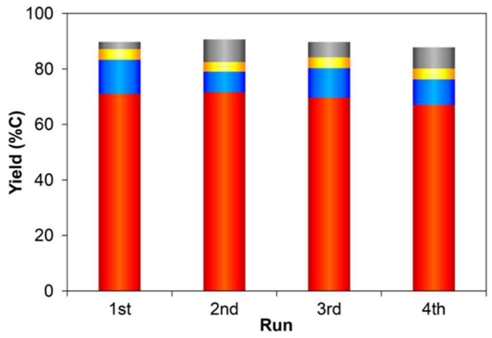

Figure 2. Reuse experiments of mix-milled K26 for the hydrolysis of cellulose (200 g L^{-1}) in 0.012% HCl. First, 473 K for 2 min, then 423 K for 60 min. Red, glucose; blue, oligomers; yellow, fructose and mannose; gray, others.

We also tried the saccharification of bagasse pulp as a real biomass substrate by an inexpensive steam-activated carbon BA50, which showed catalytic activity in cellulose conversion (Table 1, entry 5), for practical use. Taking account of the different reactivity of hemicellulose and cellulose, the mix-milled sample was subjected to the reaction at 453 K for 1 min and subsequently at 483 K for 2 min. As a result, hemicellulose was converted to xylose (84% yield) and arabinose (8.1%) and cellulose was converted to glucose (76%), fructose (2.5%), and mannose (1.5%) (Figure 3). In addition, pentoses were mainly produced in the first step, whereas hexoses were produced in the second one. This separate production of sugars will be advantageous for further use.

Next, the active sites on K26 were estimated by several physicochemical measurements. We checked that the hydrolysis activity did not result from the catalysis of sulfonic groups. The content of sulfur in K26 was less than 0.01%, corresponding to only 10^{-5}% in the whole reaction mixture. Even 10^{-4}% H_2SO_4 did not promote the hydrolysis of cellulose (Table 2, entry 17). Moreover, no strong acid peaks were observed in the NH_3-

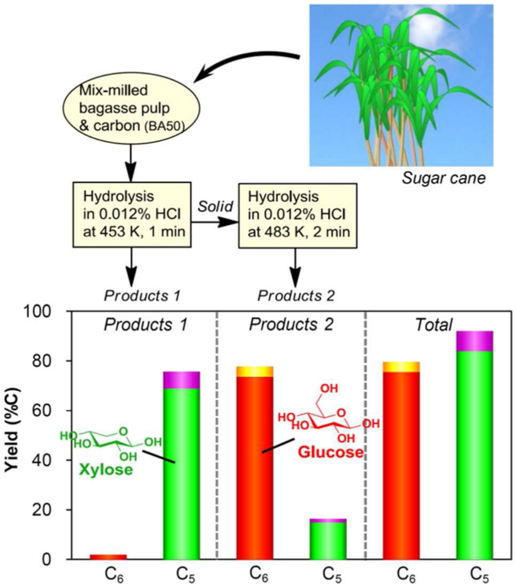

Figure 3. Hydrolysis of bagasse pulp mix-milled with BA50. Red, glucose; yellow, fructose and mannose; green, xylose; purple, arabinose.

TPD measurement (Supporting Information, Figure S9). Hence, the hydrolytic activities of K26 might be ascribed to weakly acidic groups such as carboxylic acids and phenols on the surface.

To elucidate the contributions of the functional groups for the hydrolytic activity, they were partially removed by a heat treatment[32] under He flow, denoted as HT, at 673 to 1273 K. Figure 4A depicts the hydrolytic activities of the treated K26s for the hydrolysis of singularly ball-milled cellulose against the HT temperature. For evaluating the activities, conversion and glucose yield obtained in the blank reaction without catalysts were subtracted from those of the catalytic reactions, indicated as ΔConversion and ΔGlucose (see the caption of Figure 4). Both ΔConversion and ΔGlucose gradually decreased when elevating the HT temperature, suggesting the decomposition of active sites of K26 in the HT. Then, the specific amounts of oxygenated groups of heat-treated K26s were determined by the Boehm titration[23] (Figure 4B). The amount of carboxylic acids first decreased at about 673 K, followed by the reduction of lactones. Phenolic groups were slightly more stable than lactones, which was consistent with previous results.[32] The elimination of oxygenated groups was also supported by DRIFT and TPD measurements (Supporting Information, Figures S10, S11). From these results, we concluded that the weakly acidic oxygenated groups were removed in the temperature range of the deactivation of K26. Although the lactone is not an acid, it may be in an equilibrium with the carboxylic acid and the phenol in hot-compressed water.

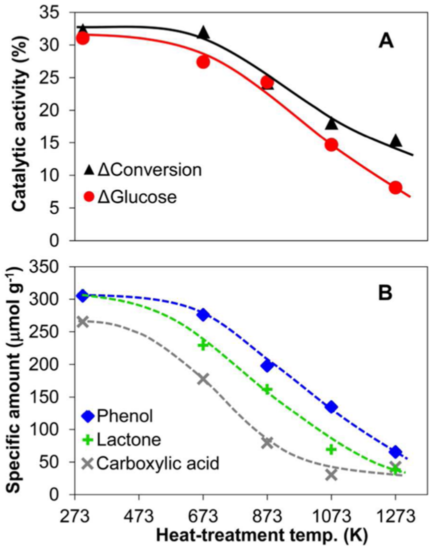

Figure 4. (A) Hydrolysis of cellulose by heat-treated K26s and (B) the specific amounts of functional groups. ΔGlucose = (yield of glucose in the catalytic reaction) − (yield of glucose in the control experiment without catalysts, 4.6%). ΔConversion = (conversion in the catalytic reaction) − (conversion in the control experiment without catalysts, 28%).

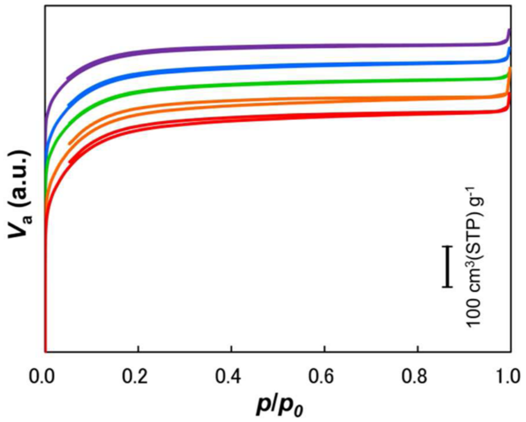

Figure 5. N_2 adsorption−desorption isotherms for heat-treated K26s at 77 K. Red, nontreated; orange, pretreated at 673 K; green, 873 K; cyan, 1073 K; purple, 1273 K. Baselines are shifted to avoid overlap of the respective isotherms.

Table 3. Morphological Properties of Heat-Treated K26s

heat treatment temp. (K)	BET specific surface area (m^2 g^{-1})	total pore volume (cm^3 g^{-1})	median particle diameter (μm)
no treatment	2270	1.00	13
673	2240	0.99	13
873	1970	0.86	13
1073	1980	0.86	12
1273	1730	0.75	12

Morphological change by the HT was also checked by N_2 adsorption and laser diffraction measurements. The heat-treated K26s provided type I isotherms, indicating similar microporous structures (Figure 5). The Brunauer−Emmett−Teller (BET) specific surface area decreased from 2270 m^2 g^{-1} to 1730 m^2 g^{-1} along with the decrease of the pore volume from 1.00 cm^3 g^{-1} to 0.75 cm^3 g^{-1} when increasing the HT temperature (Table 3). The distributions of particle diameters were maintained during the HT (Figure 6), providing almost constant median particle diameters (12−13 μm) (Table 3). It is not probable that these small morphological changes of K26 in the HT are the origin of the deactivation of K26. Instead, we propose that the catalytic activity is correlated with the specific amounts of oxygenated groups. However, the contributions of respective functional groups were not clarified in these

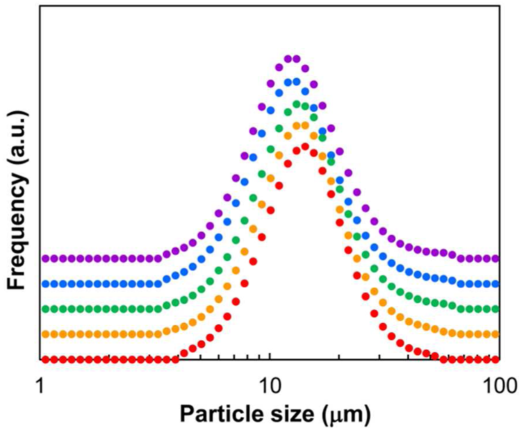

Figure 6. Distributions of particle diameters of heat-treated K26s in water. Red, nontreated; orange, pretreated at 673 K; green, 873 K; cyan, 1073 K; purple, 1273 K. Baselines are shifted to show respective distributions.

experiments because the amounts of respective oxygenated groups were similarly decreased in the HT.

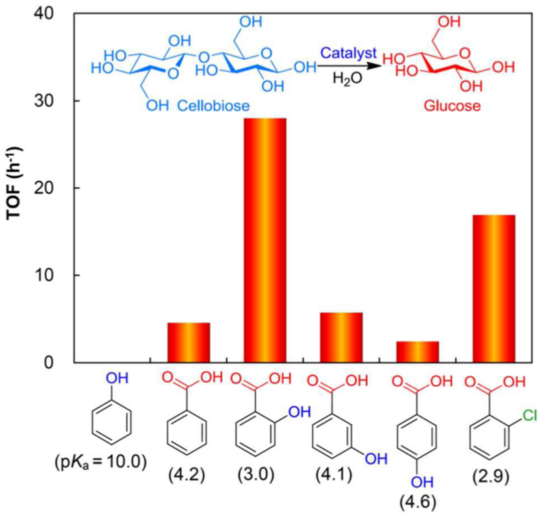

Figure 7. Hydrolysis of cellobiose by molecular catalysts at 443 K. Cellobiose 25 mM, catalyst 0.5 mM. TOF = [(mole of glucose produced in the catalytic reaction) − (mole of glucose produced without catalysts)]/[2(mole of catalyst)·(reaction time)].

The roles of carboxylic acids and phenols on K26 were studied in model reactions, in which aromatic compounds were used as molecular catalysts and cellobiose as a substrate by quantitatively evaluating the hydrolytic activities at 443 K in water (Figure 7). Phenol (pK_a = 10) and benzoic acid (pK_a = 4.2) were almost inactive (TOF = 0 h^{-1}, 4.5 h^{-1}, respectively), whereas *o*-hydroxybenzoic acid (salicylic acid, pK_a = 3.0) bearing both a carboxylic acid and a phenolic group gave a TOF as high as 28 h^{-1}. However, *m*- and *p*-hydroxybenzoic acids (pK_a = 4.1, 4.6, respectively) were nearly inactive (TOF = 5.7 h^{-1}, 2.4 h^{-1}), and *o*-chlorobenzoic acid (pK_a = 2.9, TOF = 17 h^{-1}) was also less active than salicylic acid regardless of their similar acidities. The catalytic activities can be explained by two factors: one is pK_a because the order of activity is the same as that of pK_a except for salicylic acid. The other is the structure of acids as indicated by the unexpectedly high activity of salicylic acid, which suggests the synergy of neighboring carboxylic and phenolic groups in the hydrolysis of glycosidic bonds. Capon demonstrated that the hydrolysis of a glycosidic bond is dramatically accelerated by an intramolecular adjacent carboxylic acid,[33] while opposite-side ones do not work. Katz et al. reported that even silanols (pK_a = ca. 7) can hydrolyze cellulose by optimizing the configuration of functional groups; ether bonds are formed between hydroxyl groups of cellulose chains and silanols, and then glycosidic bonds of the immobilized cellulose are activated by free silanols located near the substrate.[34,35] They also indicated that dense hydroxyl groups on alumina worked as an array of weak acidic groups for the hydrolysis of cellulose in a similar fashion to those of silanols.[36] Moreover, Hara et al. indicated that phenolic groups can adsorb glucans.[37,38] Hence, we tentatively propose that phenolic groups form ether or hydrogen bonds with hydroxyl groups of a cellulose chain, and that adjacent carboxylic acids have an opportunity to hydrolyze glycosidic bonds (Supporting Information, Figure S12). Mechanistic details will be shown in future work.

4. CONCLUSIONS

The results represented here show that simple activated carbons are effective for the hydrolysis of cellulose to water-soluble sugars, and that combining with trace HCl affords 88% yield of glucose. The good physical contact between solid substrates and solid catalysts is particularly important to achieve high performance. Mechanistic studies suggest that the active sites of the carbons are weakly acidic functional groups, in which neighboring carboxylic and phenolic groups synergistically work for the hydrolysis reaction. Notably, large-scale and quick millings are already practically available,[29] for example, in the cement and food industries, thus showing applicability of our method in the biorefinery.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional characterization data, reaction results, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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