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# Mechanochemical Synthesis of a Carboxylated Carbon Catalyst and Its Application in Cellulose Hydrolysis

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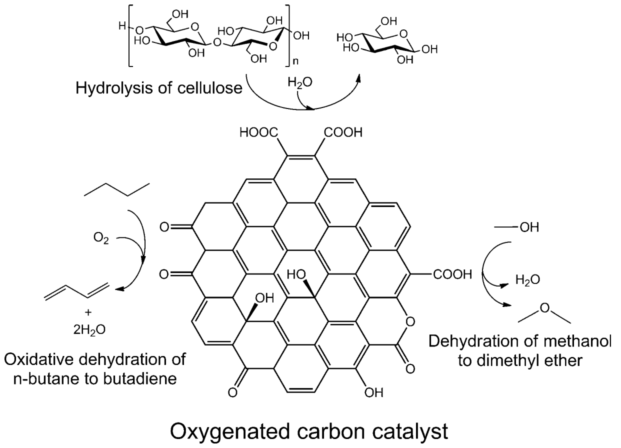
A carbon catalyst containing a high density of carboxyl groups was prepared by solvent-free mechanochemical oxidation of activated carbon by using persulfate salts as the oxidant. The mechanochemical oxidation preferentially oxidized the carbon to introduce carboxyl groups without incorporation of sulfonated groups. The material exhibited hydrophilic behavior and was easily dispersed in water. Upon mix-milling, the oxidized carbon showed good catalytic activity for the hydrolysis of cellulose, even at a low catalyst loading. Glucose was obtained in 85 % yield from mix-milled cellulose in the presence of a trace amount of HCl after a reaction time of 20 min.

Carbon is an inexpensive and widely available material that serves as a versatile catalyst and catalyst support for various chemical reactions.[1,2] Whereas carbon materials are extensively used as supports for metal catalysts, their use in the field of carbocatalysis has recently gained more attention (Scheme 1). The use of an oxygenated carbon catalyst for the dehydrogenation of hydrocarbons to the corresponding olefins is well known.[3–5] Other reactions catalyzed by oxidized carbon include the dehydration of alcohols,[6,7] the oxidation of alcohols,[8,9] esterification,[10] the electrochemical synthesis of $H_2O_2$,[11] and the reduction of $NO_x$.[12] More recently, oxygenated carbon catalysts have also emerged as useful catalysts for the hydrolysis of renewable polysaccharides such as cellulose and hemicellulose.[13–21] The active sites on the oxygenated carbon catalyst are made up of carboxyl, ketonic, and phenolic functional groups.[22] These functional groups can be introduced by oxidation of the carbon material by using chemical and thermal methods.[23] Often, only one functional group catalyzes the desired reaction. For example, the oxidative dehydrogenation of hydrocarbons is catalyzed by ketonic sites,[5] whereas the dehydration of alcohols occurs on the carboxylic acid sites.[24] Alternatively, vicinal functional groups can work together to enhance catalytic activity. This behavior is observed in the carbon catalyst used for the hydrolysis of $\beta(1\rightarrow4)$ glycosidic bonds in cellulose and hemicellulose.[14,25] In this case, vicinal carboxyl–carboxyl and carboxyl–phenolic groups work synergistically through formation of a hydrogen bond with the glucan chain followed by attack on the glycoside bond. Therefore, it is essential to develop new oxidation methods that can selectively introduce oxygenated functional group in high density to control catalytic activity. Selective introduction of carboxyl groups is most attractive, as the acidic carbon catalyst can act as a substitute for other acid catalysts.



**Scheme 1.** Examples of organic transformations catalyzed by different functional groups on an oxygenated carbon catalyst.[5,21,24]

Conventional oxidation methods that rely on brute force oxidation with the use of concentrated acids or high temperatures are not selective, and the final catalyst contains all three functional groups in different proportions. Moreover, the use of strong mineral acids to introduce large amounts of oxygenated functional groups also introduces unwanted functional groups. For example, the synthesis of graphite oxide by Hummer's method requires oxidation with $KMnO_4$ in the presence of concentrated $H_2SO_4$.[26] Evidently, the use of sulfuric acid introduces sulfonic groups, which can act as unstable catalytic sites.[27] Persulfate salts such as ammonium persulfate are reported to favor the formation of carboxylic groups.[28] However, the oxidation intensity of persulfate salt solutions is lower than that of other systems. Moreover, a sulfuric acid solution is essential for oxidation reaction in which persulfates are used, and this can cause sulfonation to a small degree.

In this paper, we report a mechanochemical approach for the oxidation of carbon to prepare a carbon catalyst consisting of a high density of carboxyl groups and its application as a catalyst for the hydrolysis of cellulose. The catalyst was prepared by mechanochemical oxidation of activated carbon by using persulfate salts as the oxidant in a planetary ball mill without using any solvent. In a typical catalyst preparation experiment, steam activated carbon was milled with the solid ox-

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idizing agent in a planetary ball mill for 5 h. The resulting mixture was washed with 5% HCl to protonate the carboxylate ions and was then washed with copious amounts of water to remove HCl and the remaining salts of the oxidizing agent. Two oxidizing agents were used for this study, Oxone (potassium peroxymonosulfate $KHSO_5$; KPS) and ammonium persulfate $(NH_4)_2S_2O_8$ (APS).

The elemental compositions of the catalysts used in this study are shown in Table 1. The oxygen content of the parent steam activated carbon (AC) was 4.6%. After mechanochemical oxidation, the oxygen content of the activated carbon milled with $KHSO_4$ (AC-M-KPS) increased to 24.4%. Similarly, the oxygen content of the activated carbon milled in the presence of $(NH_4)_2S_2O_8$ (AC-M-APS) increased to 26.6%. The sulfur content in AC-M-KPS was reduced from 0.1% to beyond the detection limit, and the sulfur content increased marginally in AC-M-APS (0.3%), as did the nitrogen content (0.0 to 0.6%). This suggests that there was little or no sulfonation of the carbon during oxidative milling. The presence of nitrogen in AC-M-APS indicates that sulfur may be present as unwashed impurities in the form of $(NH_4)_2S_2O_8$ or its corresponding reduced salt. In contrast, ball milling of activated carbon in the absence of an oxidizing agent (AC-M) caused a slight increase in the oxygen content (4.6 to 7.8%). The $O_2$ in air can act as a potential oxidant during ball milling, as carbon can react with $O_2$ under ball-milling conditions.[29] Milling of carbon under all conditions increased the ash content of the catalyst. This was a result of the corrosion of the milling media owing to mechanical abrasion. X-ray diffraction of the catalyst confirmed the presence of α-alumina in all of the milled samples (Figure S1, Supporting Information). The ash content in AC-M was very high (18.5%), as carbon alone could not dampen the mechanical force causing severe abrasion.

The carbon catalysts were analyzed by X-ray photoelectron spectroscopy (XPS), and the C 1s region between binding energies of 291 and 281 eV is shown in Figure 1. Deconvolution of the spectra revealed five peaks. The most prominent peak centered at a binding energy of 284.6 eV was assigned to the polyaromatic carbon present in the C=C bonds (Table 2). The weak and overlapping peak at a binding energy of 283.7 eV was assigned to the C−H bonds. The peak at a binding energy of 286 eV was assigned to the C−O bonds of alcohols and epoxy bridges, and that at a binding energy of 287 eV was assigned to the C=O bond in the carbonyl group. The increase in the relative areas for these two peaks was low (−1% for AC-M-KPS and 4% for AC-M-APS), which suggests that mechanochemical oxidation disfavors the formation of these functional groups. The peak centered at a binding energy of 288.9 eV was assigned to carbon in the form of O−C=O as carboxylic acid, lactone, or acid anhydride. Calculation of the atomic ratio based on the peak area revealed that 12 and 13% of the carbon atoms were present in the O−C=O environment in AC-M-KPS and AC-M-APS, respectively. Combining the elemental analysis data with the XPS data, we calculated the surface density of carboxyl groups in the AC-M-KPS sample to be

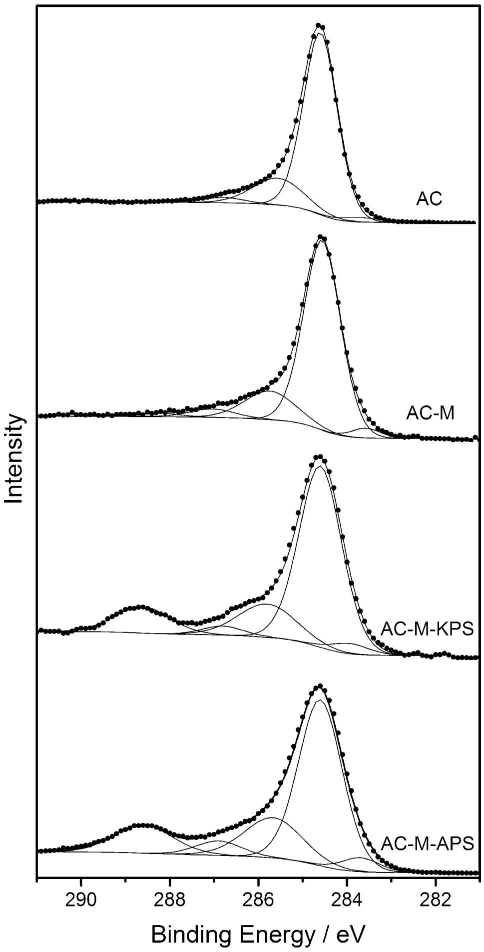

**Figure 1.** XPS analysis of the carbon catalysts.

**Table 1.** Elemental composition and surface properties of the carbon catalysts before and after mechanochemical treatment.

| Catalyst | C [%] | H [%] | N [%] | S [%] | Ash [%] | O[a] [%] | pH in NaCl solution[b] | Surface area[c] [$m^2 g^{-1}$] |
|---|---|---|---|---|---|---|---|---|
| AC | 92.1 | 0.8 | nd[d] | 0.1 | 2.4[e] | 4.6 | 6.5 | 963 |
| AC-M | 72.4 | 1.2 | nd[d] | 0.1 | 18.5 | 7.8 | 5.8 | 710 |
| AC-M-KPS | 69.1 | 1.6 | nd[d] | nd[d] | 4.9 | 24.4 | 3.1 | 406 |
| AC-M-APS | 68.9 | 1.7 | 0.6 | 0.3 | 4.1 | 26.6 | 3.3 | 453 |
| AC-A-KPS[f] | 86.3 | 0.8 | nd[d] | na[g] | 2.5 | 10.4 | 4.9 | 749 |

[a] Oxygen content was calculated by subtracting the wt% of C, H, N, S, and ash from 100 wt%. [b] pH of a suspension containing the catalyst (50 mg) in 0.1 M NaCl solution (40 mL). [c] Surface area measured by BET approximation of the $N_2$ adsorption isotherms. [d] Not detected. [e] Mainly consisted of quartz. [f] Catalyst was prepared by aqueous-phase oxidation of AC by using KPS. [g] Not analyzed.

**Table 2.** Composition of carbon atoms present in different environments based on the area of peaks in Figure 1.[a]

| Catalyst | C=C [%] | C–O [%] | C=O [%] | O–C=O [%] |
|---|---|---|---|---|
| AC | 78 | 17 | 3 | 0 |
| AC-M | 76 (−2)[b] | 16 (−1)[b] | 4 (+1)[b] | 2 (+2)[b] |
| AC-M-KPS | 65 (−13)[b] | 16 (−1)[b] | 3 (0)[b] | 12 (+12)[b] |
| AC-M-APS | 59 (−19)[b] | 19 (+2)[b] | 5 (+2)[b] | 13 (+13)[b] |

[a] Composition calculated by taking the percentage of area of the fitted peaks with respect to the total area under the curve. [b] Change in composition relative to that of the AC.

6.8 mmol g$^{-1}$. Notably, this amount is higher than that in oxidized carbons prepared by conventional oxidation methods.[30,31] The high density of carboxyl groups is a result of edge functionalization in favor of the other functional groups. This is in contrast with harsh chemical oxidation methods such as Hummer's method for the synthesis of graphene oxide, in which the formation of hydroxyl groups and epoxy bridges is favored.[26] Consequently, the mechanochemical oxidation successfully produced a carbon material bearing a high density of carboxylic groups.

We measured the pH of the dispersed catalyst in 0.1 M NaCl to evaluate the acidity of the oxidized catalyst (Table 1). AC and AC-M showed high pH values of 6.5 and 5.8, respectively, which is indicative of a low concentration of acidic groups on the surface. The oxidized AC-M-APS and AC-M-KPS catalysts showed pH values of 3.3 and 3.1, respectively. This pH is in accordance with the expected value for the presence of dense carboxylic groups on the surface of the catalyst (phthalic acid, p$K_a$ = 3.0). The FTIR spectra of the carbon catalysts are shown in Figure 2. Prominent bands in the $\tilde{\nu}$ = 1780–1680 cm$^{-1}$ region appear in the mechanochemically oxidized carbons, and these bands are indicative of $\nu$(C=O) in the O–C=O bond. Typically, vibrations of C=O stretching resulting from carboxylic acid, lactone, and anhydride groups fall in the range of $\tilde{\nu}$ = 1740 to 1700 cm$^{-1}$.[32–34] All four spectra show complex overlapping bands at $\tilde{\nu}$ = 1650–1550 cm$^{-1}$. These bands were assigned to $\nu$(C=C) in the aromatic rings and $\delta$(O–H) of adsorbed water.[32] The broad band at $\tilde{\nu}$ = 1420–1380 cm$^{-1}$ could be assigned either to in-plane $\delta$(C–H) in different C=C–H structures or to the carboxylate structure.[35] The broad band at $\tilde{\nu}$ = 1300–1000 cm$^{-1}$ was a result of multiple overlapping bands resulting from $\nu$(C–O) bonds in different environments.[32,33]

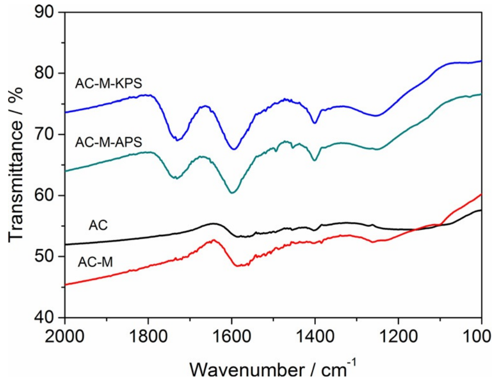

**Figure 2.** FTIR spectra of the carbon catalysts.

The textural properties of the carbon materials were also of interest, as they are heterogeneous catalysts. By analyzing the nitrogen adsorption isotherms of the catalysts (Figure S2), the Brunauer–Emmett–Teller (BET) surface areas of all the materials were determined, as shown in Table 1. Carbon milled in the absence of an oxidizing agent showed a surface area of 710 m$^2$ g$^{-1}$, which is slightly smaller than that of the parent material (963 m$^2$ g$^{-1}$). Mechanochemical oxidation reduced the area to 453 and 406 m$^2$ g$^{-1}$ for AC-M-APS and AC-M-KPS, respectively. The BET surface area is decreased by only one half and may have a limited influence during the catalytic reactions, especially in the aqueous phase, which is used for the hydrolysis of cellulose. The oxidized carbon catalyst is expected to be hydrophilic, and therefore, the available contact area in water may be larger than the BET surface area owing to swelling effects. We analyzed the adsorption of water on the surface of the untreated and oxidized carbon catalysts at 298 K (Figure S3). At a low relative pressure ($p/p_0$ = 0.1) and despite having a lower BET surface area, the mechanochemically oxidized samples adsorbed an amount of water that was four times (for AC-M-KPS) and three times (for AC-M-APS) higher than that adsorbed by the non-oxidized catalyst. Furthermore, the catalysts were easily dispersed in water and the AC-M-APS and AC-M-KPS catalyst particles did not settle even after 1 h (Figure S4). Thus, we can expect that the oxidized catalysts are suitable for aqueous-phase reactions owing to the presence of a large amount of carboxyl groups and good dispersion in water.

The prepared catalysts were used in the hydrolysis of cellulose in an aqueous-phase reaction. Contrary to traditional belief that only strong acid catalysts can hydrolyze glycosidic bonds,[27,36–42] oxygenated carbon catalysts utilize weakly acidic functional groups as active sites.[14,15,25] Unlike sulfonic acid species on carbon catalysts, the oxygenated species are much more durable under the hydrothermal reaction conditions required for the hydrolysis of polysaccharides.[16,17]

Pretreatment of cellulose is required to reduce its crystallinity. Steric hindrance owing to the crystalline state[43] and the strong intermolecular hydrogen bonds of cellulose[44] inhibit the hydrolysis reaction. In addition, hydrolysis of cellulose in the aqueous phase by using a solid acid catalyst takes place at the solid–solid interface. The reaction is slow owing to the limited contact area between the catalyst and the solid cellulose. Previously, our group reported that amorphization of cellulose and facilitation of a good solid–solid contact can be simultaneously achieved by milling the catalyst and cellulose together in a process called mix-milling.[14,21,45] Mix-milling produces a solid–solid mixture of cellulose and the catalyst; this results in a 13-fold increase in the hydrolysis rate relative to the rate of the reaction in which the components are individually milled, as this only amorphizes the cellulose. Consequently, a high yield of soluble oligomers can be obtained even at low temperature.[45] In aqueous solution, soluble glucans easily adsorb back onto the aromatic carbon surface through CH–π bonds and further hydrolysis occurs.[46,47] Thus, we performed mix-milling of the mechanochemically oxygenated carbon and cellulose prior to the hydrolysis reaction. As such, mix-milling was not expected to alter the acidic properties of the catalyst. This was confirmed by analyzing the pH of a solution prepared by dispersing mix-milled cellulose containing 50 mg of AC-M-KPS in 40 mL of 0.1 M NaCl. This dispersion showed a pH of 3.2, which was the same as that of the suspension made from 50 mg of the AC-M-KPS catalyst.

Table 3 shows the results of the hydrolysis of cellulose in distilled water. AC-M-KPS was the most active catalyst, and it gave a conversion of 98% and a glucose yield of 69% after a reaction time of 16 h at 145 °C and a cellulose to catalyst (S/C) weight ratio of 6.5 (Table 3, entry 4). AC-M-APS also showed good activity with a glucose yield of 67% under the same reaction conditions (Table 3, entry 6). In contrast, a conversion of 76% and a glucose yield of 40% were obtained in the presence of AC-M (Table 3, entry 3). The parent AC gave an even lower conversion (56%) and a low yield of glucose (27%; Table 3, entry 2). Assuming a pseudo-first-order reaction,[45] the rate constant of hydrolysis for AC-M-KPS is five times larger than that for AC. These results show that the presence of carboxyl groups imparted by mechanochemical oxidation promotes the cellulose hydrolysis reaction. We also used AC oxidized under aqueous conditions by using the same amount of $KHSO_5$ to evaluate the effectiveness of the mechanochemical oxidation. The aqueous-phase oxidation was not effective in introducing a large amount of oxygenated functional groups, as evident from the low oxygen content (10.4%) and the high pH value (4.9) of the AC-A-KPS catalyst. Evidently, this catalyst did not yield a high amount of glucose after mix-milling (33%; Table 3, entry 5). Therefore, it can be inferred that mechanochemical oxidation is essential to produce an active carbon catalyst bearing large amounts of carboxylic acid groups.

To evaluate the activity of the oxygenated carbon catalyst further, the S/C ratio of the hydrolysis condition was increased from 6.5 to 13. The yield of glucose was 61% in the reaction with AC-M-KPS (Table 3, entry 7). The glucose yield decreased to 48% in the presence of AC-M-APS under the same reaction conditions (Table 3, entry 8). The higher activity of AC-M-KPS can be attributed to the presence of a larger number of acidic functional groups on the catalyst surface, as demonstrated by the lower pH value of the catalyst dispersed in 0.1 M NaCl solution (Table 1) and its better hydrophilicity, which exposes the active sites as shown by the adsorption of water at low $p/p_0$ (Figure S3).

The reaction time was reduced substantially by increasing the temperature. After only 20 min at 180 °C in the presence of AC-M-KPS, cellulose was completely converted into soluble oligomers (Table 3, entry 9). Further hydrolysis of the oligomers under these conditions required a longer time, which reduced the selectivity because of the degradation of glucose. Soluble oligomers can be rapidly converted into glucose in the presence of a small amount of mineral acid (0.012% HCl).[14] Under these conditions, the oligomers underwent quick hydrolysis to afford glucose in a high yield of 85% (Table 3, entry 10). This is one of the highest glucose yields reported from cellulose by using a carbon catalyst.

We also tested the durability of the catalyst under hydrothermal reaction conditions (180 °C, 20 min, water). Cellobiose was chosen as a substrate to test the recyclability of the catalyst to avoid the need to produce a large amount of recycled catalyst to repeat the mix-milling. After hydrolysis of cellobiose, the yield of glucose was 33, 31, and 30% over three repeated runs (Figure S5). Hence, we conclude that the activity of the catalyst did not decrease for at least three runs under the reaction conditions used for cellulose conversion.

In conclusion, we found that mechanochemical oxidation of activated carbon with persulfate salts resulted in a highly oxygenated carbon catalyst without introducing sulfonic acid groups. Analysis of the prepared catalyst by X-ray photoelectron spectroscopy showed that the newly generated oxygenated functional groups were mainly present in the form of carboxyl groups. These catalysts were active for the hydrolysis of cellulose to produce glucose. The carbon oxidized with $KHSO_5$ showed the highest activity for the hydrolysis of cellulose at

**Table 3.** Conversions and yields of products after the hydrolysis of cellulose by using the carbon catalysts.[a]

| Entry | Catalyst | S/C[b] | $T$ [°C] | $t$ [h] | Conv. [%] | Glucose [%] | Other sugars [%] | Oligomers [%] | Levoglucosan [%] | 5-HMF [%] | Furfural [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | none[c] | – | 145 | 16 | 16 | 5.0 | 1.7 | 4.9 | 0.2 | 1.2 | 0.4 |
| 2 | AC | 6.5 | 145 | 16 | 56 | 27 | 2.9 | 19 | 0.6 | 1.6 | 0.5 |
| 3 | AC-M | 6.5 | 145 | 16 | 76 | 40 | 8.2 | 15 | 1.2 | 8.3 | 1.4 |
| 4 | AC-M-KPS | 6.5 | 145 | 16 | 98 | 69 | 4.4 | 5.8 | 1.7 | 7.5 | 1.3 |
| 5 | AC-A-KPS | 6.5 | 145 | 16 | 65 | 33 | 2.7 | 13 | 0.8 | 3.8 | 0.1 |
| 6 | AC-M-APS | 6.5 | 145 | 16 | 86 | 67 | 4.1 | 1.8 | 1.4 | 7.4 | 1.2 |
| 7 | AC-M-KPS | 13.0 | 145 | 16 | 84 | 61 | 3.4 | 10 | 1.5 | 5.8 | 1.2 |
| 8 | AC-M-APS | 13.0 | 145 | 16 | 78 | 48 | 4.0 | 8.9 | 1.3 | 7.3 | 1.1 |
| 9 | AC-M-KPS[d] | 6.5 | 180 | 0.33 | 94 | 20 | 1.6 | 68 | 0.9 | 0.3 | 0.1 |
| 10 | AC-M-KPS[d,e] | 6.5 | 180 | 0.33 | 97 | 85 | 2.6 | 1.2 | 2.8 | 2.3 | 0.3 |

[a] Cellulose and catalyst were ball milled together before the reaction. The substrate containing cellulose (81 mg) and the remaining catalyst were dispersed in water (10 mL) in a glass reactor, and reaction was performed in an oil bath. 5-HMF = 5-(hydroxymethyl)furfural. [b] Cellulose to catalyst weight ratio. [c] Cellulose was milled in the absence of the catalyst. [d] The milled substrate containing cellulose (324 mg) and the catalyst (50 mg) were charged in a high-pressure reactor along with water (40 mL). The reactor was heated to 180 °C, and this temperature was maintained for 20 min before cooling. [e] Dilute HCl (0.012 wt%) was used instead of water.

high cellulose to catalyst weight ratios of all the catalysts studied. A glucose yield of 85% was achieved in only 20 min at 180 °C in the presence of a trace amount of HCl (0.012%).

## Experimental Section

### Catalyst preparation

Steam activated carbon (AC) for the synthesis of the catalysts was supplied by Ajinomoto Fine-Techno, commercially called BA. For mechanochemical oxidation, AC (0.5 g) was milled in the presence of $(NH_4)_2SO_8$ (4.6 g, Wako Pure Chemical Industry, Ltd.) or Oxone (4.2 g, $KHSO_4$ as triple salt, Tokyo Chemical Industry Co., Ltd.). The mixture was ball milled in a 250 mL alumina pot with alumina balls (1.5 cm, 100 g) at 500 rpm for 5 h by using a Fritsch P-6 planetary ball mill. After milling, the mixture was recovered and washed with 5 wt% HCl (2×) and water until the pH of the washed solution was more than 5. Subsequently, the catalyst was dried at 110 °C for 16 h. Aqueous-phase oxidation was done by dispersing the AC (0.5 g) and $KHSO_4$ (4.2 g) in water (50 mL) and stirring for 5 h. After that, the solid was washed with 5% HCl and water several times before drying at 110 °C for 16 h.

### Catalyst characterization

The elemental composition of the catalyst was determined by using a CE440 CHN analyzer from Exeter Analytical. The ash content was calculated by measuring the weight of residue left after calcining the carbon catalyst in air at 575 °C for 10 h. The BET surface area was calculated by measuring the $N_2$ adsorption isotherm at −196 °C by using a Belsorp mini. XPS was performed by using a JEOL JPC-9010 MC instrument. Prior to analysis, a thin layer of the sample was spread on a copper tape, which was degassed in the analysis chamber overnight. Monochromatic beam of $AlK_\alpha$ X-ray was used to analyze the sample. The FTIR spectra were measured by making a KBr pellet of the carbon with a dilution of 1:5000. The pellet was analyzed by using a PerkinElmer Spectrum 100 Spectrometer.

### Cellulose hydrolysis

For mix-milling, microcrystalline cellulose (4.0 g, Merck, column chromatography grade) was first milled with the catalyst (0.616 g) in a 250 mL alumina pot by using alumina balls (0.5 cm, 200 g) for 2 h at 500 rpm in a Fritsch P-6 planetary ball mill. Hydrolysis of the milled cellulose at 145 °C was performed in a 20 mL high-pressure glass reactor supplied by ACE glass. The mix-milled cellulose/catalyst (94 mg) was charged in the reactor with water (10 mL). The reactor was sealed and placed in an oil bath maintained at 145 °C for 16 h. Hydrolysis at 180 °C was performed by using a hastelloy C22 high-pressure reactor (OM Lab-Tech MMJ-100). For this reaction, the mix-milled cellulose (374 mg) was added to the reactor with water (40 mL) or 0.012% HCl (pH 2.5, 40 mL). The reactor was sealed and heated to 180 °C, and this temperature was maintained for 20 min before the reactor was rapidly cooled to room temperature. After hydrolysis, the solids left in the mixture were separated by centrifugation. Liquid products were analyzed by a high-performance liquid chromatography system equipped with Shodex Sugar SH-1011 column and a Phenomenex Rezex RPM-Monosaccharide Pb++ column. The products were detected by using a refractive index detector. Typical error in the hydrolysis experiments was within ±2%.

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**Keywords:** carbon catalysts · carboxylic acids · hydrolysis · mechanochemistry · oxidation

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