Mechanochemical synthesis of carboxylated carbon catalyst and its application for cellulose hydrolysis

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Abstract: Carbon catalyst containing high density of carboxyl groups was prepared by solvent free mechanochemical oxidation of activated carbon using persulfate salts as oxidant. 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 cellulose hydrolysis even at low catalyst loading. Glucose yield of 85% was obtained from mix-milled cellulose in the presence of trace amount of HCl after 20 min of reaction.

Carbon is an inexpensive and widely available material that serves as a versatile catalyst and catalyst support for various chemical reactions.[1,2] While carbon materials are extensively used as a support for metal catalyst, their use in the field of carbocatalysis is recently gaining more attention (Scheme 1). Use of oxygenated carbon catalyst for dehydrogenation of hydrocarbons to corresponding olefins is well known.[3–5] Other reactions catalyzed by oxidized carbon include the dehydration of alcohols,[6,7] oxidation of alcohols,[8,9] esterification,[10] electrochemical synthesis of H_2O_2,[11] and reduction of NO_x.[12] More recently, oxygenated carbon catalyst have also emerged as a useful catalyst for the hydrolysis of renewable polysaccharides such as cellulose and hemicellulose.[13–21] 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 the oxidation of carbon material using chemical and thermal methods.[23] Often, only one functional group catalyzes the desired reaction. For example, oxidative dehydrogenation of hydrocarbons is catalyzed by ketonic sites,[5] whereas dehydration of alcohols occurs on the carboxylic acid sites.[24] Alternatively, vicinal functional groups can work together to enhance the catalytic activity. This behavior is observed in the carbon catalyst used for hydrolysis of β (1→4) glycosidic bonds in cellulose and hemicellulose.[14,25] Here, vicinal carboxyl-carboxyl and carboxyl-phenolic groups work synergistically by making hydrogen bond with glucan chain followed by attack on the glycoside bond. Therefore, it is essential to develop new oxidation methods, which can selectively introduce oxygenated functional group in high density to control the catalytic activity. Selective introduction of carboxyl groups is most attractive as the acidic carbon catalyst can act as a substitute for other acid catalysts.

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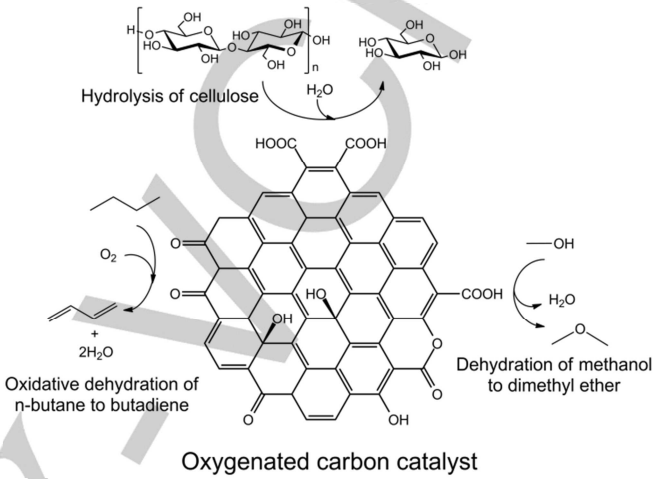

Scheme 1 Examples of organic transformations catalyzed by different functional groups on the oxygenated carbon catalyst.[5,21,24]

Conventional oxidation methods that rely on brute force oxidation using concentrated acids or high temperature are not selective and the final catalyst contains all the three functional groups in different proportion. Moreover, use of strong mineral acids to introduce large amounts of oxygenated functional groups also introduces unwanted functional groups. For example, 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, oxidation intensity of persulfate salt solutions is lower than other methods. Moreover, sulfuric acid solution is essential for oxidation using persulfates, which can cause sulfonation in small degree.

In this paper, we report a mechanochemical approach for oxidation of carbon to prepare carbon catalyst consisting of high-density carboxyl groups and application of the catalyst for cellulose hydrolysis. The catalyst is prepared by mechanochemical oxidation of activated carbon using persulfate salts as oxidant in a planetary ball mill without using any solvent. In a typical catalyst preparation experiment, a steam activated carbon was milled with the solid oxidizing agent in a planetary ball mill for 5 h. The resulting mixture was washed with 5% HCl to protonate the carboxylate ions, and then washed with copious amounts of water to remove HCl and 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 composition of the catalysts used in this study is shown in Table 1. The oxygen content of parent steam

activated carbon (AC) was 4.6%. After mechanochemical oxidation the oxygen content of activated carbon milled with $KHSO_4$ (AC-M-KPS) increased to 24.4%. Similarly, oxygen content of activated carbon milled in the presence of $(NH_4)_2S_2O_8$ (AC-M-APS) increased to 26.6%. Sulfur content in AC-M-KPS reduced from 0.1% to beyond detection limit, and the sulfur content increased marginally in AC-M-APS (0.3%) along with nitrogen (0.0 to 0.6%). This suggests that there was little or no sulfonation of 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 oxidizing agent (AC-M) caused a slight increase in the oxygen content (4.6 to 7.8%). 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 milling media due to mechanical abrasion. X-ray diffraction of the catalyst confirmed the presence of α-alumina in all milled samples (Figure S1). Ash content in AC-M was very high (18.5%), as carbon alone cannot dampen the mechanical force causing severe abrasion.

Table 1. Elemental composition and surface properties of carbon, 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	0.1	18.5	7.8	5.8	710
AC-M-KPS	69.1	1.6	nd	nd	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	na[g]	2.5	10.4	4.9	749

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

X-ray photoelectron spectra (XPS) for the C1s region of the carbon catalyst between binding energy of 291 eV and 281 eV is shown in Figure 1. The deconvolution of the spectra revealed five peaks. The most prominent peak centered at 284.6 eV was assigned to the polyaromatic carbon present in C=C bonding (Table 2). The weak and overlapping peak at 283.7 eV was assigned to the C–H bonds. The peak at 286 eV was assigned to the C–O bonds of alcohols and epoxy bridges, and that at 287 eV was assigned to the C=O bonds in the carbonyl group. The increase in 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 288.9 eV was assigned to carbon in the form of O–C=O as carboxylic acid, lactone or acid anhydride. Calculation of atomic ratio based on the peak area reveals that 12% and 13% of 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 XPS, we calculated the surface density of carboxyl groups in the AC-M-KPS as 6.8 mmol g^{-1}. Notably, this amount is higher than the 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 the harsh chemical oxidation methods such as the Hummer's method for graphene oxide synthesis, in which formation of hydroxyl groups and epoxy bridges is favored.[26] Consequently, the mechanochemical oxidation successfully produced carbon material bearing dense carboxylic groups.

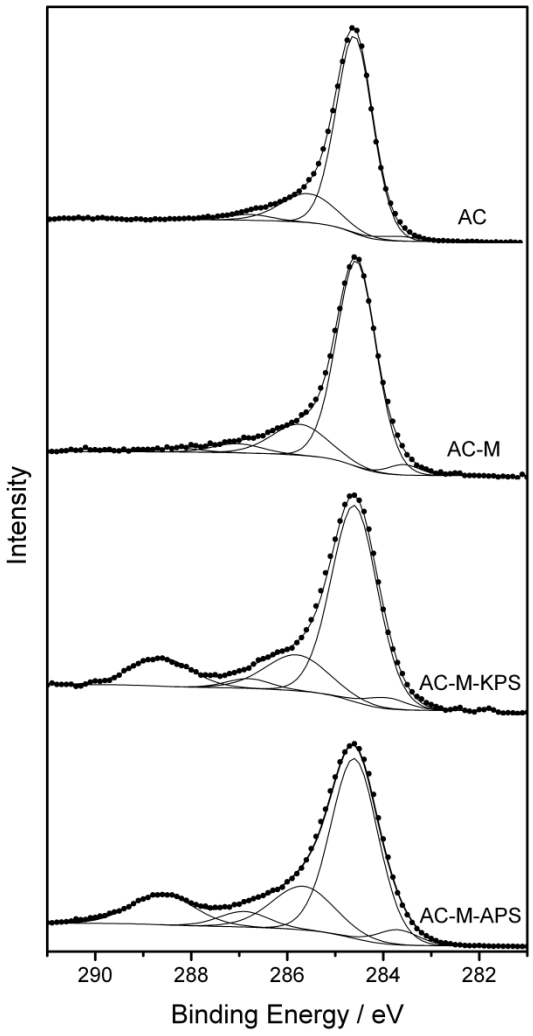

Figure 1: XPS analysis of the carbon catalysts.

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 of composition compared with AC.

We measured pH of 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, indicative of low concentration of acidic groups on the surface. Oxidized catalyst showed pH values of 3.3 and 3.1 for AC-M-APS and AC-M-KPS, 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, pK_a = 3.0). FT-IR spectra of the carbon catalysts are shown in Figure 2. Prominent bands in 1780–1680 cm^{-1} appear in mechanochemically oxidized carbons which are indicative of ν(C=O) in the O–C=O bond. Typically vibrations of C=O stretching due to carboxylic acid, lactone and anhydride groups are in the range of 1740–1700 cm^{-1}.[32–34] All four spectra show complex overlapping band at 1650–1550 cm^{-1}. These bands were assigned to ν(C=C) in the aromatic rings and δ(O–H) of adsorbed water.[32] The broad band at 1420–1380 cm^{-1} can be either assigned to in-plane δ(C–H) in different C=C–H structures, or carboxylate structure.[35] The broad band at 1300–1000 cm^{-1} was a result of multiple overlapping peaks due to ν(C–O) bond under different environment.[32,33]

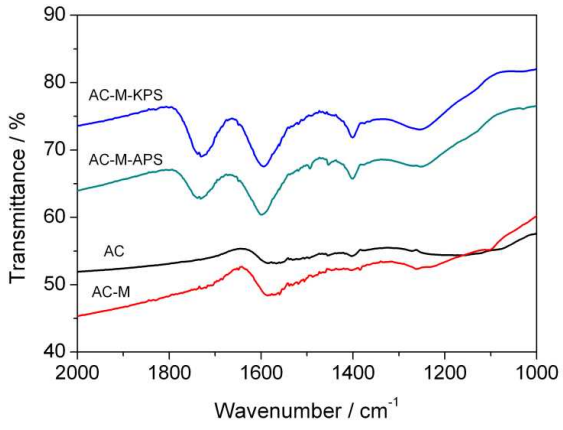

Figure 2: FT–IR spectra carbon catalysts

The textural properties of the carbon materials are also of interest as they are heterogeneous catalysts. Analyzing nitrogen adsorption isotherms for catalysts (Figure S2), the Brunauer–Emmett–Teller (BET) surface area for all materials was determined as shown in Table 1. Carbon milled in the absence of oxidizing agent showed slightly less surface area of 710 m^2 g^{-1} in comparison to the parent material (963 m^2 g^{-1}). Mechanochemical oxidation reduced the area to 453 m^2 g^{-1} and 406 m^2 g^{-1} for AC-M-APS and AC-M-KPS, respectively. The loss of BET surface area is only half, and may have limited influence during catalytic reactions, especially in aqueous phase used for hydrolysis of cellulose. The oxidized carbon catalyst is expected to be hydrophilic, and therefore available contact area in water may be larger than the BET surface area owing to swelling effect. We analyzed the adsorption of water on the surface of untreated and oxidized carbon catalysts at 298 K (Figure S3). Mechanochemically oxidized samples showed 4 times (AC-M-KPS) and 3 times (AC-M-APS) higher adsorption amount of water at low relative pressure (p/p_0 = 0.1) despite having a lower BET surface area. Furthermore, the catalyst was 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 catalyst is suitable for aqueous phase reaction due to presence of large amount of carboxyl groups and good dispersion in water.

The prepared catalyst was applied for hydrolysis of cellulose in an aqueous phase reaction. Contrary to traditional belief that only strong acid catalyst 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 catalyst, the oxygenated species are much more durable in the hydrothermal reaction conditions required for polysaccharide hydrolysis.[16,17]

Pretreatment of cellulose is required to reduce its crystallinity. Steric hindrance owing to crystalline state[43] and strong intermolecular hydrogen bonds of cellulose[44] inhibit the hydrolysis reaction. In addition, hydrolysis of cellulose in aqueous phase using solid acid catalyst takes place at the solid-solid interface. The reaction is slow due to the limited contact area between the catalyst and solid cellulose. Previously, our group reported that amorphization of cellulose and facilitation of 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, which results in a 13 fold increase in the hydrolysis rate when compared with individual milling that only amorphisizes the cellulose. Consequently, high yield of soluble oligomers can be obtained even at low temperature.[45] In aqueous solution, soluble glucans easily adsorb back on the aromatic carbon surface by CH–π bonds and further hydrolysis occurs.[46,47] Thus, we performed mix-milling of mechanochemically oxygenated carbon and cellulose prior to the hydrolysis reaction. As such, mix-milling is 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 same as that of the suspension made from 50 mg of AC-M-KPS catalyst.

Table 3. Conversion and yield of products after hydrolysis of cellulose using carbon catalyst[a]

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

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

Table 3 shows the result of cellulose hydrolysis in distilled water. AC-M-KPS was the most active catalyst resulting in conversion of 98% and glucose yield of 69% after 16h reaction at 145 °C and S/C of 6.5 (entry 4). AC-M-APS also showed good activity with glucose yield of 67 % under the same reaction conditions (entry 6). In contrast, 76% conversion and 40 % yield of glucose was obtained in the presence of AC-M (entry 3). Parent AC gave further lower conversion (56%) and yield of glucose (27%) (entry 2). Assuming 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 group imparted by mechanochemical oxidation promotes the cellulose hydrolysis reaction. We also used AC oxidized under aqueous condition using the same amount of $KHSO_5$ to evaluate the effectiveness of mechanochemical oxidation. Aqueous phase oxidation was not effective for introducing large amount of oxygenated functional groups as evident from low oxygen content (10.4%) and high pH value (4.9) of the AC-A-KPS catalyst. Evidently, this catalyst did not yield high amount of glucose after mix-milling (33%; entry 5). Therefore, it can be inferred that mechanochemical oxidation is essential to produce active carbon catalyst bearing large amounts of carboxylic acids.

To further evaluate the activity of oxygenated carbon catalyst the S/C of the hydrolysis condition was increased from 6.5 to 13. Yield of glucose was 61% in the reaction with AC-M-KPS (Table 3 entry 7). Glucose yield decreased to 48 % in the presence of AC-M-APS under the same reaction condition (entry 8). The higher activity of AC-M-KPS can be attributed to the presence of 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 better hydrophilicity that exposes the active sites as shown by the adsorption of water at low p/p_0 (Figure S3).

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

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

In conclusion, we found that mechanochemical oxidation of activated carbon with persulfate salts resulted in highly oxygenated carbon catalyst without introducing sulfonic acid groups. XPS analysis of the prepared catalyst showed that the new oxygenated functional groups generated were mainly present in the form of carboxyl groups. These catalysts were found to be active for hydrolysis of cellulose to produce glucose. Carbon oxidized with KPS showed higher activity for cellulose hydrolysis at high S/C. Glucose yield of 85 % was achieved in only 20 min at 180 °C in the presence of trace amount of HCl (0.012%).

Experimental Section

Catalyst preparation: Steam activated carbon (AC) for catalyst synthesis was supplied by Ajinomoto Fine-Techno, commercially called BA. For mechanochemical oxidation 0.5 g of AC was milled in the presence of 4.6 g of $(NH_4)_2SO_8$ (Wako Pure Chemical Industry Ltd.) or 4.2 g of Oxone® ($KHSO_4$ 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 using a Fritsch P-6 planetary ball mill. After milling the mixture was recovered and washed twice with 5 wt. % HCl and then washed several times with water until the pH of 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 0.5 g of AC and 4.2 g of $KHSO_4$ in 50 mL of water 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 using a CE440 CHN analyzer from Exeter Analytical. Ash content was calculated by measuring the weight of residue left after calcining the carbon catalyst under air at 575 °C for 10 h. BET surface area was calculated by measuring the N_2 adsorption isotherm at –196 °C using a Belsorp mini. XPS of the catalyst were obtained using a JEOL JPC-9010MC instrument. Prior to analysis, a thin layer of sample was spread on a copper tape and degassed in the analysis chamber overnight. Monochromatic beam of Al Kα X-ray was used to analyze the sample. FT-IR spectra of samples were measured by making KBr pellet of the carbon with dilution of 1:5000. The pellet was analyzed using a PerkinElmer Spectrum 100 Spectrometer.

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

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Keywords: Carbon Catalyst • Carboxylic acid • Cellulose hydrolysis • Mechanochemical Oxidation •

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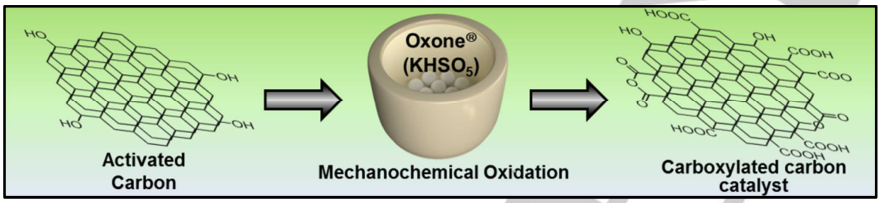

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We report a solvent free mechanochemical method for oxidation of carbon catalyst using persulfate salts. Mechanochemical oxidation preferentially introduced carboxyl groups with high density and without the incorporation of sulfonic groups. The catalyst exhibited hydrophilic behavior and was easily dispersed in water. The catalyst was active for acid catalyzed hydrolysis of cellulose after mix-milling, giving glucose in 85% yield after 20 min in the presence of dilute HCl.