# Chapter 2
# Depolymerization of Cellulosic Biomass Catalyzed by Activated Carbons

**Hirokazu Kobayashi, Mizuho Yabushita, and Atsushi Fukuoka**

**Abstract** Efficient hydrolysis of cellulosic biomass to glucose is a grand challenge for the realization of a nonfood biorefinery. In recent years, solid catalysts have attracted significant attention for biomass conversion, as they can be separated from product solutions and their functions can be designed. In this chapter, we describe activated carbons that can hydrolyze cellulose and real biomass to glucose in yields up to 88 % in the presence of a trace amount of hydrochloric acid. Creating contacts between the solid catalyst and the solid substrate by ball-milling is the key to realizing the potential of this catalytic system. Activated carbon adsorbs cellulosic molecules by van der Waals forces, CH–π hydrogen bonds, and hydrophobic interactions between the polyaromatic surface of the carbon and the axial planes of glucans, namely, hydrophobic groups. Subsequently, the weakly acidic groups of the carbon surface such as carboxylic acids cleave the glycosidic bonds of cellulose via oxocarbenium intermediates, for which the salicylic acid structure is especially effective.

**Keywords** Cellulose • Hydrolysis • Activated carbon • Ball-milling • Depolymerization

## 2.1 Introduction

Efficient hydrolysis of cellulosic biomass to glucose (Fig. 2.1) is a grand challenge for the realization of a nonfood biorefinery, as cellulose is the most abundant inedible biomass and glucose is a versatile precursor to chemicals [1, 2]. In recent years, enzymatic hydrolysis of cellulose has been widely studied at up to a $10^5$-ton-per-year scale in the USA (DuPont, KL Energy, Poet, and Cobalt Technologies), Japan (a project of New Energy and Industrial Technology Development Organization), Taiwan (Institute of Nuclear Energy Research), etc.

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M. Schlaf, Z.C. Zhang (eds.), *Reaction Pathways and Mechanisms in Thermocatalytic Biomass Conversion I*, Green Chemistry and Sustainable Technology, DOI 10.1007/978-981-287-688-1_2

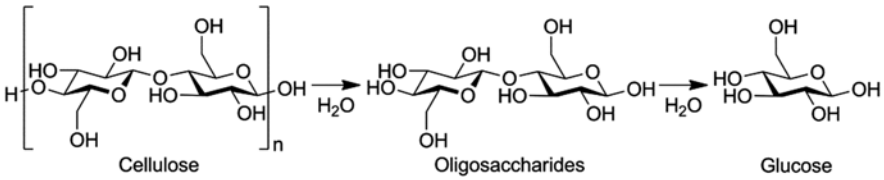



**Fig. 2.1** Hydrolysis of cellulose to glucose

However, the high cost of enzymes has remained an issue for the establishment of economical processes.

Another potential strategy to depolymerize cellulose is the utilization of solid catalysts, because they can be separated from product solutions and their functions can be designed [3]. Solid strong acids such as sulfonated carbons have been intensively studied by many groups to hydrolyze cellulose [4–12], whereas little research has focused on weakly acidic solid catalysts. However, weak acids may also be useful, as cellulase enzymes selectively hydrolyze cellulose using weak acids/bases [13]. Moreover, weak acids can survive in the presence of salts potentially derived from biomass, whereas solid strong acids readily cause cation exchange, namely, proton leaching [14]. Solid weak acids are worthwhile to investigate for the hydrolysis of cellulose.

We have focused on activated carbons because they are ubiquitous materials bearing weakly acidic oxygenated groups such as carboxylic acids and phenols. Moreover, carbon is stable under the harsh aqueous conditions required for the conversion of cellulose. In this chapter, we describe the catalysis of activated carbons for the hydrolysis of cellulose and real biomass and discuss the reaction mechanism.

## 2.2 Hydrolysis of Cellulose by Activated Carbons

### *2.2.1 Catalytic Activities of Carbons*

Various carbons were tested for the hydrolysis of ball-milled cellulose in water with the following temperature program: r.t. to 503 K in 18 min and then a rapid cool down to r.t. by blowing air [15]. The concentration of cellulose used here was 8.1 g in 1 L of water, denoted 8.1 g $L^{-1}$, and the weight-based ratio of substrate to catalyst (S/C) was 6.5. As shown in Table 2.1, alkali-activated carbon K26 gave the highest conversion of cellulose (60 %) with the formation of sugar products such as glucose (36 % yield), soluble oligosaccharides (2.5 %), fructose (2.7 %), and mannose (2.6 %). K26 was reusable three times without significant loss of activity. Other alkali-activated carbons K20 and MSP20 also had good catalytic activities (glucose yields of 35 % and 26 %, respectively). A mesoporous carbon CMK-3 [16] reproducibly afforded 12–16 % yields of glucose over several tests [15, 17, 18], and

**Table 2.1** Hydrolysis of cellulose by various carbon catalysts

| Catalyst | Acid amount[a]/ μmol $g^{-1}$ | Conv./% | Yield based on carbon/% | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Glc | Olg | Frc | Man | Lev | HMF | Others |
| None | – | 28 | 4.6 | 15 | 0.5 | 0.6 | 0.2 | 1.8 | 5 |
| K26[b] | 880 | 60 | 36 | 2.5 | 2.7 | 2.6 | 2.1 | 3.4 | 11 |
| K20[b] | 1010 | 59 | 35 | 1.7 | 1.9 | 1.3 | 2.7 | 2.9 | 14 |
| MSP20[c] | 450 | 50 | 26 | 6.3 | 1.7 | 1.6 | 1.6 | 2.1 | 11 |
| CMK-3[d] | 410 | 52 | 12 | 25 | 0.9 | 0.8 | 0.7 | 2.5 | 10 |
| BP2000[e] | 160 | 37 | 6.4 | 12 | 0.5 | 0.5 | 0.3 | 1.8 | 16 |
| XC72[e] | 75 | 35 | 5.8 | 19 | 0.6 | 0.9 | 0.2 | 1.9 | 7 |
| GO[f] | – | –[g] | 58 | 1.5 | 0.5 | 2.5 | 3.1 | 11 | –[g] |

*Reaction conditions*: ball-milled cellulose, 8.1 g $L^{-1}$; S/C = 6.5; solvent, water 40 mL; r.t. to 503 K in 18 min and then cooled down to r.t. *Products*: *Glc* glucose, *Olg* water-soluble oligosaccharides, *Frc* fructose, *Man* mannose, *Lev* levoglucosan, *HMF* 5-hydroxymethylfurfural, others (conversion) – (total yield of the shown products)

[a]Total amount of surface acidic groups quantified by the Boehm titration [20]

[b]Alkali-activated carbon synthesized in Showa Denko

[c]Commercial alkali-activated carbon, Kansai Coke and Chemicals

[d]Mesoporous carbon [16]

[e]Commercial carbon black, Cabot

[f]Commercial graphene oxide, G-22, EM Japan

[g]Cannot be determined due to the decomposition of catalyst

another group also verified the catalytic activity of a mesoporous carbon [19]. Carbon blacks BP2000 and XC72 provided similar glucose yields (5.8–6.4 %) to that of a blank experiment without catalyst (4.6 %). Thus, the catalytic activity greatly depended on the types of carbons. In addition, good yields of glucose (50–60 %) were obtained by using graphene oxides, but graphene oxides became black precipitates having low activity after the reaction. The reaction temperature of 503 K is high enough to decompose oxygenated groups of graphene oxide to CO and $CO_2$ [11], which induce its aggregation. Thus, we studied the catalysis of more typical carbon materials for the hydrolysis of cellulose.

In order to identify the active sites, the surface acidic groups on carbons were quantified by the Boehm titration using $NaHCO_3$, $Na_2CO_3$, and NaOH [20]. The most active catalyst K26 had 270 μmol $g^{-1}$ of carboxylic acids, 310 μmol $g^{-1}$ of lactones, and 310 μmol $g^{-1}$ of phenols, whereas an inactive catalyst XC72 possessed only 75 μmol $g^{-1}$ of acidic groups in total. Figure 2.2 shows a plot of yields of glucose against the total amounts of acidic groups on the carbons, showing a fairly good correlation. It was also found that the activity of K26 decreased by reducing the amount of oxygenated groups. We and Chung et al., respectively, showed that the catalytic activity of such carbons was maintained after treating the materials with sodium acetate/acetic acid buffer of pH 4.0–4.1 [14]. If the carbon catalysts were strong acids, they would be deactivated by the treatment due to ion exchange with $Na^+$. Thus, major active sites of carbons such as K26 are not strong acids but weak ones.

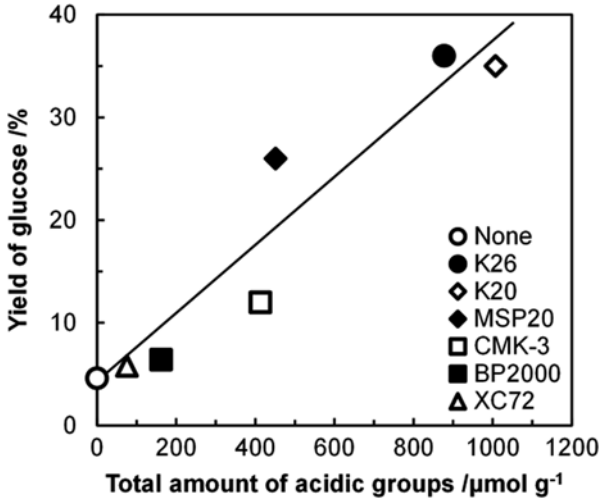



**Fig. 2.2** Correlation between total acid amounts on carbons and glucose yields (cellulose, 8.1 g $L^{-1}$; S/C = 6.5; solvent, water; r.t. to 503 K in 18 min and cooled down to r.t.)

### *2.2.2 Mix-Milling for the Hydrolysis of Cellulose by Activated Carbon*

The yield of glucose was at most 36 % in the screening tests, which must be improved for practical use of activated carbon catalysts. The hydrolysis of solid cellulose by solid catalysts is hampered by their limited collisions and therefore requires severe reaction conditions that may lead to the degradation of glucose. This degradation must be avoided while accelerating the hydrolysis of cellulose. Thus, we conceived of ball-milling cellulose and carbon together to improve their contact, denoted as mix-milling hereafter [15]. The mix-milled sample containing cellulose and K26 was used in a reaction at 418 K for 24 h, and 72 % yield of glucose was achieved (Table 2.2). On the other hand, individually milled cellulose gave only 17 % yield of glucose, thus showing that the mix-milling pretreatment dramatically improved the yield of glucose.

The effect of mix-milling was quantitatively analyzed in a kinetic study [21]. We have hypothesized that the catalytic conversion of cellulose consists of three pseudo-first-order reactions: hydrolysis of solid cellulose to soluble oligomers ($k_1$), that of soluble oligomers to glucose ($k_2$), and decomposition of glucose to by-products ($k_3$). When the mix-milling was used as a pretreatment, $k_1$ (0.17 $h^{-1}$) was as high as $k_2$ (0.16 $h^{-1}$) at 418 K, showing that solid cellulose was hydrolyzed similarly as soluble oligosaccharides in this system. Moreover, $k_1$ and $k_2$ were both *ca.* ten times greater than $k_3$ (0.017 $h^{-1}$), thus giving a good yield of glucose (72 %). In the case of individual milling, $k_1$ was as low as 0.013 $h^{-1}$, but $k_2$ and $k_3$ were 0.16 and 0.017 $h^{-1}$, respectively. In summary, the mix-milling improves $k_1$ by 13-fold but keeps $k_2$ and

**Table 2.2** Effect of mix-milling and trace HCl on the hydrolysis of cellulose by K26

| Milling pretreatment | Reaction temp./K | Reaction time/h | Solvent | Yield based on carbon/% | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Glc | Olg | Frc | Man | Lev | HMF |
| Individual | 418 | 24 | Water | 17 | 6.7 | 1.1 | 0.9 | 0.2 | 0.8 |
| Mix | 418 | 24 | Water | 72 | 2.8 | 1.4 | 1.5 | 1.4 | 4.9 |
| Mix | 453 | 0.33 | Water | 20 | 70 | 0.6 | 0.7 | 0.7 | 1.0 |
| Mix | 453 | 0.33 | 120 ppm HCl | 88 | 2.7 | 1.5 | 1.5 | 3.0 | 1.7 |

*Reaction conditions*: Cellulose, 8.1 g $L^{-1}$; S/C = 6.5. *Products*: *Glc* glucose, *Olg* water-soluble oligosaccharides, *Frc* fructose, *Man* mannose, *Le*v levoglucosan, *HMF* 5-hydroxymethylfurfural

$k_3$ constant, indicating that the mix-milling pretreatment selectively improves the rate constant of the solid-solid reaction.

Pristine, mix-milled, and individually milled cellulose samples were characterized by several physicochemical methods. X-ray diffraction and $^{13}C$ nuclear magnetic resonance spectroscopy indicated that the pristine cellulose was in the cellulose I form with 80 % crystallinity, whereas the milled ones were in amorphous form with less than 5 % crystallinities. Median diameters of secondary particles were 63 μm for the pristine cellulose, 37 μm for the mix-milled one, and 33 μm for the individually milled one; both the milling pretreatments decreased the particle sizes almost by half. The polymerization degree of pristine cellulose (1240), determined by viscometry with parameters reported elsewhere [22], was also reduced to half by the milling pretreatments (690 for mix-milled and 640 for individually milled). Thus, the mix-milling and the individual milling changed the nature of cellulose in a similar way. Therefore, the origin of the specific effect of the mix-milling can be ascribed to enhanced contact between cellulose and the carbon catalyst.

### 2.2.3 *Combination of Activated Carbon and Trace Hydrochloric Acid*

The productivity of glucose was improved by optimizing the reaction conditions of cellulose hydrolysis. First, the reaction temperature was increased to shorten the reaction time to a more practical range. At 453 K, 20 % yield of glucose and 70 % yield of oligomers, 90 % yield in total, were obtained within 0.33 h. The hydrolysis of cellulose was remarkably rapid and that of oligosaccharides was the rate-determining step under these conditions. As indicated in the kinetic study described in the previous section, increasing reaction time causes the decomposition of glucose in addition to the hydrolysis of oligosaccharides. Therefore, the second step was the acceleration of the hydrolysis of oligosaccharides, for which trace soluble acid was used as a solvent instead of pure water for the reaction of a mix-milled sample containing cellulose and K26. Optimized conditions (120 ppm HCl; 453 K; 0.33 h) gave an 88 % yield of glucose with 90 % selectivity (Table 2.2), which is one

of the best records ever achieved with solid catalysts. Accordingly, we concluded that trace HCl efficiently transformed soluble oligosaccharides into glucose. Economic costs of a trace amount of HCl and its neutralization are low, and some stainless steel reactors are tolerant to low concentrations of HCl. We believe that combining *trace* HCl with a solid catalyst is a prospective method for the conversion of cellulose. Sels et al. also proposed the use of *trace* HCl with a solid catalyst as an efficient methodology for the conversion of cellulose [23].

Reuse experiments of K26 were carried out using a high concentration of cellulose (200 g $L^{-1}$) at S/C = 6.5 in 120 ppm HCl to evaluate productivity and durability of the catalyst (Fig. 2.3). Glucose was produced in 71 % yield with a concentration of 160 g $L^{-1}$ in the first run. Although the yield of glucose was lower than that under a diluted condition (88 % yield at 8.1 g $L^{-1}$), our catalytic system still functioned well under the concentrated condition. Next, the catalyst was reused according to the following procedure. The reaction mixture was separated by centrifugation into hydrolysate and solid residue containing K26 and unreacted cellulose. The solid was washed with water, dried, and mix-milled with fresh cellulose, the amount of which was the same as that consumed in the previous reaction. The mix-milled sample was used for the next hydrolysis reaction. The yields of glucose in the second to fourth reactions were 72 %, 70 %, and 67 %, respectively, which indicated good reusability of K26.

The combination of activated carbon and HCl was applied to conversion of bagasse pulp as an example of real biomass. The bagasse sample was composed of cellulose (59 wt%), hemicellulose (27 wt%; xylan 25 wt% and arabinan 2 wt%), lignin (9 wt%), and others (5 wt%). The bagasse pulp and a commercial activated carbon bearing a relatively large amount of oxygenated groups among inexpensive

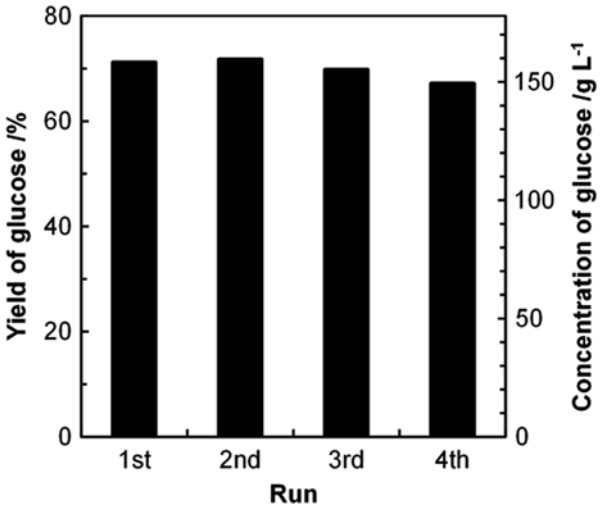



**Fig. 2.3** Reuse tests of K26 in the hydrolysis of cellulose (cellulose, 200 g $L^{-1}$; S/C = 6.5; 0.012 % HCl aq.; r.t. to 473 K in 16 min, 473 K for 2 min, and 423 K for 60 min)

ones (BA50, Ajinomoto Fine-Techno) were mix-milled, and the mixture was used for a two-step reaction in order to selectively hydrolyze hemicellulose and cellulose. The first hydrolysis conditions at 453 K for 1 min gave glucose in 1.9 % yield based on the cellulose content and pentoses in 76 % yield based on the amount of hemicellulose, and most of the cellulose fraction remained as a solid together with BA50 in this step. Subsequently, the second hydrolysis at 483 K for 2 min using the solid residue in the first reaction afforded glucose in 74 % yield and pentoses in 16 % yield. These results clearly show that our catalytic system is applicable to the hydrolysis of real biomass.

## 2.3 Mechanistic Study of the Hydrolysis of Cellulose by Activated Carbon

### *2.3.1 Elementary Steps of Hydrolytic Reactions*

Hydrolysis of cellulose by solid catalysts occurs after adsorption of the cellulose molecule on the surface of the catalyst followed by dissociation of the glycosidic bonds by the active sites. Katz et al. found that cellulose molecules grafted on silica via ether bonds were converted to oligosaccharides by surface silanol groups ($pK_a$*ca.* 7) in trace hydrochloric acid at pH 4 [24, 25]. The catalytic activity correlated with the density of surface OH groups [26]. In contrast, free cellulose cannot be depolymerized by the catalysts under the same conditions. These results indicate that even weak acids can hydrolyze glycosidic bonds of cellulose by attracting the molecule to active sites. Therefore, we studied the adsorption of cellulosic molecules on K26 and the hydrolysis step by oxygenated groups.

### *2.3.2 Adsorption of Cellulosic Molecules on Activated Carbon*

Cellobiose was adsorbed onto K26 in water at 296 K to elucidate the manner of adsorption [27]. A Langmuir-type adsorption isotherm was obtained, and the adsorption equilibrium constant ($K_{ads}$) was calculated to be 5660 $M^{-1}$ and the adsorption capacity ($C_{ads}$) to be 412 mg $g^{-1}$. Two driving forces behind the adsorption can be hypothesized based on interactions of hydrophobic and hydrophilic groups. The polyaromatic surface of carbon may interact with the hydrophobic plane of cellobiose (axial plane consists of C–H groups) via van der Waals forces and CH–π hydrogen bonds [28], whereas oxygenated groups of carbon possibly form OH–O hydrogen bonds with hydroxyl groups on the equatorial plane of cellobiose [29, 30]. To clarify which is the predominant force for the adsorption, K26 was deoxygenated at 1273 K under He flow. This treatment removed *ca.* 99 % of the oxygenated groups from K26, but this material similarly adsorbed cellobiose ($K_{ads}$ = 5270 $M^{-1}$,

**Table 2.3** Enthalpy and entropy changes for the adsorption of β-glucans on K26

| Adsorbate | $\Delta H^\circ_{ads}$/ kJ mol$^{-1}$ | $\Delta S^\circ_{ads}$/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| Glucose | −8.4 ± 1.2 | +16.5 ± 3.8 |
| Cellobiose | −14.1 ± 1.9 | +23.5 ± 3.4 |
| Cellotriose | −20.2 ± 0.8 | +32.2 ± 3.3 |

$C_{ads}$ = 342 mg g$^{-1}$). The slight decrease in $C_{ads}$ was due to the reduction of surface area by the heat treatment. It is thus concluded that the major driving force for the adsorption is the interaction between hydrophobic groups. The two-dimensional polyaromatic surface and flatly arrayed CH groups of cellobiose are well fitted to each other.

The adsorption enthalpy ($\Delta H^\circ_{ads}$) and entropy ($\Delta S^\circ_{ads}$) of cellobiose on K26 were calculated from the van't Hoff plot to quantitatively evaluate the driving forces (Table 2.3). $\Delta H^\circ_{ads}$ was −14.1 kJ mol$^{-1}$, and accordingly, the value divided by the number of CH groups presenting on one side of cellobiose (5) was −2.8 kJ mol$^{-1}$.

This value is reasonable for the CH–π interactions [28, 31]. In contrast, $\Delta S^\circ_{ads}$ of +23.5 J K$^{-1}$ mol$^{-1}$ is surprising, as the adsorption usually decreases the freedom of adsorbate. This positive entropy change is ascribed to the hydrophobic interaction (a review article is available for general hydrophobic interactions [32]). The adsorption of cellobiose onto K26 with hydrophobic groups releases water molecules restricted around the lipophilic surface, which increases freedom of the water molecules. Consequently, the adsorption of cellobiose onto K26 is driven by both enthalpy and entropy. The positive entropy change provides strong adsorption even at the high temperatures required for the conversion of cellulose, as demonstrated in a high-temperature adsorption experiment in which 230 mg of cellobiose adsorbed onto 1 g of K26 at 413 K within 10 min.

The thermodynamics of adsorption of glucose, cellobiose, and cellotriose were compared to clarify the effect of chain length. $\Delta H^\circ_{ads}$ value linearly decreased from −8.4 kJ mol$^{-1}$ (glucose) to −14.1 kJ mol$^{-1}$ (cellobiose) and −20.2 kJ mol$^{-1}$ (cellotriose), which was due to the increase in the number of CH groups. Similarly, $\Delta S^\circ_{ads}$ was elevated from +16.5 J K$^{-1}$ mol$^{-1}$ to +23.5 and +32.2 J K$^{-1}$ mol$^{-1}$ with increasing chain length, owing to the increase in adsorption in cross-sectional area. The longer the cellulosic molecule becomes, the stronger the molecule and carbon interact. Thus, K26 has a strong interaction with cellulose on the interface.

### *2.3.3 Hydrolysis of Glycosidic Bonds by Oxygenated Groups*

The role of oxygenated groups was studied in the hydrolysis of cellobiose by aromatic compounds as model catalysts at 443 K (Table 2.4) [15]. Phenol ($pK_a$ = 10) and benzoic acid ($pK_a$ = 4.2) provided low turnover frequencies (TOFs) of 0 and 4.5 h$^{-1}$, respectively. Salicylic acid ($pK_a$ = 3.0), having phenolic and carboxylic groups in vicinal positions, gave a high TOF of 28 h$^{-1}$, whereas *m*-hydroxybenzoic

**Table 2.4** Hydrolysis of cellobiose by molecular catalysts

| Catalyst | p$K_a$ | TOF[a]/h$^{-1}$ |
|---|---|---|
| Phenol | 10 | 0 |
| Benzoic acid | 4.2 | 4.5 |
| Salicylic acid | 3.0 | 28 |
| *m*-Hydroxybenzoic acid | 4.1 | 5.6 |
| *p*-Hydroxybenzoic acid | 4.6 | 2.2 |
| *o*-Chlorobenzoic acid | 2.9 | 17 |

[a]Initial rate method with reaction conditions of cellobiose 50 mM, catalyst 0.5 mM, and water solvent at 443 K for 10 min

acid (p$K_a$ = 4.1) and *p*-hydroxybenzoic acid (p$K_a$ = 4.6) were almost inactive (TOF = 5.7, 2.4 h$^{-1}$, respectively). Additionally, *o*-chlorobenzoic acid (p$K_a$ = 2.9, TOF = 17 h$^{-1}$) was significantly more active than benzoic acid, but less active than salicylic acid. Hence, the catalytic activity is determined by two factors. One is the acidity of the catalyst; strong acids can easily activate glycosidic bonds. The other is its structure; vicinal oxygenated groups are effective for the hydrolysis. Hara et al. have proposed that phenols form hydrogen bonds with hydroxyl groups of glucans [4]. Thus, we assume that the hydrogen bonding between the phenol and cellobiose increases the frequency factor of scission of glycosidic bonds by the neighboring carboxylic acid. Recently, it has been proposed that a high local density of surface weak-acid sites cooperatively works for the hydrolysis of glycosidic bonds, as change of the density strongly affects the catalytic activity of carbons [33].

Controlled experiments were conducted to clarify the dissociation mechanism of glycosidic bonds: $S_N1$ or $S_N2$. First, the methanolysis of cellobiose by K26 gave a mixture of α- and β-methylglucose from the nonreducing end glucose unit, and we observed that isomerization of methylglucose was limited under the reaction conditions. These results indicate that the reaction intermediates should be oxocarbenium ions ($S_N1$). Second, the hydrolysis of cellobiose by K26 was performed in the presence of tetraethylammonium chloride or bromide as nucleophiles. The ratio of nucleophilicity of water, $Cl^-$, and $Br^-$ is 1:1000:10,000 in water. However, chloroglucose or bromoglucose was not detected, and these reactions provided similar conversion rates of cellobiose. This result indicates that dissociation of glycosidic bonds by $S_N2$ reaction is negligible in this catalytic system. Therefore, it is concluded that the hydrolysis proceeds by the $S_N1$ mechanism.

### *2.3.4 Proposed Reaction Mechanism*

Figure 2.4 shows the proposed reaction mechanism for the hydrolysis of cellulose by activated carbons. We hypothesized that the salicylic acid structure was the active site. Carbon adsorbs a cellulose molecule by van der Waals forces, CH–π hydrogen bonds, and hydrophobic interactions. Next, phenolic and carboxylic

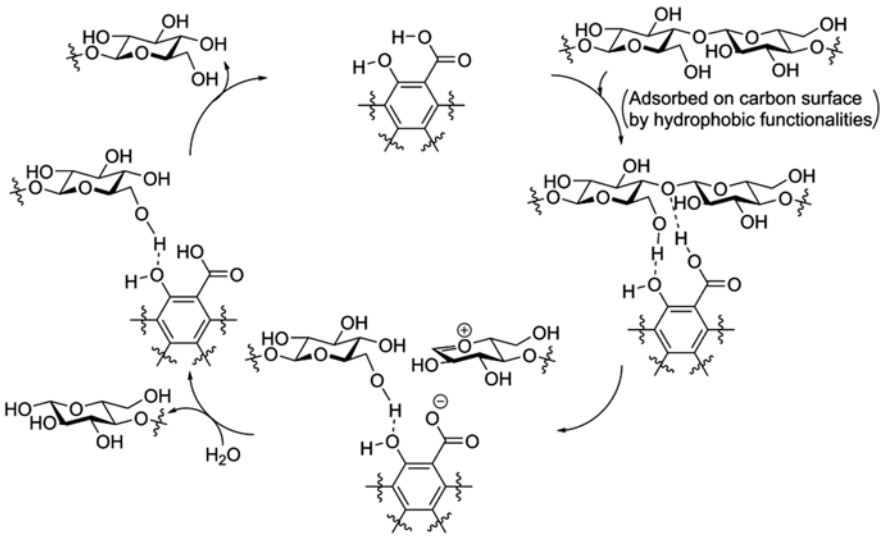



**Fig. 2.4** Proposed reaction mechanism for the hydrolysis of cellulose by activated carbon catalysts

groups of carbon form OH–O hydrogen bonds with the cellulose molecule to attract a glycosidic bond to the carboxylic group. The oxygen atom of the glycosidic bond is protonated, and subsequently scission of the glycosidic bond occurs with formation of an oxocarbenium ion. A water molecule rapidly reacts with the cation to form a sugar residue and regenerates the carboxylic acid of carbon. Finally, the remaining cellulose molecule desorbs from carbon, and the catalyst is regenerated.

It is known that cellulase adsorbs onto cellulose by a hydrophobic aromatic amino acid residue and that the enzyme hydrolyzes glycosidic bonds by a carboxylic acid and a carboxylate [13, 34]. Thus, our activated carbon catalyst and cellulase function similarly in the hydrolysis of cellulose.

## 2.4 Summary

Activated carbons can hydrolyze cellulose and real biomass to glucose in high yields with good productivity. Creating contacts between the solid catalyst and the solid substrate by ball-milling is the key to realizing the potential of this catalytic system. Activated carbon adsorbs cellulose by hydrophobic functionality and cleaves glycosidic bonds by weakly acidic groups such as carboxylic acids, for which the salicylic acid structure is especially effective.

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Cellulose Structure, Depolymerization and Conversion by Heterogeneous Catalysts
Schlaf, M.; Zhang, Z. (Eds.)
2016, X, 260 p., Hardcover
ISBN: 978-981-287-687-4