Catalysis of weakly acidic carbons for hydrolysis of cellulose

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Abstract: Hydrolysis of cellulose is a bottle-neck process in the utilization of lignocellulosic biomass. We found that a carbon material bearing weak acid sites hydrolyzes cellulose to soluble sugars in 90% yield after formation of good solid–solid contact. Carbon adsorbs cellulose by CH–π and hydrophobic interactions, and the adsorbed molecules are hydrolyzed on the acid sites.
Keywords: Solid catalyst, Carbon, Hydrolysis of cellulose.

1. Introduction

Cellulose is a polymer of glucose linked by β-1,4-glycosidic bonds (Figure 1). Hydrolysis of cellulose gives glucose, which is the most important feedstock for the production of chemicals and fuels in biorefinery.[1] However, efficient processes for the hydrolysis of cellulose have not yet been established due to the recalcitrance of cellulose. Cellulose makes many inter- and intra-molecular hydrogen bonds by OH groups on equatorial face to form two-dimensional sheets, and they stack each other using axial face consisting of CH groups by dispersion force.

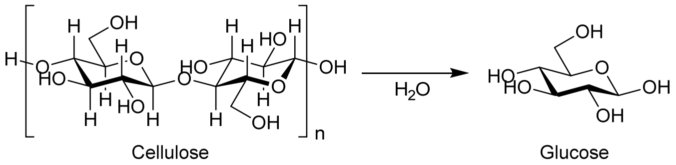

Figure 1. Conversion of sugar alcohols to monomers for plastics.

Heterogeneous catalysts are candidates for the hydrolysis of cellulose, as they can be easily removed from liquid hydrolysate after the reaction. We found that carbons bearing weak acid sites such as carboxylic groups can hydrolyze cellulose to glucose. Ball-milling cellulose and an activated carbon produces good solid substrate–solid catalyst contact. The pre-treated sample gives 90% yield of soluble sugars in the hydrolysis. Herein, we report the details of catalysis and reaction mechanism. We have found that polar and non-polar groups of carbon materials cooperatively hydrolyze cellulose, which also has both polar and non-polar groups.

2. Experimental

Microcrystalline cellulose was ball-milled together with an alkali-activated carbon (K26) in 6.5:1 (wt/wt) ratio. The sample (374 mg) and water (40 mL) were added into a high-pressure reactor and hydrolyzed at 453 K for 20 min. The solution was analyzed with a high-performance liquid chromatograph.

3. Results and discussion

Screening of several types of carbon materials was performed in the hydrolysis of ball-milled cellulose at 503 K.[2] The activity was strongly influenced by types of carbons, and an alkali-activated carbon K26 provided the highest yield of glucose (36%). We found that the activity roughly correlated with the amount of carboxylic and phenolic groups. In addition, treatment of K26 with NaCl aq. had no influence on the activity. These results show that the weak acid sites are active for the hydrolysis of cellulose.

A major factor that limits the hydrolysis rate would be the low contact chance between solid catalyst and solid cellulose. Although the rate-determining step is cleavage of a glycosidic bond, the frequency factor is proportional to the contact degree. Therefore, we ball-milled K26 and cellulose together to make a higher degree of solid–solid contact, which was named mix-milling.[2] The sample was subjected to the hydrolysis reaction for 20 min at 453 K, 50 K lower than the previous reaction (503 K). This reaction gave 20% yield of glucose and 70% yield of oligosaccharides, thus total 90% yield of soluble saccharides (Table 1, entry 3). In stark contrast, the reaction with individually ball-milled cellulose and K26 gave only 2.9% of glucose and 10% of oligomers under the same reaction conditions (entry 2), which was similar to the non-catalytic reaction (entry 1). The yield of glucose was increased to 88% by adding trace amount of HCl (0.012%) for hydrolysis of the mix-milled sample (entry 4), as soluble oligomers are easily hydrolyzed by H_3O^+ at low concentration. This system is applicable for real biomass and the catalyst is reusable after air oxidation in spite of the presence of lignin.[3]

Table 1. Hydrolysis of cellulose by K26.[a)]

Entry	Catalyst	Substrate	Pretreatment	Conv.	Yield of substrate /%	
					Glucose	Oligomers
1	None	Cellulose	Milling of cellulose	12	1.3	6.6
2	K26	Cellulose	Milling of K26 and cellulose, individually	18	2.9	10
3	K26	Cellulose	Mix-milling	93	20	70
4[b)]	K26	Cellulose	Mix-milling	98	88	2.7

a) Substrate 2 mmol-glucose unit, catalyst 50 mg, water 40 mL. 453 K, 20 min. b) 0.012% HCl (pH 2.5) instead of water.

We studied the reaction mechanism for the hydrolysis of cellulose by a carbon catalyst.[4,5] In the adsorption step, K26 adsorbed cellobiose with an equilibrium constant (K_{ads}) of 5700 M^{-1}. The value was increased upon increasing the number of glucose unit. van't Hoff plot showed that the adsorption is driven by both negative change in enthalpy and positive change in entropy. In a controlled experiment, the K26 treated at 1273 K under He to remove oxygenated groups adsorbed cello-oligosaccharides similarly to pristine K26. This result demonstrates that K26 adsorbs cello-oligosaccharides not by oxygenated groups but on polycyclic aromatic framework (Figure 2). DFT calculations supported this assumption, and indicated CH–π interactions mainly consisting of dispersion force between basal plane of carbon and CH groups on axial face of sugars. Besides, the positive entropy change was ascribed to hydrophobic interactions.

In the hydrolysis step, a kinetic study have shown that vicinal oxygenated groups are especially active for the hydrolysis reaction due to high frequency factor.[6] Indeed, carbon catalysts had larger frequency factors for the hydrolysis of cellobiose, compared to simple aromatic carboxylic acids. NMR measurements revealed that vicinal oxygenated groups make strong hydrogen bonds with cellobiose, which may increase the chance of hydrolysis (Figure 2).

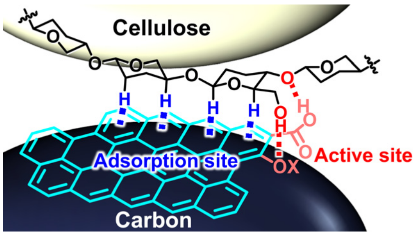

Figure 2. Schematic of cellulose hydrolysis on carbon.

4. Conclusions

We developed hydrolysis of cellulose by weakly acidic carbon catalysts. A carbon material bearing weak acid sites hydrolyzed cellulose to soluble sugars in 90% yield after formation of good solid–solid contact by mix-milling. Carbon adsorbs cellulose by CH–π dispersive force and hydrophobic interactions, and the adsorbed molecules are hydrolyzed by weak acid sites. The findings can be applied to explore new adsorbents and catalysts such as hexagonal boron nitride.[7]

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