Phosphoric acid pretreatment of cellulose for carbon catalyzed hydrolysis to glucose

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Abstract: Hydrolysis of cellulose to glucose using carbon catalyst is a promising approach for renewable chemical synthesis. In this reaction, adsorption of cellulose on carbon is necessary to achieve high yield of products. Here we report a method for adsorption of cellulose on carbon catalyst using H_3PO_4 as solvent. Cellulose was easily dissolved in H_3PO_4 and then adsorbed on carbon surface by using water as anti-solvent. Adsorption on carbon surface is preferred instead of precipitation by partially hydrolyzing the cellulose molecules to reduce their degree of polymerization. After hydrolysis up to 73 % yield of glucose can be obtained.

Keywords: Cellulose pretreatment, Hydrolysis, Carbon catalyst

1. Introduction

Hydrolysis of cellulose to glucose is a key reaction for synthesis of chemicals from renewable biomass.[1] Carbon catalyst containing weakly acidic functional groups hydrolyzes cellulose to soluble β-1,4-glucans and glucose.[2,3] Polyaromatic surface of carbon adsorbs cellulosic molecules and hydrolyzes them using carboxyl functional groups. Therefore, a major challenge in this area is to achieve efficient adsorption of cellulose on carbon materials for rapid hydrolysis.

Previously, our group reported that combined ball milling of cellulose and carbon produces a solid mixture in which cellulose is adsorbed on carbon surface.[4,5] This method increases the rate of cellulose hydrolysis 13 times in comparison to milling the carbon and cellulose separately. The increase in rate of reaction is attributed to the amorphization of cellulose and its adsorption on the surface of carbon catalyst. A major drawback of this method is the high energy consumption for the ball milling step. Therefore, it is essential to develop another cost effective method for adsorption of cellulose on carbon catalyst.

Cellulose is insoluble in most conventional solvent, which makes its adsorption rather difficult. Concentrated strong mineral acids such as H_2SO_4 are HCl can dissolve cellulose. However, they are highly corrosive and their neutralization is costly. Ionic liquids can also dissolve cellulose but the cost of ionic liquids is prohibitive. Therefore, we used H_3PO_4 as weak acid solvent to adsorb cellulose on carbon. Here we describe our research on use of H_3PO_4 as solvent for adsorption of cellulose on carbon followed by hydrolysis to glucose.

2. Experimental

Catalyst synthesis: Activated carbons (BA and Norit, 4 g each) were spread with a thickness of 3-5 mm on a quartz dish. The carbon was then oxidized under air in a furnace at 425 °C for 10 hours and named BA-Air and Norit-Air.

Cellulose pretreatment: Cellulose (Avicel PH-101, 324 mg) was placed in a vial and 0.9 mL of water was added to it. Cold H_3PO_4 (85%, 16.2 mL) was added to the mixture and stirred for 15 minutes resulting in complete dissolution of cellulose. The solution was heated at 60 °C for certain time to partially hydrolyze the dissolved cellulose molecules. Following partial hydrolysis, 324 mg of carbon catalyst was added and stirred for 10 minutes. Then 25 mL of water was added to promote cellulose adsorption on carbon surface. The solid was separated by filtration from the H_3PO_4 solution and washed with 300 mL of water to removed adsorbed H_3PO_4 and then used for hydrolysis step.

Hydrolysis: Solid residue was transferred to an autoclave using 40 mL of water and hydrolysis reaction was performed for 20 mins at 180 °C. The product solution was analyzed by HPLC to calculate product yield.

3. Results and discussion

The schematic of cellulose dissolution process is shown in Figure 1. After dissolution, the cellulose was partially hydrolyzed before adsorption on carbon materials. Partial hydrolysis reduces the degree of polymerization of cellulose causing a drop in the viscosity of solution. The effect of partial hydrolysis was to facilitate the adsorption of cellulose molecule on BA-Air. Glucose yield was only 16% without any partial hydrolysis treatment. After partial hydrolysis for 1 h at 60 °C the glucose yield increased to 73%.

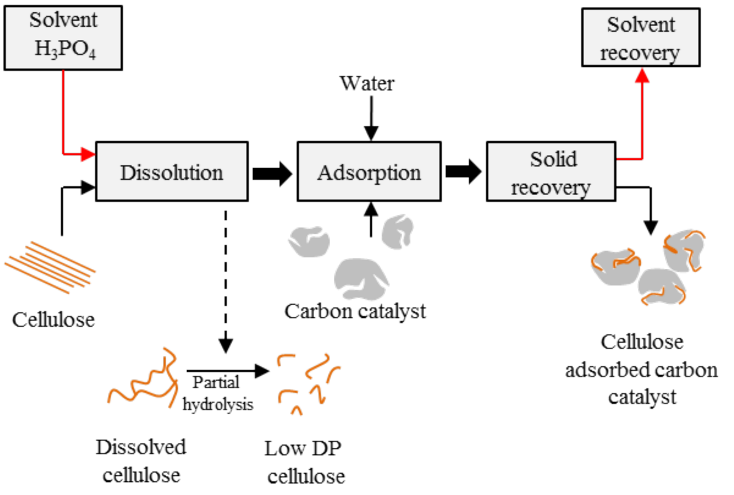

Figure 1: Schematic of cellulose pretreatment process

Presence of acidic function groups on carbon catalyst was crucial for the hydrolysis reaction. We tested the effect of number of acidic functional groups on different catalyst (Table 1). In the absence of carbon catalyst, cellulose precipitates without adsorption and glucose yield after hydrolysis was only 4.0 %. When oxidized carbon materials was used the glucose yield increased to 73% for BA-air and 58% for Norit-Air. The yield of glucose was linearly correlated with the number of weakly acidic functional groups on the carbon surface. In comparison, after milling cellulose and carbon together glucose yield was 69% under the same reaction condition.

Table 1: Yield of products after H_3PO_4 pretreatment and hydrolysis of cellulose.

Catalyst	Acidic functional groups mmol g^{-1}	Conversion %	Glucose %	Oligomers %	By-products %
No catalyst	-	35.8	4.0	9.6	0.5
BA	0.35	48.1	8.7	10.3	0.9
BA-Air	2.64	100	73.3	1.7	4.8
Norit	0.69	48.9	12.5	8.5	1.1
Norit-Air	2.10	91.4	58.1	5.7	4.8
BA-Air[a]	2.64	91.6	68.5	3.5	9.1

[a] Cellulose and BA-Air were ball milled together for 2 h at 500 rpm before hydrolysis reaction.

4. Conclusions

Phosphoric acid pretreatment was successful for adsorption of cellulose on carbon catalyst. Highest glucose yield of 73 % was obtained with BA-Air as catalyst. Yield of glucose after hydrolysis was lineraly correlated with the number of acidic functional groups on the carbon surface. In comparison, yield of glucose was 69% when combined ball milling was used as the pretreatment method. Partial hydrolysis of cellulose enhanced the adsorption by depolymerizing the cellulose molecules and reducing the viscosity of the solution.

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