



Influence of reaction conditions on heterogeneous hydrolysis of cellulose over phenolic residue-derived solid acid



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HIGHLIGHTS

- Influence of reaction conditions on hydrolysis of cellulose is discussed in detail.
- Glucose can be competitively adsorbed on the phenolic residue-derived solid acid.
- Generated glucose suppresses hydrolysis of cellulose to some extent.
- Chloride ions can promote the decrystallization of cellulose in hydrolysis process.

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ABSTRACT

A carbon-based solid acid (CSA) was prepared from phenolic residue which is the solid waste generated from the refining of crude phenol. Influence of various reaction conditions on hydrolysis of cellulose over phenolic residue-derived solid acid (PRCSA) is discussed. The results indicate that both cellulose hydrolysis and the effectiveness of PRCSA need a suitable temperature range. The glucose can be adsorbed on the surface of PRCSA due to the hydroxyl-rich structure of PRCSA. The behavior of generated glucose in competitive adsorption with unreacted cellulose on PRCSA suppresses the continuing hydrolysis of cellulose to some extent. For PRCSA, the number of effective active sites increases with the decrease of catalyst particle size. In heterogeneous hydrolysis of cellulose assisted by inorganic salts, the promotion of KCl and NaCl is remarkable, which is attributed to the decrystallization of chloride ions on cellulose and the ion exchange between cations and H^+ in $-SO_3H$ bonded to PRCSA.

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1. Introduction

Cellulose, accounting for the largest part (40–50%) of lignocellulosic biomass [1], composed of glucose linked by β -1,4 glycosidic bonds, is considered as a renewable resource of glucose. Glucose can be selectively converted into bio-ethanol, ethylene glycol, etc. [2–5], exhibiting great economic development potential in the production of fuels and chemicals for the replacement of fossil feedstocks. However, cellulose shows high chemical stability and insolubility in most solvents due to a robust crystal structure with inter- and intra-molecular hydrogen bonds. Therefore, the development of effective methods for the hydrolysis of cellulose to glucose is one of the most attractive and challenging subjects in green and sustainable chemistry [6,7].

Until now, an extensive number of studies have been reported on the hydrolysis of cellulose using mineral acids [8–10], enzyme [11,12], and supercritical water [13,14]. Despite the high hydrolysis efficiency with these processes, there exist a lot of drawbacks such as high costs of enzyme, acid corrosion, production of chemical waste, severe controls of reaction conditions, and difficult separation of products and catalysts. As will be discussed later on, the application of solid acid catalysts for hydrolysis of cellulose is currently receiving much attention because of its potential to overcome these problems [15,16]. It has been demonstrated that the CSAs show excellent catalytic activity and stability in the hydrolysis of cellulose to glucose [17–19].

Phenolic residue is the solid waste generated from the refining of crude phenol in coking plant and it contains resinous materials and a small amount of high-boiling phenols such as 3-methyl-5-ethylphenol, 2,3,5-trimethylphenol, and naphthol. Recently, we reported that the PRCSA which was readily prepared by sulfonation of carbonized phenolic residue can function as an efficient solid catalyst for the hydrolysis of cellulose [19]. It is known that the CSA generally

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Nomenclature

| | |
|-------|-------------------------------------|
| CSA | carbon-based solid acid |
| PRCSA | phenolic residue-derived solid acid |
| TOF | turnover frequency |

contains condensed aromatic carbon sheets and active groups (including $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic OH) [17,18,20–24]. Except for $-\text{SO}_3\text{H}$, the others could be derived from the corresponding parts of phenolic residue. Therefore, as the solid waste from coking plant, phenolic residue has the structural advantages to prepare CSA. Furthermore, the aliphatic side chains in phenolic residue can greatly improve the sulfonation activity of carbon precursor and enhance the catalytic performance in cellulose hydrolysis. The PRCSA has higher stability and allows for repeated reuse.

Currently, the hydrolysis of cellulose over CSAs is still at the stage of experimentation, and researchers are more focused on increasing catalyst activity, little attention has been given to the relationships between reaction conditions and hydrolysis efficiency of cellulose. Yamaguchi et al. [25] investigated the relationship between hydrolysis rate and several parameters by mathematical simulation methods to analyze the role of water in hydrolysis of cellulose. However, some information about influence of reaction conditions was not discussed deeply. More importantly, the heterogeneous hydrolysis process of cellulose over CSAs is not yet clear. Therefore, this work attempts to investigate the influence of reaction conditions (hydrolysis temperature, hydrolysis time, amount of cellulose, amount of catalyst, particle size of catalyst, addition of inorganic salts) on hydrolysis efficiency of cellulose to analyze the hydrolysis process of cellulose on the surface of PRCSA and clarify the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

As a carbon source, phenolic residue is the solid waste generated from the refining of crude phenol which is a component of coal tar in coking plant. It contains resinous materials and a small amount of high-boiling phenols such as 3-methyl-5-ethylphenol, 2,3,5-trimethylphenol, and naphthol. The resinous materials are thermal polymers of phenolic compound in the distillation process. The analysis data of phenolic residue are shown in Table 1.

The catalyst was prepared according to the following method based on a previous report [19]. Phenolic residue was carbonized in a quartz tube for 8 h at 450 °C under N_2 to produce black carbon precursor which was then ground to powder. Subsequently, the ground carbon precursor was added into concentrated H_2SO_4 (18 mol L^{-1}) according to the ratio of 1 g:20 mL and heated under N_2 flow at 150 °C for 10 h in order to introduce $-\text{SO}_3\text{H}$ to the aromatic carbon sheets. After sulfonation, the black slurry was cooled to room temperature and filtered, the residue was washed repeatedly with boiling deionized water until the filtrate was neutral and free from sulfate ions, and then dried in oven at 70 °C overnight.

Table 1
Analysis of phenolic residue.

| Sample | Proximate analysis w (%) | | | Ultimate analysis w_{daf} (%) | | | | |
|------------------|--------------------------|----------------|------------------|--|------|------|------|----------------|
| | M_{ad} | A_{d} | V_{daf} | C | H | N | S | O ^a |
| Phenolic residue | 1.15 | 1.53 | 62.85 | 82.52 | 7.83 | 0.47 | 1.79 | 7.39 |

^a By difference.

2.2. Cellulose hydrolysis

Pretreated microcrystalline cellulose by concentrated phosphoric acid [26] and PRCSA were added into Teflon-lined stainless steel autoclave in the presence of deionized water (10 mL) and reacted at required temperature for prescribed time periods under magnetic stirring. After the reaction, the autoclave was cooled by cold water immediately to avoid further reaction. The mixture was filtered to obtain the filtrate.

The yield of reducing sugar was estimated by the means of 3,5-dinitrosalicylic acid (DNS method). The amount of produced glucose in filtrate was analyzed by a high-performance liquid chromatography (HPLC).

3. Results and discussion

3.1. Hydrolysis temperature

Fig. 1 shows the effect of reaction temperature on hydrolysis of cellulose in the presence of PRCSA. Temperature is a significant parameter to affect the cellulose hydrolysis. The yield of glucose remarkably increases with increasing the reaction temperature. Like cellulase, the effectiveness of catalyst has a suitable temperature range, further increasing the temperature to 170 °C begins to result in the reduction of the glucose yield.

As shown in Fig. 1, the higher temperature generates higher inner pressure, which helps to accelerate adsorption of cellulose on PRCSA, and disrupt the crystalline structure of cellulose to make the glycosidic bond exposed to the catalyst. Until 160 °C, the yield of glucose synchronously increases as the pressure rises. But the higher pressure is unfavorable to the desorption of products from the catalyst, and the higher temperature can weaken the stability of solid acid, which can be confirmed by the fact that the hydrolysate solution obtained over 160 °C is yellow. When the catalyst is used for a long time at higher temperature, the small aromatic carbon sheets bearing $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic OH groups may be leached from the carbon skeleton, which makes the hydrolysate solution colored to yellow. In addition, the hydrolysis of cellulose is a cascade reaction, the produced glucose is not stable at higher temperature above 160 °C and is readily degraded to the water soluble and insoluble byproducts [27]. All the above parameters can reduce the yield of glucose.

3.2. Hydrolysis time

The correlation between glucose yield and hydrolysis time is shown in Fig. 2A. Prolonging the hydrolysis time favors the formation of glucose, while the hydrolysis time has little or no effect on the glucose yield after 12 h.

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