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Zinc chloride mediated degradation of cellulose at 200 °C and identification of the products

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ABSTRACT

The effect of $ZnCl_2$ on the degradation of cellulose was studied to develop conditions to produce useful feedstock chemicals directly from cellulosic biomass. Cellulose containing 0.5 mol of $ZnCl_2$/mol of glucose unit of cellulose was found to degrade at 200 °C when heated for more than 60 s in air. The major non-gaseous products of the degradation were identified as furfural, 5-hydroxymethylfurfural and levulinic acid. The maximum yields for furfural and 5-hydroxymethylfurfural are 8% and 9%, respectively, based on glucose unit of cellulose. These yields are reached after 150 s of heating at 200 °C. A cellulose sample containing 0.5 mol of $ZnCl_2$/mol of glucose unit of cellulose and 5.6 equivalents of water when heated for 150 s at 200 °C produced levulinic acid as the only product in 6% yield. The $ZnCl_2$ mediated controlled degradation of cellulose at 200 °C is shown to produce useful feedstock chemicals in low yield.

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1. Introduction

In view of declining petroleum resources, researchers have embarked on the development of new technologies for the utilization of renewable biomass resources for fuels and feedstock chemicals (Bridgwater and Grassi, 1991; Grassi et al., 1990; Horne and Williams, 1996a,b). Cellulose, the most abundant form of biomass, is the target of intensive research for the conversion into useful chemicals and fuels through thermolysis studies. (Bobleter, 1994). These approaches involve direct combustion, hydrothermolysis (Bobleter, 1994; Sakaki et al., 1996), pyrolysis (Antal and Varhegyi, 1995), non-catalytic thermal degradation in supercritical water (Adschiri et al., 1993) and liquification in reactive solvents (Yamada and Ono, 1999).

Generally, cellulose degradation at higher temperatures is difficult to control and is known to give large amount of chars. Therefore, the attention has shifted to acid catalysis (Adschiri et al., 1993; Bobleter, 1994; Mok et al., 1992) and the use of metal ions to facilitate the breakdown and subsequent transformations. Nanopowder metal oxides (Fabbri et al., 2007) and aluminum ions supported on mesoporous silica (Al-MCM-41) (Adam et al., 2005) are also known to facilitate the controlled pyrolysis of cellulose. A complex mixture of products with furfural, 5-hydroxymethylfurfural (HMF) and furfural alcohol are formed in Al-MCM-41 catalyzed reactions. Pyrolysis of willow coppice in the presence of potassium ions has been shown (Nowakowski et al., 2007) to give similar furan mixtures as well. Seri et al. (2002) reported a significant lowering of cellulose pyrolysis temperature to 250 °C with added $LaCl_3$, and HMF was identified among the products.

Magnesium chloride is also known to promote the breakdown of cellulose at temperatures as low as 105 °C when heated for longer periods like 24 h, and a small amount of HMF was isolated as a product (Shimada et al., 2007). This breakdown of the cellulose was explained (Shimada et al., 2007) to result from chelation of Mg^{2+} with glycosidic oxygen. Even though found in small yields, furan derivatives such as furfural and HMF (Lewkowski, 2001) are formed as the major products in this metal catalyzed pyrolysis at relatively low temperatures. These furans can be considered as practical renewable resources based feedstock materials useful in the replacement of some fossil raw materials (Corma et al., 2007; Gandini and Belgacem, 1998; Lichtenthaler, 2002). Particularly, HMF is a very useful bifunctional heterocyclic system (Lewkowski, 2001) that can be transformed to a number of chemicals. The current preparation of HMF involves the dehydration of less abundant fructose (Román-Leshkov et al., 2006), and a direct preparation from abundant polysaccharides would be a very attractive proposition.

Williams and Horne (1994) studied the effect of a variety of metal salts on the cellulose pyrolysis using thermogravimetric – differential thermal analysis (TG-DTA), without the analysis of the products and showed that a number of metal salts are effective in lowering the degradation temperature. This effect is small in catalytic reactions and significant lowering can be seen at higher loadings of certain metal ions. Careful analysis of Williams and Horne's TG-DTA data revealed that Zn^{2+} ions at 5% loading is the most effective in lowering the cellulose degradation temperature (Williams and Horne, 1994), so we have selected to study the effect

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of further increasing the amount of $ZnCl_2$. In this communication we describe the effect of non-catalytic amounts of $ZnCl_2$ in further lowering the pyrolysis temperature and identification of the products formed at 200 °C under different reaction conditions.

2. Methods

2.1. Materials

Filter paper (Whatman No. 1, oven dried at 105 °C for 24 h) shredded into fine strips was used as the cellulose samples. A $ZnCl_2$ stock solution (1.00 M) was prepared by dissolving anhydrous $ZnCl_2$ (Fluka, ACS Analytical grade) in deionized water. ^1H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury plus spectrometer operating at 400 MHz and thermogravimetric analysis was carried out on a Perkin–Elmer Diamond TG/DTA system. Recovered Zn was determined on a Varian Spectra AA 220FS atomic absorption spectrometer using an air-acetylene flame. Error bars in Fig. 1 are drawn using Microsoft Excel error bar calculator.

2.2. The effect of $ZnCl_2$ concentration

Four $ZnCl_2$ impregnated cellulose samples were prepared by slowly adding 0.10, 0.20, 0.40 and 0.50 mL of $ZnCl_2$ (1.00 M) solutions via a syringe to celluloses samples of 0.162 g, (1.0 mmol of glucose unit of cellulose) each on watch glasses. The samples were stirred with a glass-rod during the addition of $ZnCl_2$ solution to assure even impregnation of $ZnCl_2$. These were then air-dried at room temperature by keeping in a fume hood for 24 h, providing cellulose samples impregnated with $ZnCl_2$ (0.1, 0.2, 0.4 and 0.5 mol/mol of glucose unit of cellulose). Thermogravimetric analysis was performed in air using 8–10 mg portions of these samples in the temperature range 20–620 °C to determine the initial degradation temperatures and the results are shown in Table 1. The initial degradation temperature was measured as the temperature range that corresponds to 90–70% weight loss in the thermogravimetric analysis curve. A cellulose sample without added $ZnCl_2$ was analyzed as the reference for the experiment.

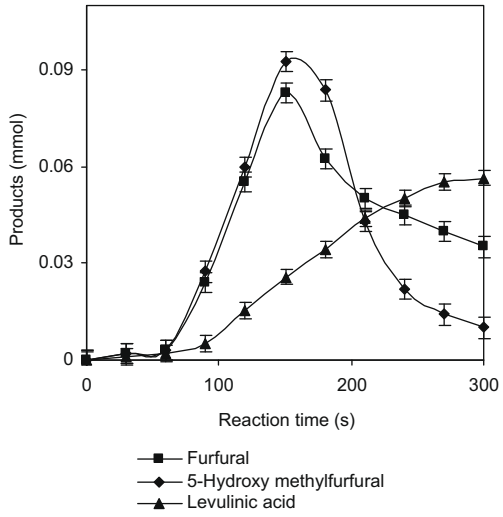

Fig. 1. Changes in the product composition during the degradation of cellulose (1.0 mmol glucose unit) containing 0.50 mmol $ZnCl_2$ at 200 °C in air.

Table 1
Change in initial degradation temperature range with the addition of $ZnCl_2$ to cellulose.

$ZnCl_2$ content (mol/mol of glucose unit of cellulose)	Initial degradation temperature range °C
0	338–354
0.1	320–340
0.2	224–256
0.4	203–248
0.5	192–238

2.3. The effect of reaction time

A $ZnCl_2$ impregnated cellulose sample was prepared by adding 5.0 mL of $ZnCl_2$ (1.00 M) solution via a syringe to cellulose (1.620 g, 10 mmol of glucose unit of cellulose) on a watch glass. This sample was then air-dried at room temperature for 24 h in a fume hood and divided into 10 equal portions by weighing and transferred into 10 glass reaction tubes and sealed to give 10 equal samples of cellulose impregnated with $ZnCl_2$ (0.5 mol/mol of glucose unit of cellulose). Reactions were carried out by immersing the reaction tubes in a preheated oil bath at 200 °C for a specific time and cooling in water to terminate the reaction after the specific period. The cooled tubes were opened and the contents were repeatedly extracted with CH_2Cl_2 (3×10 mL) and then the filtered CH_2Cl_2 extracts were concentrated under reduced pressure at 40 °C. Residue after evaporation of the solvent was analyzed by recording proton NMR spectrum in $CDCl_3$. Products were identified by comparison of the NMR data with NMR spectra of authentic samples of furfural, 5-hydroxymethylfurfural and levulinic acid. The quantitative analysis was performed by standard addition method using authentic samples and manual integration of the ^1H NMR peaks. This experiment was duplicated and the average number of mmoles of products formed per 1.0 mmol of glucose unit of cellulose during the course of the reaction is plotted in Fig. 1.

2.4. The effect of added water

A $ZnCl_2$ (0.5 mol/mol of glucose unit of cellulose) impregnated cellulose sample was prepared from 0.162 g of cellulose as described in Experiment 2.3 and transferred to glass reaction tube and water (0.10 mL, 5.6 mmol) was added and sealed. The reaction was carried out by immersing the reaction tube in a preheated oil bath at 200 °C for 150 s and cooling in water to terminate the reaction, which was worked out and the contents were analyzed as described for the samples in the Experiment 2.3. Proton NMR analysis showed that the only product formed is levulinic acid (0.06 mmol, 6% yield based on glucose unit of cellulose).

2.5. Recovery of $ZnCl_2$ from the reaction and analysis of char produced in the degradation of cellulose

A $ZnCl_2$ (0.5 mol/mol of glucose unit of cellulose) impregnated cellulose sample was prepared from 0.81 g of cellulose as described in the Experiment 2.3 and transferred to a glass reaction tube and

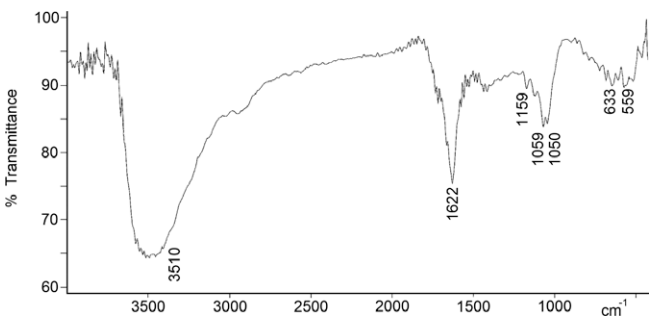

Fig. 2. FT-IR spectra of the char formed in the pyrolysis of $ZnCl_2$ (0.5 mol/mol of glucose unit of cellulose) impregnated cellulose at 200 °C for 150 s.