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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.

Keywords

cellulose; pyrolysis; zinc chloride; 5-hydroxymethylfurfural

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 (Bridgewater and Grassi, 1991; Grassi et. al., 1990; Horne and William, 1996a; Horne and William, 1996b). 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; Sakakai 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 (Fabri et. al., 2007) and aluminum ions supported on mesoporous silica (Al-MCM-41) (Adam et. al., 2007) are also

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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 hrs, 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 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 and methods

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 400MHz 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 the figure 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 hr., 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 to 10 mg portions of these samples in the temperature range 20 to 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.

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 hr. in a fume hood and divided into ten equal portions by weighing and transferred into ten 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 figure 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 sealed. The reaction was carried out by immersing the tube in a preheated oil bath at 200 °C for 150 s and cooling in water to terminate the reaction. The resultant charred product was repeatedly washed with CH_2Cl_2 (3×25 mL) to remove furfural, HMF and levulinic acid formed. Then residue was dried in vacuum at room temperature for 24 hr. to remove the traces of CH_2Cl_2 and the resultant char was transferred to an Erlenmeyer flask and magnetically stirred with 25 mL of 1.0 M aqueous HCl at room temperature for 3 hr., and then the aqueous acid layer was separated by centrifugation of the solution. The char residue was repeatedly extracted with two more 25 mL portions of 1.0 M aqueous HCl and the combined acid layer was transferred to a 100 mL volumetric flask and diluted with distilled water to make 100 mL of recovered zinc solution. The $[\text{Zn}^{2+}]$ in this solution was determined using atomic absorption spectroscopy employing the standard curve method. Duplicate experiments recovering zinc, using aqueous acid extraction yielded 82% recovery of the zinc chloride. The resulting char residue was dried under vacuum for 24 hr. at room temperature to give 0.36 g (44 % yield, average of two experiments) of char, which was analyzed by FT-IR spectroscopy to investigate the nature of the char formed, and this IR spectrum is shown in figure 2.

3. Results and discussion

Initial degradation temperatures (Table 1) of the cellulose were measured for 90 to 70% weight loss in the sample from the thermogravimetric analysis curve, and this result showed that increasing the ZnCl_2 molar ratio decreases the degradation temperature. The sample containing 0.5 mol of ZnCl_2 /mol of glucose unit of cellulose showed the lowest initial degradation temperature range of 192 to 238 °C, which is about 130 °C reduction in the average temperature compared to pure cellulose (338 to 354 °C). Product analysis during the course of the reaction was performed for cellulose containing 0.50 mol of ZnCl_2 /mol of glucose unit by heating at 200 °C in air and the results are shown in figure 1. The samples heated for 30 and 60 s remained white without any decolorization and the CH_2Cl_2 extract of the cellulose after the reaction did not leave any residue after evaporation of the solvent, showing that no significant degradation occurs in the first 60 s of the reaction. Samples heated for more than 60 s showed gradual darkening from brown to black chars. Proton NMR spectra of the extracted samples showed the formation of three products: furfural, 5-hydroxymethylfurfural and levulinic acid with minute amounts of unidentifiable products. These unidentifiable minor products constitute less than 1% of the total products in the mixture. Gradual increase of the three major products were observed for the period of 60 to 150 s and the maximum yields of furfural, 5-hydroxymethylfurfural were observed as 8 and 9 % respectively at 150 s (Figure 1). 5-Hydroxymethylfurfural concentration rapidly decreased during the 150 to 300 s period and this is probably due to the decomposition of 5-hydroxymethylfurfural to levulinic acid. Similar decomposition of HMF to levulinic acid is known (Horvat, 1985) in mineral acids as well. The optimum yields of 0.083 mol of furfural and 0.0925 mol of HMF per mol of glucose unit in cellulose were produced at 150 s of reaction, and in addition to this 0.0258 mol of levulinic acid was also formed during this time. Therefore a total of 0.2013 mol of products are formed per mol of glucose unit, and which can be expressed as 20.13 % degradation cellulose into non-gaseous products.

The proposed mechanism for the ZnCl_2 mediated degradation of cellulose is shown in figure 3. In the initial step of the mechanism coordination of glycosidic oxygen of cellulose with zinc, which is acting as the Lewis acid would help the breakdown of the glycosidic linkage. This oxygen-zinc coordination could lower the activation energy of the reaction, thus lowering the reaction temperature to 200 °C. It is reasonable to expect that ZnCl_2 in the impregnated cellulose sample exists in the hydrated form, where 3.2-3.6 water molecules exists in the coordination sphere of the Zn^{2+} ions (Salmon, 1989). Hydrolysis of the cellulose to glucose is shown in the second step of the mechanism, where these coordinated water molecules from the hydrated ZnCl_2 participates as a nucleophile to give D-glucose. It is well known that dehydration of D-glucose at higher temperatures gives mixtures of furfural and 5-hydroxymethylfurfural. Paine et. al. (2008) has recently proposed a common mechanism for this complex dehydration process during the pyrolysis of D-glucose using ^{13}C labeled D-glucose. This mechanism can explain the production of furfural and 5-hydroxymethylfurfural as secondary products in this reaction. Decomposition of HMF to levulinic acid at high temperature is also well known (Girisuta et. al., 2006; Horvat, 1985) and the gradual formation of levulinic acid is also observed as a result of this reaction. Reaction mixtures analyzed for D-glucose or other reducing sugars failed to produce any positive results, indicating that D-glucose readily dehydrates to secondary products observed.

Sample with added water produced levulinic acid in 6% yield as the only non gaseous product. We have demonstrated that 82% of the ZnCl_2 used in the reaction can be recovered by extraction of the remaining char residue with dilute hydrochloric acid. The IR spectrum of the residue is shown in figure 2, which shows a strong absorption at 1622 cm^{-1} indicative of $\text{C}=\text{C}$ of polyaromatic ring systems of the polymeric compounds (Morterra and Low, 1983). The broad absorption in the region of 3510 cm^{-1} is due to OH groups in the polymeric char and

adsorbed water on the surface may also contribute to this peak. In addition to this two moderate absorptions at 1050 and 1059 cm^{-1} are observed for possible C-O stretching absorptions of phenoxy and aromatic ether groups. It is interesting to note that similar IR spectra were observed by Morterra and Low (1983) for a cellulose sample pyrolyzed above 350 °C, indicating that ZnCl_2 mediated pyrolysis produces a similar char at a much lower temperature of 200 °C. This lowering of the pyrolysis temperature is significant as it produces useful furan compounds from abundant biomass with lower expenditure of energy compared to the previously studied direct pyrolysis of cellulose.

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Figure 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

Figure 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

Figure 3.
Proposed mechanism for the ZnCl_2 mediated degradation of cellulose to D-glucose

Table 1Change 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