

Effect of the polymorphs of cellulose on its pyrolysis kinetic and char yield



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ABSTRACT

In this study, we show that the polymorph type of cellulose is an important factor for its pyrolysis behavior. By using TGA, XRD and FTIR, we characterized the pyrolysis kinetics and char yields of amorphous cellulose, cellulose II and cellulose I. All these celluloses with various polymorphs were regenerated from the same source material, microcrystalline cellulose; thus, the lattice difference among these samples was the only factor affecting their thermal pyrolysis. We found that the char yield of cellulose I was the highest among all cellulose polymorphs. With the addition of 5% phosphoric acid, the char yield of cellulose I at 800 °C was as high as 37.4%. The char yield of cellulose I at 800 °C is more than 10% higher than that of cellulose II regardless the addition of additives. This study highlights that the lattice structures of cellulose affects both its thermal pyrolysis kinetics and the char yield. For improving the char yield of cellulose, both structural factors and impregnated additives play independent and important roles.

1. Introduction

Cellulose is sustainable natural resources with many attractive advantages, such as biocompatibility, biodegradability, non-toxicity, good thermal/chemical stability, and low cost [1–3]. Most researches of cellulose focus on how to replace non-renewable petroleum-based materials by this almost inexhaustible material. Based on the chemical formula of cellulose, it contains 44.4 wt% of carbon elements. The potential usages for cellulose as cheap carbon precursor have been widely explored, such as carbon fibers, carbon aerogels and carbon membranes [4–7]. However, the major limitations of cellulose-based carbon materials is their low carbon yield [4]. Despite its theoretic relatively high carbon yield, the actual char yield of cellulose is only 10–30 wt% [4,8–11]. To improve the carbon yield of celluloses, researchers found that a slower heating treatment was helpful [12]. Also, impregnating cellulose with proper additives has been found as a facile and effective way to improve its char yield [10,13–22]. Many works have shown that phosphoric acid (H₃PO₄), sulfuric acid and their derivatives are effective dehydrating agents to improve the char yield of cellulose.

It's well known that cellulose has various types of polymorphs, for example cellulose I (native cellulose), cellulose II (regenerated cellulose) and more [23,24]. Due to their different packing structures, the theoretic modulus of cellulose I is 138 GPa, whereas cellulose II is only

88 GPa [25]. It is believed that the mechanical properties of carbonized cellulose I and II and their pyrolysis processes could be significantly different. For the effects of cellulose's crystalline structures on its pyrolysis, few papers reported that there were different depolymerization and pyrolysis pathways in highly crystallized region and amorphous region during thermal treatment [26,27]. For the polymorphs of cellulose, Henrique et al. studied the thermal decomposition kinetics of cellulose nanocrystals with lattice forms of cellulose I and II, and observed that both polymorph type of cellulose and the acid used for extraction affected the thermal decomposition kinetics of the nanocrystals [28]. Mukarakate et al. treated cellulose powder by H₃PO₄ and NaOH to regenerate cellulose with different polymorphs and crystallinities, and found that both crystallinity and polymorphs of cellulose affected the primary products during fast pyrolysis [29]. However, due to their varied sources and treatment methods, many factors which could affect the pyrolysis of cellulose were unable to be ruled out, such as molecule weight, crystallinity and functional groups. How the polymorph and crystallinity of cellulose would affect its char yield with and without the impregnation of proper additives is an important question, but is still unclear. In this study, we tried to find out how the lattice structures or polymorphs of cellulose affected its pyrolysis and char yield. We regenerated cellulose with various lattice structures including cellulose I, cellulose II, and amorphous cellulose, from same source material, microcrystalline cellulose (MCC). The regenerated

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cellulose had the exactly same molecule weight and chemical structures (there are no different functional groups in the regenerated cellulose), except for different lattice structures. Thus, the cellulose structure would be the only factor affecting the pyrolysis and char yields of these celluloses. Additionally, we chose H_3PO_4 as impregnated chemical, and studied the pyrolysis and char yields of different polymorphs of cellulose with the addition of H_3PO_4 . Our results would be helpful to answer how the physical or lattice structures of cellulose affect its char yields without and with additives, and suggest how to further tune cellulose's structures to improve its char yield.

2. Experimental

2.1. Materials and sample preparation

H_3PO_4 (AR) was purchased from Sinopharm Chemical Reagent co. Ltd. (Beijing, China). Deionized water ($> 15 \text{ M}\Omega$) was prepared by an ultra-pure water system (model ROP-15L, Heal Force Bio-Meditech, Shanghai, China). MCC (cotton linter) was purchased from Henan Henrui Food Additive Ltd Corp. (Zhengzhou, China). The amorphous, type I and type II celluloses were prepared from the MCCs and the detailed procedures were described elsewhere [30]. For the impregnation of cellulose samples with H_3PO_4 , the concentrated H_3PO_4 solution was first diluted to 1% by deionized water; then, cellulose samples (grinded powder form) were soaked with certain amount of the diluted acid solution (acid/cellulose wt/wt 5/95); finally, the soaked cellulose was vacuum dried at 60°C for 24 h.

2.2. Characterizations

The structural parameters of cellulose samples were measured by X-ray diffraction (XRD, Bruker D8 Advance, German) at a 2θ scanning speed of $4^\circ/\text{min}$. The obtained XRD curves were analyzed by Jade software. The crystallinity (CI) of type I or type II cellulose was calculated by Segal method [31] or Revol method [32] as shown in Eqs. (1) and (2), respectively.

$$CI_{\text{TypeI}} (\%) = \frac{I_{002} - I_{18}}{I_{002}} \times 100\% \quad (1)$$

$$CI_{\text{TypeII}} (\%) = \frac{I_{110} - I_{15}}{I_{110}} \times 100\% \quad (2)$$

Where, I_{002} is the peak intensity of the (002) planes of cellulose I, I_{110} is the peak intensity of the (110) planes of cellulose II, I_{18} and I_{15} are the diffraction intensity of amorphous cellulose at 2θ of 18° and 15° , respectively. X-ray Photoelectron Spectroscopy (XPS) were carried out on a Kratos Analytical Axis Ultra DLD spectrometer (Shimadzu Corporation Kratos Ltd., Japan) equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) operated at 25 kV. The measurements were conducted under vacuum lower than 2×10^{-10} mbar. High-resolution spectra of C1 s and O1 s were performed using the CasaXPS program. The C1 s (C–C) peak at 284.8 eV was used to check the binding energy scale. Thermal gravimetric analysis (TGA) was measured with a Netzsch STA409C thermogravimetric analyzer (NETZSCH, German). Approximately 10 mg of samples were heated from ambient temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen environment. When the cellulose samples began to decompose, the crossing temperature of tangents to two branches of the TGA major loss curve was defined as initial temperature (T_{ini}), the mass loss rate reached its maximum was referred as the maximum weight loss rate (DTG_{max}) and this temperature was defined as the maximum mass loss temperature (T_{max}). The Fourier transform infrared spectra (FTIR) were measured by IR spectroscopy (Bruker Vertex 80 v, USA) under vacuum circumstance. Raman spectra were performed by using a $\lambda = 532 \text{ nm}$ (2.33 eV) diode laser source operating at 25 mW and a Holoprobe Kaiser optical spectrometer equipped with a holographic notch filter and CCD camera.

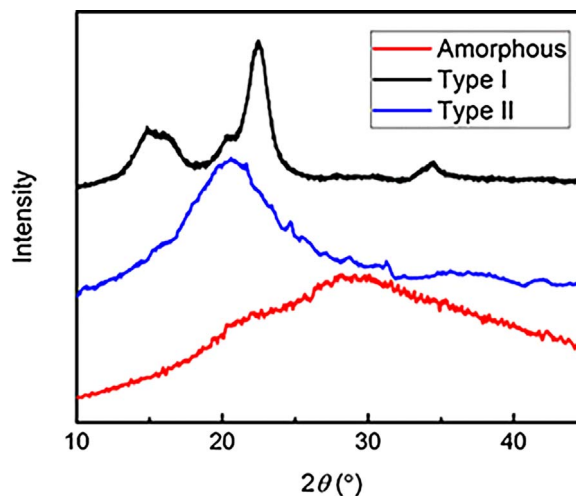


Fig. 1. XRD curves of all celluloses used in this study.

Data were collected for 30 s over a range of $500\text{--}4000 \text{ cm}^{-1}$.

3. Results and discussion

3.1. Effect of the polymorphs of cellulose on its char yields

The cellulose I (type I), cellulose II (type II) and amorphous cellulose (AM) were all regenerated cellulose from the same source MCC. The regeneration involved no chemical changes, and the only difference between these regenerated celluloses was their different lattice structures. The XRD curves of these regenerated celluloses are shown in Fig. 1.

The thermal decomposition behaviors of all celluloses were measured by TGA, and their TGA and DTG curves without and with the addition of H_3PO_4 are plotted in Fig. 2. The crystallinity of these celluloses, TGA data, and char yields at 800°C are summarized in Table 1. The major weight loss occurred in the temperature range between 180 and 400°C . Comparing the pyrolysis behaviors of neat celluloses, the amorphous cellulose showed two types of pyrolysis behaviors based on its DTG curve (Fig. 2B1). The temperature of the maximum weight loss (T_{max}) of the celluloses followed the sequence of cellulose I < cellulose II < amorphous. The differences in thermal decomposition processes indicate that the three regenerated cellulose have different dehydration and depolymerization characteristics. The char yields of the celluloses followed the opposite orders, the char yield of the amorphous cellulose was the lowest, 16.5 wt%, increased to 18.2 wt% for cellulose II, and to 19.5 wt% for cellulose I. The char yield of the cellulose I was 18.2% higher than the amorphous cellulose, and was 7.2% higher than the cellulose II. As it is well known, cellulose is composed by linearly connected β -(1-4) glycosidic groups, and hydroxyl groups readily form inter and intramolecular hydrogen bonding. The cellulose I are packed in a parallel orientation and all hydroxymethyl groups are positioned in *tg* conformation; whereas, hydroxymethyl groups of cellulose II are in *gt* conformation [33]. The different conformations of hydroxymethyl groups lead to different intra- and intermolecular hydrogen bonding, and this structural change could possibly affect the dehydration and depolymerization reactions of cellulose during pyrolysis and lead to different char yields. Additionally, because of their conformation differences, cellulose I has a much higher modulus (140 GPa) than cellulose II (90 GPa) than amorphous cellulose ($< 20 \text{ GPa}$). Regarding their different mechanical properties and crystalline structures, the carbon materials produced from these celluloses are expected to have different yields, structures and mechanical properties.

Although the theoretic char yields of cellulose is 44.4 wt%, the actual char yields of neat cellulose was lower than 20% regardless its

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