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Thermogravimetry–mass spectrometry on the pyrolysis process of Lyocell fibers with and without catalyst

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Abstract

We analyzed the pyrolysis behaviors of Lyocell fiber, a novel man-made cellulosic fiber, with and without catalyst, using thermogravimetry–mass spectrometry (TG–MS) coupling technology. The temperature for maximum weight loss in the control Lyocell fibers was between 260 and 340 °C, and the fibers were completely decomposed at 460 °C. The temperature for maximum weight loss in the catalyzed fibers shifted to 130–300 °C, and 11% of the weight still remained at 460 °C. With TG–MS, we monitored the evolution profiles of several volatile compounds: hydrogen (H_2, $m/z = 2$ a.m.u.), methane (CH_4, $m/z = 16$ a.m.u.), water (H_2O, $m/z = 18$ a.m.u.), carbon monoxide (CO, $m/z = 28$ a.m.u.), methanol (CH_3OH, $m/z = 32$ a.m.u.), carbon dioxide (CO_2, $m/z = 44$ a.m.u.), and ethanol (C_2H_5OH, $m/z = 46$ a.m.u), and found three of them – H_2O, C_2H_5OH and CO_2 – depended strongly on temperature during the pyrolysis. In addition, we concluded that weight loss was attributed to the evaporation and/or volatilization of H_2O, C_2H_5OH and CO_2, which benefits the removal of hetero-atoms, such as hydroxyl groups from the cellulosic rings during the carbon formation. We also proposed possible reaction mechanisms for the removal of water. Interestingly, C_2H_5OH and CO_2 presented similar MS signal changes, implying that they were synchronously generated during pyrolysis. All results indicated that the catalyst positively altered and accelerated the pyrolysis and increased the carbon yield.

Keywords: Lyocell fiber; Pyrolysis; TGA; Mass spectroscopy; Carbon fiber

1. Introduction

Lyocell cellulose fibers are characterized by a round, uniform, and dense cross-section, with high crystallinity and chain orientation. Compared to the conventional rayon precursor materials, their mechanical properties, including tensile strength and tensile modulus, are superior (Wu & Pan, 2002), so that the Lyocell based carbon fibers (CF) are expected not only to maintain the advantages of the rayon-based carbon fibers but also to have mechanical properties better suiting the requirements of advanced composite materials. However in our previous work, the strength of the Lyocell-based carbon fiber was much lower than expected (Wu, Gu, Gong, & Pan, 2006; Wu, Gong, Zhang, & Pan, 2007; Wu & Pan, 2002). One possible reason for this low strength is that the heat-treating conditions we used were not suitable for Lyocell owing to its higher degree of fibrillation or more densely packed structure.

The whole process of converting the Lyocell precursor to carbon fiber can be divided into two main stages: pyrolysis (thermal decomposition, <400 °C), a more complex and important stage (Tang & Bacon, 1964; Watt and Perov, 1985), and carbonization (high-temperature treatment, >400 °C). A more thorough investigation of the thermal stability, and decomposition of Lyocell fibers under a wide range of conditions is desirable to produce carbon fibers with better quality, by resorting to, for instance in this paper, the thermogravimetry–mass spectrometry (TG–MS).

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TG–MS spectrometry is a suitable tool for studying the mass change during the pyrolysis and carbonization processes, and has been used in a wide variety of qualitative and quantitative studies of the thermal degradation of polymers, the identification of pyrolysis products, and the thermal decomposition mechanisms (Raemakers & Bart, 1997). In determining and measuring individual gaseous species released during a process evolving over time, TG–MS technique is highly preferred when compared to TG alone, which is only able to measure the total volatile as a single group (Liu, Lv, Yang, He, & Ling, 2005; Statheropoulos & Kyriakou, 2000).

In this work, we used quantitative TG–MS to simultaneously track the evolution profiles of decomposed products during heat-treating process of Lyocell at temperature range from room temperature to 600 °C. The main purpose of this research is to trace the reactions that may occur as Lyocell is been converting to carbon fiber, which will help us explore the mechanisms for such pyrolysis process and thus optimize the heat-treating conditions including the temperature and exposing duration so as to improve the strength of carbon fibers.

2. Experimental

2.1. Samples

The detailed information on the Lyocell precursors used was provided in our previous publications (Wu & Pan, 2002; Wu et al., 2006). Two kinds of samples were prepared: the control Lyocell fibers and catalyzed Lyocell fibers, the latter being pre-treated in an acid aqueous solution containing certain amount of Lewis acid and amine salt; more specifically, we have employed sulfuric acid and urea correspondingly in this study.

2.2. The TG–MS instrumentation

A simultaneous thermal analyzer (Netzsch-STA449, Germany) coupled with a quadruple mass spectrometer (Balzers QMG511, Switzerland) was applied for the TG–MS analysis. First, two samples, the control Lyocell and catalyzed Lyocell, were heated at 80 °C in vacuum for 48 h to release physically adsorbed water in the fibers. Then, about 4 mg of each sample was heated from ambient temperature up to 600 °C at heating rate of 5 °C/min in air in a TG furnace. Mass spectrometry settings were: mass scan speed, 1 a.m.u/s; mass filtering time, 0.03 s; and the vacuum of system under 2.67 mPa.

3. Results and discussion

3.1. TG and DTG analysis

The TG curves for both the control and catalyzed Lyocell samples more or less have a reversed S-shape (Fig. 1). Each TG curve consists of four regions of weight loss at different temperature ranges (Table 1). Weight loss begins after the fibers experience heat. Until up to 130 °C, both the control and catalyzed samples exhibit similar thermal characteristics, the weight loss of each sample being about 8–10% w/w, consistent with previous data (Tang & Bacon, 1964; Watt and Perov, 1985). This loss is mainly the result of eliminating the residual of the physically adsorbed water from the precursors, for the major portion of the physically adsorbed water was released already during the sample preparation.

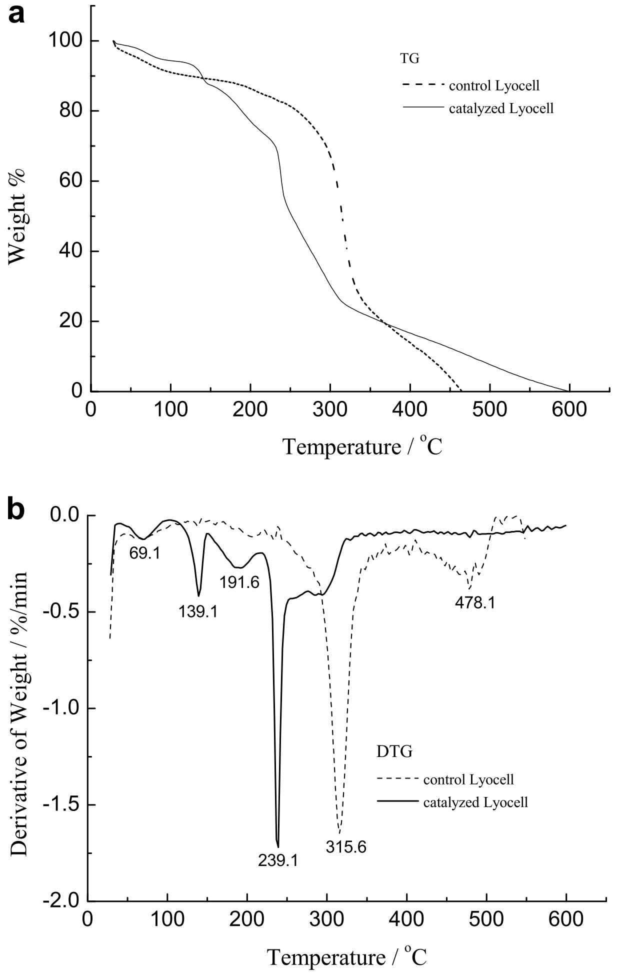


Fig. 1. (a) TG and (b) DTG curves of control Lyocell (- - -) and catalyzed Lyocell (—).

Table 1
The temperature and weight loss percent of TG

	First stage	Second stage	Third stage	Fourth stage
Control Lyocell				
Temperature/°C	30–150	150–260	260–340	340–460
Curie point/°C	70	200	315	475
Weight loss/%	10	9	61	20
Catalyzed Lyocell				
Temperature/°C	30–130	130–225	225–300	300–600
Curie point/°C	69	139	239	305
Weight loss/%	8	22	48	22

Once the temperature arises to 130 °C, the difference between the TGA curves of the two precursors becomes obvious. Weight loss for the control Lyocell continues from 130 to 260 °C at the slow speed, then a considerable loss, almost 61%, appears at the range from 260 to 340 °C, followed by a 20% loss from 340 to 460 °C. The maximum loss rate appeared around 315 °C, according to the accompanying DTG curve. However, the catalyzed sample shows a more rapid pyrolysis response, with a 22% weight loss from 130 to 225 °C, the maximum loss occurring at 239 °C and the total loss reaching 78%, leaving a solid residue of 11% at 460 °C, at which the control Lyocell is 100% burned off.

Meanwhile the DTG curve of the catalyzed Lyocell shows three visible minor peaks at 69, 139 and 190 °C, no such presence in the control Lyocell curve, indicating that the catalyst indeed influences the pyrolysis reactions. Although extensive research has shown that the chemical reactions taking place during cellulose pyrolysis were too complex to be described clearly (Tang & Bacon, 1964; Watt and Perov, 1985), it is apparent that the catalyst we selected accelerates the pyrolysis process of Lyocell fibers, lowering the temperature of maximum mass loss shift and thus resulting higher yield of carbon at a given ending temperature. This finding confirms that the catalyst is effective in facilitating the conversion process from the Lyocell precursor to carbon fiber. This quantitative analysis obtained from TG/DTG may serve as a basis for kinetic analysis, which will be addressed in our future work.

Lyocell fiber is a cellulosic material (Wu & Pan, 2002) whose repeat unit contains hydrogen and oxygen, each releasing five molecules of water, and hence giving a weight loss of 55.5% during pyrolysis, based on the reaction formula (1).

$$(C_6H_{10}O_5)_n \xrightarrow{\Delta} 6nC + 5nH_2O \quad (1)$$

However, more than 55.5% of the total weight loss is observed in both the control and the catalyzed samples, revealing the occurrence of other reactions physical or chemical responsive for causing other mass loss. Like many celluloses, for Lyocell fiber the main chemical processes take place during the pyrolysis stage, where the maximum loss of mass and greatest changes occur in structural, mechanical, and physicochemical properties. Although our TG–DTG analysis so far has confirmed the maximum mass loss and our previous research (Wu et al., 2007) found notable changes in the structure and properties at this stage, we would like to examine in detail such specific changes and reactions as deprivation of water, alcohol and light gases, by means of the MS investigation.

3.2. The mass spectrometry detection

Cellulose pyrolysis occurs in two consecutive major reactions: dehydration and depolymerization. Dehydration reaction results in the formation of CO, CO_2, H_2O, and the other (carbonyl or organic acid) volatiles through intra-ring scission of the glucose unit in the cellulose chain (Pappa, Mikedi, Tzamtzis, & Statheropoulos, 2003; Price, Horrocks, Akalin, & Faroq, 1997; Scheirs, Camino, & Tumiatti, 2001), whereas depolymerization occurs at higher temperature level and releases chemicals like transglycosylation and 1,6-anhydro-β-D-glucopyranose (levoglucosan), along with some gaseous fraction containing CO, CO_2, and heavy oil fraction containing other volatile materials. Although depolymerization is ineluctable during the pyrolysis, researchers (Julien, Chornet, & Overend, 1993; Pappa et al., 2003; Tang & Bacon, 1964; Watt and Perov, 1985) strive to reduce the chances of forming such negative byproducts as levoglucosan, which debase the properties of the resulting carbon fibers.

From the gas evolution profiles, we obtained information about the starting formation temperature, the completion temperature, the maximum formation temperature, as well as the sequence of formation of products. In this work, the evolution profiles of 7 compounds, hydrogen (H_2, $m/z = 2$), methane (CH_4, $m/z = 16$), water (H_2O, $m/z = 18$), carbon monoxide (CO, $m/z = 28$), methanol (CH_3OH, $m/z = 32$), carbon dioxide (CO_2, $m/z = 44$), and ethanol (C_2H_5OH, $m/z = 46$) were monitored simultaneously during the pyrolysis of the samples. However, only three volatiles – water, ethanol, and carbon dioxide – have shown noticeable changes in weight with temperature. Liu et al. (2005) also found that the MS signals of H_2O and CO_2 changed, reaching their maximums during the pyrolysis of a wood-derived rayon fiber, but did not detect any change in C_2H_5OH. Here, we will specifically illustrate the deprivation of hydroxyl group and atoms C and O through volatilization of H_2O, CO_2 and C_2H_5OH, so as to examine the reactions more carefully.

3.2.1. –OH deprivation by volatilizing water

The ion intensities of H_2O for both the control and catalyzed Lyocell samples in Fig. 2 have exhibited

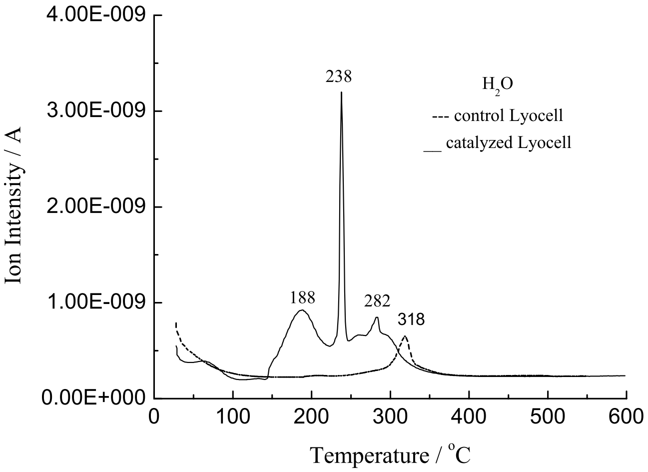


Fig. 2. H_2O evolution curves during pyrolysis process in air (- - - control Lyocell and — catalyzed Lyocell).

fluctuations, confirming the evolution of water during the pyrolysis. In the control Lyocell case, only one characteristic peak appears in the range of 290–340 °C, with a maximum at 318 °C. This temperature range is close to what reported by Scheirs et al. (2001). Comparing Fig. 1 with Fig. 2, it is easy to see that the temperature range (290–340 °C) and peak (318 °C) of the H_2O MS change basically correspond to those during weight loss (range = 260–340 °C; peak = 315.6 °C), indicating that dehydration reaction is a main contributor to weight loss when no catalyst present.

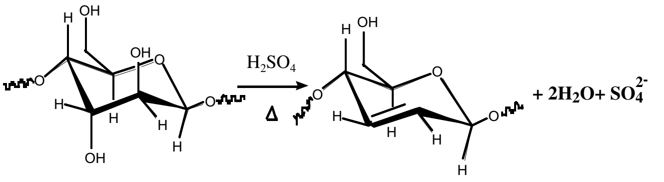
Scheirs et al. (2001) also summarized the mechanisms of water evolution from cellulose in three distinct temperature regions: (1) loss of absorbed water at low temperatures (<220 °C), (2) loss of chemical water at moderate-to-high temperature range (220–550 °C), and (3) loss of chemical water at high temperatures (>550 °C). In this work, the main MS change of H_2O occurs around 290–340 °C, indicating that water is evolved mainly via the chemical dehydration because the physical adsorbed water has largely been released during the pre-drying process before the TG–MS detection.

When the catalyst is introduced to the precursor however, multiple peaks are found at several temperature ranges: the first one appears around 140–220 °C; the second one, the narrowest and highest, occurs at 220–250 °C, with a maximum at 238 °C; the third one appears at 270–290 °C. When compared with the weight loss results, the first peak temperature range, 130–225 °C, corresponds with that of the second stage in weight loss (Table 1), and the second peak has the quite similar maximum temperature, 238 °C, to that for the maximum weight loss (Fig. 2). Such correspondence in temperature (in both the control and catalyzed Lyocell cases) proves further that the evaporation/volatilization of H_2O is mainly responsible for the sample weight loss. This result agrees as well with other studies that water accounts for the highest proportion in weight relative to other products generated, such as CO_2 (Degroot, Pan, Rahman, & Richards, 1988).

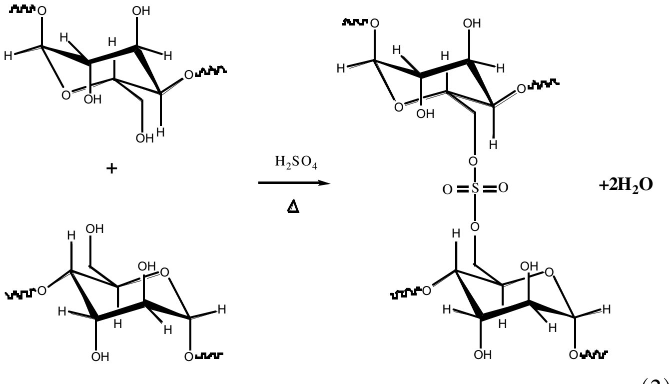
It is instructive to also compare the catalyzed sample with the control one. With the catalyst, the onset of dehydration and the maximum rate of the water loss are shifted to the region of lower temperature (Fig. 2). Moreover, the ion intensity of H_2O in the catalyzed sample is stronger than that in the control case, revealing that more H_2O is withdrawn from catalyzed Lyocell. The results agree with those of Cullis, Mirschler, & Khattab (1990), who investigated the actions of some sulfates as flame retardants for cellulose, and found the yield of water was increased greatly from 11.4% to 26% when cellulose was treated in a solution with pH from 7.0 to 0.5, correspondingly (Julien et al., 1993).

The mechanism how the hydrogen groups are deprived from the cellulosic rings becomes more complicated after the catalyst is introduced to the precursor. Although the detailed mechanism cannot be determined based on MS signals only, it is safe to conclude that dehydration at lower temperature diminishes the hydrogen and oxygen atoms from the cellulose molecule earlier, thus lessening the chance of depolymerization. This reduction brings about a greater carbon yield, as shown by the TG analysis.

The catalyst containing sulfuric acid provides more H^+, which attracts with hydroxyl groups to form water. In other words, the water is eliminated with the participation of the hydroxyl groups and H^+. Since these H^+ ions are more active than those H free radicals generated from the cellulosic units themselves, the water evaporates at lower temperature in the catalyzed case. Although we do not have a complete account for all the related reactions, there are at least two possible mechanisms in water elimination: via substitution reaction or inter-molecular reaction. Formula (2) suggests that the catalyst H_2SO_4 provides H^+ to deprive the –OH groups at C_2, and C_3, thus bringing about a double C bond. If however the –OH groups are from other cellulose molecules as in the case of the control sample, as shown in formula (3), an intermolecular bond is formed which leads to the conversion of linear polymers into a space-network featuring an enhanced thermal stability.



(2)



(3)

Mamleev, Bourbigot, & Yvon (2007) on the other hand believed that cross-linking competes with depolymerization so that if the cellulose is cross-linked at the beginning of pyrolysis by adding the catalyst, more light gases and char, rather than heavy molecules of tar, would be generated thus leading to a higher yield of carbon.

However, the complete picture of the water deprivation is likely to be more complicated, considering that -OH can be withdrawn from different positions, such as C_2, C_3 and C_6 simultaneously. Therefore, precisely when, where, and how water is evolved from cellulose is still uncertain (Scheirs, Camino, & Tumiatti, 2001). Additionally, other competing reactions, such as alcohol volatilization, may be involved as discussed below.

3.2.2. –OH withdrawn by volatilizing alcohols

The abundant –OH groups in the cellulosic units of Lyocell fiber also provide favorable opportunities for alcohol volatilization that competes with water deprivation. Some research has reported that methanol and ethanol are the main components of the alcohols generated (Watt and Perov, 1985), a conclusion confirmed by our study as illustrated in Fig. 3, where methanol CH_3OH does not show intensive MS signal change along with temperature, whereas ethanol C_2H_5OH behaves more actively (shown in Fig. 4).

From Fig. 4, one can easily see that the MS signals of ethanol in the control sample have two characteristic peaks, one at 275–330 °C with central point at 318 °C and a second appearing at 405–500 °C with a maximum at 475 °C. These changes are different from those of water, which has only one peak at 290–340 °C. Eliminating ethanol from the cellulosic ring leads to the ring opening because ethanol contains two C atoms. The temperature range of the first MS peak of ethanol mostly covers the range of water peak, indicating that hydroxyl groups in cellulosic rings provide random chances to form either water or ethanol. The second peak of ethanol at the higher temperature where no water MS is detected, indicates that more cellulosic ring cleavage happens at higher temperature.

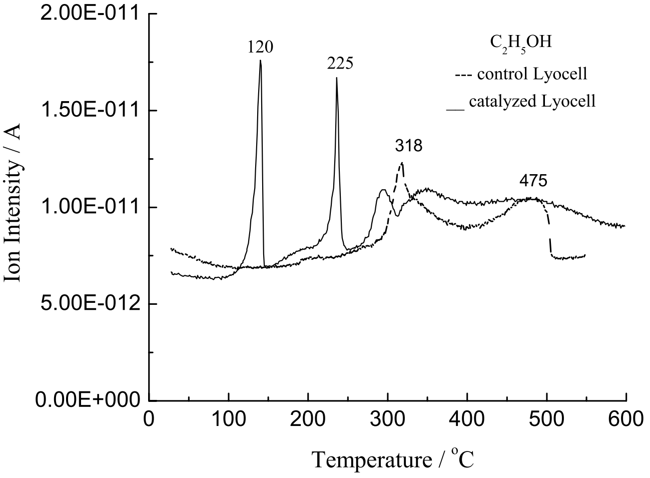


Fig. 4. C_2H_5OH evolution curves during pyrolysis process in air (- - - control Lyocell and — catalyzed Lyocell).

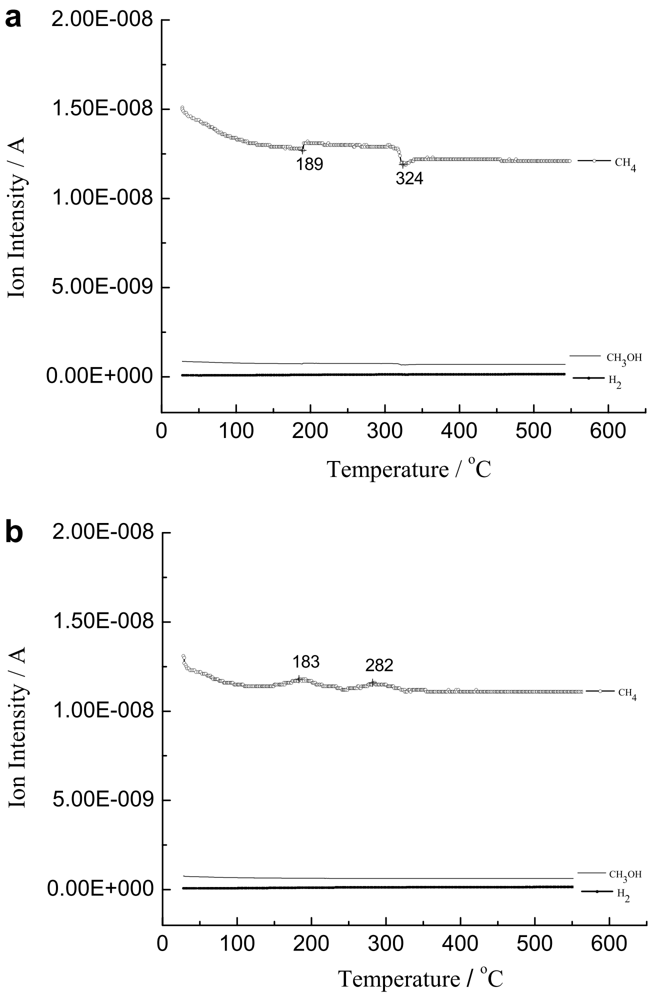


Fig. 3. Evolution curves of CH4 (–◦–), H2 (–•–) and CH3OH (—) for (a) control Lyocell and (b) catalyzed Lyocell.

In case of the catalyzed Lyocell, the first two MS peaks of ethanol appear at 110–145 °C and at 210–245 °C, earlier than those in the control Lyocell, respectively, revealing that the catalyst also accelerates the deprivation of ethanol, which occurs at lower temperatures and within much narrower ranges than those in control Lyocell. The MS signals still fluctuates above 250 °C, indicating that the deprivation of ethanol continues in both samples, but are relatively weak at the higher temperature range (250–400 °C), meaning that the majority of –OH groups have been withdrawn to form ethanol and water at 110–245 °C range already.

Other research has reported that if dehydration takes place later accompanied by depolymerization, starting at about 250 °C, what formed then will be predominantly levoglucosan (Liu, Lv, Yang, He, & Ling, 2005; Pappa, Mikedi, Tzamtzis, & Statheropoulos, 2003). So the early removal of –OH groups actually precludes or reduces the subsequent reaction to form the undesirable levoglucosan at or above 250 °C. Hence, some research suggested holding the temperature in the initial stages below 250 °C (Watt and Perov, 1985), whereas we show here that using a catalyst to accelerate the deprivation of –OH at lower temperature is an alternative way in improving the carbon yield.

3.2.3. Evolution of CO_2

Gases, such as H_2 ($m/z = 2$), CH_4 ($m/z = 16$), CO ($m/z = 28$), and CO_2 ($m/z = 44$), are primary gaseous products during cellulosic fibers pyrolysis. In this work, we found that the MS signals of H_2 possess negligible fluctuations at higher temperatures (Fig. 3). Both CH_4 and CO show similar changes along with temperature in the control

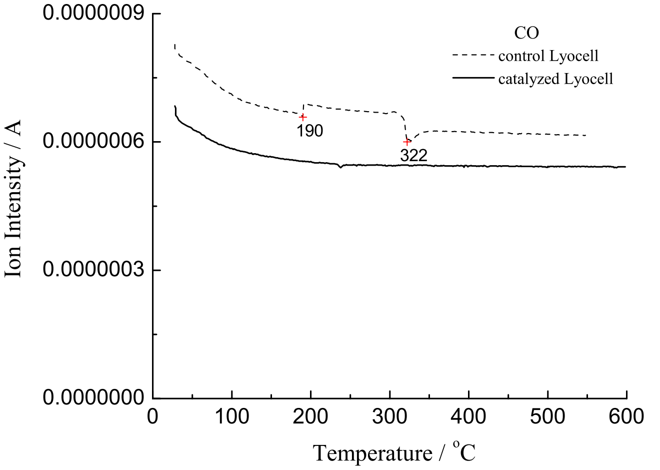


Fig. 5. CO evolution curves during pyrolysis process in air (- - - control Lyocell and — catalyzed Lyocell).

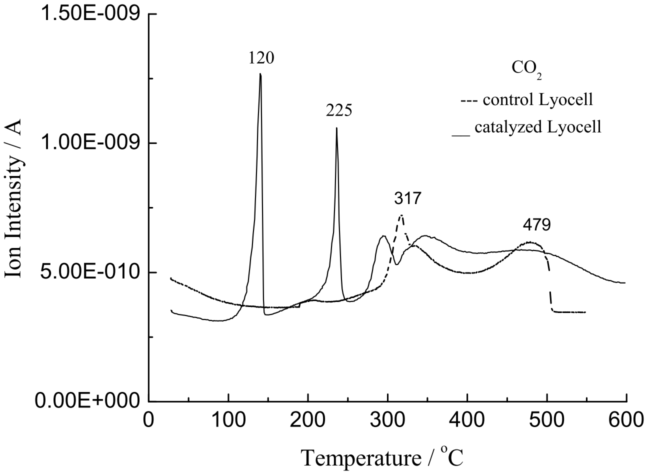


Fig. 6. CO_2 evolution curves during pyrolysis process in air (- - - control Lyocell and — catalyzed Lyocell).

Lyocell case (Figs. 3a and 5), but temperature affects the evolution of CO_2 strongly for both samples in air (Fig. 6). This effect is attributed to the presence of oxygen, by which the evolution of CO_2 seems to be favored over CO.

Interestingly, the MS signals of CO_2 present similar profiles to those of ethanol in both samples, but the H_2O profiles depict totally different pictures. Furthermore, the temperature ranges corresponding to the peaks of both CO_2 and C_2H_5OH are almost identical. The CO_2 MS peaks of the catalyzed Lyocell possess lower onset temperature and much narrower temperature ranges, again indicating that the catalyst also has the same accelerating effects on deprivation of CO_2 as it does on C_2H_5OH. This similarity indicates the concurrence of CO_2 and C_2H_5OH deprivations. As discussed in last section, the withdrawal of C_2H_5OH is related to the cellulose ring-open; therefore, the product of CO_2 also contributes to the ring-open.

Tang and Bacon (Tang and Bacon, 1964) proposed that the thermal cleavages of C–O and C–C linkages can result in the formation of large amounts of CO and CO_2, leaving a residue containing four-carbon atoms. In our work, generated CO_2 was more dominant than CO because of the supply of oxygen from air. Along with the elimination of C_2H_5OH and CO_2, a certain amount of atom C is also removed from the cellulose structure, an unfortunate yet inevitable dissipation. However, with the rings opening, oxygen and hydrogen are further eliminated from the glycoside links of the original cellulose, which benefits the conversion from the cellulose structure to the graphete (graphite-like) structure which directly affects the properties of the resulting carbon fiber.

4. Conclusions

We analyzed the pyrolysis behaviors of Lyocell fiber with a TG–MS coupling technology. During a pyrolysis process, although both the control and catalyzed Lyocell fibers undergo great weight loss, the control precursor is completely burned off at 460 °C, whereas the catalyzed one still retains 11% of the mass at the same temperature. In other words, addition of the catalyst accelerates the pyrolysis and lowers the temperature required. Our MS analysis proves that the weight loss is partly attributed to the volatilization of H_2O, C_2H_5OH, and CO_2, whose evolutions of MS signals were found to possess a much stronger dependence on temperature than those of other volatile compounds, such as H_2, CH_4, CO, and CH_3OH. We also found that C_2H_5OH and CO_2 are synchronously generated during pyrolysis, and the hydroxyl groups in the samples are withdrawn by volatilizing both H_2O and C_2H_5OH, benefiting the removal of hetero-atoms from the cellulosic rings. It can be concluded that both carbon yield and the quality can be improved with the aid of the catalyst when the hetero-atoms, such as hydroxyl group or oxygen, are removed earlier at lower temperature ranges.

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