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Catalytic mechanism of sulfuric acid in cellulose pyrolysis: A combined experimental and computational investigation

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ABSTRACT

Sulfuric acid (H_2SO_4) is widely used as a strong acid catalyst in biomass pyrolysis process, and exhibits prominent catalytic effects on the pyrolytic reactions and product distribution. In this study, the fundamental catalytic mechanism of H_2SO_4 on cellulose pyrolysis process was investigated via combined experimental and computational methods. Both thermogravimetric analysis (TGA) and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) experiments were performed to reveal the pyrolytic characteristics and product distribution in the H_2SO_4 -catalyzed pyrolysis of cellulose. In addition, quantum chemistry methods were employed to build the reaction models and investigate the major H_2SO_4 -assisted reactions in initial cellulose pyrolysis process, i.e., depolymerization of the cellulose chain, bridged dehydration, ring-opening, ring-contraction and dehydration of the free hydroxyl groups. The results indicate that the H_2SO_4 -assisted depolymerization via C1–O1 bond scission and bridged dehydration reactions take place in a two-step mechanism involving a sulfate ester intermediate. While other reactions occur via a one-step mechanism involving only hydroxyl group or both hydroxyl and sulfonic groups of H_2SO_4 . The activation energies of above reactions are all decreased by adding H_2SO_4 , and thus lowering the degradation temperature of cellulose. Among all initial pyrolytic reactions, dehydration reactions which are inconspicuous in the non-catalytic process, become very important in the catalytic process, because their activation energies are decreased dramatically by adding H_2SO_4 (from 322.7 to 372.1 to 152.2–237.7 kJ/mol). The promoting effect on the dehydration reactions plays a vital role in the increased char yield and significant change of organic volatile product distribution. Through the promoted dehydration reactions, unsaturated structures of cellulose are formed, which is favorable for the formation of certain dehydrated products at the expense of depolymerized and ring scission products.

1. Introduction

Conventional fast pyrolysis of biomass is a non-selective thermal conversion process to obtain a very complex liquid product known as bio-oil. The complex chemical composition and poor properties of crude bio-oil significantly limit its utilization in current industries [1]. In order to solve this problem, catalytic pyrolysis has been proposed as a promising way to selectively control the biomass pyrolysis process towards specific bio-oils [2,3]. Inorganic acids have been widely utilized to catalyze the biomass pyrolysis process, including H_2SO_4 [4,5], phosphoric acid (H_3PO_4) [6,7] and nitric acid (HNO_3) [8]. These acid catalysts are very effective to significantly alter the biomass pyrolysis characteristics as well as product distribution, and can be utilized to prepare value-added chemicals [7,8].

H_2SO_4 is a common strong inorganic acid, and has been widely

employed for catalytic pyrolysis of biomass and its primary components (cellulose, hemicellulose and lignin). The catalytic effect of H_2SO_4 on cellulose pyrolysis has been preliminarily elucidated as summarized by the following three aspects. Firstly, the initial decomposition temperature of cellulose will be significantly decreased by H_2SO_4 . This fact has been confirmed by previous work [7–10] according to TGA studies on the H_2SO_4 impregnated cellulose. Secondly, the promoting effect of H_2SO_4 on dehydration and charring reactions changes the yields of solid, liquid and gas products. Char and water yields increase, while that of organic liquid compounds (organic fraction of bio-oil) decreases. Such catalytic effects will be promoted along with the increase of H_2SO_4 content [8–11]. Thirdly, pyrolytic product composition will also be altered by H_2SO_4 . In regard to the liquid products, H_2SO_4 can significantly decrease the yield of levoglucosan (LG) which is the typical depolymerized product and also the most abundant pyrolytic product in

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bio-oil. Meanwhile, yields of several dehydrated products can be increased, such as 1,4:3,6-dianhydro- α -D-glucopyranose (DGP), furfural (FF) and levoglucosenone (LGO). Detailed H_2SO_4 -catalyzed product distribution generally differed in previous studies due to different impregnation methods, pyrolytic conditions and H_2SO_4 contents [7]. However, the basic conclusions were not controversial based on the fact that H_2SO_4 could promote dehydration and cross-linking reactions [12].

Currently, the published studies on H_2SO_4 -catalyzed pyrolysis of cellulose mainly paid attention to the catalytic behaviors of H_2SO_4 , neglecting deep insight into the catalytic mechanism. In regard to the catalytic center of H_2SO_4 (proton or acid ion), different viewpoints were raised. Nimlos et al. [13,14] proposed the proton-catalyzed mechanism for ethanol pyrolytic reactions based on the quantum chemistry calculation. It was found that protonated ethanol/carbohydrates would readily undergo dehydration reactions with relatively low activation energies. On the contrary, Julien et al. [8] regarded that the pyrolysis reactions were mainly catalyzed by the sulfate ion. In comparison of catalytic pyrolysis of cellulose over different inorganic acids [4–8], both similarities and distinctions exist, indicating that both the proton and the acid ion should play vital roles in influencing the pyrolytic reactions of cellulose. In addition, the stability of ions is questionable under a fluent gas condition in the pyrolysis process, especially the carrier gases (usually N_2 and He) having low dielectric constants [15]. Therefore, it is necessary to consider the global effect of the acid molecule on the cellulose pyrolysis.

In the present study, catalytic effect of H_2SO_4 on cellulose pyrolysis was investigated in detail using computational chemistry methods. Three model compounds, i.e., 1,4-dimethyl-glucose, 4-methyl-glucose and 1-methyl-glucose were selected to investigate the effect of H_2SO_4 on major cellulose initial decomposition reactions, i.e., depolymerization of cellulose chain, bridged dehydration, ring-opening, ring-contraction and dehydration of the free hydroxyl groups, as shown in Fig. 1. Structural analyses and kinetic analyses were conducted based on the computational results. Meanwhile, TGA and Py-GC/MS experiments were performed to combine with the computational investigation to give an insight into the catalytic mechanism of H_2SO_4 on cellulose pyrolysis.

2. Methods

2.1. Experimental section

2.1.1. Materials

Microcrystalline cellulose (Avicel PH-101, Sigma) was employed for the pyrolysis experiments. H_2SO_4 impregnated cellulose was prepared by the incipient wetness impregnation method [16]. H_2SO_4 solutions

with different concentrations were prepared by adding concentrated H_2SO_4 (AR, 98%) to different volumes of deionized water. Then 1 g cellulose was added to 3 ml diluted H_2SO_4 solution to obtain a gel-like paste. The mixture was treated in the KQ-500DE ultrasonic sonicator (Kunshan Utranonis Istrument, CO., LTD, 40 kHz) for 7 h. Then the sample was dried (35 °C in air for 2 h) and ground to obtain fine powders. The sample was stored in a desiccator for experiments. A total of six samples were prepared with the H_2SO_4 contents of 0 wt%, 1.0 wt%, 3.0 wt%, 5.0 wt%, 10.0 wt% and 20.0 wt%, respectively.

2.1.2. TGA analysis

TGA experiments of the H_2SO_4 impregnated cellulose samples were performed on an STA600 thermogravimetric analyzer (Perkin Elmer). The samples (10 mg) were heated from room temperature to 900 °C at a heating rate of 20 °C/min under nitrogen gas (20 mL/min).

2.1.3. Py-GC/MS Experiments

Fast pyrolysis experiments were conducted by using the CDS Pyroprobe 5200HP pyrolyzer (Chemical Data Systems) connected with a Perkin Elmer GC/MS (Clarus 560). The experimental samples were prepared by filling the cellulose sample in the middle of the quartz tube, and quartz wool was placed at both ends to hold the sample. In each sample, the quantity of the H_2SO_4 impregnated cellulose varied to ensure the pure cellulose quantity of 0.20 mg. As a result, the actual quantities of the pretreated cellulose samples were precisely weighed to be 0.20 mg, 0.20 mg, 0.21 mg, 0.21 mg, 0.22 mg and 0.25 mg, corresponding to H_2SO_4 contents of 0 wt%, 1.0 wt%, 3.0 wt%, 5.0 wt%, 10.0 wt% and 20.0 wt%, respectively. An analytical balance (XS105, METTLER TOLEDO) with a readability of ± 0.01 mg was used for weighing.

Pyrolysis was performed under 500 °C for 20 s with a heating rate of 20 °C/ms. The pyrolysis vapor went into GC/MS for analysis with carrier gas (helium, 99.999%, 1 mL/min). GC separation was achieved by an Elite-35MS capillary column (30 m \times 0.25 mm i.d., 0.25 μm of film thickness) with a split ratio of 1:80. The GC oven was heated from 40 °C to 280 °C at a heating rate of 15 °C/min, then was held at 280 °C for 2 min. The GC/MS interface was held at 280 °C. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. The chromatographic peaks were identified according to NIST library, Wiley library and the literature data. For each sample, the experiments were replicated for at least three times to confirm the reproducibility of the reported results.

2.2. Computational section

2.2.1. Computational methods

Gaussian 09 package [17] was used for all density functional theory

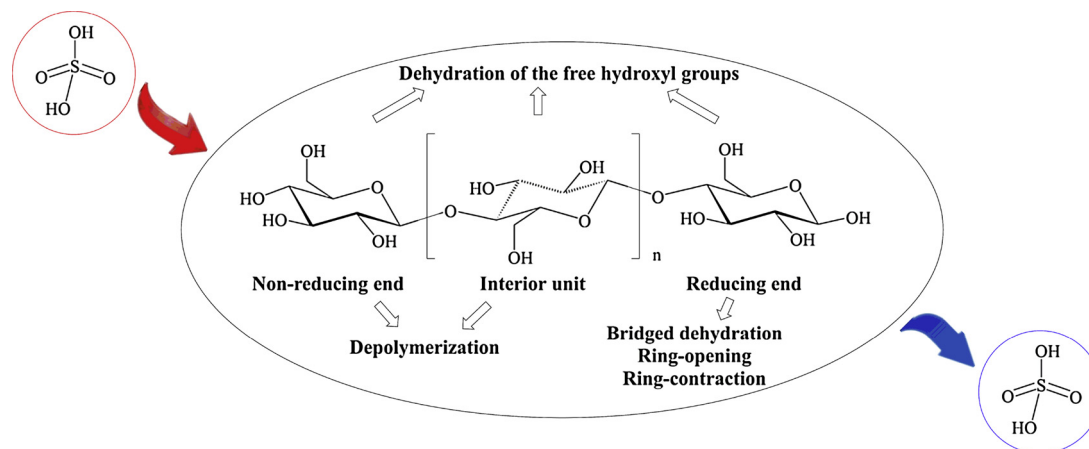


Fig. 1. Major H_2SO_4 -catalyzed pyrolytic reactions in initial cellulose pyrolysis process.

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