



Fast pyrolysis of cellulose with solid acid catalysts for levoglucosenone



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ABSTRACT

Various metal oxides, such as zirconia, titania, and alumina, were screened as solid acid catalysts in the fast pyrolysis of cellulose for levoglucosenone production. The liquid yields were affected by the properties of the catalyst, and an increase in levoglucosenone was observed with the addition of mesoporous metal oxides. Good catalytic properties were observed for anatase titanium oxide with an optimum surface area and pore diameter resulting in a levoglucosenone yield that was as much as 4.98%. The activities of calcined sulfated zirconia increased substantially compared to zirconia-impregnated sulfuric acid without calcination. In the presence of solid super-acid $\text{SO}_4^{2-}/\text{ZrO}_2$, cellulose produced levoglucosenone in a 7.25% yield.

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1. Introduction

Levoglucosenone (LGO) is the major product from the pyrolysis of phosphoric acid pre-treated waste paper [1]. LGO is a multifunctional C6-monomer suited for organic synthesis [2]. In addition, LGO is an optically active compound that can be used as a chiral synthon in the synthesis of a wide variety of biologically active products [3,4] and for the preparation of chiral auxiliaries applied in other reactions [4]. LGO is a versatile and available chiral building block from the carbohydrate family [3–6].

LGO can be produced with high selectivity and yield from the fast pyrolysis of cellulose/biomass impregnated with phosphoric acid at 500 °C [7]. Microwave irradiation of phosphoric acid pre-treated cellulose was also recently determined to be effective [8]. The aforementioned studies on the preparation of LGO were primarily limited to the catalytic pyrolysis of cellulose by phosphoric acid. The use of phosphoric acid has disadvantages associated with corrosion, inefficient recovery, and environmental concerns due to water pollution. In addition, phosphoric acid can decompose into toxic substances during heating. Therefore, it is necessary to develop a safe, efficient, and environmentally friendly catalyst.

Liquid acids that possess well-defined acid properties and solid acids may contain a variety of acid sites [9]. In general, these

catalysts are classified by their Brønsted or Lewis acidity, the strength and number of sites, and the textural properties of the support (i.e., porosity and surface area) [10]. The active sites on the surface of the metal oxide may promote cellulose dehydration and inhibit its rapid degradation increasing the yield of LGO. In contrast to liquid acids, the utilization of solid acid catalysts would avoid the complex pretreatment process and offer the potential for catalyst recycling. An analytical pyrolysis procedure was utilized to study the effect of zeolites and nanopowder metal oxides on the distribution of chiral anhydrosugars evolved from pyrolysis of cellulose. Zeolites and nanopowder metal oxides exhibited a strong influence on the pyrolytic behavior of cellulose, and the nanosized characteristics of aluminum titanate resulted in the highest LGO yields (i.e., $19 \pm 5\%$) at 500 °C [11]. Preparative pyrolysis of cellulose mixed with nanopowder aluminum titanate at 350 °C yielded LGO and LAC (1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one) as the major products with yields reaching 22 wt.% and 8.6 wt.%, respectively [12]. Recently, we proposed a new process for LGO production [13] based on the catalytic fast pyrolysis of cellulose using sulfated zirconia. A LGO yield of 8.14 wt.% was obtained at 335 °C in the presence of $\text{SO}_4^{2-}/\text{ZrO}_2$. The structure of the parent ZrO_2 was retained after it was recycled. However, the sulfated zirconia can be gradually deactivated by leaching of sulfate groups when a small amount of water is present in the pyrolysis process.

In addition, the textural properties (i.e., porosity and surface area) of the catalyst may affect the catalytic activity, and the acid supported on the catalyst can promote the formation of LGO. The aim of the current work was to investigate the influence of the structure and sulfur content of the catalysts on the formation of

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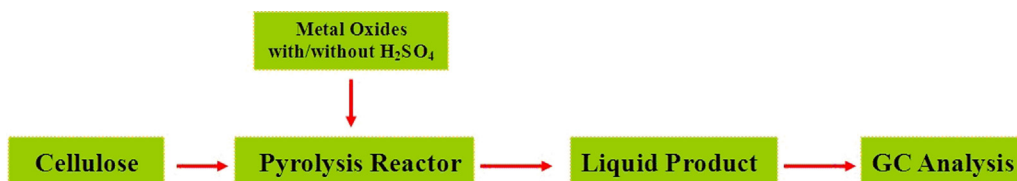


Fig. 1. Schematic representation of the experimental process.

LGO from cellulose. The experiment process is shown in Fig. 1. ZrO_2 , TiO_2 and other metal oxides with/without sulfuric acid were tested to determine the catalytic activity of the fast pyrolysis of cellulose in a fixed bed reactor. The yield and selectivity of LGO were studied under optimized pyrolysis conditions. The effect of the morphological structure on the catalytic activity of the catalysts is discussed.

2. Materials and methods

2.1. Materials

The cellulose used in this study was commercial α -cellulose (Aladdin, China). The metal oxides (i.e., ZrO_2 , TiO_2 , and Al_2O_3) were obtained from Saint-Gobain NorPro and Aladdin (China). HZSM-5 was purchased from Shanghai Pengrui Chemical Technology Co., Ltd. (China) and calcined at $500^\circ C$ in air for 5 h prior to the reaction.

1,2,4,5-Tetramethylbenzene (99%, Aladdin, China) was used as the internal standard. LGO with 96.4% purity was obtained from fast pyrolysis of phosphoric acid pretreated cellulose and purified by vacuum distillation [14]. LGO was used as an internal calibration to analyze the content of LGO. All of the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without a further purification.

The cellulose-impregnated sulfuric acid was obtained by suspending 100 g of cellulose in 1000 mL of a 0.05 M sulfuric acid solution [15]. The suspension was stirred for 5 h, filtered, and dried at $105^\circ C$ for 24 h.

2.2. Catalysts

The preparation of sulfated metal oxides involved the dispersion of 50 g of metal oxide in 500 ml of 1 M sulfuric acid for 24 h. Then, the suspension was filtered and dried at $105^\circ C$ for 12 h. The solid was divided into two parts. One part of the product was calcined at appropriate temperatures (i.e., $600^\circ C$ for ZrO_2 , and $500^\circ C$ for TiO_2) for 2 h to obtain sulfated metal oxides, which were designated SO_4^{2-} /metal oxide. The other part was used directly as sulfuric acid impregnated metal oxides and designated metal oxide- H_2SO_4 . The particle sizes of all of the catalysts were 150–250 μm via crushing.

2.3. Characterization of catalysts

Nitrogen adsorption–desorption isotherms were measured by a Micromeritics ASAP 2020 system. The specific surface areas of all of the samples were calculated according to the Brunauer–Emmett–Teller (BET) equation at relative pressures between 0.0 and 0.2.

The X-ray diffraction (XRD) analysis was conducted on a Philips X' Pert PROS X-ray diffractometer using a $Cu K\alpha$ radiation source. The diffractograms were measured within the range of 10 – $70^\circ (2\theta)$. Crystalline phases were identified by comparison with the reference data from ICDD files.

2.4. Catalytic fast pyrolysis experiments

The fast pyrolysis of cellulose samples was performed using a vertical flow reactor under nitrogen flow (60 – 70 ml min^{-1}) at $335^\circ C$. The pyrolysis unit has been previously described in detail [13]. The quartz tube equipped with a thermocouple was heated by a furnace. 3 g of cellulose was mixed with catalysts, fed into the reactor and maintained for 15 min at the preset temperature. The volatile products were condensed by liquid nitrogen. The experiments were conducted at least three times to confirm the reproducibility of the reported procedures. The RSD of the data was less than 3%.

2.5. Analysis of liquid products

The liquid product was analyzed by gas chromatography (GC1690, Kexiao, China) employing a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu m$ fused-silica capillary column (OV1701, China). A fraction of the liquid product mixed with 1,2,4,5-tetramethylbenzene that was used as the internal standard was diluted with acetone for the measurement. Nitrogen was used as the carrier gas. The detailed operating conditions were as follows: injection port: $250^\circ C$ in split mode; detector (FID): $250^\circ C$. The oven temperature was maintained at $40^\circ C$ and then heated to $250^\circ C$ at a rate of $10^\circ C/\text{min}$, which was maintained for 5 min at this temperature.

Table 1
Detailed characteristics of the metal oxides.

Samples	Chemistry	Product code ^b	Surface area (m^2/g)	Median pore diameter (nm)	Total pore volume (Hg) (cm^3/g)	Phase
HZSM	Si/Al: 25	–	352	0.6	0.18	–
Z1	ZrO_2^a	–	14	50	0.08	Monoclinic
Z2	ZrO_2	SZ31108	70	10/40	0.30	Monoclinic
T1	TiO_2	ST51122	3	>160	>0.15	>95% rutile
T2	TiO_2	ST31119	40	28	0.30	Anatase
T3	TiO_2	ST61120	150	15	0.38	Anatase
A1	Al_2O_3	SA6178	175	13	0.82	γ, δ
A2	Al_2O_3	SA6175	260	10	0.83	γ

^a ZrO_2 purchased from Aladdin.

^b Both the catalysts and the characterization data were provided by Saint-Gobain NorPro.

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