DOI: 10.1002/cssc.201000210

Catalytic Fast Pyrolysis of Cellulose to Prepare Levoglucosenone Using Sulfated Zirconia

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Sulfated zirconia was employed as catalyst for fast pyrolysis of cellulose to prepare levoglucosenone (LGO), a very important anhydrosugar for organic synthesis. The yield and the selectivity of LGO were studied in a fixed-bed reactor at different temperatures and cellulose/catalyst mass ratios. The experiments of catalyst recycling were also carried out. The results displayed that from 290 to 400 °C, the liquid and solid accounted for more than 95 wt% of products, and the higher temperature led to more liquid and less solid products. The introduction of SO_4^{2-}/ZrO_2 could promote cellulose conversion and

Introduction

With the increasing concern on fossil-fuel storage and environmental problems, the utilization of renewable biomass resources, such as lignocellulose, cellulose, and so on, will play a more and more important role in the future. Cellulose, a fiber which is a bulk component of plant biomass, is very fascinating biopolymer and sustainable raw material in nature.^[1] It can be converted to a variety of high-value chemicals by different technologies, such as fast pyrolysis, which is now an accepted feasible and viable technique to produce renewable liquid fuels, chemicals, and derived products.^[2] Fast pyrolysis of biomass is a thermal decomposition process that occurs in the absence of oxygen, with quick decomposition and rapid vapor condensation, to convert biomass mainly into a liquid product (known as bio-oil) with yields as high as 70-80 wt %.^[3] There are many valuable compounds in bio-oils, such as furfural, hydroxyacetaldehyde, levoglucosan, and thus, they have the potential for useful chemicals recovery. However, most of the chemicals in bio-oils are in low contents, making their recovery not only technically difficult but also economically unattractive. The commercialization of bio-oils for value-added chemicals requires production of specific bio-oils with high contents of target products.^[4]

Catalytic fast pyrolysis offers a possible way to drive the pyrolysis of biomass (including cellulose) towards the products of interest. Various valuable compounds have been produced from catalytic pyrolysis of cellulose or biomass, such as levo-glucosan (1,6-anhydro- β -D-glucopyranose, LGA),^[5] levoglucosenone (1,6-anhydro-3,4-dideoxy- β -D-pyranosen-2-one, LGO)^[6] and (1*R*,5*S*)-1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC).^[7]

LGO is a multifunctional C_6 monomer that forms from thermal degradation of acid-pretreated cellulose, which is a very important anhydrosugar for organic synthesis due to its

LGO production. The temperature had a similar effect on the yield and selectivity of LGO at different cellulose/catalyst mass ratios. The maximum yield was obtained at 335 °C. Although the structure of the parent ZrO₂ was retained after recycles, which was confirmed by X-ray diffraction and N₂ adsorption-desorption measurements, the activity of SO_4^{2-}/ZrO_2 could only be partially recovered by simply calcination. The catalytic activity decrease could be mainly attributed to SO_4^{2-} leaching, and the activity could be restored by further impregnation of H₂SO₄.

unique structure and the introduction of chiral centers.^[8] LGO is a reactive enone owing to its carbonyl and olefinic bond.^[9] This property is very important for modification and cycloaddition reactions.^[10] LGO can be used in the synthesis of various natural products (such as tetrodotoxin,^[11] multistriatin,^[12] rare sugars,^[13] Ras activation inhibitors^[14]) and used to prepare chiral auxiliaries for application in other reactions.^[15] Other uses of LGO can be found elsewhere.^[8, 16]

The chemical synthesis of LGO and its enantiomer from various precursors has been described.^[17] The traditional method of cellulose pyrolysis for preparation of LGO is still a viable and economically feasible procedure.^[16a] LGO is produced in very low yields from fast pyrolysis of cellulose or biomass, but can be promoted in the acid-catalyzed pyrolysis process. According to a series of studies performed by Dobele et al., fast pyrolysis of cellulose or biomass impregnated with phosphoric acid can produce LGO with high selectivity.^[18]

It is known that solid acids have many advantages compared with liquid acids.^[19] The utilization of solid acid catalysts can avoid the complex pretreatment process, and offer a significant advantage on catalyst recycles. Zirconium dioxide, one of the transition metal oxides, is prepared as a carrier which

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	Supporting Information for this article is available on the WWW under

http://dx.doi.org/10.1002/cssc.201000210.

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has received increasing interest in recent years due to its special catalytic properties and thermal stability; sulfated zirconia is considered as an excellent solid superacid. In this study, we used sulfated zirconia as a catalyst to explore the catalytic activity of fast pyrolysis of cellulose in a fixed-bed reactor. The yield and the selectivity of LGO were studied at different temperatures and cellulose/catalyst mass ratios. The catalyst recycling was also investigated.

Results and Discussion

The effect of temperature

To investigate the effect of temperature on the fast pyrolysis of cellulose, we analyzed the yields of the liquid and solid products under different temperatures (from 290 to 400 °C) in the presence and absence of SO_4^{2-}/ZrO_2 catalyst. The cellulose/catalyst mass ratio was 3:2. Under all conditions, the liquid and solid components accounted for the vast majority of products (>95 wt%, Figure 1). The low production of gas should be due to the low temperatures used in this study.



Figure 1. Temperature and the SO_4^{2-}/ZrO_2 catalyst effects on the liquid and solid products.

The temperature facilitated the production of liquid component. As shown in Figure 1, with the temperature rise from 290 to 400 °C, liquid products increased from 15.1 wt% to 72.5 wt% in the absence of the catalyst and 40.8 wt% to 73.2 wt% with the presence of the catalyst, respectively. Meanwhile, the yield of the residual solid was down to 25 wt% at 400 °C. The significant increase of liquid production by the SO_4^{2-}/ZrO_2 catalyst at low temperature may be due to the promotion of the depolymerization and dehydration of the glucan chains in cellulose and the heat transfer in the process of fast pyrolysis. The effect of SO_4^{2-}/ZrO_2 was masked by the effect of the temperature when the temperature was above 350 °C.

Next, the optimum temperature for the LGO production was investigated. Figure 2a shows the LGO content in the liquid products at the different temperatures. In the absence of the catalyst, the LGO content increased from 290°C to 320°C, and then decreased with increasing temperature. The introduction



Figure 2. Temperature effects on LGO production in the presence and absence of SO_4^{2-}/ZrO_2 (the cellulose/catalyst mass ratio was 3:2).

of SO₄²⁻/ZrO₂ catalyst led to a great increase in the LGO content at all temperatures. However, the LGO content decreased from 14.1 wt% to 5.4 wt% as the temperature increased from 290 to 400 °C. It was reported that the dehydration of cellulose led to the formation of LGO.^[20] The dehydration reaction with the lower activation energy occurred easily at lower temperature. At higher temperature, degradation became the dominant reaction during the catalytic pyrolysis. Therefore, higher temperature was more appropriate for the formation of liquid products, but had negative effects on the production of LGO. Taken together, the yield of LGO based on the cellulose is shown in Figure 2b. At 335 °C, we obtained the maximum amount of LGO in both the presence and absence of the catalyst, and the introduction of catalyst could significantly promote the LGO production (Table 1). Thus, the optimal temperature for preparation of LGO should be around 335 °C.

The effect of mass ratio and type of catalyst

At all test temperatures, the yield of LGO increased when cellulose to SO_4^{2-}/ZrO_2 mass ratio changed from 3:0 to 3:2 (Table 1). However, when the mass ratio was 3:3, the yield of LGO slightly increased at lower temperature, whereas it decreased at 350 °C, which indicated that the higher temperature

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Table 1. The effect of cellulose/catalyst mass ratio on the yield of LGO (based on cellulose) at different temperatures.						
<i>T</i> [°C]	3:0	SO4 ²⁻ 3:1	/ZrO ₂ 3:2	3:3	ZrO ₂ 3:2	$H_3PO_4^{[a]}$
320 335 350	1.93 % 2.21 % 1.60 %	6.67 % 7.07 % 5.39 %	7.15 % 7.76 % 7.00 %	7.16% 8.14% 6.46%	2.92% 4.10% 4.29%	5.60 % 7.62 % 6.70 %
[a] The loading of H_3PO_4 was 3 wt% based on dry cellulose.						

and/or excess catalyst were not appropriate for LGO production.

Phosphoric acid was proven to be an efficient catalyst for LGO formation;^[18,24] however, it was not preferred because of the problems of corrosion, inefficient recovery, and environmental disadvantages associated with water pollution. 3% phosphoric acid-loaded cellulose was tested under the same conditions employed in this study. As shown in Table 1, more LGO was produced under our conditions than those under conventional pyrolytic conditions (3–5%).^[25] Compared with phosphoric acid, the SO_4^{2-}/ZrO_2 exhibited comparable activity, and it could produce more LGO under optimized conditions. ZrO_2 only showed a mild catalyst effect. Therefore, SO_4^{2-}/ZrO_2 was an effective catalyst for the preparation of LGO. It could substitute phosphoric acid for LGO preparation due to the easy recovery and simplified cellulose pretreatment steps.

In our liquid products, the water content varied in the range of 30–50 wt% depending on the experimental conditions. Some oligosaccharides were also observed. The organic components in liquid product obtained at 335 °C were analyzed by GC–MS (Figure 3). Although the changes of the chromatographic peak areas could not strictly represent the changes of the product yield, the result was useful for a primary evaluation of the catalytic effects on the volatile organic product yield. LGA, LGO, and some other anhydrosugars were obtained by fast pyrolysis of cellulose without catalyst (Figure 3a). LGA



Figure 3. GC–MS traces of pyrolysis liquid obtained from the fast pyrolysis of a) pure cellulose at 335 °C and b) cellulose in the presence of SO_4^{2-}/ZrO_2 at 335 °C. The asterisks indicate the anhydrosugars which were not investigated in this study.

was the dominant product in the liquid, which was consistent with the previous study.^[21] With SO₄²⁻/ZrO₂ catalyst, the amount of two major components of LGA and LGO were significantly altered (Figure 3 b); the amount of LGA was reduced, whereas LGO was increased. The yield of furfural was also improved. The initial thermal decomposition of cellulose was the depolymerization of the cellulose polymer to form various anhydrosugar derivatives, among which LGA was most prevalent.^[22] LGO was formed by the elimination of two molecules of water from LGA,^[23] which could be promoted by catalysis. The result indicated that the solid acid catalyst had a higher dehydration activity and better LGO selectivity.

Recycling of the catalyst

The catalytic activity of the recycled sulfated zirconia was evaluated as follows. The solid, after pyrolysis of the cellulose/catalyst mixture, was calcined at 600 °C in air until the black char was completely eliminated. The recovered catalyst was then utilized for subsequent pyrolysis experiments at 335 °C and treated again as described above.

LGO was still the principal component in the liquids resulting from three consecutive pyrolyses. According to Table 2, the yields of LGO decreased from 7.8% (fresh catalyst) to 5.4% (once regenerated catalyst), and 4.6% (twice regenerated cata-

Table 2. The effects of catalyst recycle on the LGO content and yield at 335 °C, and sulfur content in the catalysts (the cellulose/catalyst mass ratio was 3:2).				
Samples	fresh catalyst	once regenerat- ed catalyst	twice regenerat- ed catalyst	once re- claimed cata- lyst
LGO content (wt%)	11.78	8.42	7.33	12.74
LGO yield (wt%)	7.76	5.42	4.61	8.45
Sulfur con- tent (wt %)	1.57	0.60	0.44	1.71

lyst), indicating that the efficiency of the catalyst was downregulated. However, if the used catalyst was impregnated with 1 m sulfuric acid for 1 h, followed by calcination at 600 °C in air, the efficiency of the new obtained catalyst, designated as once reclaimed catalyst, was recovered or even better than that of the fresh one. This result together with the catalyst sulfur content analysis indicated that the loss of catalytic activity of SO_4^{2-}/ZrO_2 was mainly attributed to SO_4^{2-} leaching during the pyrolysis process.

The effect of sufuric acid

To further investigate the effect of sulfuric acid on the formation of LGO, the cellulose was treated with sulfuric acid solutions of different concentrations and pyrolyzed at 335 °C. The results are summarized in Table 3.

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Table 3. The effects of sulfuric acid on liquid and LGO production at 335 $^\circ\text{C}.$				
С _{Н2SO4} [м]	0.01	0.05	0.10	0.15
Sulfur content (wt%) Liquid yield (wt%) LGO in liquid (wt%) LGO yield (wt%)	0.02 58.70 10.03 5.89	0.03 57.04 11.54 6.58	0.05 53.90 9.17 4.94	0.11 48.14 8.96 4.31

With the treatment concentration increasing, the sulfur content, and thus the sulfuric acid content on the cellulose also increased. Higher sulfuric acid content resulted in lower liquid yield. The highest yield of LGO, 6.6 wt%, was achieved when the concentration of sulfuric acid solution was 0.05 M. Raising or reducing the sulfuric acid concentration from this amount did not favor LGO formation. When the concentration reached 0.15 M, the LGO yield was only 4.3 %, which meant that excess sulfuric acid was not good for LGO formation. It was also shown that the sulfuric acid was less effective than sulfated zirconia. Sulfuric acid was very difficult to handle during the cellulose pretreatment process due to its high corrosiveness and reactivity. Furthermore, it was hard to control the sulfuric acid loading amount on cellulose. Therefore, sulfuric acid was not recommended for LGO preparation.

Characterization of catalysts

The parent ZrO_2 crystal and textural structure changes could also be related to the decrease of the catalytic activity, and thus, detailed characterization of the catalysts were carried out.

Various catalyst samples were subjected to X-ray diffraction (XRD) analysis (Figure 4). Samples of ZrO_2 and SO_4^{2-}/ZrO_2 primarily consisted of monoclinic phase of ZrO_2 , which had almost no change even after the recycling of the catalyst. It was consistent with the fact that the monoclinic phase is the thermodynamically more stable phase for bulk zirconia be-



Figure 4. X-ray diffraction patterns of ZrO_2 and SO_4^{2-}/ZrO_2 (1 for once regenerated catalyst, 2 for twice regenerated catalyst, and 3 for once reclaimed catalyst).

tween room temperature and about 1500 K.^[26] The average crystallite size of zirconia was also calculated. No obvious change was found, suggesting that zirconia was a highly thermal stable support.

The N₂ adsorption–desorption isotherms of the catalysts were measured to analyze the different textural properties among the fresh and reused catalysts. The results of the specific surface area and pore volume of zirconia and sulfated zirconia are shown in Table 4. Brunauer–Emmett–Teller (BET) surface area of zirconia was 42.3 m²g⁻¹ and the pore volume was about 0.18 cm³g⁻¹. The specific surface area and pore volume of various sulfated zirconia samples changed slightly.

Table 4. The specific surface area and pore volume of zirconia and sulfat- ed zirconia (1 for once regenerated catalyst, 2 for twice regenerated catalyst, and 3 for once reclaimed catalyst).				
Samples	Pore volume [cm ³ g ⁻¹]	BET surface area [m ² g ⁻¹]		
ZrO ₂	0.18	42.3		
SO_4^{2-}/ZrO_2	0.19	43.2		
SO ₄ ²⁻ /ZrO ₂ -1	0.18	42.0		
SO ₄ ²⁻ /ZrO ₂ -2	0.19	44.7		
SO_4^{2-}/ZrO_2-3	0.19	45.6		

 $\rm N_2$ adsorption–desorption isotherms of all catalysts are shown in Figure 5 a. The isotherms of $\rm ZrO_2$ illustrated a clear H1-type hysteresis loop in the relative pressure range between 0.4 and 0.9, implying that this material had very regular mesoporous channels. Desorption Barrett–Joyner–Halenda (BJH) pore volume distributions are given in Figure 5 b. The most concentrated pore diameter was about 12 nm. The four SO₄^{2–}/ ZrO₂ catalysts exhibited similar isotherms and pore volume distributions as the ZrO₂, suggesting that they retained their structure after the impregnation and calcination process.

XRD and N₂ adsorption–desorption isotherm analysis data both suggested that the regenerated catalysts had similar characteristics to the fresh catalyst. Therefore, the parent ZrO_2 was very stable and could be recycled for LGO production.

Conclusions

In this study, extensive experiments were performed to investigate the catalytic fast pyrolysis of cellulose over different catalysts. It was found that SO_4^{2-}/ZrO_2 could promote cellulose conversion and LGO production.

In presence of the SO_4^{2-}/ZrO_2 , the yield of LGO reached the maximum at 335 °C under selected reaction conditions. It was believed that the optimum temperature for preparation of LGO was in the range from 320 °C to 350 °C. The temperature had a similar effect on the yield of LGO when the cellulose/ SO_4^{2-}/ZrO_2 catalyst mass ratio was changed from 3:0 to 3:3. Compared with phosphoric acid, the SO_4^{2-}/ZrO_2 exhibited comparable activity. It was an effective catalyst for the preparation of LGO preparation. Sulfuric acid also displayed certain catalytic activity to produce LGO, but due to the complicated pre-



Figure 5. Textural properties of ZrO_2 and SO_4^{2-}/ZrO_2 . (1 for once regenerated catalyst, 2 for twice regenerated catalyst, and 3 for once reclaimed catalyst).

treatment process and environmental issue, sulfuric acid was not a good candidate for LGO production.

Although the fresh catalyst could be recovered by calcination, the activity of regeneration catalysts decreased due to SO_4^{2-} leaching. As zirconia is a thermally stable carrier, the activity of the catalyst could be restored by impregnation of sulfuric acid. Currently more experiments are under progress to explore the effects of the sulfur content and the type of solid acids on the cellulose pyrolysis and LGO production. Detailed catalytic mechanism is also under investigation. More work will also be carried out to optimize the catalytic pyrolysis process.

Experimental Section

Preparation

ZrOCl₂·8H₂O (150 g) was dispersed in deionized water (1500 mL) and precipitated with NH₃ solution (25 wt%) to the final pH of 9. The precipitate was washed, filtered, dried at 105 °C for 12 h, and then calcined at 600 °C for 2 h. The obtained powder was ZrO₂. The product was impregnated with sulfuric acid (1 m) for 1 h. Finally, the suspension was filtered, dried and calcined at 600 °C for 2 h, and SO₄²⁻/ZrO₂ was obtained.

The procedure of impregnation cellulose with phosphoric acid was similar to the one described in the literature.^[25] The cellulose used

in this study was commercial α -cellulose (Aladdin). The acid pretreated cellulose was obtained by suspending cellulose (20 g) in anhydrous ethanol (100 mL) with 85% H₃PO₄ (0.71 g). The suspension was stirred for 1 h, evaporated under vacuum, and dried at 105 °C for 24 h.

The cellulose impregnated sulfuric acid was obtained as follows: The cellulose (10 g) was suspended in sulfuric acid solutions (100 mL) with different concentrations (0.15 m, 0.1 m, 0.05 m, and 0.01 m). The suspension was stirred for 5 h, filtered by sand cored funnel, and dried at 105 °C for 24 h.

Characterization

The sulfur content on sulfuric acid-treated cellulose and SO_4^{2-}/ZrO_2 catalyst were analyzed by high frequency infrared carbon and sulfur analyzer (LECO CS-600, USA) using ASTM E1915–01 standard test methods.

The XRD patterns were recorded on a Philips X' Pert PROS X-ray diffractometer using a Cu K α radiation source. The diffractograms were measured within the range of 10° to 70° (2 θ). Crystalline phases were identified by comparison with the reference data from the International Centre for Diffraction Data (ICDD) files. The average crystallite size of zirconia was calculated according to the Scherrer formula, using the XRD data of prominent lines.

Nitrogen adsorption–desorption isotherms were measured by a Micromeritics ASAP 2020 system. The specific surface areas of all samples were calculated according to the BET equation in the range of relative pressures between 0.0 and 0.2. The thermodynamic-based BJH method was used to calculate the pore size distributions from the adsorption and desorption branches of the isotherms. The total pore volume was determined from the adsorption and desorption branches of the nitrogen isotherms at $P_s/P_0 = 0.97$.

Equipment

The fast pyrolysis of cellulose processes was carried out in the vertical flow reactor under nitrogen flow ($60-70 \text{ mLmin}^{-1}$) in the range of 290–400 °C. The pyrolysis unit was composed of a feeding system, a pyrolysis system, and a condensation system, as shown in Figure 6. The reactor was a quartz tube (diameter of 20 mm, length of 600 mm, and thickness of 1 mm) equipped with a thermocouple and heated by a furnace.

In the fast pyrolysis experiments, cellulose (3 g) was mixed with various amounts of catalysts, fed into the reactor with a certain speed, and kept for 15 min at a preset temperature. The experiments were conducted at least three times to confirm the reproducibility of the reported procedures. The volatile products were collected in a consequent condenser tube bathed in liquid nitrogen. The condensed pyrolysis liquid products were estimated by the weight difference of the condenser and the connecting tube before and after the experiment. The solid residue was also collected and weighted to determine the yield of solid, and then calcined at 600 °C to regenerate the catalyst.

Analysis of liquid products

A fraction of the liquid product mixed with durene as the internal standard had been diluted by anhydrous ethanol for its measurement by gas chromatography (GC 1690, Kexiao, China) employing a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ um}$ fused-silica capillary column (OV 1701,

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Figure 6. The configuration of the pyrolysis reactor.

China). The operating conditions were as follows: carrier gas: nitrogen; injection port: 250 °C in split mode; detector (FID): 250 °C; column temperature: 40 °C; oven temperature program: heated up to 250 °C at a rate of 10.0 °C min⁻¹ and held at final temperature for 5.0 min. Levoglucosenone with 96.4% purity was used as an internal calibration to analyze the content of levoglucosenone. Levoglucosenone was produced in house by fast pyrolysis of phosphoric acid-pretreated cellulose and purified by vacuum distillation (see the Supporting Information, Figure S1).^[16a]

The organic components of pyrolysis oil were analyzed by GC–MS (Agilent 5975C), using a 30 m×0.25 mm×0.25 um HP-5MS fusedsilica capillary column. The injector temperature was kept at 280 °C in split mode. Helium (99.999%) was used as the carrier gas with a constant flow. The oven temperature was held at 40 °C for 3.0 min, then heated to 150 °C at a rate of $5.0 \,^{\circ}$ Cmin⁻¹, finally heated to 280 °C at a rate of $10.0 \,^{\circ}$ Cmin⁻¹, and held for 5 min at that temperature. The mass spectrometer was operated in El mode. Confident identification of the chromatographic peaks could be achieved based on the National Institute of Standards and Technology (NIST) MS library.

Acknowledgements

We gratefully acknowledge the financial support provided by Knowledge Innovation Program of the Chinese Academy of Science (KGCX2-YW-3306), National Basic Research Program of China (2007CB210205) and Key Program of National Natural Science Foundation of China (50930006).

Keywords: biomass · carbohydrates · heterogeneous catalysis · pyrolysis · zirconium

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Received: July 12, 2010 Revised: September 20, 2010 Published online on November 12, 2010