



Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Catalytic fast pyrolysis of cellulose to produce furan compounds with SAPO type catalysts

Xu Chen^{a,1}, Yingquan Chen^{a,1}, Zhen Chen^b, Danchen Zhu^a, Haiping Yang^{a,*}, Peng Liu^b, Tao Li^{b,*}, Hanping Chen^a^a State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan Hubei, 430074, PR China^b School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

ARTICLE INFO

Keywords:

Catalytic fast pyrolysis
Furans
Cellulose
SAPO type catalysts
Metal modification

ABSTRACT

Furans, such as furfural (FF) and 5-hydroxymethyl-furfural (HMF), are recognised as target high-value chemicals produced through catalytic fast pyrolysis (CFP) of biomass. In this work, a series of SAPO type catalysts were introduced in the CFP of cellulose to promote the generation of furans. Results indicate that under the catalysis of SAPO type catalysts, the formation of furans is promoted while the content of sugars decreases considerably. AlCu-SAPO-34 and ZrCu-SAPO-18 performed best for furan formation: their furans peak area% was 56.94% and 63.86%, respectively. Furthermore, these two catalysts had more mild acidity (lower density and strength), which favoured the formation of furans. Meanwhile, 500–600 °C was selected as the optimum operation temperature when using SAPO catalysts. The formation of furans with SAPO type catalysts may be favoured because the catalyst promotes the direct conversion of oligosaccharides to furans.

1. Introduction

Fast pyrolysis is one of the most promising methods for the conversion of biomass to liquid fuel bio-oil [1]. However, bio-oil contains hundreds of oxygenates, which have negative effects, causing the bio-oil to have low heating value, high corrosiveness, high viscosity, and instability [2]. Catalytic fast pyrolysis (CFP) has attracted considerable attention due to its ability to upgrade the quality of bio-oil over a range of deoxygenation processes [3,4]. Furthermore, the direct conversion of biomass to hydrocarbon transport fuel via CFP has also been studied [5–7]. To obtain hydrocarbon transport fuel, oxygen in the input biomass must be completely removed from the liquid products during CFP, which may raise the cost of CFP and reduce the atom utilisation efficiency [8]. To overcome this, many researchers have replaced the liquid product with specific oxygenates, and these studies have demonstrated that CFP for specific oxygenates not only has a higher atom utilisation efficiency than hydrocarbon transport fuel, but also that they have potential for use as high-value chemicals [3,9].

Of the specific oxygenates reported, furans are garnering increased attention. Furfural, 5-hydroxymethyl-furfural and furandicarboxylic acid were included in the top 15 target structures that can be generated from carbohydrates in the Bozell and Petersen report in 2010 [10].

These furan compounds are widely used as organic solvents or reagents for the production of medicines, resins, fuel additives, etc. [11–13]. They are considered to be a bridge between renewable energy and petrochemicals [14].

Generally, furan compounds can be produced from biomass with acidic catalysts through hydrolysis-dehydration reaction or pyrolysis process. Summaries of previous studies on furan compound (mainly furfural (FF) and 5-hydroxymethyl-furfural (HMF)) production are listed in Table 1. Comparatively, hydrolysis-dehydration technology is more mature: furfural was produced in large amounts for the first time by the Quaker Oats Company one hundred years ago. Organic/inorganic acids [15,16], acidic salts [17] and solid acids [18–20] are used as catalysts for the production of furan compounds through biomass hydrolysis-dehydration reaction. However, for catalytic fast pyrolysis, which can produce furan compounds in a shorter time, most studies have only focused on organic/inorganic acids and acidic salts, which are difficult to recycle. The utilisation of these volatile and acidic catalysts also causes environmental problems. Thus, it is essential to develop environmentally friendly solid acid catalysts for furan compound production in biomass pyrolysis.

Various solid acid catalysts have been employed in biomass catalytic fast pyrolysis. Zeolite catalysts, HZSM-5 in particular, are most

* Corresponding authors at: 1037 Luoyu Road, Wuhan, Hubei, 430074, PR China.

E-mail addresses: chxu@hust.edu.cn (X. Chen), chenyingquan@hust.edu.cn (Y. Chen), zhende_888@126.com (Z. Chen), chen_19930501@163.com (D. Zhu), yhping2002@163.com (H. Yang), pengliu@hust.edu.cn (P. Liu), taoli@hust.edu.cn (T. Li), hp.chen@163.com (H. Chen).¹ These authors contributed equally to this work.<https://doi.org/10.1016/j.jaap.2017.12.004>Received 17 August 2017; Received in revised form 7 December 2017; Accepted 7 December 2017
0165-2370/ © 2017 Elsevier B.V. All rights reserved.

Table 1
Summaries of previous studies on furan compounds production (mainly furfural (FF) and 5-hydroxymethyl-furfural (HMF)).

| Feedstock | Catalyst | Method | Product | Ref. |
|------------------------------|------------------------------------------------------------------------------------------------------|------------------------|---------|---------|
| Xylose, xylan and straw | HCl, H ₂ SO ₄ , HNO ₃ , etc. | hydrolysis-dehydration | FF | [16] |
| Corn stover | Maleic Acid | hydrolysis-dehydration | FF | [15] |
| Corn cob | FeCl ₃ and acetic acid | hydrolysis-dehydration | FF | [17] |
| Hemicellulose | Hbeta and HUSY | hydrolysis-dehydration | FF | [20] |
| Cassava waste | Sulfonated carbon-based catalyst | hydrolysis-dehydration | FF | [18] |
| Fir wood | (NH ₄) ₂ HPO ₄ and (NH ₄) ₂ SO ₄ | pyrolysis | FF | [51] |
| Biomass | ZnCl ₂ | pyrolysis | FF | [52–56] |
| Corn cob | H ₂ SO ₄ | pyrolysis | FF | [57] |
| Corn cob | H ₂ SO ₄ , H ₃ PO ₄ , ZnCl ₂ , etc. | pyrolysis | FF | [58] |
| Fructose, glucose and xylose | HCl, H ₂ SO ₄ and H ₃ PO ₄ | hydrolysis-dehydration | HMF | [14] |
| Fructose | Formic acid and acetic acid | hydrolysis-dehydration | HMF | [59] |
| Fructose | TiO ₂ and ZrO ₂ | hydrolysis-dehydration | HMF | [60] |
| Glucose | Amberlyst-15 and hydrotalcite | hydrolysis-dehydration | HMF | [19] |
| Fructose | Without catalyst | pyrolysis | HMF | [12] |

extensively studied. Wang, et al. [21] studied the influence of HZSM-5 on cellulose pyrolysis and found that the predominant product from cellulose pyrolysis, levoglucosan, is first converted to furan compounds and then further transformed to aromatics and olefins. So, if the second step (furan compounds to aromatics and olefins) can be suppressed through modification of the physicochemical properties of the zeolite catalysts, the yield and selectivity of the furan compounds can be increased. Then it will be possible to produce furan compounds through catalytic pyrolysis with solid acid catalysts. Based on this, in this study several SAPO type catalysts are prepared and used during cellulose fast pyrolysis to obtain high yield, high selectivity furan compounds. SAPO type catalysts are used since their pore size may limit the transformation space for the conversion from furans to aromatics, and thus suppress the second step described above. On the other hand, the mild acidity of SAPO catalysts caused by the framework composition [22] may be favourable for the formation of furans [23]. Moreover, it is known that furans can be formed through the dehydration of cellulose or carbohydrates during pyrolysis [24], and SAPO type catalysts were found effective to promote the dehydration reaction of biomass [25–28]. However, the hydrolysis-dehydration reactions occur in liquid phase at lower temperature. While, for fast pyrolysis, the reactions occur mostly in gas phase at higher temperature (> 400 °C). However, to date, the influence of SAPO materials on the formation of furan compounds during biomass pyrolysis remains unclear. Hence, the performance of SAPO materials during biomass pyrolysis should be further studied. As is known, appropriate strength, number and sort of acid sites must be needed to maximize the yield of furans [23]. The incorporation of different metals may change the acid property of SAPO type catalysts. On the hand, the presence of Cu²⁺ [29], Zr²⁺ [30], Fe³⁺ [31] and Al³⁺ [32] were found favourable for the production of furfural. Thus, those metal modifications of SAPO type catalysts were investigated to identify the best catalyst. In addition, a possible mechanism for the formation of furan compounds is also discussed.

2. Experimental section

2.1. Sample

Cellulose used in this study was provided by Sigma–Aldrich Co., Ltd., and the particles were dried at 105 °C prior to the experiments.

2.2. Catalyst preparation

SAPO-34 (H-SAPO-34, Cu-SAPO-34, ZrCu-SAPO-34 and AlCu-SAPO-34) and SAPO-18 (H-SAPO-18, Cu-SAPO-18, Fe-SAPO-18 and ZrCu-SAPO-18) molecular sieves were used as catalysts in this study. H-SAPO-34 and H-SAPO-18 were prepared according to the synthesis routes reported by Yu, et al. [33] and Smith, et al. [34], respectively.

Metal-modified molecular sieves (M-SAPO-34/SAPO-18, where M indicates that the sieve contains a different metal) were prepared by the following procedure. A certain amount of metal nitrates was dissolved in deionised water to obtain 0.1 M metal ion aqueous solution. Then, H-SAPO-34/H-SAPO-18 was dispersed into the above solution with a solid-liquid ratio of 1:50 (g/g) and stirred over a hot water bath at 70 °C for 12 h. Finally, the mixtures were filtered and washed with deionised water, dried at 110 °C for 12 h, and then calcined at 600 °C for 5 h. The catalysts from different molecular sieves and metal nitrates are denoted as: H-34 for H-SAPO-34, Cu-34 for Cu-SAPO-34, ZrCu-34 for ZrCu-SAPO-34, AlCu-34 for AlCu-SAPO-34, H-18 for H-SAPO-18, Cu-18 for Cu-SAPO-18, Fe-18 for Fe-SAPO-18 and ZrCu-18 for ZrCu-SAPO-18.

2.3. Catalyst characterisation

The acidity of the samples was measured with a Micromeritics Chemisorb 2720 system using Temperature-Programmed Decomposition (TPD) of ammonia (NH₃-TPD). NH₃-TPD was conducted with 50 mg catalyst. First, the catalyst was heated to 600 °C for 30 min in He to remove adsorbed water. Once the sample had been saturated with NH₃ at 50 °C for 30 min, the He was flushed for 30 min. Finally, the catalyst was heated to 600 °C at a heating rate of 10 °C/min (To totally eliminate the influence of physisorbed NH₃, the data recording can be done from 100 °C).

The structure and compositions of obtained catalysts were characterized by X-Ray Diffraction (XRD, X'Pert PRO, PANalytical B.V, Netherlands) and X-Ray Fluorescence (XRF, EAGLE III, EDAX Inc, America) [33], respectively. The XRD analysis was operated at 40 kV and 40 mA in the range of 5°–40° with a step wise of 0.017°.

2.4. Experimental methods

The pyrolysis experiment was carried out in a CDS 5250 pyrolyzer with direct connection to a gas chromatograph equipped with mass spectrometry (GC–MS, HP7890 series GC with an HP5975 Mass Selective detector). For cellulose fast pyrolysis, the cellulose was packed between two layers of quartz wool and put into a quartz sample tube. The internal diameter and length of the quartz tube were 2 mm and 38 mm, respectively. In the catalytic pyrolysis experiments, a mixture of cellulose and catalyst (physically mixed) were added as feedstock into the quartz sample tube. The sample masses of cellulose and catalyst were 0.3 mg and 2.4 mg, respectively. For a typical run, the heating rate was set at 10 °C/ms (the set point of the furnace) to ensure fast pyrolysis. The reaction time (solid residence time) and pyrolysis temperature (set point of the furnace) were 15 s and 600 °C (when considering the influence of temperature, the set temperature were 400 °C, 500 °C, 600 °C, 700 °C and 800 °C), respectively.

To avoid the potential condensation of pyrolytic volatiles before the

Download English Version:

<https://daneshyari.com/en/article/7606395>

Download Persian Version:

<https://daneshyari.com/article/7606395>

[Daneshyari.com](https://daneshyari.com)