

Catalytic Pyrolysis of Kapok Fiber for Production of Olefins

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Received May 30, 2019; Accepted July 12, 2019; Published July 14, 2019

Pyrolysis of kapok fibers over mesoporous molecular sieves of MCM-41, Zr-MCM-41 and Cr-MCM-41 (the mole ratio of Si:Zr or Si:Cr=50) was studied by using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). Pure silicon MCM-41 showed weak acidity during pyrolysis with furfural as the main product. Zr-MCM-41 showed the dual-functionality of acid and base with both furfural and hydroxy acetone present in the products. Cr-MCM-41 was more acidic with more furfural produced. The optimal conditions for producing olefins were found to be 600°C and the ratio of kapok fiber to catalyst being 1:10 with the Zr-MCM-41 catalyst. The main products obtained via pyrolysis of kapok fiber were acetic acid, furfural, 2,4-di-tert-butylphenol, olefins, and alkanes. The excess of the catalyst and the high temperature of the reaction had certain effects on the pyrolysis of biomass to produce olefins, such as 1-decene, 1-dodecene, 1-undecene, 1-tridecene and heptadecane.

Keywords: Kapok fibers; GCMS; Pyrolysis; MCM-41; Zr-MCM-41; Olefin

Introduction

Energy sources are not only closely related to the country's political stability and economic development, but also the motivating power for the economic growth and the national progress [1]. The advance of energy technologies is an important driving force for the development of the human society.

The Earth has not only a large amount of fossil energy, namely coal, oil and natural gas, but also a large amount of renewable clean energy such as hydropower, wind and sunlight. The traditional fossil fuels greatly promoted the development of human society. After the industrial revolution, due to the relatively low cost of the fossil fuels, people's interest in biomass had greatly reduced. Global energy development is over-reliant on the fossil energy [2]. For example, the fossil coal is being continuously mined, resulting in growing number of problems, such as resource constraints and excessive CO₂ emissions. The resultant greenhouse effect, global warming, environmental pollution, and other issues seriously threaten the survival and the development of human beings. Due to these concerns, scientists have raised interest in renewable energy. In the past few decades, researchers have been dedicated for exploring and developing new renewable energy sources, including the solar energy, wind energy, hydropower generation, biomass energy, geothermal energy, and the ocean energy [3]. Among them, the biomass energy (*i.e.*, bioenergy), accounting for 14% of the world's total primary energy consumption, is

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the fourth largest energy source in the world, playing an important role in the entire energy system [4].

So far, the world's annual biomass production has reached 180 billion tons, or 3×10^{22} J, 10 times the actual energy consumption in the world. Under the ideal conditions, the biomass potential on Earth could reach 180~200 times the actual energy consumption [5, 6]. The use of the biomass as an energy and chemical source is conducive to not only the energy conservation and emission reduction, but also the adjustment of the energy consumption while promoting the economic development. In order to further develop the bioenergy technology and effectively improve the biomass conversion, it is indispensable to explore the principle of the conversion process [7].

Pyrolysis is one of the mostly studied biomass utilization technologies to produce energy products and fine chemicals [8, 9]. Catalytic pyrolysis has the advantages of selective conversion and fast reaction, a promising method to improve the quality of final products [10, 11]. For this study, kapok fibers were catalytically pyrolyzed over mesoporous molecular sieves of MCM-41 modified with Zr and Cr. The impact of these catalysts on the pyrolysis of kapok fiber was investigated by using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS).

Materials and Methods

Materials

Kapok fibers were collected locally at Shenzhen, China during the spring 2018. The kapok fibers were dried at 100°C for 24 h to remove the moisture. The dried fibers were ground to fine powders, with the compositions shown in Table 1. The fibers contain cellulose, lignin, pentosan (hemicellulose), and extractives.

Table 1. The compositions of the kapok fiber (wt%)

Ash	Extractives			Cellulose	Klason lignin	Pentosan
	Hot water	NaOH	Phenyl			
1.43	4.10	26.96	1.93	43.73	11.36	37.43

Catalysts of mesoporous molecular sieves of MCM-41, Zr-MCM-41 and Cr-MCM-41 were provided by the Wuhan Institute of Technology [12]. The mole ratios of Si/Zr in Zr-MCM-41 and Si/Cr in Cr-MCM-41 were 50.

Pyrolysis Coupled with Gas Chromatograph/Mass Spectrometer (Py-GC/MS)

Prior to pyrolysis, the kapok fibers were mixed with the catalyst of MCM-41, Zr-MCM-41 or Cr-MCM-41 to make a feedstock-to-catalyst weight ratio of 1:2, 2:1, 1:10 and 10:1. The mixtures were ground in a mortar and placed in an oven at 100°C for 10 h.

Pyrolysis of kapok fibers was conducted in a sample cup of Frontier PY-2020iD pyrolyzer (Fukushima, Japan). Prior to the pyrolysis, a sample of 0.5 mg was weighted by using a METTLER TOLEDO XP6 Automated-S microbalance (Columbus, OH, USA). For each experiment, the pyrolyzer was pre-heated to the desired temperature (400°C, 500°C or 600°C), and then purged with ultra-purity helium to remove oxygen. The pre-weighted sample was allowed to drop into the pyrolyzer, whereby the sample was pyrolyzed for 30 s. The volatilized products were injected directly into a Shimadzu

GCMS-QP2010 gas chromatograph/mass spectrometer (Shimadzu, Japan) equipped with an Agilent DB-5MS capillary column (Santa Clara, CA, USA).

Results and Discussion

Impact of Ratio of Feedstock to Catalyst

The effect of the ratio of the feedstock to catalyst (R) on pyrolysis was explored. Firstly, catalytic pyrolysis was conducted with Zr-MCM-41 at the feedstock to a catalyst ratio (R) of 1:2 and 2:1 at the pyrolysis temperature of 600°C. The total ion chromatogram (TIC) of these two conditions are shown in Figure 1. The results showed an obvious profile change upon the change in the catalyst ratio. Therefore, R was further decreased to 1:10. This ratio was compared to the R of 10:1, with the resultant TIC shown in Figure 2. Figure 2 exhibits evidently higher peak height, higher peak area, and more abundant products at the ratio of the feedstock to catalyst of 1:10. Consequently, a lower R value is preferred in the subsequent experiment.

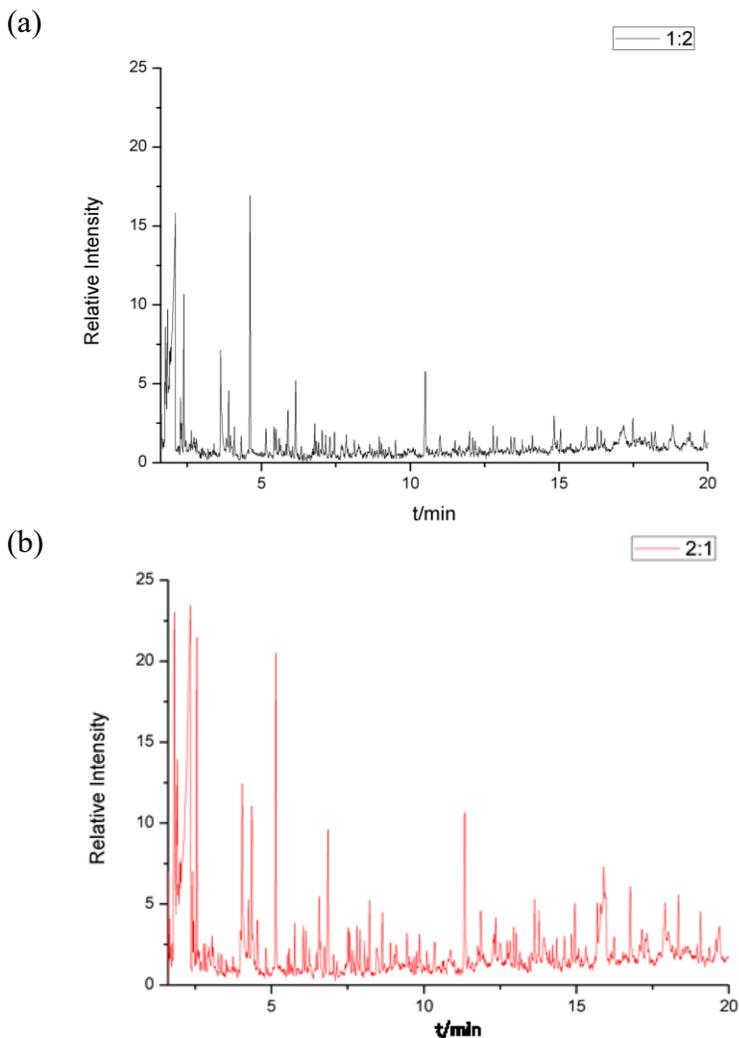


Figure 1. TIC of pyrolysis of kapok fibers with a feedstock to Zr-MCM-41 ratio of (a) 1:2 and (b) 2:1

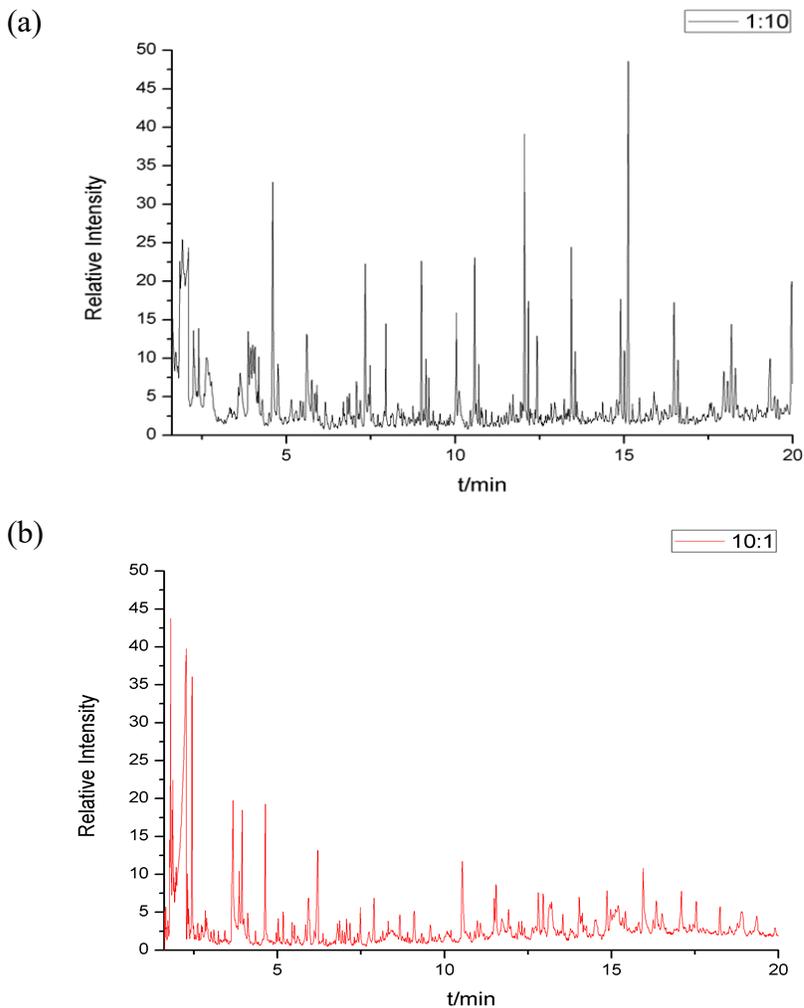


Figure 2. TIC of pyrolysis of kapok fibers with a feedstock to Zr-MCM-41 ratio of (a) 1:10 and (b) 10:1

Impact of Pyrolysis Temperature

The biomass components are difficult to be cracked under low pyrolysis temperature. Contrarily, when the pyrolysis temperature is too high, the pyrolytic products become more complicated with more gaseous products. Accordingly, pyrolysis temperature was chosen as 400°C, 500°C, and 600°C. Figure 3 shows the TIC of catalytic pyrolysis of kapok fibers over Zr-MCM-41 with $R = 1:10$.

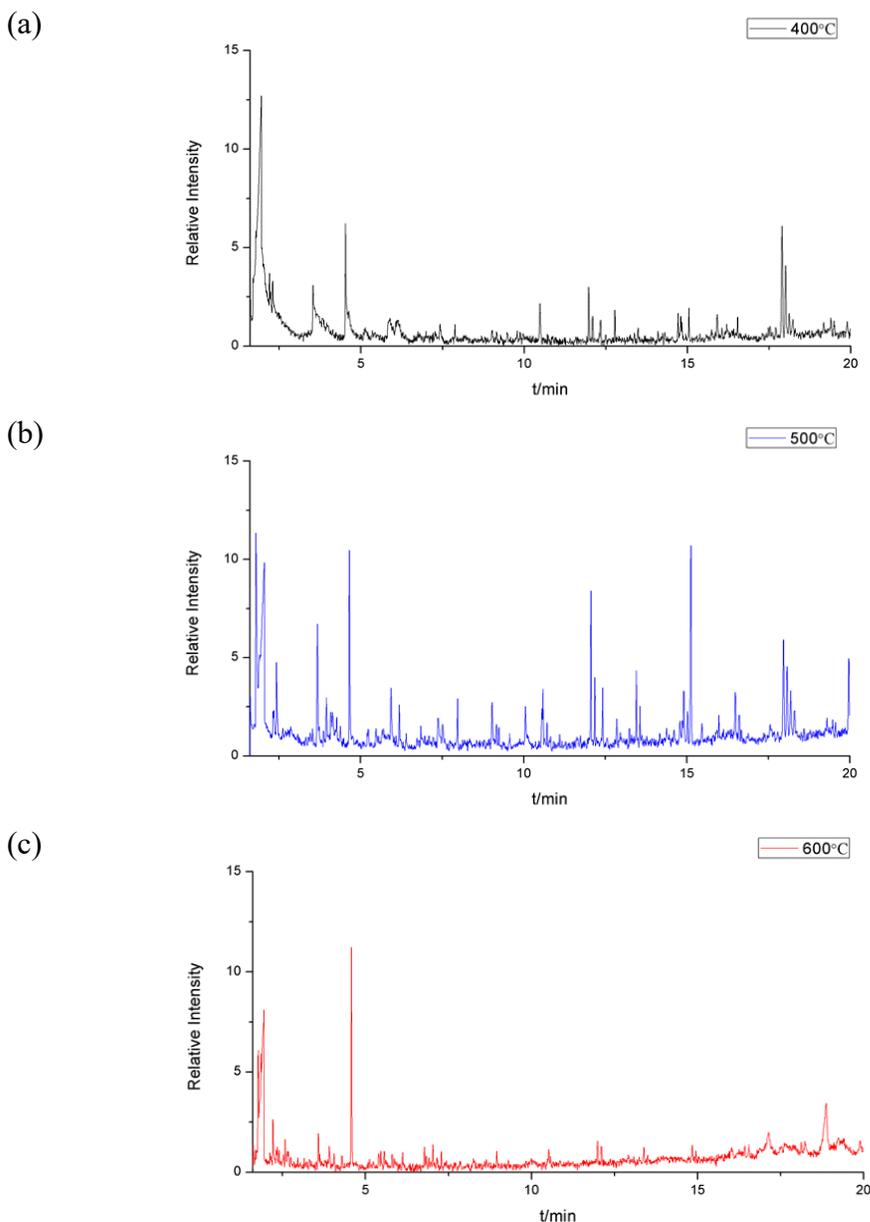


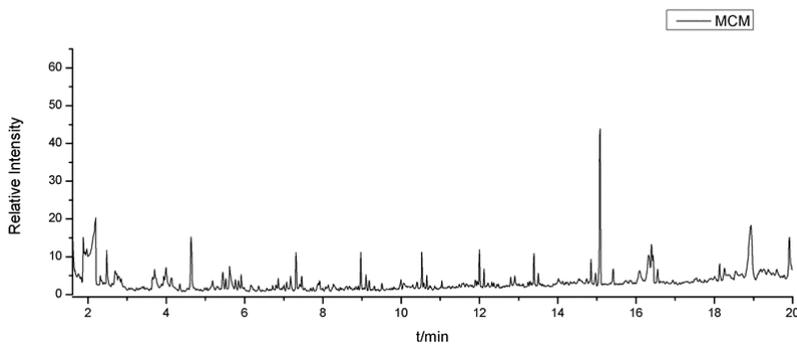
Figure 3. TICs of pyrolysis of kapok fibers at the feedstock to Zr-MCM-41 ratio of 1:10 and (a) 400°C, (b) 500°C and (c) 600°C

The number of chemicals produced at 400°C was less, and it is apparent that the kapok fiber was not fully catalytically cracked. The reactions at 500°C showed more chemicals than that of 400°C, though there were similar small molecular chemicals. At 600°C, cracking of the feedstock was relatively complete, and new substances were formed obviously. Therefore, the following experiments were pyrolyzed at 600°C.

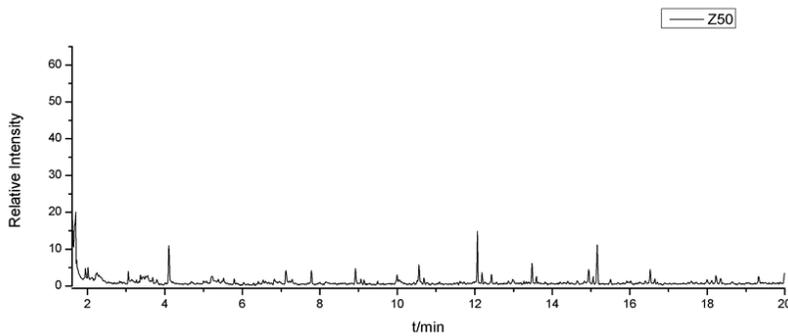
Impact of MCM-41 Catalysts

The experiments on MCM-41 catalysts were conducted at $R = 1:10$ and 600°C for 30 s. The TICs of MCM-41, Zr-MCM-41 and Cr-MCM-41 are shown in Figure 4, while produced chemicals are summarized in Tables 2- 4, respectively.

(a)



(b)



(c)

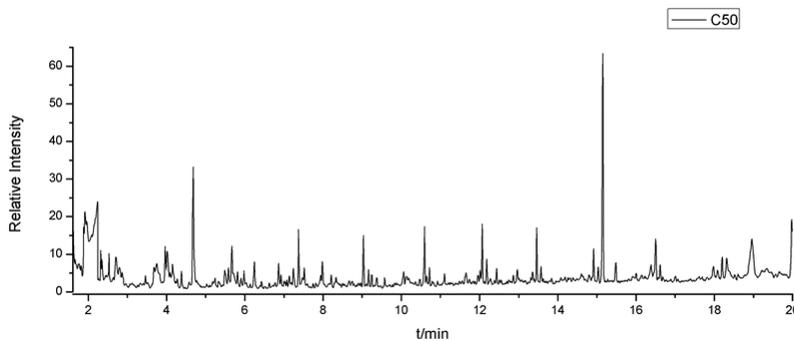


Figure 4. TICs of pyrolysis of kapok fibers over (a) MCM-41, (b) Zr-MCM-41 and (c) Cr-MCM-41 at $R = 1:10$ and 600°C

Table 2. Pyrolytic products obtained from catalytic (MCM-41) Py-GC-MS analysis

RT (min)	Possible chemical	Similarity (%)	Formula	Areas (%)
2.196	Acetic acid	94	C ₂ H ₄ O ₂	21.55
3.993	1-Octene	91	C ₈ H ₁₆	1.94
4.634	Furfural	83	C ₅ H ₆ O	6.87
5.620	1-Nonene	94	C ₉ H ₁₈	3.7
7.316	1-Decene	95	C ₁₀ H ₂₀	3.73
8.967	1-Undecene	95	C ₁₁ H ₂₂	3.36
9.101	Undecane	92	C ₁₁ H ₂₄	1.36
10.529	1-Dodecene	94	C ₁₂ H ₂₄	3.3
10.653	Dodecane	93	C ₁₂ H ₂₆	1.02
12.002	(3Z)-3-Hexadecene	91	C ₁₆ H ₃₂	2.95
12.116	Tridecane	92	C ₁₃ H ₂₈	1.47
13.394	1-Pentadecene	95	C ₁₅ H ₃₀	2.48
14.850	Pentadecene	94	C ₁₅ H ₃₀	2.11
15.080	2,4-Di-tert-butylphenol	96	C ₁₄ H ₂₂ O	18.1
16.320	1-Heptadecene	91	C ₁₇ H ₃₄	5.87
18.931	Oleic acid	85	C ₁₈ H ₃₄ O ₂	20.19

Table 3. GC-MS analysis of pyrolytic products obtained with Zr-MCM-41

RT (min)	Possible chemical	Similarity (%)	Formula	Areas (%)
2.096	Acetic acid	91	C ₂ H ₄ O ₂	11.9
2.251	4-Methyl-2-penten-1-ol	84	C ₆ H ₁₂ O	1.32
2.401	Hydroxy acetone	86	C ₃ H ₆ O ₂	1.06
4.591	Furfural	89	C ₅ H ₄ O ₂	8.14
4.750	1-Heptene,2,4-dimethyl-	91	C ₉ H ₁₈	2.38
5.604	1-Nonene	95	C ₉ H ₁₈	4.51
7.332	1-Decene	96	C ₁₀ H ₂₀	4.67
7.944	2-Ethylhexanol	95	C ₈ H ₁₈ O	2.01
9.000	1-Undecene	96	C ₁₁ H ₂₂	3.9
9.134	Undecane	94	C ₁₁ H ₂₄	1.58
10.034	4-Methoxystyrene	88	C ₉ H ₁₀ O	3.36
10.571	1-Dodecene	95	C ₁₂ H ₂₄	4
10.696	Dodecane	95	C ₁₂ H ₂₆	1.31
12.051	1-adamantancarboxylic acid, 5-tetradecyl ester	82	C ₂₅ H ₄₄ O ₂	6.3
12.163	Tetradecane	88	C ₁₄ H ₃₀	2.78
12.428	o-phthalic anhydride	93	C ₈ H ₄ O ₃	2.69
13.442	(3Z)-3-Hexadecene	96	C ₁₆ H ₃₂	3.36
13.549	Tetradecane	94	C ₁₄ H ₃₀	1.38
14.898	1-Pentadecene	96	C ₁₅ H ₃₀	2.78
15.012	Pentadecane	95	C ₁₅ H ₃₂	1.9
15.124	2,4-Di-tert-butylphenol	97	C ₁₄ H ₂₂ O	10.14
16.481	1-Heptadecene	95	C ₁₇ H ₃₄	6.34
16.599	Hexadecane	93	C ₁₆ H ₃₄	1.83
18.300	Nonadecane	91	C ₁₉ H ₄₀	1.7
19.330	Myristic acid	91	C ₁₄ H ₂₈ O ₂	2.2
19.464	(1-Methyldecyl)cyclohexane	87	C ₁₇ H ₃₄	0.93
19.553	2-hexyl-1-Decanol	88	C ₁₆ H ₃₄ O	0.77
19.964	1-Nonadecene	96	C ₁₉ H ₃₈	4.68

Table 4. GC-MS analysis of pyrolytic products obtained with Cr-MCM-41

RT (min)	Possible chemical	Similarity (%)	Formula	Areas (%)
2.236	Acetic acid glacial	94	C ₂ H ₄ O ₂	21.53
4.683	Furfural	95	C ₅ H ₄ O ₂	12.54
5.667	1-Nonene	95	C ₉ H ₁₈	2.85
7.374	1-Decene	95	C ₁₀ H ₂₀	4.39
9.031	1-Undecene	95	C ₁₁ H ₂₂	3.7
10.594	1-Dodecene	94	C ₁₂ H ₂₄	5.17
12.068	2-Dodecenal, (2E)-	84	C ₁₂ H ₂₂ O	4.33
12.181	Tridecane	91	C ₁₃ H ₂₈	1.77
13.46	(3Z)-3-Hexadecene	95	C ₁₆ H ₃₂	3.71
14.915	1-Pentadecene	95	C ₁₅ H ₃₀	2.5
15.150	2,4-Di-tert-butylphenol	97	C ₁₄ H ₂₂ O	21.59
16.500	1-Heptadecene	94	C ₁₇ H ₃₄	3.77
18.199	1-Nonadecene	94	C ₁₉ H ₃₈	2.31
18.959	Oleic acid	85	C ₁₈ H ₃₄ O ₂	9.83

Analysis of the above experimental results indicated that there were numerous products obtained via catalytic pyrolysis of kapok fibers. Acetic acid was obtained in all cases with basically the highest peak area. Furfural was another major product. In addition, 2,4-di-tert-butylphenol was produced during pyrolysis using different catalysts with a retention time of ~15 mins. After the retention time of ~5.6 mins, more olefins were formed, including 1-decene, 1-dodecene, 1-undecene, 1-tridecene, heptadecene, etc. Those that catalytic pyrolysis over the modified molecular sieve catalyst contributed to the production of olefins.

CONCLUSIONS

Catalytic pyrolysis of kapok fibers was investigated with various MCM-41 catalysts, the feedstock to catalyst ratios, and the reaction temperatures.

(1) The main products obtained via pyrolysis of kapok fiber were acetic acid, furfural, 2,4-di-tert-butylphenol, olefins and alkanes.

(2) Pure silicon MCM-41 showed its weak acidity during the reaction with the furfural as the main product. Zr-MCM-41 showed the dual-functionality of acid and base, and both furfural and hydroxy acetone were present in the products. Cr-MCM-41 was more acidic and resulted in more furfural.

(3) The excess of the catalyst and the high temperature of the reaction had certain effects on the pyrolysis of biomass to produce olefins.

ACKNOWLEDGMENTS

This work was partially supported by Natural Science Foundation of Guangdong Province (2017A030310133) and the College of Chemistry and Environmental Engineering at Shenzhen University.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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