



Catalytic fast pyrolysis of mushroom waste to upgraded bio-oil products via pre-coked modified HZSM-5 catalyst



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HIGHLIGHTS

- HZSM-5 catalyst was modified with pre-coked by methanol to olefins reactions.
- Modified HZSM-5 catalyst contributed to the carbon yields of hydrocarbons.
- Coke yields decreased gradually with increasing of pre-coked percentage.
- Obtained oxygenates decreased at first and then increased at studied pre-coked percentage ranges.

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ABSTRACT

In this paper, HZSM-5 catalyst was modified by pre-coked to cover the strong external acid sites by methanol to olefins reaction, and the modified catalysts were then applied to conduct the catalyst fast pyrolysis of mushroom waste for upgraded bio-fuel production. Experiment results showed that the strong external acid sites and specific surface area decreased with pre-coked percentage increasing from 0% to 5.4%. Carbon yields of hydrocarbons increased at first and then decreased with a maximum value of 53.47%. While the obtained oxygenates presented an opposite variation tendency, and the minimum values could be reached when pre-coked percentage was 2.7%. Among the achieved hydrocarbons, toluene and *p*-xylene were found to be the main products, and the selectivity of *p*-xylene increased at first and then decreased with a maximum value of 34.22% when the pre-coked percentage was 1.3%, and the selectivity of toluene showed the opposite tendency with a minimum value of 25.47%.

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1. Introduction

Concerning the quite heavy dependence on fossil fuels and environmental impacts of greenhouse gas emissions associated with massive consumption of fossil energy, some efforts are currently made to find or invent renewable and alternative resources which are environmentally friendly and with a high reliability and stability (Abnisa and Wan, 2014; Wang et al., 2013b; Zhang et al., 2015b). In this regard, bioenergy is now accepted as a promising alternative that can attribute to meeting the fossil energy needs and enhancing the environmental problems (Akhtar and Saidina, 2012). Among the utilizations of bioenergy, catalytic fast pyrolysis (CFP) is particularly interesting and technically reliable, as well as economically feasible for converting bioenergy into bio-fuel products (Liu et al., 2013; Lu et al., 2012). This technology has attracted increasing attentions as its role in producing the highest bio-fuel

yields (~75 wt.%) under conditions of moderate temperature (500–600 °C) and short pyrolytic vapor residence time (~1 s) (Borges et al., 2014). In this sense, CFP can be selected as a recommend approach to seek the stated objective of biomass application.

Among various researched catalysts used in CFP process, HZSM-5 zeolite dominated the pronounced performance for shape selectivity and liquid products deoxygenation (Tamiyakul et al., 2015; Brebu et al., 2010; Zhang et al., 2014). The 3-dimensional intersecting pore structure of HZSM-5 is characterized by well-defined 10-membered rings with straight channels of 0.53 × 0.56 nm and sinusoidal channels of 0.51 × 0.55 nm, in which oxygenated organic compounds will be removed and hydrocarbons will be formed when primary pyrolytic volatile matters passed through the catalyst layer (Zhang et al., 2015a). However, it is important to note that there are several critical problems associated with HZSM-5 catalyst, such as the high coke production and short life-cycle. Coke is a kind of large molecule aromatic compound generated and accumulated on the surface of HZSM-5 catalyst, which leads to the blockage of the pore opening mouth and thus a

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deactivation of catalyst will be caused (Bertero and Sedran, 2016). Note that the strong external acid sites of HZSM-5 are responsible for coke formation, and a promising measure for decreasing the coke yield is to lower the strong external acid sites but meanwhile retain the internal acid sites (Zhang et al., 2014). In this sense, pre-coked treatment showed great promise for eliminating the strong external acid sites and improving the stability and activity of HZSM-5 zeolites (Chia and Trimm, 2005; Kim et al., 2011). Al-Khattaf (2007) found that the controlled pre-coking process, which could be obtained by exposing the zeolite to organic compounds at moderate temperature, showed significant effect for the enhancement of *p*-xylene selectivity during toluene disproportionation. Bauer et al. (2007) also revealed that in terms of inactivation of external surface acidity, specimens modified by pre-coking were proved to be more effective compared to those by one-cycle silica deposition. However, at the best of our knowledge, the effect of pre-coked percentage of HZSM-5 on products distribution achieved from CFP of MW has not been investigated and analyzed yet.

Mushroom waste (MW) is a representative kind of biomass energy, which consists of wood chip, cottonseed hull and corn cob. A pronounced way to utilize it is catalytic fast pyrolysis, which can convert MW into fuels or other high value-add chemicals. In this contribution, experiments on selectively eliminating the external strong acid sites were conducted by pre-coking of HZSM-5 through methanol to olefins (MTO) reaction. In contrast with fresh HZSM-5 catalyst, the pre-coked catalyst already has some cokes deposited on the external surface, and thus the strong external acidity and activity will be reduced. Subsequently, the modified catalysts with different pre-coked percentages were used to conduct the CFP of MW using Py-GC/MS. The effects of pre-coked percentages on products distribution of CFP of MW were investigated. The rest of this paper can be organized as follows: in Section 2 the experimental materials and set up are introduced; in Section 3 the effects of pre-coked percentages on products distribution, such as hydrocarbons, phenols, alcohols and so forth, as well as the selectivities of aromatics, were analyzed and discussed in detail; and in Section 4, the conclusions are drawn.

2. Materials and methods

2.1. Materials

Mushroom waste (MW) was obtained from a farm in Xuzhou, Jiangsu province, China. Before the experiment, some pretreatments of mushroom waste were carried out, which could be shown as follows: (1) Dried at 105 °C for 24 h in a drying oven; (2) Pulverized and grinded mechanically; (3) Sifted through a 60-mesh sieve and then kept in a sealed bottle. The ultimate analysis of dried MW was conducted and the results were as follows: 41.8 wt.% carbon, 6.4 wt.% hydrogen, 41.9 wt.% oxygen, and 4.7 wt.% nitrogen. Simultaneously, the proximate analysis of air-dried MW was also carried out, and the results were: 8.32 wt.% moisture, 76.59 wt.% volatile, 5.08 wt.% ash, and 10.01 wt.% fixed carbon.

2.2. Pre-coked treatment process of HZSM-5

It should be noted that more than 20 reaction mechanisms of methanol to olefins (MTO) have been proposed by different researchers, and among them, a hydrocarbon pool mechanism, which was firstly presented by Kolboe and co-workers, have attracted much more attention (Li et al., 2011). The hydrocarbon pool mechanism reveals that some certain organic active centers known as hydrocarbon pool intermediates act as co-catalysts within the cages of zeolites to which olefins are eliminated and

methanol is added (Wang et al., 2013a). The fresh HZSM-5 catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) was pre-coked by MTO reaction, and the treatment process was illustrated as Fig. 1. An injection pump and heat tape were used to generate methanol vapors and nitrogen was applied as carrier gas with a constant flow rate of 300 ml/min. Meanwhile, in order to obtain a high contact efficiency of methanol vapors and HZSM-5 catalyst, a vertical tube furnace was utilized to conduct the pre-coked experiments. The reaction temperature was controlled by temperature controller system, and in this experiment, the temperature was kept at 450 °C. When the methanol vapors were introduced into the reactor, they passed through the HZSM-5 catalyst layer, resulting the MTO reactions and thus, some cokes would be formed on the catalyst. Posterior to each experiment, some pre-coked HZSM-5 catalysts were combusted at 800 °C for 2 h in a muffle furnace, and the coke yield was calculated by the weight difference. Here, a parameter called pre-coked percentage was used to evaluate the pre-coked degree, and it was defined as the total mass of coke to HZSM-5 catalyst. In this paper, HZSM-5 catalysts with different pre-coked percentages (1.3%, 2.7%, 3.8%, 4.5% and 5.4%) were analyzed and studied, and they were achieved by adjusting and varying the MTO reaction time. Besides, the HZSM-5 catalysts used in the experiments were bought from the Catalyst Plant of Nankai University, Tianjin, China.

2.3. Experimental methods of CFP

A CDS Pyroprobe 5200 pyrolyzer was used to conduct the CFP experiments. The probe is a quartz tube, open at both ends, and heated by platinum resistance. Before the experiment, some packed quartz wool, 0.50 mg HZSM-5 catalysts and 0.50 mg feedstock specimens (MW) were put in the quartz in sequence. Besides, the pyrolysis temperature was kept for 20 s with a heating rate of 20 °C/ms, the helium with a high-purity (99.999%) purchased from Nanjing Maikesi Nanfen Special Gas Co., Ltd., which was utilized as carrier gas at a stable flow of 1.0 mL/min.

The pyrolysis vapors passed through the quartz tube into a gas chromatography/mass spectrometry (7890A/5975C, Agilent) via the helium sweeper gas stream. The interface and injector temperature of GC/MS was 300 °C and 275 °C, respectively. A capillary called HP-5MS with a size of 0.25 mm × 0.25 μm × 30 m was used to conduct GC separation. The split ratio was set at 1:80, and the

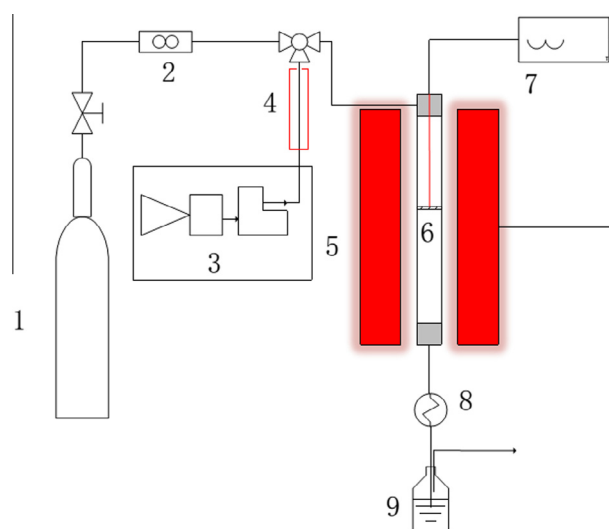


Fig. 1. Pre-coked treatment process of HZSM-5 catalyst by MTO reaction: 1 – N_2 gas cylinder; 2 – Flowmeter; 3 – Injection pump (methanol); 4 – Heat tape; 5 – Vertical tube furnace; 6 – HZSM-5 catalyst; 7 – Temperature controller and thermocouple; 8 – Heat exchanger; 9 – Gas-washing bottle.

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