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The conversion of biomass to light olefins on Fe-modified ZSM-5 catalyst: Effect of pyrolysis parameters

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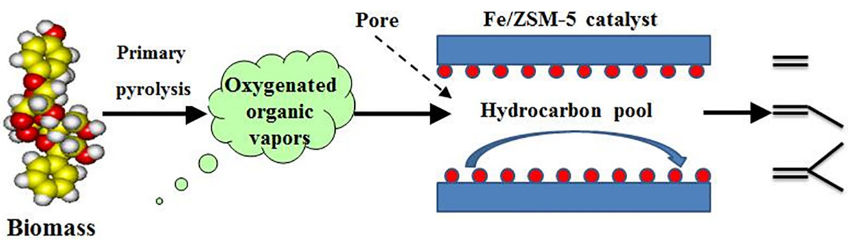
HIGHLIGHTS

- Ex-situ pyrolysis leads to higher yields of olefins compared to in-situ pyrolysis process.
- The optimal Fe-loading on ZSM-5 is 3 wt% for the selective production of light olefins
- The highest yield of light olefins was obtained for cellulose with 6.98 C-mol%.
- The yields of light olefins follow the decreasing order of cellulose, corn stalk, hemicelluloses and lignin.

GRAPHICAL ABSTRACT



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ABSTRACT

Light olefins are the key building blocks for the petrochemical industry. In this study, the effects of in-situ and ex-situ process, temperature, Fe loading, catalyst to feed ratio and gas flow rate on the olefins carbon yield and selectivity were explored. The results showed that Fe-modified ZSM-5 catalyst increased the olefins yield significantly, and the ex-situ process was much better than in-situ. With the increasing of temperature, Fe-loading amount, catalyst to feed ratio, and gas flow rate, the carbon yields of light olefins were firstly increased and further decreased. The maximum carbon yield of light olefins (6.98% C-mol) was obtained at the pyrolysis temperature of 600 °C, catalyst to feed ratio of 2, gas flow rate of 100 ml/min, and 3 wt% Fe/ZSM-5 for cellulose. The selectivity of C_2H_4 was more than 60% for all feedstock, and the total light olefins followed the decreasing order of cellulose, corn stalk, hemicelluloses and lignin.

1. Introduction

Light olefins (such as ethylene, propylene and butylene) are the key building blocks in the petrochemical industry, which can be used to produce polyethylene, polypropylene, butadiene and others (Dong et al., 2014; Izquierdo et al., 2012; Zakaria et al., 2012). To date, light olefins are mainly produced from the steam cracking of naphtha or other light alkane feedstock, and methanol conversion. With the growing of environmental deterioration and declining fossil energy resources, these current utilization technologies are not sustainable in the long term for light olefins production. Biomass has received more and more attentions as the only carbon-containing renewable energy (Awad et al., 2018; Das and Sarmah, 2015a; Das and Sarmah, 2015b; Martín-

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Lara et al., 2018). Using biomass as raw materials can provide a renewable way to light olefin production, and it is of great significance in increasing light olefin demand markets.

The conversion of light olefins from biomass pyrolysis were influenced by the reaction condition and feedstock composition (Jae et al., 2014). Catalytic fast pyrolysis (CFP) of biomass with zeolite provides a promising way to convert pyrolysis vapors directly into light olefins (Carlson et al., 2011). During CFP process, a number of catalysts have been developed, ZSM-5 catalyst shows more light olefins production by reacting with the oxygenate intermediates (Li et al., 2014), others also founded that metal-loaded ZSM-5 catalysts are more efficient than ZSM-5 catalysts (Galadima and Muraza, 2015; Hong et al., 2013). For the conversion process of methanol to olefins (MTO), methanol to propylene (MTP) and Fischer-Tropsch synthesis, Fe/ZSM-5 is widely used and found to improve the yields of light olefins efficiently, while the formation of aromatics and paraffins are reduced (Inaba et al., 2007; Machado et al., 2005). However, limited researches of Fe/ZSM-5 on biomass catalytic pyrolysis for light olefin have been reported, and Fe/ZSM-5 is found to produce the highest yield of light olefins compared to Mg, K, Ga and Ni/ZSM-5 (Zhang et al., 2013). Also the yields of C_2Hm from pyrolysis vapors followed the order of 4Fe/HZSM-5, HZSM-5 and 4Zr/HZSM-5 (Li et al., 2016).

To date, literature related to the production of light olefins from biomass catalytic pyrolysis, are noticeably lower than those from the common feedstocks (such as naphtha and light diesel) (Gayubo et al., 2004; Gong et al., 2011). The yield of light olefins is mainly determined by the ability of catalyst and cracking conditions, thus the catalysts and cracking conditions are needed to be optimized. However, there were no systematic studies concerning optimizing catalysts and reaction conditions of biomass pyrolysis to light olefins (Galadima and Muraza, 2015; Iisa et al., 2016; Wang et al., 2014). Most researchers just simply reported a comparison of the distribution of light olefins and aromatic by in-situ and ex-situ catalytic fast pyrolysis, and found that light olefins are mainly obtained from ex-situ pyrolysis, while aromatic from in-situ pyrolysis. Also, only few researchers have put their attentions on the effects of catalyst and cracking conditions during biomass catalytic pyrolysis (Gong et al., 2011; Hu et al., 2017; Huang et al., 2012). Huang et al. (Huang et al., 2012) investigated the effects of temperature, residence time, the catalyst/feed ratio and La content on the biomass and three components by in-situ catalytic fast pyrolysis, and found that biomass with high content of cellulose can produce more olefins. Hu et al. (Hu et al., 2017) studied the effect of HZSM-5 on the formation of light olefins from biomass catalytic fast pyrolysis, and the maximum carbon yield of aromatics + olefins is 21.7%.

In this study, catalytic pyrolysis of biomass with Fe-modified ZSM-5 catalyst for selective light olefins production was carried out in a fixed bed reactor. The effects of in-situ and ex-situ process, temperature, Fe loading, catalyst to feed ratio and gas flow rate on the product yields and selectivity were explored. The optimal conditions for light olefins production were obtained. The study may be helpful to the further understanding of different parameters on biomass to light olefins deeply.

2. Methods

2.1. Materials

2.1.1. Feedstock

In this study, hemicelluloses, cellulose, lignin and corn stalk were used as biomass feedstock. Hemicelluloses, cellulose, and lignin were purchased from Sigma–Aldrich Co., Ltd., while corn stalk samples were obtained from Wuhan, Hubei province, China. The particle sizes of 0.105–0.3 mm were selected for each trial. All raw materials were dried at 105 ± 5 °C overnight and kept in a desiccator before each experiment. The proximate and ultimate analyses of the raw materials were measured using SDTGA-2000 (Las Navas Company, Spain) and an elemental analyzer (Vario EL II CNHS/O, Germany). The lower heating value (LHV) of the raw materials were measured using an oxygen bomb calorimeter (Parr 6300, American), and the results are shown in Table 1.

2.1.2. Catalysts

ZSM-5 zeolite catalysts used have a three-dimensional regular pore system with a Si/Al ratio of 25 and the pore size of 5.5–5.6 Å, which were supplied by Nankai University Catalyst Co. Ltd. (Tianjin, China). Fe/ZSM-5 catalyst was prepared by impregnation method. Taking 3 wt% Fe/ZSM-5 catalyst for example, 5.0 g of ZSM-5 zeolite was impregnated in 100 ml Fe nitrate solution (1.08 g $Fe_2(NO_3)_3.9H_2O$) at the room temperature, and then rotary-evaporated at 70 °C, and dried overnight at 105 °C. The sample was calcinated at 550 °C for 5.5 h.

For catalyst characterization, temperature programmed desorption (TPD) was used to analyze the acidity of catalysts (ChemiSorb 2720, Micromeritics Instrument Corporation, Norcross, GA). Firstly, 50 mg catalyst sample was put into the U-tube, after being purged for 30 min by helium gas at the rate of 40 ml/min, the sample was heated from room temperature to 700 °C and kept for 60 min. Then, the sample was cooled to 50 °C, using NH_3 as the carrier gas at a rate of 40 ml/min to achieve adsorption for 30 min. Subsequently, helium gas was once again taken as carrier gas and the treatment maintained for 30 min at a gas flow rate of 40 ml/min. Finally, catalyst was heated to 700 °C with 40 ml/min helium gas to desorb NH_3 at 10 °C/min (Li et al., 2016). In this case, the NH_3-TPD profiles of catalysts were recorded.

2.2. Reactor setup

The schematic diagram of biomass catalytic pyrolysis for light olefins is presented in Fig. 1. The system consists of a quartz reactor with the ID of 30 mm and height of 700 mm and has two reaction zones, a fixed-bed reactor, a gas condensing system with ice and water mixture, a gas cleaning section followed by gas-sampling and measurement system. A cylindrical furnace with two heating zones is employed to supply the heat needed in the pyrolysis reactions. In the quartz tube reactor, two porous plates are equipped and some pieces of quartz fiber are located on the plates.

2.2.1. In-situ catalytic pyrolysis

During in-situ catalytic pyrolysis, feedstock and catalyst are mixed together and loaded on the top porous plate of the 1st-heating zone. Pure N_2 (99.99%) is used as the carrier gas. Before the two heating zones was both increased to the set temperatures (400, 500, 600 or 700 °C), the quartz reactor was flushed with pure N_2 (99.99%) at a flow rate of 300 ml/min for 30 min. Then sample (1.0 g) mixed with catalyst is quickly put onto the top porous plate, and maintained at a constant temperature for 30 min with N_2 flow rate of to ensure the complete reaction, and the gas rate of N_2 was changed to 50, 100, 200 or 300 ml/min. During the experiment process, bio-oil was collected in the gas condensing system, and non-condensable gases were collected in a gas-sampling system. After the experiment, turn off the furnace, while keep the carrier gas on until the quartz reactor reaches the room temperature to avoid the oxidation of char. The amount of bio-oil was determined based on the weight differences of the condensing system, and the amount of char was determined by the weight difference of the feedstock after experiment, the amount of gaseous products was calculated by the results of GC (Agilent 6890N) analysis.

2.2.2. Ex-situ catalytic pyrolysis

During ex-situ catalytic pyrolysis process, feedstock was loaded on the top porous plate of the quartz reactor, and catalyst was placed on the bottom porous plate as shown in Fig. 1. The 1st and 2nd heating zones were heated independently and kept at the same temperature. The pyrolysis vapors passed through the catalyst layer and reacted