



Modification and regeneration of HZSM-5 catalyst in microwave assisted catalytic fast pyrolysis of mushroom waste



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ABSTRACT

In this contribution, HZSM-5 zeolites were modified by ethylene diamine tetraacetic acid (EDTA) to selectively eliminate the strong external acid sites, and the modified catalysts were then used to conduct the microwave assisted catalytic fast pyrolysis (MACFP) of mushroom waste (MW). Experiment results showed that the modification of HZSM-5 with EDTA had no significant effect on topological structure, and the surface area and total acid sites decreased while the pore volume increased within the modification time regions. Among the modified catalysts, an EDTA treatment for 2 h (labeled as 2H-Z5) performed prominent promise for removing oxygenated chemicals and promoting the aromatic species as well as inhibiting the formation of coke. Simultaneously, the effects of various regeneration steps for deactivated 2H-Z5 catalysts on products distribution were studied, and the highest relative content of hydrocarbons (19.9%) and the lowest coke yield (3.48%) could be obtained under the third regeneration cycle condition.

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1. Introduction

Bio-fuel, achieved from thermal conversion or liquefaction of bioenergy as an abundant and renewable energy source, has attracted more and more attention in the past few years [1,2]. Despite some high value-added chemicals are found in the bio-oil, which includes hydrocarbons, alcohols, furans, phenols and so forth, its application is still limited as a consequence of the high oxygen content, low calorific value, high corrosion behavior and chemical instability [3,4]. Upgrading of biomass derived bio-oil provides an effective and efficient process to attain an energy benefit with a minimum effect on environment [5]. In this regard, catalytic fast pyrolysis (CFP) of biomass shows great promise for increasing the hydrocarbons and reducing the generation of oxygenated chemical compounds [6,7].

Among various catalysts which have been investigated and tested for the conversion of bio-energy into bio-fuels, HZSM-5 has been proved to be the most efficient for considerably improving the components of bio-oil by both decreasing the oxygenated chemicals and promoting gasoline like constituents through various reactions, such as dehydration, decarbonylation, decarboxylation and aromatization [8,9]. However, the high production of coke during the CFP process leads to catalyst deactivation and short recycle life. Due to the high price and large amount of HZSM-5 catalysts consumed in the industry, it is worth noting that efficient modifi-

cation, recycle and reuse of catalysts in a continuous operating system is necessary [10]. In this sense, researches on modification, regeneration and reuse of HZSM-5 zeolites are of fundamental interest to obtain their practical implementation.

Previous studies related to the modification and regeneration of catalysts by various techniques were reported intensively [10–14]. For the modification of HZSM-5, Huang et al. [15] modified HZSM-5 zeolites by CuO and MoO₃ for the thermal conversion of pine sawdust, and they indicated that Mo(3%)-Cu(3%)/HZSM-5 treatment promoted the highest yield of C₆ ~ C₁₂ hydrocarbons. Sheng et al. [16] analyzed the effect of steam treatment on HZSM-5 during ethanol dehydration to ethylene, and they detected that the total amount of acid sites of HZSM-5, especially the strong acid sites, decreased after steam treatment, which led to the improvement of catalytic stability. Li et al. [17] conducted a comparative research on catalytic conversion of methanol and propanal, and it was observed that the post-modification step by Ga(NO₃)₃ and NH₄HF₂ had significant effects on structure and acidity of HZSM-5 zeolites, and the catalyst lifetime was dramatically improved. In the sense of catalyst regeneration, Ma and van Bokhoven [12] studied the deactivation and regeneration of H-USY catalysts during the catalytic fast pyrolysis of lignin, and they concluded that the regeneration of H-USY was possible to a large extent, and the products distribution were affected by the regeneration cycles. Lopez et al. [10] used TG/FTIR to research the regeneration of H-USY and HZSM-5 catalysts through the catalytic cracking of polyethylene, and it was found that the volatile matters showed slight variation during the regeneration process.

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Note that the strong external acid sites are responsible for the coke formation due to the shape selectivity of HZSM-5 zeolites makes it difficult to form coke in the internal pores, a promising process to lower the strong external acid sites but retain the internal weak sites is to selectively eliminate the strong acid sites by dealumination [18]. For this reason, ethylene diamine tetraacetic acid (EDTA) showed prevalent ability to remove the framework aluminums [19]. Simultaneously, compared to some other pyrolysis heating reactors, microwave assisted catalytic fast pyrolysis (MACFP) dominates a series of superiorities for well-distributed of heat, easy operation and energy conservation, which has been extensively used and studied [20–22]. However, at the best of our knowledge, the MACFP of mushroom waste (MW) over EDTA modified HZSM-5 catalysts, and the subsequent regeneration of modified HZSM-5 catalysts, have not been studied and reported yet. In this regard, our objective here is to investigate the effects of various EDTA modifications and regeneration steps of HZSM-5 catalysts on products distribution through MACFP of MW, and thus the optimum EDTA treatment condition and regeneration cycle process will be determined and an upgraded bio-oil production will be obtained.

2. Materials and methods

2.1. Materials

Mushroom waste (MW) was collected from a farm in Xuzhou, Jiangsu province, China. Prior to experiment, the MW samples were dried at 105 °C for 24 h in a drying oven, and then the specimens were smashed and grinded. Finally, a 60-mesh sieve was used to screen the feedstock specimens, and after the pretreatment, the MW experimental samples were deposited in a sealed bottle. The component analysis of the MW samples (dry basis) were carried out and the results were shown as follows: 34.5% cellulose, 38.1% hemicellulose, 23.1% lignin and 4.3% extractives. The ultimate analysis of dried MW was conducted and the C, H, O and N were 41.8 wt%, 6.4 wt%, 41.9 wt%, and 4.7 wt%, respectively. Note that the proximate analysis results for air-dried MW could be shown as follows: 5.08 wt% ash, 76.59 wt% volatile, 10.01 wt% fixed carbon, and 8.32 wt% moisture.

2.2. EDTA modification of HZSM-5

EDTA, which was used to conduct the chemical modification of HZSM-5, was achieved from Nanjing Chemical Reagent Co. Ltd. Simultaneously, the HZSM-5 zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) were purchased from the Catalyst Plant of Nankai University, Tianjin, China. The EDTA modification procedures could be organized as follows: (i) Deionized water was used to prepare 0.33 mol/L EDTA solution, and a magnetic stirrer at 80 °C water bath was applied to intensively mix the solution and HZSM-5 (the zeolite to solution mass ratio was 1:10) for 1 h, 2 h, 3 h and 4 h, respectively. (ii) A Buchner funnel was utilized to conduct vacuum filtration steps of mixture, and a Ph-meter was used to measure the filtrate (until neutral). (iii) The EDTA modified HZSM-5 catalysts were dried in an air-circulating oven at 120 °C for 2 h, and then a muffle was used to calcine the modified HZSM-5 samples for 4 h at 550 °C. Note that in this contribution, the studied modified HZSM-5 catalysts were designated as 1H-Z5, 2H-Z5, 3H-Z5 and 4H-Z5 according to the EDTA modification time.

2.3. Characterization of catalysts

XRD patterns were carried out by Bruker D8 Focus using $\text{CuK}\alpha$ radiation with a step of 0.02 at a current of 40 mA and a voltage of

40 kV. The scanning range of 2θ was from 5° to 50° with a 10 min^{-1} scanning rate. The pore characteristics and surface features of the parent and modified HZSM-5 specimens were conducted by a Belsorp-Max adsorption instrument. BET and Langmuir methods were used to calculate the specific surface area. NH_3 -TPD was conducted by the FineSorb 3010 automatic temperature programmed chemical adsorption equipment to investigate the acidity performances of various specimens. For a typical run, 100 mg specimens were introduced in a U-shaped quartz cell and the temperature was fixed at 873 K with a He steam for 1 h, and then cooled down to 423 K. Finally, the samples were saturated by some NH_3 gas, then the NH_3 -TPD was conducted with a fixed heating rate of 15 °C/min from 150 to 650 °C.

2.4. Experimental procedure

Fig. 1 presented the schematic diagram of MACFP process. Obviously, the MACFP experiments were conducted in a bench scale with a microwave oven (power: 750 W; frequency: 2.45 GHz). A self-designed quartz fixed bed reactor was placed into the microwave oven cavity, and the stream inlet tube was connected to the N_2 gas system, and the stream outlet was connected to the condensation system. Furthermore, a K-type thermocouple was used to measure the reaction temperature. It should be noted that due to the strong absorptive ability for microwave, some SiC samples were utilized as microwave absorbent [21,23].

For a typical run, 10 g MW feedstock specimens were introduced onto the surface of SiC bed, and some SiC particles and 10 g HZSM-5 catalysts were mixed uniformly at first, and then the mixtures were placed on the mesh sieve to form a fixed bed for upgrading the primary volatile matters. Prior to each experiment, N_2 was purged into the reactor to keep an inert atmosphere with a flow rate of 50 mL/min. After sufficient purging, the power supply was started and the pyrolysis process was proceeded. After reaching the desired reaction temperature of 550 °C, the temperature control system was used to maintain the temperature, and for each experiment, the reaction time was fixed at 20 min. The pyrolytic volatile matters passed through the condensation system, and then the condensable products were collected as bio-oil. The incondensable gas were gathered in a gas collection bag. After each experiment, in order to determine the coke yield, the spent HZSM-5 catalysts were collected and then were calcined in a muffle for 4 h at 800 °C, and thus the coke yield could be determined. Furthermore, the carbon yield of bio-oil was calculated by the weight difference of condensation collector before and after each MACFP experiment, and the water content in the liquid products was identified by Karl Fischer Titration. Simultaneously, the char yield was determined by the weight difference of the reactor before and after each experiment. Besides, the carbon yield of gas was calculated by the difference based on the law of mass conservation.

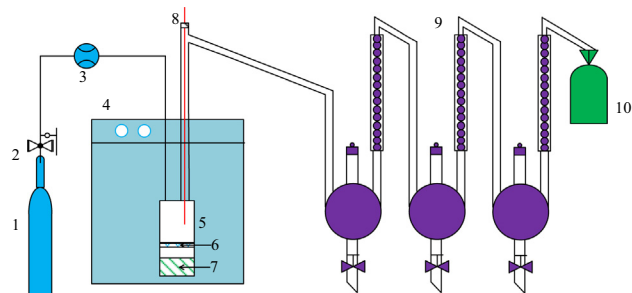


Fig. 1. Schematic diagram of MACFP system. (1) N_2 gas; (2) pressure regulator; (3) flow meter; (4) microwave oven; (5) quartz glass reactor; (6) HZSM-5 catalysts; (7) pyrolysis feedstock samples; (8) thermocouple (K-type); (9) condensation system; (10) gas collection bag.

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