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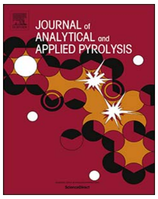

Catalytic fast pyrolysis of rice straw to aromatic compounds over hierarchical HZSM-5 produced by alkali treatment and metal-modification

Hao Chen[a], Hao Cheng[a,b], Feng Zhou[c], Kequan Chen[b], Kai Qiao[c], Xiuyang Lu[a], Pingkai Ouyang[a,b], Jie Fu[a,*]

[a] *Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China*
[b] *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*
[c] *Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC, Fushun 113001, China*

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ABSTRACT

The synthesis of highly selective catalysts for the catalytic fast pyrolysis (CFP) of biomass into valuable aromatics remains a challenge. This report describes the synthesis of hierarchical ZSM-5 catalysts by the NaOH desilication of conventional HZSM-5 for the CFP of rice straw to aromatics in a Tandem μ-reactor system coupled directly to a GC/MS equipped with FID and TCD. Catalysts were treated with a mild HCl wash and metal loading to increase the catalytic activity and reduce the deactivation. The effects of acidity, mesoporosity and incorporation of metals on the production of aromatics were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption and desorption (N_2-BET) and temperature-programmed desorption of NH_3 (NH_3-TPD). The highest total acidity, especially the strong acidity, of the hierarchical ZSM-5 treated by 0.2 and 0.4 NaOH followed by HCl washing (AHZ-0.2 and AHZ-0.4) gave the highest yields of aromatics. Suitable mesopores introduced by alkali treatment enhanced mass transfer of reactants, increasing the yield of aromatics. Finally, the loading of a suitable amount of Ni and Cu produced more aromatics than standard HZSM-5 due to the improved decarboxylation/decarbonylation reactions leading to higher yields of olefins.

1. Introduction

Currently, the utilization rate of traditional fossil fuels is much faster than their regeneration rate which is leading to a shortage of fossil fuels, and their concomitant CO_2 emissions are resulting in serious environment pollution [1,2]. Therefore, it is necessary to development a new kind of environmental friendly and sustainable method for energy production [3,4]. Lignocellulosic biomass, which is abundant in nature, has a lot of potentials as a renewable source of energy [5]. Several pathways to convert lignocellulosic biomass into biofuels and chemicals are under development, and they are generally classified as either thermochemical processes or biochemical processes [6,7]. In recent years, catalytic fast pyrolysis (CFP) has been viewed as a promising route for the conversion of biomass to chemicals and fuels, and the optimization of catalysts for the pyrolysis of bio-oils is geared towards increasing the substitution of oxygen and oxygen-containing functionalities [7,8].

ZSM-5 zeolite has been reported to be the most active and selective catalyst for the production of aromatics from various biomass feedstocks owing to its moderate pore structure, strong acidity, and high hydrothermal stability [9–11]. However, the sizes of the biomass molecules are limited by diffusion into the micropores, which causes coke formation at continuously elevated temperatures. To solve this problem, many modifications of ZSM-5 have been investigated, and the most significant is the introduction of mesopores connected to micropores in the ZSM-5. Li et al. [12] synthesized the hierarchical ZSM-5 by NaOH treating, which showed that the hierarchical structure in ZSM-5 improved the yield of aromatics and decreased the formation of undesired coke during the CFP of beech wood. Zhang et al. [13] and Park et al. [14] showed that hierarchical ZSM-5 performed well in the CFP of biomass due to that the mesopores connected to micropores improved the access to available catalytic active sites, and then improved the conversion of large molecules and preserved aromatization capacity through the microporosity of ZSM-5. The post-synthesis treatments tend to produce intracrystal mesopores. Alkali treatment of conventional microporous ZSM-5 is a simple and effective method for creating intracrystalline mesopores and generating more open mesopores that are accessible to large molecules in the ZSM-5 zeolites rather than creating

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[*] Corresponding author.
E-mail address: jiefu@zju.edu.cn (J. Fu).

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the zeolite fragments that would be produced via direct synthesis [15–21].

Metal modification is another important method to improve the catalytic activity of ZSM-5. Mullen et al. [22] showed that Fe-modified HZSM-5 was more selective for the formation of benzene and naphthalenes compared to the standard HZSM-5, while the selectivity for p-xylene, ethylbenzene and trimethylbenzene decreased with the addition of Fe. Du et al. [23] found that the impregnation of Cu or Ga in HZSM-5 increased the yield of aromatics, suggesting that some transition metals can promote the aromatization functionality of H-ZSM5. The incorporation of metals promoted the deoxygenation mainly through decarboxylation and/or decarbonylation processes [24] and produced more olefins to produce aromatics. Thus, the addition of metals to the hierarchical ZSM-5, which combines the advantage of both the metals and the hierarchical structure, should further improve the catalytic performance of CFP of biomass to produce aromatics.

In this study, rice straw was used for the CFP to produce aromatics over catalytic hierarchical HZSM-5 synthesized by alkali treatment. To further improve the yield of aromatics for CFP of rice straw, the modification of catalyst by HCl washing and incorporation of metals were measured. The effects of acidity, mesoporosity and incorporation of metals on the production of aromatics were investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), N_2 adsorption and desorption (N_2-BET) and temperature-programmed desorption of NH_3 (NH_3-TPD). The objective of this work is to understand the relationship among the properties of ZSM-5, selectivity for the products and coke formation during the CFP of biomass to achieve the maximum utilization of renewable resources for the production of valuable chemicals.

2. Experimental and materials

2.1. Materials

Rice straw used in the study was purchased from a farm (Henan, China). HZSM-5 was purchased from Nankai University (Tianjin, China). $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Ga(NO_3)_3{\cdot}9H_2O$ were purchased from Aladdin (AR, China). NaOH and HCl were purchased from Sinopharm Chemical Reagent Limited Corporation (AR, China). Ethylene, propylene, butylene, benzene, toluene, xylenes, naphthalene, trimethylbenzene and methyl naphthalene as the external standards, which were all purchased from Aladdin (AR, China).

2.2. Catalyst synthesis

Hierarchical ZSM-5 were synthesized using the following procedure: 1 g of HZSM-5 and 40 mL of NaOH (0.2–1.0 M) were mixed and heated at 65 °C for 1 h. Then, the slurry was rapidly cooled to room temperature, filtered, washed with deionized water and dried at 110 °C overnight. Finally, the alkali-treated zeolites were ion-exchanged with NH_4Cl (1.0 M) at 80 °C for three times to generate the protonated material which was then subjected to calcination at 550 °C for 5 h. The catalysts were denoted as AZ-x, where the x referred to the concentration of NaOH used.

For the HCl washed samples, the desilicicated AZ-x were treated with 0.1 M HCl at 65 °C for 5 h, and the zeolites were then filtered, washed with deionized water and dried at 110 °C for 12 h. The catalysts were denoted as AHZ-x, where the x referred to the concentration of NaOH used.

The metal-modified hierarchical HZSM-5 catalysts were prepared using an incipient-wetness impregnation with an aqueous solution of different metal salts on AHZ-0.2. After impregnation, the samples were dried at 110 °C for 12 h and calcinated at 550 °C (5 °C/min) for 4.5 h. Metal-modified hierarchical HZSM-5 samples were named as M/HZ-0.2 (M represents the metal).

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer with Cu-Kα radiation at 40 kV and 40 mA. Diffractions were carried out in the 2θ range of 5–50° at a speed of 4°/min. N_2 adsorption and desorption isotherms (N_2-BET) were measured on a Micromeritics 3Flex adsorption instrument, Micromeritics. Samples were degassed for 12 h under N_2 at 300 °C prior to the measurements. The microporous volume, micropore surface area, and external surface area were calculated using the t-plot method. The mesoporous volume and size distribution were determined from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. Temperature-programmed desorption of NH_3 (NH_3-TPD) were measured on a chemisorption physisorption analyzer connected to a thermal conductivity detector (TCD). Typically, 50 mg of zeolites was pretreated at 120 °C in He (20 mL/min) for 2 h and then cooled to 80 °C, followed by ammonia adsorption for 40 min. NH_3-TPD were carried out in the temperature range of 80 ∼ 700 °C at a ramping rate of 10 °C/min. The morphologies of the zeolites were examined by transmission electron microscopy (TEM) on a Tecnai G2 microscope operated at 200 kV. The metal loadings of the catalysts were determined by coupled plasma optical emission spectrometry (ICP-OES).

2.4. CFP of rice straw

The CFP of rice straw was conducted in a Tandem microreactor system (Rx-3050 TR, Frontier Laboratories, Japan) coupled directly to a Agilent 7890B gas chromatography/5975N mass spectrometry (GC/MS) for immediate identification and quantification of the pyrolysis products. The furnace consisted of two reactors, the temperatures of which could be controlled individually between 40–900 °C. The interface between the furnaces and GC can be heated to 100–400 °C and was operated at 300 °C to minimize condensation of pyrolysis products.

Firstly, we crushed the straw using grinding miller and then collected the particles below 0.15 mm through mesh. Then the solid was further purified using Soxhlet extraction with ethanol and methylbenzene ($V_{ethanol}$: $V_{methylbenzene}$ = 1: 1) for 24 h. After washed by deionized water, the straw particles were dried at 110 °C for 12 h. The biomass and catalyst were mixed using agate mortar. To ensure sufficient mixing, all samples were grinded for at least 30 min. For a typical test, approximately 5 mg of a catalyst-to-rice straw mixture (20:1 by weight) was used. Helium (He) was used as the pyrolysis gas and the carrier gas, and the pyrolysis vapor was swept into a gas chromatograph (Agilent 7890 B) equipped with a three-way splitter coupled to three detectors, a mass spectrometer (5977A MSD), a flame ionization detector (FID), and a thermal conductivity detector (TCD). The oven temperature program was set as below: holding at an initial temperature of 40 °C for 4 min, and then increasing the temperature by the rate of 10 °C/min to 260 °C with a dwell time of 6 min. A liquid nitrogen bath (MicroJet Cryo-Trap, MJT-1030E) was used to focus the pyrolysis vapors of volatile components, such as CO, CO_2 and olefin hydrocarbons, before they passed through the column. The condensable pyrolysis products were separated with an Ultra alloy-5 capillary column (30 m × 0.250 mm and 2 μm film thickness). Products were quantified by injecting calibration standards with known concentrations of the target species into the furnace under the same experimental condition. The yields of CO and CO_2 were quantified by the TCD and the other organic products were quantified by the FID using external standards. The unaccounted material was unrecovered coke deposited on the walls of the sample cups. The analysis of organic products were quantified by external standard method using ethylene, propylene, butylene, benzene, toluene, xylenes, naphthalene, trimethylbenzene and methyl naphthalene as the external standards. The concentrations for each products were in the range of 0–8 g/L. Those compounds not account for standards were tentatively identified by MS. The electron ionization of MS was 70 eV and the acquisition mode was full scan. The structural assignment was based on