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Enhancement in the aromatic yield from the catalytic fast pyrolysis of rice straw over hexadecyl trimethyl ammonium bromide modified hierarchical HZSM-5

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ABSTRACT

Modified H-type ZSM-5 (HZSM-5) catalysts were prepared using hexadecyl trimethyl ammonium bromide (CTAB) as mesopore templates to enhance the activity for the catalytic fast pyrolysis of rice straw for aromatics compounds. A certain quantity of CTAB added into the HZSM-5 (HZ) forming hierarchical structure exhibited an improvement in the yield of the aromatics and a decrease in the yield of coke in comparison with that of bare HZ. In contrast, excessive CTAB addition resulted in a decrease in aromatic yield and an increase in coke yield. The effects of crystallinity, textural properties, morphological structure and acidity distribution on the production of aromatic compounds were measured by XRD, BET, TEM and NH_3-TPD. The good crystallinity, small amount of mesopore formation and highest total acidity discovered in HZ-0.01 (the mole ratio of CTAB/SiO_2 is 0.01) provided the highest aromatic compound yield of 26.8% and the lowest coke yield of 39.2%.

1. Introduction

Lignocellulosic biomass has been considered as the most abundant renewable resource, which can be used for the synthesis of bio-based chemicals and liquid biofuels (Stocker, 2008; Schaetz et al., 2012; Huber and Corma, 2007). Thermochemical or biochemical methods have been developed as the routes for the production of bio-based chemicals and biofuels from lignocellulosic biomass. However, these technologies usually require multiple steps that significantly increase the cost in the process of biomass conversion, which means that lignocellulosic biomass is not currently used in industrial production processes (Wang et al., 2014). In recent years, a thermochemical technology of catalytic fast pyrolysis (CFP) has been viewed as one of the most prevailing and promising methods for the production of renewable liquid fuels such as aromatic compounds (Zhang et al., 2015; Lei et al., 2011). In this single-step process, rice straw, as the most abundant biomass agricultural waste around the world, was regarded as a suitable raw material for the CFP technology (Cheng et al., 2012; Binod et al., 2010; Hsu et al., 2010).

CFP proceeds likely as two main steps: thermal depolymerization as well as the decomposition of biomass into pyrolysis vapors, and the subsequent deoxygenation to aromatic and olefin compounds along with CO, CO_2, H_2O and coke (Wang et al., 2014; Cheng et al., 2012). The deoxygenated process tends to require a zeolite catalyst, and ZSM-5 has shown best performance for the aromatic production from the CFP of lignocellulosic biomass compared with that of other zeolite catalysts (Jae et al., 2014; Perego and Bosetti, 2011; Foster et al., 2012). For instance, Jae et al. (2011) systematically studied the production of aromatics from the CFP of glucose using a series of zeolites with different pore sizes and found that HZSM-5 zeolite exhibited the highest yield of aromatic and lowest yield of coke. Carlson et al. (2009) reported the CFP of glucose, xylitol, cellobiose, and cellulose over five catalysts including silicalite, beta, Y-zeolite, silica–alumina, and ZSM-5. The results showed that ZSM-5 exhibited the highest yield of aromatic with 30% and the lowest yield of coke (Carlson et al., 2009). The catalytic performance characteristics of H-ferrierite, H-mordenite, H-beta, H-Y and HZSM-5 for the catalytic pyrolysis of hemicellulose were compared, and the results indicate that HZSM-5 was most effective for the production of aromatics (Mihalcik et al., 2011). The HZSM-5 catalyst also has shown good catalytic activity for the production of aromatics from the conversion of lignin (Ma et al., 2012). Therefore, HZSM-5 showed good catalytic performance for the CFP of lignocellulosic biomass, which mainly consisted of cellulose, hemicellulose and lignin.

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Although HZSM-5 was demonstrated to be the most effective in the CFP of lignocellulosic biomass to produce valuable aromatics, it also faces many problems (Ding et al., 2017). Due to the microporous structure of a typical HZSM-5 zeolite, bulky reactants and intermediates face diffusion limitations, making it difficult to access active pore sites, and these reactants and intermediates end up blocking the channels, thereby causing the deactivation of the catalyst (Wang et al., 2014; Ding et al., 2017; Schmidt et al., 2013). To overcome this problem, many studies has been conducted that introduce an additional mesoporous structure into micropores of HZSM-5. One method was the desilication of HZSM-5 with alkaline solutions, which has been widely studied and showed good performance for the CFP of lignocellulosic biomass (Zhang et al., 2013; Qiao et al., 2017; Li et al., 2014). In alkali treatment method, the mesopores are introduced into ZSM-5 crystals with extraction of silicon atoms from the zeolite framework. The main drawback of the desilication method is the loss of zeolite material owing to the leaching process and the relatively limited quantity of mesopores (Schmidt et al., 2013). Another method that introduces a mesopore transport network was the use of a hard-templating or a soft-templating technique during the synthesis process of ZSM-5 (Choi et al., 2006; Schmidt et al., 2001). Zhao et al. (2009) reported that hierarchical ZSM-5 can be synthesized by the introduction of CTAB, however, they did not apply the synthesized hierarchical ZSM-5 to any catalytic application. Chen et al. (2016) reported the nano-sized ZSM-5 zeolite was synthesized by a modified seed-induced method with CTAB, which showed a high stability and high propylene selectivity from the conversion of methanol. However, the effect of the introduction amount of mesotemplate during the synthesis process of HZSM-5 for the CFP of lignocellulosic biomass has not been studied systematically.

In this work, hierarchical HZSM-5 was prepared by an emulsion method using conventional TPAOH and CTAB as micro- and mesopore templates for the CFP of rice straw. The catalytic performance of HZSM-5 with different CTAB quantities for the CFP of rice straw was compared. The effects of crystallinity, textural properties, morphology structure and acidity distribution on the production of aromatic compounds were investigated by X-ray diffraction (XRD), N_2 adsorption-desorption (BET), transmission electron microscopy (TEM) and temperature-programmed desorption of NH_3 (NH_3-TPD) methods. The objective of this work is to provide a useful method for improving the selectivity to aromatic compounds and reducing coke formation during the CFP of rice straw using hierarchical HZSM-5 with the addition of CTAB.

2. Materials and methods

2.1. Materials

Rice straw was purchased from a farm (Henan, China). $NaAlO_2$ (99%), tetraethyl orthosilicate (TEOS, > 99%) and hexadecyl trimethyl ammonium bromide (CTAB, AR) were obtained from Aladdin, Shanghai. NH_4Cl (AR) and tetrapropylammonium hydroxide (TPAOH, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized water was prepared in house. Prior to use, the rice straw was chopped by a grinder and screened with a 100-mesh sieve, extracted with ethanol and toluene by a Soxhlet apparatus, and then dried at 110 °C for 12 h.

2.2. Synthesis of the catalysts

A series of hierarchical HZSM-5 samples were synthesized using an emulsion method with TPAOH and CTAB as micro- and mesopore generating templates. First, a 0.16 g of $NaAlO_2$ was added to 13.5 mL of deionized water in a round-bottom flask under an ice-water bath condition with magnetic stirring at 600 r/min for 30 min. A 6.2 g portion of TEOS was added to the above solution with magnetic stirring for another 30 min, creating an oil (TEOS)-in-water emulsion. Second, 4.9 g of TPAOH was dissolved in deionized water to form a 25% aqueous solution, and the mixture was dropped gradually into the above emulsion under ice-water bath conditions with magnetic stirring at 1000 r/min for 4 h. Thereafter, a calculated amount of CTAB was added into the above emulsion with magnetic stirring at 800 r/min for 6 h at room temperature, forming the ZSM-5 precursor. Third, the ZSM-5 precursor was crystallized in a 100 mL autoclave at 170 °C for 3 days. The precipitate was separated via filtration and washed thoroughly with deionized water until a pH of approximately 7 was attained. The obtained precipitate was further dried in a forced air oven at 110 °C overnight. Then, the ZSM-5 precursor was suspended in a solution of 1.0 mol/L NH_4Cl aqueous solution, heated to 80 °C with magnetic stirring and maintained for 8–12 h by an ion-exchange method three times. Lastly, the solids were calcined at 550 °C for 6 h. The obtained catalysts were denoted as HZ-x, where x refers to the molar ratio of CTAB/SiO_2. The catalyst without the addition of CTAB was denoted as bare HZ for comparison.

2.3. Catalytic fast pyrolysis of rice straw

The CFP experiments were performed in a tandem μ-reactor system (Rx-3050 TR, Frontier Laboratories, Japan), connected directly to a gas chromatography-mass spectrometry (GC–MS, Agilent 7890B-5977A MSD) system for identification and quantification of the pyrolysis products. The furnace includes two reactors, which can be individually temperature-controlled from 40 °C to 900 °C. The interface between the furnaces and GC–MS equipment was heated to 300 °C to minimize the condensation of the pyrolysis products.

In a typical experiment, approximately 5 mg mixtures with a mass ratio of 20:1 (catalyst: rice straw) were added into a furnace. Helium was used as both the pyrolysis gas and carrier gas, and the pyrolysis vapors were swept into a GC equipped with a three-way splitter coupled to three detectors, a mass spectrometer, a flame ionization detector (FID), and a thermal conductivity detector (TCD). A liquid nitrogen bath MicroJet Cryo-Trap (MJT-1030E) was equipped for focusing the pyrolysis vapors of volatile components such as CO, CO_2 and olefin hydrocarbons before they passed through the column, contributing to a good separation effect. The condensable pyrolysis products were separated with an Ultra alloy-5 capillary column.

2.4. Analysis method

The liquid products were quantified by injecting calibration standards with known concentrations of the target species into the furnace under the same experimental conditions. Quantitative analysis of CO and CO_2 was performed with the TCD using calibration curves for each compound of the standard gas mixtures. Quantitative analyses of other products were performed with an FID using calibration curves for each compound. The carbon content in the rice straw and residue after pyrolysis was quantified by elemental analysis (Vario Micro). All data regarding the product distribution was calculated as the molar ratio of carbon in a specific product to the moles of carbon in the rice straw. The selectivity to the aromatic compounds was calculated as the molar ratio of carbon of the target aromatic compound to total aromatic products. The unaccounted contents included unrecovered coke deposited on the walls of the sample cups, small amounts of alkanes and large molecular weight compounds unidentified by GC. The reported uncertainties are the standard deviations, which were determined by replicating three experiments.

2.5. Characterization techniques

Powder X-ray diffraction (XRD) patterns were performed on a PANalytical Empyrean 200895 with Ni filtered Cu Kα radiation (λ = 0.154 nm) at 30 mA, 40 kV. The samples were scanned using a 2θ range of 5°–50° at a speed of 4°/min.