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Improving activity of ZSM-5 zeolite catalyst for the production of monomeric aromatics/phenolics from hydrolysis lignin via catalytic fast pyrolysis

Hooman Paysepar[a], Kasanneni Tirumala Venkateswara Rao[a], Zhongshun Yuan[a], Hengfu Shui[b], Chunbao (Charles) Xu[a,b,*]

[a] *Department of Chemical and Biochemical Engineering, Western University, London, Ontario N6A 5B9, Canada*
[b] *School of Chemistry & Chemical Engineering, Anhui University of Technology, Ma'anshan 243002, Anhui Province, PR China*

A R T I C L E I N F O

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A B S T R A C T

This work aimed to further enhance the activity of ZSM-5 zeolite catalyst for the production of monomeric aromatics/phenolics from hydrolysis lignin via catalytic fast pyrolysis. To this end, various treatment approaches including acidification with H_2SO_4 and H_3PO_4 and metal (Ni) loading were performed on the ZSM-5 zeolite. Catalytic fast pyrolysis (CFP) of hydrolysis lignin (HL) was conducted at 450 °C using ZSM-5 zeolites with various strengths of acidity (ZSM-5 and Ni-ZSM-5 with moderate Lewis and Bronsted sites, H_2SO_4-ZSM-5 and H_3PO_4-ZSM-5 with more Bronsted sites). The results show that the yield of monomeric aromatic compounds increased considerably by increasing the Bronsted acid site and total acidity of the catalyst. With the best catalyst, H_2SO_4-ZSM-5, the total monomeric aromatics/phenolics yield increased to 151 mg/g-HL, compared to 68 mg/g-HL without catalyst, 84 mg/g-HL with ZSM-5, 96 mg/g-HL with H_3PO_4-ZSM-5, and 85 mg/g-HL with Ni-ZSM-5. The H_2SO_4-ZSM-5 demonstrated to be thermally stable and has superb resistance to carbon/coke deposition, owing to its microporous structure, relative large BET surface area and presence of strong Bronsted acid sites.

1. Introduction

The fundamental requirements of developing biorefining technologies for transforming raw biomass into chemicals and fuels is the processing cost, efficiency and quality/values of the produces, which are all related to the development of inexpensive and effective catalysts. For example, fast pyrolysis though being the industrially realized biomass conversion technology is limited by the poor quality of pyrolysis bio-oil, consisting of hundreds of oxygenated organic compounds that are corrosive, instable and with a poor heating value [1]. Catalytic fast pyrolysis (CFP) has demonstrated to be cost-effective approach to improving the overall quality of the bio-oil through the catalytic cracking and de-oxygenation of pyrolysis vapor phase to low molecular weight bio-oil products with reduced oxygen content (and hence better quality for both fuel and chemical applications) [2,3].

Solid acid catalysts such as alumina and aluminosilicate zeolites (e.g., ZSM-5, Zeolite Y, Zeolite X) have widely used for CFP of biomass for producing high-quality bio-oils, owing to their unique chemical and structural properties (acidity, high surface area, and porous structure, etc.), although the application of solid acid catalysts in CFP of biomass has some challenges related to active sites poisoning and variations in the pore structure of the catalyst by coke/carbon deposition [4]. Compared with the alumina-based catalysts, zeolite catalysts perform well in terms of its Bronsted acidity and stability, both of which are important factors in CFP of lignocellulosic biomass for production of bio-oils. Different types of zeolites with variation in the Si/Al ratio would greatly affect the overall structure (such as surface area/porosity, acidity and acid strength, type of acid sites - Bronsted/Lewis sites, etc.) [5,6]. Ma et al. [7] showed that with increasing Si/Al ratio, the total acidity and the number of Bronsted acid sites on the zeolite catalyst decreased. In the work by Du et al. [8], effects of different Si/Al ratios of zeolite catalyst were investigated with respect to the yield of aromatic hydrocarbons in catalytic pyrolysis of microalgae, where three HZSM-5 catalysts with varied Si/Al ratios (30, 80, and 280) was compared, and it was shown that by increasing Si/Al ratio the aromatics yield decreased. It was also shown that the maximum yield of aromatics was achieved with HZSM-5 at Si/Al ratio of 80, which provides moderate acidity to achieve high aromatics production and reduce the coke

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[*] Corresponding author.
E-mail address: cxu6@uwo.ca (C.C. Xu).

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formation in the process. In a work by Engtrakul et al. [1], effect of ZSM-5 acidity on aromatic product selectivity during upgrading of pine pyrolysis vapor was investigated. They showed that by increasing acid site concentration, the formation rate of aromatic and cyclization products increased. In a work by Zheng et al. [9], effects of acidity of HZSM-5 catalyst on yield and selectivity of aromatics during catalytic upgrading of biomass pyrolysis vapor were examined. They showed that increasing total acidity of the zeolite catalyst promoted the yield of monomeric aromatic hydrocarbons. Elfadly et al. [10] reported production of aromatic hydrocarbons from catalytic pyrolysis of lignin over acid-activated bentonite clay, where it was aslo demonstrated that yield of aromatic hydrocarbons increased by acidification of the bentonite with strong acid (HCl). The HCl-activation was believed to enhance the activity of the catalyst by improving its textural properties and increasing the strong Bronsted acid sites.

According to the study reported so far, zeolites with higher total acidity and more Bronsted acid sites were also demonstrated to be favorable for the production of monomeric aromatics/phenolics from CFP of HL. Among all zeolites tested (Zeolite X, Zeolite Y and ZSM-5), ZSM-5 with moderate total zeolite catalysts but more strong Bronsted acid sites was determined to be the best catalyst for production of monomeric aromatics/phenolics from CFP of HL at 450 °C.

There have been much research focusing on effects of various Si/Al molar ratios and hence varying degrees of acidity of zeolite catalysts (a higher Al/Si ratio generally corresponding to higher acidity for zeolite catalysts [11]) on products distribution in catalytic pyrolysis of biomass. The main objective and novelty of the present study was to improve the performance of ZSM-5 zeolite catalyst (with a fixed Si/Al ratio of 80) in catalytic fast pyrolysis for the production of monomeric aromatics/phenolics from hydrolysis lignin by increasing the strength of the acidity with sulphuric and phosphoric acids or incorporation metals (metal-supported solid acids are common catalysts for hydro-deoxygenation or hydrocracking of bio-oils [3]). To this end, acidification treatment (with H_2SO_4 and H_3PO_4) and metal (Ni) loading were performed on the ZSM-5 zeolite, and the catalytic performance of these catalysts was evaluated by conducting CFP of HL at 450 °C using ZSM-5 zeolites with various strengths of acidity (ZSM-5 and Ni-ZSM-5 with moderate Lewis and Bronsted sites, H_2SO_4-ZSM-5 and H_3PO_4-ZSM-5 with more Bronsted sites).

2. Materials and methods

2.1. Materials

The ZSM-5 (CBV-8014) powder in ammonium form with Si/Al molar ratio of 80 was purchased from Zeolyst International (PA, USA). The hydrolysis lignin was supplied by FPInnovations, which is a by-product extracted from aspen using a proprietary hardwood fractionation process (or called TMP-Bio™ process) developed by FPInnovations [12]. The HL contains approximately 50–60% lignin weight balanced by residual cellulose and carbohydrates and the molecular weight of HL is not measurable due to insolubility in any a common solvent. Nickel nitrate hexahydrate was purchased from Sigma-Aldrich. Reagent grade phosphoric acid (≥85.0%) and acetone were purchased from Caledon Laboratories Ltd (ON, Canada), ACS reagent grade sulfuric acid solution (≥98.0%) was supplied from VMR, USA, and di-*n*-butyl ether was provided by Alfa Aesar, USA.

2.2. Catalyst preparation

2.2.1. Preparation of acidic ZSM-5 activated by H_2SO_4 and H_3PO_4

Acidified ZSM-5 was prepared by wet impregnation method. In a typical run, 10 g of ZSM-5 was immersed and stirred into the 100 g of 0.5 mol/L of acid solution for 0.5 h (1:10 solid to liquid ratio in weight). Then, the slurry was filtered and washed several times with distilled water for removing any unreacted SO_4^{-2} or PO_4^{-3} ion. The product was dried overnight in an oven at 105 °C in air. The powder form catalyst was then calcined in a muffle furnace at 450 °C for 4 h in air. To be consistent with the preparation Ni-ZSM-5 catalyst, the H_2SO_4-ZSM-5 or H_3PO_4-ZSM-5 was also in-situ treated in 140 mL min^{-1} H_2 flow at 550 °C for 4 h before being used for CFP of HL.

2.2.2. Preparation of Ni-ZSM-5

Ni-ZSM-5 supported catalyst (5 wt.% Ni with respect to the weight of the support) was prepared by wet impregnation method. In a typical run, 0.625 g of nickel nitrate hexahydrate was dissolved in 20 mL of distilled water and 4 g of ZSM-5 (CBV-8014) was added under magnetic stirring for 4 h. The excess water was removed by oven drying at 105 °C in air overnight. The supported Ni catalyst was then calcined in a muffle furnace in air at 550 °C for 4 h. The calcined catalyst was in-situ reduced by H_2 flow (140 mL min^{-1}) at 550 °C for 4 h before it was used for CFP of HL.

It should be also noted that before being used for CFP of HL, all catalyst powders were pelletized then crushed and sieved to particles of a size range of 420–850 μm.

2.3. Catalyst regeneration

For catalyst regeneration, the spent catalyst was completely washed by acetone and dried in an oven overnight, followed by calcinations in a muffle furnace at 500 °C in air for 4 h.

2.4. Catalyst characterization

The crystalline structure of the fresh/spent/regenerated zeolite catalysts were characterized by X-ray diffraction (XRD) on a Rigaku–MiniFlex powder diffractometer (Woodlands, USA), using Cu-K_α (λ = 1.54059 Å) over the 2θ range of 10°–70° with a step width of 0.02°. Textural properties of the fresh/spent/regenerate catalysts were measured by N_2 isothermal adsorption at 77 K (NOVA 1200e surface area and pore size analyzer). The specific surface area was calculated using Brunauer-Emmett-Teller (BET) method. Total pore volume was estimated using the volume of N_2 gas adsorbed at a relative pressure (P/P°) of 0.99. Density functional theory (DFT) was used to calculate the pore size distribution based on N_2 desorption isotherm. The total acidity of the catalysts was measured by NH_3-Temperature Program Desorption (NH_3-TPD), carried out on a Quantachrome ChemBET Pulsar TPR/TPD automated chemisorption analyzer. In a typical experiment, about 0.1 g of the sample was pre-treated at 300 °C for 1 h under a flow of helium (99.9%, 120 cm^3 min^{-1}). After pretreatment, the sample was saturated with anhydrous ammonia at 100 °C for 10 min and subsequently flushed with He at the same temperature to remove any physisorbed ammonia. Then, TPD analysis was carried out by heating the sample in helium from ambient temperature to 600 °C at 10 °C min^{-1} and the desorbed ammonia was measured by a thermal conductivity detector. The carbon/coke deposition for spent catalysts was characterized by thermogravimetric analysis (TGA) on a PerkinElmer Pyris 1 TGA by heating the spent catalyst in 20 cm^3 min^{-1}flow of air from 40 °C to 800 °C at 10 °Cmin^{-1}. The strength of the Bronsted and Lewis acid sites of the zeolites was measured by pyridine FT-IR. A small amount of zeolite (0.2 g) was oven dried at 105 °C for 2 h. Then 50 μL of pyridine was added to the catalyst followed by oven-drying at 105 °C for another 2 h. Thereafter, 2 mg of catalyst was mixed with 200 mg of KBr and pressed to make a disc that was subsequently analyzed by FT-IR to examine the Bronsted and Lewis acid sites on the catalyst.

2.5. Catalytic fast pyrolysis and vapor upgrading process

CFP experiments were carried out in a drop-tube/fixed bed reactor made of SS 316 L tube (3/4 inch O.D., 26.5-inch length). The schematic diagram of the reactor is shown in Fig. 1. The reactor was heated in an electric furnace whose temperature was controlled by a calibrated