A survey of catalysts for aromatics from fast pyrolysis of biomass

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ABSTRACT

A comparative evaluation of ten catalysts for biomass pyrolysis was performed using poplar (DN-34) as the feedstock. Five of the catalysts consisted of HZSM-5 with different silica:alumina ratios (SAR, 23, 30, 55, 80 and 280). The other five catalysts were sulfated zirconia (SO_4^{2-} ZrO_2), 20% SO_4^{2-} ZrO_2 dispersed on a mesoporous MCM-41 silica support, Al–MSU–S alumnosilicate exhibiting a foam-like mesopore structure, Al–MSU–S aluminosilicate exhibiting wormhole mesopores, and a bauxite waste product known as red mud. Analytical pyrolysis in tandem with GC/MS showed that all of the catalysts except for HZSM-5 resulted in low aromatic chemical production. Highly acidic sulfated zirconia catalysts were not selective to aromatics and produced significant coke and non-condensable gases. Mesoporous MSU–S catalysts exhibiting high pore volume and acidity also gave high gas and coke yields. Among the HZSM-5 catalysts evaluated, those with the lowest SAR provided the highest yields of total aromatics and the lowest levels of undesired coke.

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1. Introduction

Monoaromatic compounds, such as benzene, toluene, ethylbenzene and xylenes (BTEX), are used as octane boosters in gasoline and as precursors to polymers such as polyethylene terephthalate. Renewable approaches for making such aromatics from biomass will reduce the U.S. dependence on fossil petroleum and mitigate the negative impacts of climate change. One approach for depolymerizing biomass into the chemical precursors of aromatic compounds is fast pyrolysis. Biomass fast pyrolysis involves the rapid heating of biomass in the absence of oxygen at temperatures of around 500 °C. The generalized products of pyrolysis include a solid product known as char, non-condensable gases and a condensable vapor.

Catalysts aid decarboxylation and decarbonylation reactions of the vapor product to produce a new set of vapor products such as hydrocarbons, alcohols and a solid carbonaceous residue on the catalyst surface known as coke. Several researchers have used zeolite catalysts to convert carbohydrate and biomass feeds into aromatics [1–6]. Acidic catalysts enable cracking reactions that remove oxygen in the form of non-condensable gases [7]. HZSM-5 is a crystalline aluminosilicate where the ratio of silicon to aluminum in the crystal structure can be modified, affecting the hydrophilicity and the concentration of Bronsted acid sites [8]. As acids sites are necessary for cracking and aromatics production, changing the acidity of HZSM-5 was accomplished by varying the silica:alumina ratio (SAR) to study its effect.

Pyrolysis of lignocellulosic woody biomass or herbaceous crops produces lignin derivatives such as phenolic molecules [9]. The kinetic diameter of many lignin derivatives is larger than the 5.5–5.6 Å dimensions of the HZSM-5 micropores [6,10]. Therefore, although HZSM-5 is highly acidic, it is limited by low mass transfer rates for several molecules generated upon biomass pyrolysis. Mesoporous catalysts have large pores that reduce diffusion limitations and increase surface area for catalytic reactions. Surface area increases the available acidic sites for reactions that may increase conversion and reduce coke yields. Thus, mesoporous catalysts may be beneficial for generating valuable chemicals by biomass pyrolysis and many biomass–catalyst permutations warrant further study. In this regard, five additional catalysts are compared to HZSM-5 for their potential to produce aromatics; namely Al–MSU–S exhibiting foam-like mesopore structure, Al–MSU–S exhibiting wormhole mesopores, highly acidic sulfated zirconia, sulfated zirconia dispersed on mesoporous MCM-41 support and red mud, a hazardous waste from bauxite mining.

Al–MSU–S catalysts have acidity as well as hydrothermal stability, necessary for highly corrosive applications such as fast pyrolysis [11]. Sulfated zirconia (SO_4^{2-}-ZrO_2) is an environmentally benign super acid shown to be active in a number of reactions such as isomerization, cracking, alkylation and acylation [12]. Its potential for pollution control such as selective NOx reduction has been demonstrated although its applications for upgrading pyrolysis oil have not been well explored [13]. Due to its low surface area, this catalyst has not seen many commercial applications [14]. Sulfated zirconia on the mesoporous aluminosilicate MCM-41 support is a relatively unexplored catalyst design that can provide greater surface area and catalyst porosity. Transition metal modified MCM-41 has been shown to increase selectivity for hydrocarbons and reduce oxygenates (organic molecules with oxygen functional groups such as acetic acid, glycolaldehyde, etc.) from biomass pyrolysis vapors [11,15,16]. Therefore, the preparation of sulfated zirconia supported on mesoporous MCM-41 is demonstrated and its activity in upgrading pyrolysis vapor is investigated.

To improve economic feasibility of biomass pyrolysis to aromatics, inexpensive catalysts are necessary. One such catalyst is red mud, which is produced as a waste during bauxite refining for aluminum. The disposal of red mud is an environmental concern [17,18]. Red mud is composed of many transition metal oxides, favors hydrogenation reactions and may prove to be an inexpensive catalyst for biofuel applications [17,19] .

An objective of the present study was to screen catalysts while simulating a pyrolysis process followed by catalysis. Separating the pyrolysis step from catalysis allows for better process control and easier collection of bio-char, a valuable by-product, which itself has many applications. Thus, in the present investigation, five different varieties of HZSM-5 along with five additional acidic and mesoporous catalysts are explored for producing aromatics from biomass pyrolysis. These ten catalyst varieties were selected for properties such as acidity, mesoporosity or low cost, that may help improve the efficiency of the biomass pyrolysis to aromatics process. Though prior research has explored the use of HZSM-5 for converting neat sugars [1,20], cellulose [21], lignin [22] and biomass [2,23] as feedstock, the impact of catalyst properties such as surface area and acidity has not been assessed in tandem with the use of raw biomass. Deoxygenation and aromatization activity of sulfated zirconia, red mud and Al–MSU–S and their comparison with the conventional HZSM-5 catalyst has not been studied. The present investigation begins to suture these knowledge gaps and in addition, explores and compares several varieties of HZSM-5 in terms of catalyst properties and aromatic product yields.

2. Experimental

2.1. Catalysts

ZSM-5 catalysts with the following silica–alumina ratios 23, 30, 55, 80 and 280 were obtained from Zeolyst Co. (Conshohocken, PA) in ammonium cation form. In order to obtain the acidic HZSM-5 form, the catalyst was calcined in air at 550 °C for 4 h prior to use. The properties of the catalysts, as measured by Zeolyst, were similar in surface area (400–425 m^2/g), pore size (~0.6 nm) and pore volume (~0.14 m^3/g).

The (2%) Al–MSU–S foam (henceforth referred to as foam) and (2%) Al–MSU–S worm (worm) were synthesized from zeolite beta seeds as precursors and the polymers cetyltrimethylammonium bromide (CTAB) and tallow tetramine as structure-directing agents. A detailed procedure for preparing these catalysts is described elsewhere [24,25]. Red mud was obtained from Professor Marcel Schlaf at the University of Guelph. The red mud was sourced as slurry from the Rio Tinto Alcan mining facility in Canada and contained about

50% w/w iron oxide. The slurry was water washed and dried at 120 °C [19].

Sulfated zirconia catalyst (henceforth referred to as SZ) was prepared by hydrolysis of $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonia, treating with 0.5 M H_2SO_4 and calcination at 650 °C. The sulfated zirconia supported in mesoporous material (20% SO_4^{2-} ZrO_2 MCM-41, henceforth referred to as MSZ) was prepared by dispersion of $ZrOCl_2 \cdot 8H_2O$ (20% ZrO_2) on to MCM-41 support using the incipient wetness method followed by drying at 105 °C for 12 h [6]. The mixture was treated with ammonia gas leading to formation of amorphous $Zr(OH)_4$. The sample was then water washed, treated with 0.5 M of H_2SO_4 solution at room temperature for 10 min and calcined at 650 °C in air for 3 h.

2.2. Catalyst characterization

Surface area measurements and pore size distribution analysis were done by nitrogen adsorption at 78 K (−195 °C) in a Micromeritics ASAP 2010 instrument. Prior to measurements, the sample was out-gassed in the degas port of the apparatus at 220 °C for 24 h. NH_3-TPD measurements were performed by volumetric adsorption in a Micromeritics AutoChem 2910 instrument. A thermal conductivity detector and an Ametek Dycor M100M Quadrupole Mass Spectrometer were used for continuous monitoring of the desorbed NH_3. Prior to NH_3 adsorption, approximately 0.5 g of catalyst was thermally pretreated in He (99.999%) at a flow rate of 50 cm^3 min^{-1} at 410 °C for 1 h followed by cooling to ambient temperature in He. After pretreatment, each catalyst was saturated at ambient temperature with NH_3 (99.998%) at a flow rate of 50 cm^3 min^{-1} for 1 h and then subsequently purged with He (50 cm^3 min^{-1}) for 2 h to remove all physisorbed NH_3. Desorption of chemisorbed NH_3 was carried out in He flow with the catalyst being heated from ambient temperature to 700 °C at a rate of 10 °C min and held for 30 min. The resulting NH_3 peak was quantified by calibrating the area using a gas standard.

2.3. Pyrolysis–GC/MS and TGA

Experiments were conducted using a microscale pyrolysis unit, CDS Pyroprobe 5250 (CDS Analytical Inc., Oxford, PA) interfaced to a Shimadzu QP-5050A gas chromatograph/mass spectrometer (Shimadzu Corp., Columbia, MD). A lignocellulosic feedstock, poplar (DN-34, *Populus x euramericana*, cv. 'Eugenei'), was used as biomass for all experiments. The poplar was dried at 60 °C to a moisture content of ~8%, ground to a particle size of less than 0.5 mm and stored at room temperature [26]. For biomass pyrolysis experiments, approximately 0.5 mg of ground biomass sample was packed between quartz wool in a quartz tube. For catalytic pyrolysis experiments, approximately 0.5 mg of biomass was packed between quartz wool. Catalyst, with a 5:1 weight ratio of catalyst to biomass, was added on both sides followed by more quartz wool to hold the sample in place. Six or more replicates of each sample were run. In a scaled-up process, pyrolysis may occur in a separate pyrolysis reactor and the vapors may be conveyed to a separate catalyst reactor. To simulate this separation between the two steps, quartz wool was used inside the sample tube. This prevented mixing of the biomass and catalyst and allowed the pyrolysis of biomass to occur first. The product vapors diffuse away from the biomass due to the helium stream inside the pyroprobe and come in contact with the catalyst for the catalysis step.

Pyrolysis proceeded by setting the pyroprobe at 650 °C (pyrolysis temperature of 500–550 °C) with a hold time of 20 s at the maximum heating rate setting of 999 °C/s. The GC used a Restek rtx-1701 column (Restek, Bellefonte, PA), 60 m × 0.25 mm with a 0.25 μm film thickness. The column gas flow was 1 cm^3/s with a split ratio of 1:100 so as to not overwhelm the mass