



On the effectiveness of tailored mesoporous MFI zeolites for biomass catalytic fast pyrolysis



David P. Gamliel^a, Hong Je Cho^b, Wei Fan^b, Julia A. Valla^{a,*}

^a Department of Chemical & Biomolecular Engineering, University of Connecticut Storrs, 191 Auditorium Road, Unit 3222, Storrs, CT 06269, USA

^b Department of Chemical Engineering, University of Massachusetts, Amherst, 686 N. Pleasant Street, Amherst, MA 01003-9303, USA

ARTICLE INFO

Article history:

Received 5 February 2016

Received in revised form 5 April 2016

Accepted 23 April 2016

Available online 30 April 2016

Keywords:

Heterogeneous catalysis

Biomass conversion

Catalytic fast pyrolysis

ZSM-5

Hierarchical zeolites

ABSTRACT

Optimum catalyst design plays a pivotal role in maximizing catalytic fast pyrolysis (CFP) bio-oil yield and quality. This work investigates the use of mordenite framework inverted (MFI) zeolites with hierarchical pore structures as potential catalysts to address the aforementioned challenges. Mesoporous MFI catalysts were created using both top-down and bottom-up approaches, were characterized and evaluated as CFP catalysts. CFP with mesoporous catalysts resulted in higher yields to aromatics and lower coke and char yields. The results of this study indicate that there is a maximum amount of mesopore volume required for optimal acid site accessibility leading to increased bio-oil production. After this maximum, intermediate aromatic hydrocarbons continue to polymerize to form bulky poly-cyclic aromatic hydrocarbons (PAHs) and coke.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Thermochemical conversion of biomass has already begun to contribute renewable energy and fuels to the ever-expanding industrial market [1]. One prevalent technique for conversion of biomass to fuels and commodity chemicals is fast pyrolysis; the rapid heating of biomass to elevated temperatures (400–700 °C) under an inert atmosphere [2]. During the pyrolysis process lignin, cellulose and hemi-cellulose, break down to form liquid oxygenates, such as phenols, furans and soluble sugars. Fast pyrolysis in the presence of an upgrading catalyst is known as catalytic fast pyrolysis (CFP). Intermediate pyrolysis oxygenates contact the catalyst acid sites, where they react to form single ring aromatic compounds, naphthalenes, poly-cyclic aromatic hydrocarbons (PAHs) and/or coke. Aromatic product selectivity can be enhanced based on the choice of catalyst. Thus, catalyst design is crucial for improving yields to valuable chemicals.

Significant scientific effort has been devoted to the design of the ideal CFP catalyst. Zeolitic materials have widely been accepted as the most promising CFP catalysts owing to their well-defined shape selective microporous structure and high acidity [3]. Jae et al. [4] studied CFP of glucose with a wide variety of aluminosilicate catalysts. They created a volcano curve correlating average zeolite pore

diameter and aromatic yield, and found that the mordenite framework inverted (MFI) zeolite has the ideal pore size and acidity for production of aromatics from biomass pyrolysis. As a result, ZSM-5 with a Si/Al ratio between 15 and 40 has been the catalyst of choice for many studies in the field of biomass CFP [5–8]. However, low bio-oil yields, with low aromatics content, and formation of coke on catalyst continue to hamper the commercialization of biomass CFP technology.

One possible source of the aforementioned challenges may be the presence of transport limitations in the catalyst pore structure. Bulky oxygenates formed during the initial stages of pyrolysis may not be able to efficiently reach the active sites within the catalyst micropores. For example, many of the oxygenates formed from lignin pyrolysis have dimensions larger than the effective pore opening of ZSM-5 [9]. Application of a mesoporous catalyst can be advantageous, as enlarging the pore structure results in increased accessibility of reactants to catalyst acid sites [10]. There are two broad approaches for the creation of mesoporous zeolites; the so-called top-down and bottom-up strategies. Top-down methods involve introduction of mesoporosity by post-synthetic methods, such as: desilication [11–14], dealumination (steaming or acid treatment) [15,16] and desilication in the presence of surfactant [17,18] or a pore directing agent [19–21]. Bottom-up methods rely on introduction of mesoporosity during hydrothermal zeolite synthesis. Common bottom-up methods include exfoliation and pillaring of layered zeolites, hard templating, supramolecu-

* Corresponding author.

E-mail addresses: valla@engr.uconn.edu, jul.valla@gmail.com (J.A. Valla).

lar templating and self-assembly of zeolite crystals or nanocrystals [22–26].

Mesoporous MFI type zeolites for biomass CFP have been studied by several research groups. Park et al. [27] prepared mesoporous ZSM-5 zeolites using top-down and bottom-up techniques [23,28], and studied their effectiveness in upgrading sawdust pyrolysis vapors. They observed that upgrading with any of the mesoporous catalysts resulted in higher solid yields, compared to upgrading with a commercial ZSM-5 zeolite. Additionally, they concluded that upgrading with the mesoporous ZSM-5 catalyst synthesized with the bottom-up approach resulted in significantly higher yields to mono-aromatic hydrocarbons (MAHs) and less PAHs than the commercial ZSM-5, due to the synergistic effects of acidity and mesoporosity. Upgrading with the mesoporous ZSM-5 created using the top-down approach resulted in significant amounts of oxygenates, most likely as a result of lower zeolite acidity compared to the parent ZSM-5. Park et al. [29] also compared pyrolysis of miscanthus with a commercial ZSM-5 zeolite and templated mesoporous ZSM-5 zeolite. They found improved yields to aromatics and phenols with the mesoporous zeolite, concluding it was the most adequate for biomass CFP. Puértolas et al. [30] studied upgrading of bio-oil over hierarchical zeolites with different Si/Al ratios prepared by desilication. They observed an increase in the solid yield (coke) and a decrease in the liquid yield over their hierarchical zeolites, compared to the parent material. On the other hand, they noted an increase in aromatic products yield of up to 50% using the mesoporous materials. They attributed these differences to changes in acidity, preferential decarbonylation over hierarchical zeolites and increased pore accessibility.

Foster et al. [31] pyrolyzed maple wood and biomass model compounds in the presence of mesoporous and microporous MFI zeolites. They found that CFP with mesoporous catalysts favored the formation of alkyl aromatics, fewer liquids and more solids. Li et al. [10] performed CFP of beech wood with a series of desilicated ZSM-5 catalysts. Contrary to Foster et al., they found that increasing the mesopore volume increased the aromatic yield, particularly to naphthalenes, and decreased the coke yield. They determined that beyond a mesopore volume of $0.127 \text{ cm}^3 \text{ g}^{-1}$, the aromatics previously gained were lost to coke.

The above review highlights the current debate on the effects of mesoporous MFI catalysts on CFP bio-oil composition and coke yield. The objective of this work is to gain a better understanding of how hierarchical pore structure MFI zeolites affect diffusion and reaction during CFP, and consequently, product yields and bio-oil quality. Top-down and bottom-up techniques were employed to create a wide variety of MFI-type catalysts with ranging mesoporosity. Each catalyst has been characterized to determine the pore structure, acidity and crystallinity. CFP of cellulose and miscanthus has been performed with the MFI zeolites to determine how the intrinsic properties of the various mesoporous catalysts affect CFP of a model and real biomass.

2. Materials and methods

2.1. Preparation of hierarchical MFI zeolite

2.1.1. Bottom-up methods

Preparation of 100 nm MFI zeolite was carried out using a method reported in literature [32]. Briefly, 6.00 g of tetraethylorthosilicate (TEOS, Sigma Aldrich) was added to 3.66 g of 40% tetrapropylammonium hydroxide solution (TPAOH, Alfa Aesar or SACHEM). The resulting mixture was stirred at 80°C for 24 h. Thereafter, the solution containing 2.37 g of distilled water, 0.23 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%, Sigma Aldrich) and 0.29 mL of 10 M NaOH solution was added to the mixture. The molar composition of

the final gel was $1 \text{ SiO}_2 : 0.25 \text{ TPAOH} : 0.0167 \text{ Al}_2\text{O}_3 : 0.05 \text{ Na}_2\text{O} : 9.45\text{H}_2\text{O}$. The prepared gel was crystallized at 170°C for 24 h. The solid product was collected by centrifugation. The H-form of the 100 nm MFI zeolite was obtained by calcination at 550°C for 12 h in air. This material is referenced as MFI-100 nm.

Mesoporous MFI zeolite was prepared using a method reported in the literature [22]. Concisely, 0.23 mL of 10 M NaOH solution was mixed with 20.80 g of 1 M TPAOH (Sigma Aldrich). Subsequently, 12.50 g of Ludox HS-40 (Sigma Aldrich) was added dropwise to the mixture. A transparent solution was formed after stirring the mixture for 1 h. 0.57 g of aluminum isopropoxide (98%, Sigma Aldrich) was added and completely dissolved into the solution by stirring for 30 min. The final composition of the mixture was $1 \text{ SiO}_2 : 0.25 \text{ TPAOH} : 0.017 \text{ Al}_2\text{O}_3 : 0.014 \text{ Na}_2\text{O} : 16.44\text{H}_2\text{O}$. Hydrothermal treatment was carried out in a Teflon-lined autoclave at 135°C for 2 days with a rotation speed of 3 rpm. The obtained product was thoroughly washed by filtration with distilled water, followed by drying overnight at 100°C . The collected sample was calcined in a furnace at 550°C for 12 h in air. This material is referred to as MFI-Meso in this study. Ion exchange was performed with 1 M aqueous solution of NH_4NO_3 (95%, J.T. Baker) at 80°C for 3 h and repeated three times. The final product was obtained in the H-form by calcination at 550°C for 8 h in air.

2.1.2. Top-down methods

The parent zeolite for all materials created using top-down approaches was a ZSM-5 zeolite with a Si/Al ratio of 40 (Zeolyst International), referenced in this study as MFI-Pa.

Desilication by alkaline treatment was employed for the top-down introduction of mesoporosity. It was accomplished by stirring MFI-Pa in 0.1 M NaOH (MFI-DS-Mild) or 0.3 M NaOH (MFI-DS-Strong) solution at 65°C for 30 min. Each material was then subjected to an acid wash in 0.01 M HCl (25°C , 6 h), followed by three ion exchanges with 0.1 M NH_4NO_3 (25°C , 6 h), drying overnight between each step. The final material was calcined in air at 550°C for 6 h to convert the material to the H-form.

It has been suggested that the use of surfactant during desilication is a more refined way of introducing mesoporosity without crystal destruction via redeposition of extracted silica around micelles of surfactant on the zeolite surface [17,18]. Thus, desilication in the presence of surfactant was performed by stirring 3.0 g of MFI-Pa in 0.05 M cetyl-trimethylammonium bromide (CTAB, Sigma Aldrich) and 0.1 M NaOH (MFI-SA-Mild) or 0.3 M NaOH (MFI-SA-Strong) at 65°C for 30 min. The acid wash, ion exchange and calcination are the same as for the desilication procedure. Table 1 outlines the preparation strategy for each of the materials presented in this work.

2.2. Characterization of hierarchical MFI zeolites

The physical properties of each material including surface area and pore size distribution were determined using N_2 sorption, which was carried out using a Micromeritics ASAP 2020 Physisorption Analyzer. Prior to analysis, each sample was calcined then degassed for 12 h at 120°C under vacuum. Isotherms were recorded at 77 K, and the Brunauer–Emmett–Teller (BET) method was used to estimate surface area. The non-local density functional theory (NL-DFT) method was applied to the adsorption branch of each isotherm to calculate the pore size distribution using a model specifically designed for N_2 adsorption on H-form zeolites [33,34]. Briefly, this method was developed as a hybrid between statistical mechanical calculations and experimentation methods. The model takes into account variation in N_2 fluid density as it enters the zeolite micropores and mesopores, and was originally developed with MCM-41 as a reference [35].

Download English Version:

<https://daneshyari.com/en/article/38704>

Download Persian Version:

<https://daneshyari.com/article/38704>

[Daneshyari.com](https://daneshyari.com)