Applied Catalysis B: Environmental 95 (2010) 365–373

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Highly valuable chemicals production from catalytic upgrading of radiata pine sawdust-derived pyrolytic vapors over mesoporous MFI zeolites

Hyun Ju Park [a], Hyeon Su Heo [a], Jong-Ki Jeon [b], Jeongnam Kim [c], Ryong Ryoo [c], Kwang-Eun Jeong [d], Young-Kwon Park [a,*]

[a] *School of Environmental Engineering, University of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, Republic of Korea*
[b] *Department of Chemical Engineering, Kongju National University, 275 Buedae-Dong, Cheonan, Chungnam 330-717, Republic of Korea*
[c] *Center for Functional Nanomaterials and Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea*
[d] *Green Chemistry Research Division, KRICT, Daejeon 305-600, Republic of Korea*

ARTICLE INFO

Article history:
Received 1 February 2009
Received in revised form 23 December 2009
Accepted 19 January 2010
Available online 25 January 2010

Keywords:
Mesoporous MFI zeolite
Gallium
Catalytic upgrading
Fast pyrolysis
BTX aromatics

ABSTRACT

The catalytic upgrading of pyrolytic vapors derived from radiata pine sawdust was carried out over mesoporous MFI zeolite synthesized using an amphiphilic organosilane. Its catalytic activity was compared with those of conventional HZSM-5 and mesoporous material from HZSM-5 (MMZ_{ZSM-5}). The effect of gallium incorporation into mesoporous MFI zeolite on the product distribution and chemical composition of bio-oil was also investigated. The catalysts synthesized were characterized using ICP, XRD, N_2-sorption, NH_3-TPD, and H_2-TPR methods. After catalytic upgrading, products were analyzed by GC–TCD, GC–FID, GC–MS, and Karl Fischer titration. The mesoporous MFI zeolite exhibited the best activity in deoxygenation and aromatization during the upgrading of pyrolytic vapors. In particular, mesoporous MFI zeolite showed high selectivity for highly valuable aromatics, such as benzene, toluene, and xylenes (BTX), even though it decreased the overall organic fraction of the bio-oil. The incorporation of gallium into the mesoporous MFI zeolite increased both the organic fraction of the bio-oil and resistance to coke deposition. Moreover, the selectivity for BTX aromatics was enhanced when the appropriate amount of gallium was introduced.

1. Introduction

The importance of alternative energy development has increased rapidly due to the high international crude oil prices and environmental concerns over global warming being aggravated by the use of fossil fuels. Bio-oil is recognized as one of the representative renewable energy sources because the existing infrastructure in the petroleum industry is available for the production of chemicals or the next-generation hydrocarbon biofuels from bio-oil without significant modification [1]. Moreover, since bio-oil is CO_2 neutral and has a negligible sulfur, nitrogen and ash content, it has fewer adverse effects on the environment during energy production and consumption than conventional fossil fuels. For this reason, considerable efforts have been made to maximize the production of useful bio-oil [2–7]. However, bio-oil is produced as an unstable complex, requiring improvements in quality. Currently, the improvement methods for yielding high quality bio-oil can be classified into two routes: simple physical upgrading (hot-gas filtration, emulsification, and solvent addition), and upgrading with catalysts (hydrotreating, mild hydrotreating, and catalytic vapor cracking) [8]. The latter has been the focus studies thus far because it offers significant improvements ranging from simple stabilization to high quality fuel products [9].

Over the past few decades, a number of studies have examined the upgrading of bio-oil over solid acid catalysts, such as pure and modified zeolites [10–22]. According to these reports, among the various zeolite-based catalysts used, HZSM-5 is the most effective for cracking or reforming bio-oil. The catalytic performance of HZSM-5 has been attributed to the shape-selectivity, ion exchange capacity, and unique solid acid characteristics. However, HZSM-5 with micropores within a 5.1 Å × 5.6 Å range is limited by the low mass transfer rates, particularly in the case of large molecules.

Since the discovery of the mesoporous M41S family [23], MCM-41-based materials have been examined as potential upgrading catalysts in biomass-derived vapors, with the effects of acidity and metal incorporation being the main focus of the investigation [24–28]. Based on their results, it was reported that Al-substituted MCM-41 materials are promising catalysts for the production of high quality bio-oil. More recently, considerable progress has been made in the catalytic pyrolysis of biomass. Highly hydrothermal and stable mesoporous aluminosilicates, MMZ and MSU-S, were applied to the catalytic pyrolysis of biomass [29–31], showing high

---

* Corresponding author. Tel.: +82 2 2210 5623; fax: +82 2 2244 2245.
E-mail address: catalica@uos.ac.kr (Y.-K. Park).

0926-3373/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2010.01.015

selectivity for specific compounds as well as excellent catalytic activity. In particular, MMZ materials exhibited remarkable catalytic stability and activity, even after two regenerations. Despite the merit of mesoporosity, MCM-41-type mesoporous materials have lower acidity than microporous aluminosilicate zeolites. The low acidity is due to the amorphous nature of the MCM-41 frameworks, which can only provide weak Brönsted acid sites. However, in bio-oil upgrading, strong Brönsted acid sites play a leading role as the active sites for catalytic cracking and reforming reactions.

Recently, Ryoo and co-workers developed a method for synthesizing highly mesoporous zeolites using organosilane surfactants as the mesopore generating agent [32,33]. Various zeolites, such as MFI, BEA and LTA, were synthesized successfully with a narrow distribution of mesopore diameters. The mesoporous were disordered but the pore diameters were uniform and tunable by the synthesis conditions. In the case of MFI, there was a notable decrease in the concentration of Brönsted acid sites [34]. However, the acidity was sufficient for the presence of mesopores to impart the zeolites with high catalytic activities for the transformation of large molecules exceeding the size of the zeolite micropores [35,36].

The catalytic performance of mesoporous MFI zeolite on the upgrading of Japanese larch bio-oil was evaluated in this preliminary study. However, the much larger mesopores (6.2 nm) of the mesoporous MFI zeolite induced an increase in the concentration of undesirable products, such as polycyclic aromatic hydrocarbons (PAHs) and coke [37]. In order to prevent the formation of undesirable large molecules and increase the amount of BTX compounds, it is important to control the catalyst porosity or modify the catalyst itself.

This study examined the catalytic upgrading of pyrolytic vapors derived from radiata pine sawdust over mesoporous MFI zeolites synthesized using organosilane surfactants with a shorter chain length, which possess high acidity and porosity with catalytic activities comparable to those of an MMZ and conventional HZSM-5. In addition, the effects of Ga-incorporation into the mesoporous MFI catalyst on the product distribution and composition were examined in detail with the aim of increasing the concentration valuable chemicals, such as BTXs.

2. Experimental

2.1. Catalyst preparation

A mesoporous MFI catalyst with a Si:Al molar ratio of 20 was synthesized using the procedure reported in the literature [32,35]. An amphiphilic organosilane, [(3-trimethoxysilyl)propyl] dodecyldimethylammonium chloride (TPDAC) ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_nH_{2n+1}]Cl$, $n = 12$), was used as a mesopore-directing agent. [(3-Trimethoxysilyl)propyl] hexadecyldimethylammonium chloride (TPHAC) was used to synthesize a larger mesoporous MFI catalyst. For comparison, a mesoporous material from a zeolite (MMZ) with a similar Si:Al molar ratio was prepared using the procedure reported in previous studies [30,31]. A commercially available zeolite, HZSM-5 (Zeolyst International Company), and cetyltrimethylammonium bromide (CTAB) were used as the framework source and template, respectively. Both catalysts were calcined, ion exchanged four times with a 1.0 M ammonium nitrate solution at 80 °C to convert them into the NH_4^+ form, and finally calcined again at 550 °C to convert them to their H^+ form. Hereinafter, the mesoporous MFI catalyst and MMZ material are referred to as Meso-MFI, and MMZ_{ZSM-5}, respectively. Various Ga/Meso-MFI catalysts were prepared using the appropriate amount of an aqueous gallium nitrate (Aldrich, 99.9 purity) solution using the incipient wetness method. The prepared catalysts were dried overnight at 110 °C, calcined in air at 550 °C for 5 h, reduced in a hydrogen stream at 500 °C for 4 h, and finally calcined in air at 550 °C for 5 h to generate the highly dispersed active Ga^{3+} species [38,39].

2.2. Characterization of catalysts

The catalysts synthesized in this study were characterized as follows: the X-ray diffraction (XRD) patterns were obtained with a Cu K_α X-ray source using a Rigaku D/MAX-III instrument at room temperature to determine the catalyst crystallinity. The acidity was examined using the NH_3-temperature-programmed desorption (TPD) method with a TPD/TPR 2900 analyzer (Micromeritics Instrument Co.). Prior to the measurements, the samples were first treated in a He stream at 500 °C and then cooled to 100 °C. NH_3 adsorption was then carried out at 100 °C. After purging the samples in a He stream for 2 h to completely remove the physically adsorbed NH_3, the catalysts were heated to 700 °C at a heating rate of 10 °C/min. The desorbed NH_3 was detected using a thermal conductivity detector (TCD). The reducibility of the Ga-incorporated mesoporous zeolites was examined using the H_2-temperature-programmed reduction (TPR) method with BELCAT. Before the TPR measurements, the samples were treated in a He stream at 110 °C for 30 min, cooled to room temperature, and then reduced in a mixture gas stream of 20% H_2/Ar at a flow rate of 30 mL/min and a heating rate of 5 °C/min to 800 °C. Hydrogen consumption during reduction was detected using a TCD. The N_2 adsorption/desorption isotherms were obtained at −196 °C using a Micromeritics ASAP 2000 with the Brunauer–Emmett–Teller (BET) surface area calculated from the linear portion of the BET plot. The micropore volume and external surface area were evaluated using the t-plot method, and the pore size distribution obtained using the Brunauer–Joyner–Halenda (BJH) model. Inductively coupled plasma analysis was used to determine the Si:Al molar ratio. After upgrading, the amount of coke deposited on the catalysts was determined by thermogravimetric analysis (TGA [TGA 2050, TA Instruments]) in the presence of air at a heating rate of 5 °C/min.

2.3. Reaction procedure

Radiata pine, which is a representative wood species in Korea, was used in the catalytic upgrading of wood-derived pyrolytic vapors. The sawdust used in these experiments was screened to size ranges of 0.3–0.5, 1.0–1.7, and 1.7–2.4 mm, and dried in an oven (J-NDS1, JISICO) at 110 °C for 24 h to minimize the water in the oil product. After drying, the water content in all wood sawdust was <1 wt.%. Table 1 lists the characteristics of the radiata pine sawdust used in this study.

The pyrolysis of radiata pine sawdust and subsequent catalytic upgrading of pyrolytic vapors were carried out in a fixed bed reactor system. Fig. 1 shows a schematic diagram of the pyrolysis and catalytic upgrading apparatus. The upgrading system was installed consecutively at the latter part of the main pyrolysis reactor. The main pyrolysis reactor was U-type quartz with an inner volume of 50 mL, a height of 160 mm, and an internal diameter of 15 mm, into which the radiata pine sawdust (5.0 g) was charged. The fixed catalyst bed reactor was a tubular quartz type, with a height of 70 mm, an internal diameter of 15 mm, and filled with the catalyst (0.5 g). All the catalysts were pelletized, crushed, and screened through standard sieves (1.7–2.4 mm). For non-catalytic pyrolysis, the catalyst was replaced with quartz beads to maintain the same space velocity within the fixed catalyst bed. Prior to the experiments, all experimental systems were purged with inert nitrogen at a flow rate of 50 mL/min for 1 h. Both reactors were indirectly heated electrically to the desired reaction