Monocyclic aromatic hydrocarbons production from catalytic cracking of pine wood-derived pyrolytic vapors over Ce-Mo$_2$N/HZSM-5 catalyst

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HIGHLIGHTS

- Catalytic upgrading of biomass pyrolytic vapors was performed using Ce-Mo$_2$N/HZSM-5.
- The optimal loading of Mo$_2$N on the HZSM-5 was screened.
- A series of transition metal modified catalysts were tested for MAHs preparation.
- Possible catalytic mechanism was explained.
- Sources of aromatics were investigated with single biomass components.

GRAPHICAL ABSTRACT
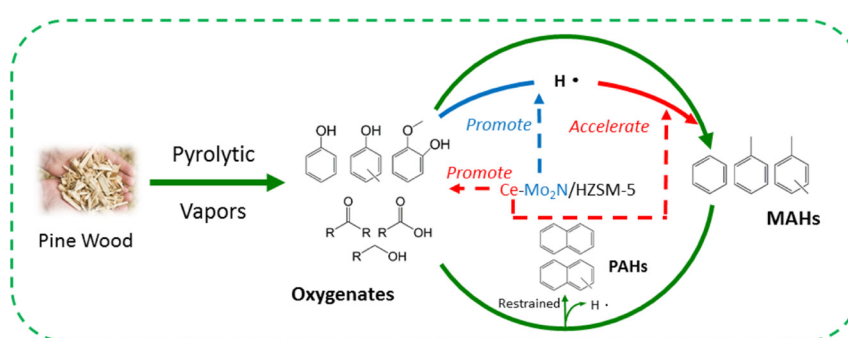
ABSTRACT

A series of Mo$_2$N/HZSM-5 and transition metal modified Mo$_2$N/HZSM-5 catalysts were prepared for the catalytic upgrading of pine wood-derived pyrolytic vapors for the selective production of monocyclic aromatic hydrocarbons (MAHs), while restraining the formation of polycyclic aromatic hydrocarbons (PAHs). Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments were performed to determine the effects of several factors on selective MAHs production, including Mo$_2$N loading on HZSM-5, transition metal (Fe, Ce, La, Cu, Cr) modification of Mo$_2$N/HZSM-5, pyrolysis temperature, and catalyst-to-biomass ratio. In addition, quantitative experiments were conducted to determine the actual yields of major aromatic hydrocarbons and the source of aromatic hydrocarbons from basic biomass components. Results indicated that among the various catalysts, the Ce-10% Mo$_2$N/HZSM-5 exhibited the best performance on promoting the formation of MAHs and restraining the generation of PAHs. Under the optimal conditions, the actual yields of MAHs and PAHs from Ce-10%Mo$_2$N/HZSM-5 catalytic process were 99.8 mg/g and 7.5 mg/g, while those from HZSM catalyst were only 77.2 mg/g and 23.7 mg/g respectively. Furthermore, the possible catalytic mechanism of the Ce-Mo$_2$N/HZSM-5 catalyst was proposed based on the catalyst characterization.

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1. Introduction

Fast pyrolysis of lignocellulosic biomass materials mainly produces a liquid product known as bio-oil which has potentials to be upgraded into liquid fuels or valuable chemicals (Bridgwater, 2012; Buller et al., 2015). Crude bio-oil from conventional fast pyrolysis process has

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complex chemical composition, mainly including anhydrosugars, acids, ketones, aldehydes, furans, phenolics and aromatics. The highly oxygenated nature and complex composition of crude bio-oil results in various poor properties for liquid fuel application as well as great difficulty for valuable chemical extraction (Wang et al., 2017; Shi et al., 2017). Therefore, upgrading of crude bio-oil is necessary to improve fuel properties or enrich valuable chemicals. Catalytic pyrolysis is one of the promising upgrading ways to obtain, I) bio-oils with low oxygen contents for liquid fuel applications (Yildiz et al., 2014); II) bio-oils with specific individual compounds such as levoglucosenone (Ye et al., 2017a), 4-ethyl phenol (Lu et al., 2016), 4-vinyl phenol (Qu et al., 2013); III) bio-oils with specific groups of valuable compounds like phenolics (Z.B. Zhang et al., 2015), furans (Lu et al., 2009) and aromatic hydrocarbons (Zhang et al., 2017). Among these target products, monocyclic aromatic hydrocarbons (MAHs) are promising products for both liquid fuels and chemical materials applications.

Currently, various catalysts have been developed and applied on biomass pyrolysis or pyrolytic vapors cracking to convert oxygenates into aromatic hydrocarbons. The commonly used catalysts mainly include microporous zeolites (Cheng and Huber, 2011; Zhang et al., 2014), mesoporous catalysts (Lappas et al., 2012), and metal oxides (Auta et al., 2014; Peng et al., 2014). Among the various catalysts, zeolites such as Proton-exchanged Zeolite Socony Mobil-5 (HZSM-5) exhibit the best performance on aromatic hydrocarbons production owing to their proper acidity, high surface area, regular pore structure and excellent shape-selectivity. However, zeolite catalysts are not only effective to produce MAHs, but also capable of catalyzing the polymerization of MAHs and oxygenates into polycyclic aromatic hydrocarbons (PAHs) (up to 50%). PAHs are a class of toxic substances that are harmful to human health. Moreover, they are coke precursors to cause catalyst deactivation (Jackson et al., 2009; Mihalcik et al., 2011). In order to efficiently produce MAHs accompanied with low PAHs, two methods have been mainly utilized by introducing extra hydrogen sources into biomass pyrolysis system or modification of zeolite catalysts. With the addition of hydrogen and ethanol, Wang et al. (Wang et al., 2016) developed a two-stage hydrogenation cracking process aiming at improving the selectivity of both oil phase and MAHs. Results showed that an oil product with the MAHs content of about 70% was obtained when using HZSM-5 catalyst for cracking stage. Modification of zeolite catalysts with different metals is also effective on regulating the selectivity of MAHs and PAHs. Sun et al. adopted Fe/ZSM-5 catalyst for catalytic fast pyrolysis of biomass to obtain a bio-oil rich in aromatic hydrocarbons with MAHs to PAHs ratio of 2:1 (Sun et al., 2016). A series of metal modified HZSM-5 catalysts were designed by Thangalazhy-Gopakumar et al. to alleviate the formation of PAHs to improve the MAHs content, and concurrently prolong the catalyst life by reducing coke deposition (Thangalazhy-Gopakumar et al., 2012). Among Co, Ni, Mo, and Pt modified catalysts, Pt/ZSM-5 obtained the highest MAHs with the carbon yield 34.9 wt% under a hydrogen atmosphere. Vichaphund et al. (Vichaphund et al., 2015) prepared Ga/HZSM-5 by an impregnation method to obtain a bio-oil with MAHs to PAHs ratio of 6.7:1. Metals of La (Huang et al., 2012) and Zn (Wang et al., 2014) were also utilized for zeolite modification, but no significant improvement was detected on the selectivity of MAHs. Besides, bimetallic zeolite catalysts were also reported for preparing aromatic hydrocarbons (Cheng et al., 2014; Cheng et al., 2016). Ni-Mo/HZSM-5 and Co-Mo/HZSM-5 catalysts were both effective in producing aromatic hydrocarbons, but no specific results on MAHs were discussed.

In this work, with the aim to selectively produce MAHs and simultaneously suppress the formation of PAHs, zeolite HZSM-5 was modified with transition metal nitride Mo_2N and transition metals including Fe, Cu, Cr, La and Ce. Mo_2N was reported to possess excellent ability of hydrogenolysis and dehydrogenation (Neylon et al., 1999), which was beneficial to inhibit the formation of PAHs so as to increase the selectivity of MAHs (Zheng et al., 2013; Lu et al., 2018a). Transition metals were also confirmed to be active in regulating biomass pyrolysis process. The

Mo_2N/HZSM-5 and transition metal modified Mo_2N/HZSM-5 catalysts were used for the catalytic cracking of pine wood-derived pyrolytic vapors. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments were conducted to investigate the formation characteristics of aromatic hydrocarbons affected by the Mo_2N loading on HZSM-5, transition metal modification of Mo_2N/HZSM-5, pyrolysis temperature and catalyst-to-biomass ratio. Quantitative analysis was conducted to determine the actual yields of major aromatic hydrocarbons. Moreover, the sources of aromatic hydrocarbons were explored with the three basic biomass components. In addition, the possible catalytic mechanism was proposed based on the catalyst characterization results.

2. Experimental

2.1. Materials

Biomass materials used in this study included microcrystalline cellulose (Avicel PH-101), xylan (isolated from birch wood), pine wood, and milled wood lignin (MWL) from pine wood. Microcrystalline cellulose and xylan from Sigma were used as purchased. Pine wood was collected from Beijing, and ground to sieve particles within the size of 0.2–0.3 mm. The sieved particles were dried at 105 °C for 4 h before experiments. The chemical composition of the pine wood was determined to be 45.8 wt% cellulose, 19.1 wt% hemicellulose, 30.7 wt% lignin, 4.1 wt% extractive, and 0.3 wt% ash. MWL was isolated from the pine wood according to literatures (Zhang et al., 2010; Wen et al., 2013). Typically, pine wood particles within the size of 0.18–0.25 mm were extracted in a Soxhlet extractor using toluene and ethanol (v:v, 2:1) as the solvents for 24 h. After drying, the extracted solids were ball milled for about 50 h. The ball-milled materials were then suspended in dioxane and water (v:v, 96:4) for extraction for 24 h. After filtration, the filtrate was concentrated and transferred into deionized water, then freeze-dried to obtain the crude MWL. Further purification of MWL was achieved by the following extraction steps using 90% acetic acid, 1,2-dichloroethane/ethanol (2:1, v/v), diethyl ether, and petroleum ether. Finally, the MWL sample was obtained after drying.

For the catalyst preparation, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, $Fe(NO_3)_3\cdot9H_2O$, $Ce(NO_3)_3\cdot6H_2O$, $La(NO_3)_3\cdot6H_2O$, $Cu(NO_3)_2\cdot3H_2O$, and $Cr(NO_3)_3\cdot9H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. HZSM-5 was provided by Nankai University Catalyst Co., Ltd.

2.2. Catalyst preparation

Mo_2N/HZSM-5 catalysts with different Mo_2N loadings were prepared via incipient wetness impregnation and temperature-programmed reduction method using HZSM-5 as the support and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ as the active precursor. Taking 10%Mo_2N/HZSM-5 as an example, 0.37 g $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ was firstly dissolved into 2 mL deionized water, and then was impregnated onto 2.70 g HZSM-5. The mixture was stirred and subjected to ultrasonic treatment for 2 h, and then dried at 105 °C for 12 h. After calcination at 500 °C in N_2 for 4 h, MoO_3/HZSM-5 was obtained. MoO_3/HZSM-5 was further reduced in NH_3 with the temperature program as follows: from room temperature to 300 °C in a heating rate of 10 °C·min^{-1}, from 300 °C to 500 °C in a rate of 0.5 °C·min^{-1}, from 500 °C to 700 °C in a rate of 1 °C·min^{-1}, and finally kept at 700 °C for 2 h. The obtained solid was fresh Mo_2N/HZSM-5 with large amounts of NH_x (x = 1–3) and H existing on the catalyst surface (Wei et al., 1997a). Due to the high activity of NH_x and H, Mo_2N/HZSM-5 catalyst should be passivated before exposed to the air. Therefore, after cooled down to room temperature, the fresh catalyst was passivated under O_2 (1 vol%, N_2 protection) for 4 h to form a thin protective layer (consisting of molybdenum oxides) (Wei et al., 1997b). The regeneration process under H_2 atmosphere (6 vol%, Ar protection, 500 °C, 3 h) was required to reduce the oxides layer before used for catalysis and characterization