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Research paper

Catalytic conversion of guaiacol as a model compound for aromatic hydrocarbon production

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ABSTRACT

Guaiacol, a mono-aromatic compound containing a hydroxyl and a methoxyl group, is one of the main products from lignin pyrolysis. In order to investigate the feasibility of aromatic hydrocarbons production from lignin, guaiacol was employed as the model compound for the catalytic conversion over HZSM-5 zeolites with different Si/Al ratios in a fixed-bed reactor under the temperatures from 500 °C to 800 °C. With the increased temperature, the yield of both aromatic hydrocarbons (such as benzene, toluene, styrene, naphthalene and 2-methylnaphthalene) and coke was increased from the mass fraction of 1.83%–24.27% and from 1.17% to 12.81%, respectively. At 600 °C, the yield of benzene was promoted by the HZSM-5 catalyst with high Si/Al ratio (200) by the mass fraction of 2.94% and up to 1.94% for that of toluene. The production of monocyclic aromatic hydrocarbons (especially for benzene and p-xylene) was favored with the loading of Ni on HZSM-5(25), while the formation of polycyclic aromatic hydrocarbons was notably inhibited. The coke deposition was slightly increased with the increased loading of Ni during the catalytic conversion of guaiacol. The demethoxylation and dehydroxylation reactions were considered to be promoted by the increase of Brønsted acid sites, while the methyl substitution reaction was slightly influenced by the total acidity of catalyst. The experimental results provided the conceptual and technical support for the catalytic pyrolysis of lignin to produce aromatic hydrocarbons.

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1. Introduction

Lignin, a natural complex polymer composed of three kinds of aromatic units with different linkages, is a potential feedstock for the production of aromatic chemicals and gasoline additives (such as benzene and xylene) [1]. Guaiacol-type compounds, one of the main derivatives from the pyrolysis of lignin, accounted for the mass fraction of 15% of the liquid product [2]. Conversion of those guaiacol-type compounds to aromatic hydrocarbons would be a promising way for utilizing lignin. The difficulty of the cleavage of the phenolic hydroxyl group from the benzene ring resulted in the limitation of the formation of aromatic hydrocarbons from the cracking of guaiacol-type compounds [3].

Corma et al. [4] studied the conversion of two oxygenates (glycerol and sorbitol) from pyrolysis of biomass over six different catalysts, finding that the ZSM-5 catalyst could give the highest

production of olefins and aromatics. HZSM-5, H-beta and HY zeolites were used in the catalytic fast pyrolysis of lignin model compounds containing β -O-4 linkages by Neumann et al. [5]. HZSM-5 was found to be the most effective catalyst for producing the products such as BTX and alkylbenzenes. The strength, type and amount of acidity of HZSM-5 zeolite affected by Si/Al ratio play an important role in the conversion of the pyrolytic derivatives from biomass. Adjaye and Bakhshi [6,7] reported that HZSM-5 was the outstanding catalyst for the high yield and selectivity of hydrocarbons production due to its abundant acid sites. Foster and co-workers [8] reported that the ZSM-5 zeolite with the highest aluminum content presented the highest selectivity to smaller aromatic hydrocarbons such as benzene and toluene from the catalytic pyrolysis of glucose. Valle et al. [9] found 1%Ni/HZSM-5(30) catalyst produced a high yield of aromatics with the content of BTX higher than the mass fraction of 60% in the upgrading of crude bio-oil into hydrocarbons. Highest aromatic hydrocarbon selectivity attributed to the presence of strong Brønsted acid sites in HZSM-5 catalyst was demonstrated in the catalytic upgrading of bio-oil [10]. Coke deposition was proved to be a major cause of the catalyst

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deactivation. The zeolite pore structure and the acidic properties, which were influenced by the type of catalysts and loading metal, play an important role in coke deposition for zeolite catalysts [11–13]. It needs to be noted that HZSM-5 zeolite can be widely used for conversion of the biomass-derived bio-oils for the production of aromatic hydrocarbons. However, the mechanism of the catalytic conversion of specific compounds from lignin over HZSM-5 is not sufficiently investigated, confining the highly-valued commercial utilization of lignin.

In order to fill the knowledge gap, guaiacol as one of the prominent compounds from the pyrolysis of lignin was selected to undergo the catalytic conversion over different HZSM-5 catalysts in a fixed bed reactor. The characteristics of the original and Ni-modified HZSM-5 catalysts were characterized using BET, XRD, NH₃-TPD, and Pyridine-FTIR to understand the inherent mechanism of catalytic conversion of guaiacol to aromatic hydrocarbons and the performance of coke deposition.

2. Materials and methods

2.1. Materials

Guaiacol (purity >99.999%, reagent grade) was purchased from Aladdin Company, P.R.China and used as feedstock directly without any treatment. Commercial HZSM-5 zeolites separately with Si/Al ratio of 25, 38, 50, and 200 were provided by Catalyst Plant of Nankai University, China. Ni-modified HZSM-5 (Ni/HZSM-5) was prepared by a typical wet impregnation method using aqueous solutions of Ni(NO₃)₂·6H₂O salt. Nickel loadings of 1, 3 and 5% mass fraction of the catalyst were obtained this way. The impregnation time was extended to about 24 h; the remaining paste was then dried in air at 105 °C for 4 h and calcined at 600 °C for 5 h. All catalysts were crushed and sieved to 50–60 mesh to obtain the particle size in the range of 0.25–0.3 mm. The Ni-modified catalysts were reduced in a H₂ flow (100 cm³ min⁻¹) at 600 °C for 1 h before the catalytic conversion experiments.

2.2. Characterization of catalysts

The various catalyst samples were analyzed by low-temperature N₂ adsorption (ASAP 2020 M) to determine the surface area (BET method), pore volume (calculated by the amount of the nitrogen adsorbed at P/P₀ = 0.99) and micropore parameters (t-plot method).

X-ray diffraction (XRD) measurements were also performed using Smartlab XRD-3 diffractometer with Cu K α radiation. The XRD patterns were accumulated in the range of 3–55° (2 θ).

NH₃-TPD experiments were carried out by temperature-programmed desorption of NH₃ (FINESORB-3010) to estimate the strength of acid sites on the catalysts. Approximately 100 mg of the sample was used in each trial. The sample was loaded in a U-shaped quartz tube and pretreated in a He stream at 500 °C for 1 h. The temperature was reduced to 120 °C and pulse chemisorption was executed by injecting 5% volume fraction of NH₃ in N₂ (20 cm³ min⁻¹) pulses through the catalyst bed for 30 min. After the adsorption of NH₃, the sample was scoured with He flow (20 cm³ min⁻¹) at 120 °C for 1 h to obtain a smooth baseline. Finally, NH₃-TPD was performed in a He stream from 120 to 700 °C with a 10 °C·min⁻¹ heating rate. The whole desorption process was detected with thermal conductive detector (TCD).

Fourier-Transform Infrared (FT-IR) spectroscopy experiments using pyridine as a probe molecule were performed on a Frontier FT-IR spectrometer (PE Company) for the determination of the Brønsted and Lewis type acid sites of the catalysts. Self-supported wafers of the catalyst were pressed and placed in the cell. Then,

the sample was outgassed at 350 °C for 2 h. Pyridine was adsorbed onto the sample at room temperature for 30 min and followed by desorption at 150 °C and 350 °C. It is generally acknowledged that the band at 1545 cm⁻¹ attributed to pyridinium ions corresponds to the Brønsted acid sites and the band at 1450 cm⁻¹ ascribed to pyridine coordinates to the Lewis acid sites [14]. The quantitative determination of acid sites was performed with the constants proposed by Emeis [15].

2.3. Catalytic conversion of guaiacol

The catalytic pyrolysis experiments were carried out on a fixed bed reactor, as shown in Fig. 1. The fixed-bed reactor was a quartz tube with an inner diameter of 20 mm and a length of 300 mm coupled with an effective heating section. The quartz tubular reactor was heated by the electrical heating coils and the temperature can be monitored by K-type thermocouples. In each experiment, about 0.5 g of the prepared catalyst was placed on the sand core of the reactor and silica sand was used as an inert solid carrier for comparison. Guaiacol was injected from the top of the reactor at the rate of 4 g h⁻¹ by a syringe pump. It was quickly evaporated and flew across the catalyst bed by carrier gas at the flow rate of 100 cm³ min⁻¹. The nitrogen was applied as carrier gas and the flow was controlled by the mass flow controller. The liquid product was collected by the two-step condensation system. Both two condensation equipment employed the mixture of water and ice to cool the condenser, where ethanol was used to absorb the volatile stream. The weight hourly space velocity (WHSV) was set to be 8 h⁻¹ according to the previous reports [16,17].

The chemical composition of the liquid captured from the catalytic conversion of guaiacol was analyzed by GC/MS (Agilent Technologies 7890A/5975C) via the helium sweeper gas stream. The GC separation was performed using a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μ m). The GC inlet was 280 °C and the split ratio was 30:1. The oven temperature was programmed from 40 °C (3 min) to 180 °C (2 min) with a 5 °C·min⁻¹ heating rate and then ramp at 10 °C·min⁻¹ to 280 °C where it was held for 2 min. Typical operating conditions of MS were ionization energy 70 eV, and scan rate of 35–550 amu per second. Peak was identified using the NIST mass spectrum library and some published data [18–20]. Some of the identified phenolic compounds and aromatic hydrocarbons were quantified based on the external standard method. The authentic compounds (purity >99.999%, reagent grade, Aladdin or Keshi) were used as standards to produce calibration curves. The coke yield deposited on the reacted catalyst was estimated by thermogravimetric analyzer (ZRT-1). Each catalytic pyrolysis experiment was performed at three times. The experimental results can be obtained as the average value from the duplicated experimental runs.

3. Results and discussion

3.1. The characterization result of catalysts

The physicochemical properties of the HZSM-5 with different Si/Al ratio and the Ni-modified HZSM-5(25) zeolites used in the catalytic conversion of guaiacol are presented in Table 1. Among the HZSM-5 zeolites having different Si/Al ratio, the BET surface area of HZSM-5(200) was the largest one (about 366.1 m² g⁻¹), while that of HZSM-5(50) was the smallest (only 287.46 m² g⁻¹). As the Si/Al ratio of HZSM-5 was decreased from 200 to 25, the surface area and pore volume of micropore were respectively increased from 115.74 m² g⁻¹ to 200.24 m² g⁻¹ and from 0.052 cm³ g⁻¹ to 0.093 cm³ g⁻¹.

The porosity characteristics of HZSM-5(25) catalyst were found

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