Upgrading of lignin pyrolytic-oil model compounds in a catalytic dielectric barrier discharge plasma reactor

Xinxin Liu[a,b,1], Tao He[a,d,*,1], Yuanzheng Ge[a,b], Guomin Li[c], Jingli Wu[a], Zhiqi Wang[a], Guangbo Liu[a], Jinhu Wu[a,*]

[a] Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] School of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, PR China
[d] Key Laboratory of Low-Carbon Conversion Science & Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China

ARTICLE INFO

ABSTRACT

Catalytic upgrading of anisole and guaiacol in an atmospheric dielectric barrier discharge (DBD) plasma reactor was studied. Compared to thermal upgrading in a fixed bed, the DBD plasma method can convert the model compound to benzene and toluene with high selectivity under relatively low temperature. The synergistic effect between H_2 plasma and Ni-Mo/SiO_2 catalyst is crucial to the high deoxygenation rate. The primary reactions occurring during the DBD upgrading process include demethylation, methyl transfer, and hydrogenolysis. XRD spectra indicate that phase change should not be the primary reason for catalyst deactivation; GC–MS, NH_3-TPD, and regeneration experiments show that carbon deposition is the cause for deactivation. NH_3-TPD analysis reveals that a combination of medium and strong acid sites plays an important role in the hydrogenolysis of phenols to benzenes. The present work shows DBD catalytic upgrading as a promising route for the C−O bond hydrogenolysis reaction.

1. Introduction

The consumption of depleting fossil fuels leads to a tightening of the energy supply and deterioration of the ecological environment, which has raised increasing concern [1,2]. The bio-oil from biomass pyrolysis is renewable, enabling it to meet the requirements of sustainable development and green chemistry [3,4]. Nevertheless, the high oxygen content (10–45 wt.%) of bio-oil results in a series of undesirable properties, including limited heating value, poor thermal-chemical stability, high viscosity and corrosiveness [5–7]; therefore, a chemical upgrading process is indispensable.

Phenols and ethers account for a large portion of lignin-related bio-oil [8]. Hydrodeoxygenation (HDO) is a bio-oil refining approach that can significantly reduce the oxygen content and improve the energy density [9,10]. Generally, the HDO reaction is performed in the liquid phase, which needs high H_2 partial pressure. Compared with the liquid phase reaction, gas phase upgrading (HDO or hydrogenolysis) reaction is fast [11]. HDO reaction can be catalyzed by precious metal and transition metal catalysts [12–15]. For example, Sun et al. [16] compared the activity of different precious metals (Pd/C, Pt/C, Ru/C, Fe/C,

Cu/C and Pd-Fe/C) for gas phase HDO of guaiacol; the results showed that the final major product was phenol. The active transition metals, Ni and Mo, are also widely used in bio-oil upgrading due to their low cost and good hydrogenation properties [17,18]. Jin et al. [19] synthesized a series of Ni-containing catalysts supported on activated carbon, SBA-15, SiO_2, and r-Al_2O_3. Testing the catalysts' activity for anisole HDO in an autoclave with 0.5–3.0 MPa H_2 pressure, these researchers observed that the Ni catalyst supported on silica materials exhibited a better deoxygenation activity with a conversion of 95% for Ni/SiO_2. In another related study, Smirnov et al. [20] investigated the HDO performance of anisole catalyzed by Ni-Mo/SiO_2 (300 °C, 6 MPa H_2 pressure), which showed high hydrogenation activity for the C−O bond and aromatic ring, leading to undesired ring saturation and high H_2 consumption.

From an economical point of view, high hydrogen pressure and consumption are not cost-effective [21]. Recently, researchers attempt to use a dielectric barrier discharge (DBD) plasma reactor for bio-oil model compound upgrading. DBD is a stable plasma source that works at low temperature [22]. The free electrons in the plasma are powered by the acceleration of the electric field, resulting in high-energy

electrons with energies of 1–10 eV [23]. These electrons collide with the bio-oil reactant molecules and may lead to selective cleaving of the C−O bond [24]. In previous work, Hamed et al. [25,26] studied the effects of different carrier gases, the applied voltage and pulse frequency on DBD reactor performance. These researchers demonstrated that the DBD reactor was suitable for anisole upgrading, obtaining a maximum anisole conversion of 72.7% under a He atmosphere. DBD plasma, combined with a catalyst, could generate a synergistic effect that may facilitate the deoxygenation reaction. Mohammad et al. [27,28] tested the upgrading of anisole in the presence of Pt, Ni-Mo, Co-Mo, Pt-Re, and Ni-Mo/Al_2O_3 catalyst in a DBD reactor; the maximum anisole conversion (81%) was achieved by the Ni-Mo/Al_2O_3 catalyst. The above studies have shown that plasma catalytic deoxygenation is a promising method for bio-oil upgrading, but such issues as time-on-stream performance, H_2 effect, and the results of other oxygen-containing functional groups have not been thoroughly elucidated to date.

In the present work, anisole and guaiacol are chosen as model compounds of lignin-derived bio-oil. Upgrading of the two model compounds in the DBD catalytic reactor using a SiO_2-supported nickel-molybdenum catalyst were investigated, including the deoxygenation performance, products distribution, synergistic effect, and catalyst analysis.

2. Experimental

2.1. Materials and catalyst synthesis

$Ni(NO_3)_2 \cdot 6H_2O$ (≥ 98 wt%), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (≥ 99 wt%) as the catalyst metal source, anisole (≥ 98 wt%), and guaiacol (≥ 98 wt%) were all AR grade commercial chemicals. SiO_2 with an initial surface area of $500 \, m^2/g$ were commercial supports and ground to 250–425 μm. He or H_2 (99.99%) was used as the carrier gas.

The supported nickel-molybdenum catalyst (Ni-Mo/SiO_2) was prepared progressively by incipient wetness impregnation of SiO_2 with the aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ overnight [29]. The sample was later aged at room temperature for 12 h, placed in an oven at 110 °C for 4 h, and calcined at 550 °C (ramp rate 5 °C/min) in air for 5 h. The theoretical mass loading of the Ni fraction (NiO) and Mo fraction (MoO_3) was 15% respectively.

2.2. Experimental apparatus and procedure

The DBD plasma catalytic reactor schematic diagram is shown in Fig. 1. The tubular plasma reactor is made of alundum with an outer diameter of 26 mm and a wall thickness of 2.5 mm, acting as the dielectric medium. The inner electrode is a stainless steel rod with a diameter of 12 mm, which is connected to the high voltage pulse generator and placed in the center of the reactor. The outer electrode is a
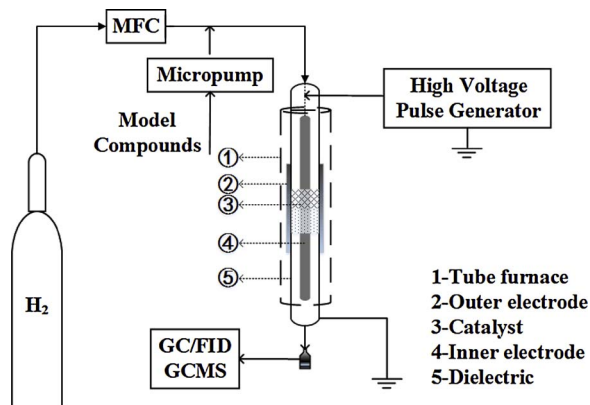

Fig. 1. Schematic of the catalytic DBD reactor.

stainless steel wire mesh wrapped around the outer wall of the alundum tube and connected to the ground. The length of the outer electrode is 20 cm, which determined the discharge zone and the catalyst is fixed in the middle of discharge zone. The outer temperature-controlled electrical tube furnace is used for heat preservation and evaporation of the liquid feed. In a typical run, the catalyst is first reduced by H_2 (450 °C, 40 min). The outer furnace is set to 200 °C for full evaporation of the liquid feed. The DBD reactor works with the input of 60 V and 1.5 A at atmospheric pressure. Carrier gas (H_2 or He) is controlled at 100 ml/min, and the liquid model compound is injected from the top of the DBD reactor using the pump with a constant flow rate of 0.08 ml/min. Lastly, the deoxygenated products are cooled by ice-water and collected every 30 min for off-line analysis by GC-7980 II (Techcomp) with an FID detector and TM-1 column (20.0 m × 0.32 mm, 0.25 μm film thickness). The GC parameters used for analysis are as follows: a detector temperature of 240 °C, injector temperature of 220 °C, and an oven temperature program: 70 °C for 1 min, 10 °C/min to 170 °C, 20 °C/min to 230 °C and hold for 2 min. The gas-phase products were analyzed by a GC-2060 with a TCD detector. GC–MS (Agilent Tech, DB-1 column) was used for polycyclic aromatic hydrocarbons analysis; the temperature program for the GC oven: 70 °C for 1 min, 10 °C/min to 340 °C and hold for 10 min.

2.3. Characterization of catalyst

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation under an instrumental setting of 40 kV and 40 mA, and a scan range of 10–80°. NH_3 temperature programmed desorption (NH_3-TPD) was performed by a Micromeritics ASAP 2020C to test the acidic property of the catalyst. Before NH_3 adsorption, the sample was pretreated at 650 °C under a helium flow, and NH_3 desorption temperature started from 50 °C to 650 °C at a rate of 10 °C/min.

3. Results and discussion

All experiments were conducted in duplicate. For analysis of the result, several equations are defined as follows:

$$\text{Anisole/guaiacol conversion (\%)} = \frac{\text{moles of the reactant consumed}}{\text{moles of the reactant fed}} \times 100 \tag{1}$$

$$\text{Deoxygenation rate (\%)} = \frac{\text{moles of the O-free aromatic product}}{\text{moles of the reactant fed}} \times 100 \tag{2}$$

$$\text{Selectivity } S_i \text{ (\%)} = \frac{\text{moles of product i}}{\text{total moles of the condensable organic products}} \times 100 \tag{3}$$

3.1. Upgrading of anisole and product distribution

Anisole upgrading over the SiO_2-supported Ni and Mo catalyst, with H_2 serving as the carrier gas, in the plasma ambient was first investigated. Fifteen types of condensable compounds were detected and quantified by GC and GC–MS, including benzene, toluene, m-xylene, p-xylene, o-xylene, trimethylbenzene, ethyltoluene, anisole, phenol, 4-methylanisole, o-cresol, p-cresol, 2,6-dimethylphenol, tetramethylbenzene, and 2,4-dimethylphenol. Fig. 2 shows the anisole conversion and deoxygenation rate with respect to time on stream (TOS). In the first 60 min TOS, the anisole conversion was maintained at more than 99% and later decreased from 99.7% to 92.3% at 90 min. Similar to the conversion trend, a maximum deoxygenation rate of 98.0% was obtained in the first 60 min TOS, and declined to 86.5% at 90 min, showing signs of catalyst deactivation.