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Research article

Liquefaction of kraft lignin over the composite catalyst $HTaMoO_6$ and Rh/C in dioxane-water system

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ABSTRACT

A catalytic routine was developed for kraft lignin depolymerization in dioxane-water systems, in which the catalyst $HTaMoO_6$ with strong Bronsted acidity and a hydrogenation catalyst (Rh/C) were employed simultaneously. The performance of the composite catalysts was tested in a series of experiments with various reaction temperatures, reaction time and catalyst ratios. Under the optimized conditions, a higher petroleum ether soluble fraction yield of 58.7% was obtained at 320 °C for 24 h. Besides, a higher liquid product yield of 95.6% was achieved at 290 °C for 2 h. Specially, the main compositions of the petroleum ether soluble fraction are monomers and dimers, which can be used as liquid fuel. These results demonstrated that the composite catalyst $HTaMoO_6$-Rh/C can effectively catalyze the depolymerization of the kraft lignin into small molecule liquid fuel components.

1. Introduction

Faced with the depletion of fossil fuel and the growing environmental problems, it is necessary to explore sustainable energy supply, such as solar, nuclear, tide and biomass. Lignin, as a main natural macromolecular organic compound in lignocellulosic biomass, was mainly composed of phenyl-propane units linked by carbon-carbon (C—C) bonds and carbon-oxygen (C—O) bonds, with 4-O-5, β-O-4 and α-O-4 as the most abundant linkages [1–8], which was a promising substitute for fossil fuels. On the one hand, lignin can be depolymerized to obtain high-value chemical additives and precursors for plastics, cosmetics, pharmaceutics, spices and many other industrial products [5,9,10] through subsequent refining and processing. On the other hand, several works were reported concerning the conversion of lignin to high-quality bio-oil that can be used as the liquid fuel component [11,12].

Kraft lignin was a major by-product in the process of industrial pulp and paper making in the form of black liquor [1,2,10,13–15], which generated > 40–50 million tons per year [3,6,16–18]. Currently, a large number of kraft lignin is directly discharged into the environments or just treated as a low-value fuel burnt to provide heat during the pulp and paper processing [19]. However, those treatment methods were wasteful and unsustainable. As a result, it is of great significance to establish an innovative catalytic method for more effective depolymerization of kraft lignin, which could ensure both sustainability and profitability.

In recent years, various approaches for lignin depolymerization have been investigated extensively including physical methods [20], biological methods [21,22] and chemical methods [23,24]. Among these methods, the chemical method gained most research interest, which includes pyrolysis [25,26], hydrogenolysis [16,27], hydro/solvothermolysis [28], hydrodeoxygenation [29,30] and so on. Therefore, a variety of catalytic systems have been developed in the past few years. Among them, the depolymerization of lignin with a noble metal catalyst [5,9,11,13,27,31,32] has undergone a preliminary exploration. Yang et al. [9] tested the lignin pyrolysis with the common noble metal Rh supported on active carbon in isopropanol system. High-quality bio-oil was obtained and oxygenated-chain compounds were reduced. Normally, the noble metal catalyst acts as a hydrogenation catalyst for O-removal process to obtain value-added aromatic chemicals and high-quality small-molecular bio-oil. Compared with noble metal catalysts, the transition metal catalysts are gaining more and more focus. However, non-noble metal catalysts generally require more severe reaction conditions [8,11,16,17,24] to achieve a certain depolymerization, which is still a pending challenge.

Some catalysts, such as graphene, g-C_3N_4, $HTaMoO_6$ ($HTaWO_6$,

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$HNbMoO_6$, $HNbWO_6$ and so on) [33] and transition metal sulfide (like Mo-S, V-S, W-S, Ni-S and Ti-S) [34–36] are well received by researchers because of their special structure and chemical properties. Among these, $HTaMoO_6$, an ion-exchangeable metal oxide, offers attractive features owing to its acid catalytic activity for Friedel-Crafts alkylation, esterification and hydrolysis [37]. Similarly, Ma et al. [38] took $LiTaMoO_6$ and Ru/C as a composite catalyst in the 0.3 M phosphoric acid system to investigate the depolymerization of cellulose in different raw biomass, reaching a hydrocarbon yield of 84%. Kazunari et al. [39] also reported the application of $HNbMoO_6$ and its exfoliated nanosheets in the hydrolysis of sucrose to glucose and fructose, achieving a glucose yield of 82%. These results demonstrated the excellent catalytic performance of this catalyst. Inspired by their works, the catalyst $HTaMoO_6$ was synthesized and applied for lignin depolymerization. Compared with traditional pore catalyst, this catalyst shows two main advantages. Firstly, the amorphous three-dimensional network structure of lignin would easily clog the pores and deactivate the traditional pore catalyst, whereas, the active sites of $HTaMoO_6$ were mainly distributed on the surface, which avoided the clogging to some extent. Secondly, the catalyst $HTaMoO_6$ exhibited a strong Bronsted acidity. These characteristics of the catalyst made it easier for lignin macromolecules to reach the active sites of $HTaMoO_6$ and promoted the lignin depolymerization. To the best of our knowledge, the compound $HTaMoO_6$ was rarely used by other researchers for the depolymerization of kraft lignin.

In this study, the catalyst $HTaMoO_6$ and a noble hydrogenation catalyst Rh/C are selected separately from the ion-exchangeable metal oxides ($HNbWO_6$/$HTaWO_6$/$HNbMoO_6$/$HTaMoO_6$) and hydrogenated catalysts (Ru/C/Pt/C/Pd/C/Rh/C/Raney Ni) as the composite catalyst to depolymerize kraft lignin in the dioxane-water system. The effects of catalyst ratio, reaction temperature and reaction time on product yields were investigated. Simultaneously, the chemical compounds and elemental content of the resulting products were examined by GC–MS and the elemental analyzer. Furthermore, the different characterization methods including NH_3-TPD, FT-IR, SEM and XRD were applied to study the characteristics of the catalyst during the process of cycle experiments.

2. Materials and methods

2.1. Materials

Indulin AT™ (Kraft lignin) was bought from MeadWestvaco (Shanghai, China). Li_2CO_3 (99.998%), WO_3 (99.8%), MoO_3 (99.9%), Ta_2O_5 (99.99%), Nb_2O_5 (99.95%), Rh/C (5 wt%), Ru/C (5 wt%), Pd/C (5 wt%) and Pt/C (5 wt%) were purchased from Aladdin (Shanghai, China). Analytical reagents, including nitric acid (65.0%–68.0%), 1,4-dioxane (≥99.5%), acetone (≥99.5%), ethyl acetate (≥99.5%) petroleum ether (60 °C–90 °C), methanol (≥99.5%) and Kari Fischer Reagents (without pyridine, 3–5 mg/mL) were provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The standard samples including acetophenone (≥99.0%), 4-ethylphenol (97%), 4-ethylguaiacol (99%), Vanillion (99%) and vanillyl benzylalcohol (97%) were purchased from Aladdin (Shanghai, China), and others including guaiacol (≥99.0%), 4-methylguaiacol (99%), 4-propylguaiacol (98%), acetovanillone (99%) and homovanillic acid (98%) were from J&K Scientific Ltd. (Shanghai, China). Above all, all the reagents in this work were used after received without further purification.

2.2. Catalyst preparation

The stoichiometric mixture of $LiCO_3$, A_2O_5 (A = Ta or Nb) and BO_3 (B = Mo or W) were calcined at 600 °C for 24 h for A = Ta, B = Mo [37,40] (at 580 °C for 24 h for A = Nb, B = Mo [37,41], at 800 °C for 24 h for A = Ta, B = W [42–46] and at 760 °C for 72 h for A = Nb, B = W [42–44,46]) in the air. Then the obtained precursors were subjected to proton exchange by shaking 2.0 g $LiABO_6$ in 250 mL cone bottle with 150 mL nitric acid (1 M) solution for 14 days at room temperature. During the proton exchange period, the solution was replaced for twice with fresh nitric acid (1 M). After that, the catalyst was collected by centrifugation and washed with deionized water. Finally, it was dried overnight in the oven at 70 °C.

2.3. Experimental method

The experiment was carried out in a 50 mL stainless steel autoclave. The initial hydrogen pressure was 2 MPa. The catalyst was added according to the required mass ratio of the two catalysts. What's more, the ion-exchangeable metal oxides and the hydrogenated catalysts were weighed separately, and then added directly to the reactor without further treatments. Then, 0.4 g substrate was charged, followed by the addition of 30 mL mixed solvent composed of 1, 4-dioxane and water (9:1, v/v). The autoclave was heated to a given temperature with a rate of 5 °C/min under magnetic stirring at a speed of 600 rpm. Once the reaction ended, the reactor was cooled to below 200 °C in the air, and then placed in cold water quenching to room temperature. As shown in Fig. 1, the reaction mixture was centrifuged to obtain the supernatant solution, from which a tiny aliquot was taken and analyzed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC–MS) to determine the content and type of aromatic monomers. The remaining reaction supernatant was divided into two equal parts. Both parts were concentrated by rotary evaporator at 40 °C and weighed. Then the total weight of the both condensed liquors was taken as the weight of the liquid product. Furthermore, the water content of the liquid product was approximately 1.5% measured by Karl Fischer moisture analyzer (see Table S1). Besides, the centrifugal residue was dried at 80 °C and weighed. Then, one part of the obtained liquid product was extracted with 30 mL of ethyl acetate, and filtered. The filtrate was evaporated by rotary evaporator at 40 °C. The enriched

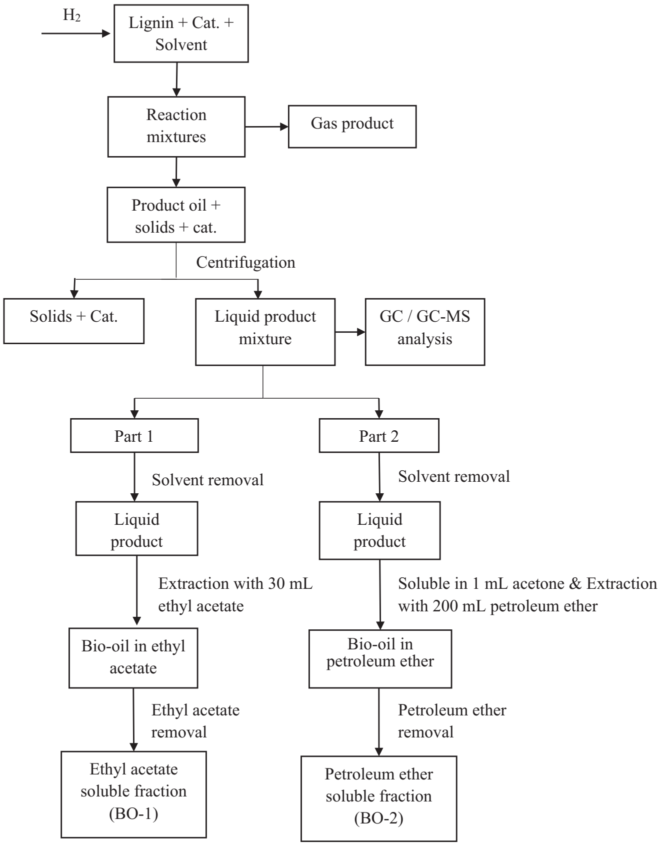

Fig. 1. Workup procedure for product mixture.