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Catalytic ethanolysis of Kraft lignin to small-molecular liquid products over an alumina supported molybdenum nitride catalyst

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ABSTRACT

An alumina supported molybdenum nitride catalyst (Mo_2N/Al_2O_3) is examined for the ethanolysis of Kraft lignin in supercritical ethanol in a batch reactor with an initial nitrogen pressure of 0 MPa (gauge). No char or tar is formed in this process. The Mo loading as well as the nitriding temperature in the catalyst preparation process has a great influence on the activity. The best performance is obtained over 30 wt% Mo_2N/Al_2O_3 catalyst nitrided at 700 °C. The overall yields of sulfur-free small-molecular products achieve the maximum value of 1189 mg/g lignin, with aliphatic compounds accounting for 907 mg/g lignin and aromatic compounds 282 mg/g lignin, respectively. Both the product yields and the molecular distribution are also strongly dependent on the reaction time and temperature. Furthermore, the Mo_2N/Al_2O_3 catalyst exhibits an excellent recycle performance with no significant activity loss after at least three runs. After reaction, the bulk structure of Mo_2N/Al_2O_3 catalyst was well-preserved only with a slight surface oxidation.

1. Introduction

Lignin, as one of the three essential components of lignocellulosic biomass, is a three-dimensional amorphous biopolymer consisting of various methoxylated phenylpropanoid building blocks [1,2], which are now mainly obtained from fossil-based industry. It accounts for 15-30% by weight and 40% by energy of all the lignocellulosic biomass. Kraft lignin was a bulk waste of the pulping and paper industry for a long time, and in recent three decades, it has been isolated from the black liquor due to the environmental regulations in the commercialized countries. Therefore, efficient utilization of Kraft lignin will not only address the issue of environmental impacts, but also become an attractive and promising approach for the production of alternative fuels and chemicals due to its high heating value and unique aromatic nature. However, in the present time Kraft lignin is just used as a low-grade boiler fuel or in the production of a number of low value-added materials, *e.g.*, flocculating and dispersing reagents in construction [3–6].

A number of strategies, *e.g.*, pyrolysis, liquid phase reforming and hydroprocessing, have been adopted in the utilization of Kraft lignin [5]. For pyrolysis, the aromatic hydrocarbon yield of 17.5% was obtained over a $Mo_2N/\gamma\text{-}Al_2O_3$ catalyst at 700 °C [7]. For the liquid phase processes, water and ethanol were used as hydrogen-donor solvents. In supercritical water, the yield and selectivity of the products depended on the reaction conditions and capping reagents [6,8,9]. The yield of water-soluble products for the depolymerisation of alkali lignin reached 16.4 wt% at 390 °C for 0.1 h with p-cresol as the capping reagent. Zakzeski et al. [10] found that the solubility of Kraft lignin in a hot ethanol-water mixture was much higher than that in pure water at 225 °C, and 17.6 wt% selectivity to aromatic products was obtained over an H_2SO_4 promoted Pt/Al_2O_3 catalyst. Jongerius et al. [11] obtained 9 wt% overall yield of monoaromatic products in a similar process with Pt/Al_2O_3 and NaOH as co-catalysts at 225 °C for 2 h under 5.8 MPa argon. The same group investigated the hydrodeoxygenation performance of the lignin-derived products over $CoMo/Al_2O_3$ and Mo_2C/CNF catalysts, and obtained 6 wt% and 7 wt% yields of monoaromatic products, respectively. An activated carbon supported tungsten phosphide catalyst gave 6.7 wt% yield of phenols in a hot compressed water-ethanol solvent without an additional capping reagent [12]. However, all the above-mentioned works suffer from several challenges, *e.g.*, low yields, corrosion, high temperature and pressure, and char or tar formation that causes the clogging issues.

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Ethanolysis strategy made an interesting advance. Ford et al. [13] converted woody biomass solids to a liquid mixture of C2-C6 aliphatic alcohols and methylated derivatives in supercritical methanol at 300–320 °C and 16–22 MPa using a copper-doped porous metal oxide. Cheng et al. [14] found that the acetone-methanol soluble products from the degradation of lignin in supercritical ethanol had a lower molecular weight than those obtained in water. Recently, we reported the catalytic ethanolysis of Kraft lignin over α-$MoC_{1\text{-}x}$/AC and Mo/Al_2O_3 catalysts at 280 °C for 6 h, and obtained 1640 and 1390 mg/g lignin small-molecular products, respectively, on the two catalysts without any char or tar formation [15,16]. Huang et al. [17] reported a Kraft lignin conversion result with 23 wt% yield of monomeric aromatics without formation of char or tar at 300 °C under inert atmosphere over a $CuMgAlO_x$ catalyst. Several other Mo-based catalysts, *e.g.*, MoS_2, Mo_2C and $NiMo/Al_2O_3$, were reported to be active in the conversion of biomass in the hydrogen-donor solvents [18–20]. Compared with noble metals, molybdenum nitride was proved to exhibit the similar performance regarding hydrogen activation [21], and successfully applied for the hydrodeoxygenation of guaiacol, a kind of lignin model compound [22,23]. Besides, on the premise of high yields, the synthesis of molybdenum nitride in the atmosphere of N_2/H_2 mixture is more accessible and cleaner than that of other Mo-based materials.

Herein, an alumina supported molybdenum nitride catalyst is applied to catalyze the ethanolysis reaction of Kraft lignin in supercritical ethanol. The nitriding temperature and Mo loading of the Mo_2N/Al_2O_3 catalyst are investigated to explore the optimal preparation conditions and related catalytic activity. Besides, the effect of reaction conditions on the yield of products is also investigated. With the aid of XRD and XPS analysis, the bulk structure of Mo_2N/Al_2O_3 catalyst and the valence state of Mo species for the catalytic ethanolysis of Kraft lignin are discussed.

2. Experimental

2.1. Materials

The Kraft lignin purchased from Sigma-Aldrich (product number 471003) was used without further purification. The weight-average molecular weight (Mw) and number-average molecular weight (Mn) of the lignin are 60,000 and 10,000 g/mol, respectively. The original lignin contains 49.5 wt% C, 4.71 wt% H, 0.15 wt% N, 2.80 wt% S and 19.4 wt% ashes [15]. The Kraft lignin was dried overnight at 100 °C prior to use. The weight loss was less than 0.2%. Solvents and chemicals, including ethanol, p-cresol, ammonia water and ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AR reagent grade, Tianjin Guangfu Technology Development Co. Ltd.) were used as received. The alumina support was kindly offered by CNOOC Tianjin Chemical Research & Design Institute. The deionized water was prepared with an Ulupure ultrapure water purification machine (UPH-1-10).

2.2. Catalyst preparation

The alumina supported molybdenum nitride catalyst was synthesized with an incipient-wetness impregnation method. For a typical preparation, 3.00 g alumina of 40–60 mesh were impregnated at ambient temperature overnight with the 3.60 g ammonia solution containing ammonium molybdate (for Mo loading of 10, 20, 30, and 46 wt %, the dosage of ammonium molybdate was 0.61, 1.38, 2.36 and 4.70 g, respectively). In the impregnation process, ammonia solution was added to improve the solubility of ammonium molybdate which was completely dissolved even at the loading of Mo up to 46%. No external material issues were observed. Then the mixture was dried at 110 °C for 12 h. The precursor underwent nitridation in a flow of N_2 and H_2 (v:v = 1:5) mixture accompanied with a four-stage temperature programmed procedure, which was set from 20 to 350 °C at a heating rate of 10 °C/min, and then from 350 to 500 °C at a heating rate of 1 °C/min. Finally, the temperature was increased to the preset value at a heating rate of 2 °C/min and held at that temperature for 2 h. After cooling to ambient temperature, the samples were directly used in the reaction without exposing to air. The materials used for XRD characterization were passivated in a flow of 100 ml/min (STP) industrial nitrogen (including small amount of oxygen) at ambient temperature for 3 h. The passivation was utilized to avoid the excessive oxidation before the characterization.

2.3. Catalyst characterization

X-ray diffraction patterns (XRD) of the passivated materials were measured with a powder diffractometer (Bruker AXS D8-S4), equipped with a Cu-Kα radiation source. It was operated at 40 kV and 40 mA, and the scanning was carried out in the 2θ range between 30 ° and 80 ° at a rate of 1.8 °/min.

The texture of the samples was determined with a nitrogen adsorption-desorption experiment using a Quantachrome Autosorb-1 system. The samples were outgassed under high vacuum degree at 250 °C for 6 h before measurement.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Perkin-Elmer PHI-1600 spectrometer using monochromatic Mg Kα radiation. Binding energy was calibrated with respect to the signal for C1 s at 284.8 eV.

2.4. Lignin ethanolysis reaction

The reaction of Kraft lignin was carried out in a 300 mL batch reactor (Parr 4566, made of Hastelloy) equipped with a temperature controller (Parr 4848). In a typical run, 1.00 g lignin, Mo_2N/Al_2O_3 catalyst (0.46, 0.23, 0.15 and 0.10 g corresponding to 10, 20, 30 and 46 wt% Mo loading) and 100 mL ethanol were loaded into the reactor. The reactor was purged with high-purity nitrogen for five times and sealed with an initial pressure (gauge) 0 MPa. Then the reactor was heated to the required temperature and kept for the desired reaction time under the constant stirring of 400 rpm. At the end of reaction, the reactor was quickly cooled to ambient temperature by immersing into a cold-water bath. The products in the gas phase were absorbed with alkaline hydrogen peroxide for the quantitative analysis of sulphur element. The liquid products were obtained through filtration and rotary evaporation prior to the analysis.

2.5. Product analysis

The products collected from the gas phase were measured and confirmed using a HIDEN HPR20 mass spectrometer, and the sulphur content of the absorbed products in the gas phase was quantified with DX600 ion chromatography produced by Dionex.

The products in the reactor were separated into ethanol soluble portion and residue (R1) after filtration. The residue was washed using diluted hydrochloric acid (pH = 2) to dissolve the ashes and weighed after drying (R2). The ethanol soluble products were enriched with removing a part of the ethanol with a rotatory evaporator. Then Agilent 6890-5973 GC-MS and Agilent 6890 GC-FID were applied for qualitative and quantitative analysis of the liquid products, respectively. The compounds were confirmed by comparing the mass spectra obtained from the samples to standard spectra in the system's database (NIST 2.0). An internal standard method was adopted for the quantitative calculation of product yield. P-cresol was used as an internal standard. The working conditions and programs for both Agilent GCs were the same as reported in our previous work [15,16]. The oven temperature program was set from an initial temperature of 45 °C to a final temperature of 250 °C at a rate of 10 °C/min, and then kept at 250 °C for 2 min. Both chromatographic column used were HP-5 MS capillary column (30m × 0.25 mm × 0.25 μm). A split ratio of 50 was used for the GC-FID and GC-MS analysis. The scanning m/z range of mass