Alumina supported molybdenum catalyst for lignin valorization: Effect of reduction temperature

Xiaolei Ma, Kai Cui, Wenyue Hao, Rui Ma, Ye Tian, Yongdan Li *

Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Technology, State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- An alumina supported molybdenum catalyst is employed in lignin conversion.
- In supercritical ethanol, C6–C10 chemicals are produced with high yield.
- The products consist of alcohols, esters, benzyl alcohols, monophenols and arenes.
- Metallic Mo is much more active than the oxide.
- The reduction temperature has a strong influence on the catalytic performance.

GRAPHICAL ABSTRACT
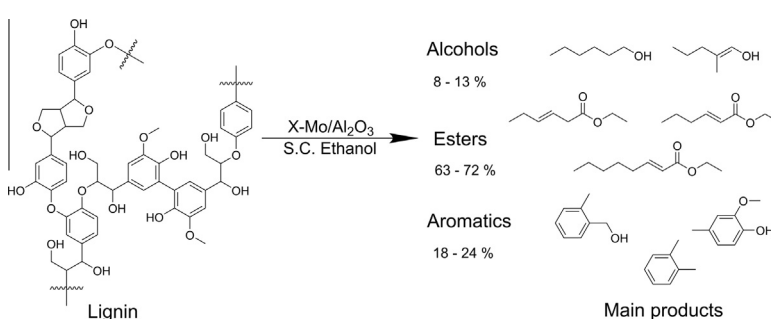
ARTICLE INFO

ABSTRACT

Alumina supported molybdenum catalysts were prepared with an impregnation method. The activity of the catalyst in the ethanolysis of Kraft lignin to C6–C11 molecules, *i.e.* alcohols, esters, monophenols, benzyl alcohols and arenes, was tested in a batch reactor at 280 °C with initial 0 MPa nitrogen. The complete conversion of lignin to small molecular chemicals was achieved without the formation of tar or char. The reduction temperature during the catalyst preparation was proved to have a profound effect on the activity of the catalyst. The overall product yield firstly increases and then decreases with the increase of the reduction temperature in a range of 500–800 °C. The maximum yield up to 1390 mg/g lignin was obtained with the catalyst reduced at 750 °C. Furthermore, the catalyst showed an excellent recyclability, where no significant loss of the catalytic activity was exhibited after 5 runs.

1. Introduction

Due to the growth of population and the development of industry, the world is experiencing a rapid increase of the consumption of traditional fossil-based fuels, which leads to a great concern of the energy future (Chu and Majumdar, 2012). The development of affordable, environmentally benign and energy efficient processes for production of fuels and chemicals from sustainable resources becomes an urgent challenge. In this respect, plant biomass with noteworthy features like the huge abundance, geographical universality, and renewability as well as low cost, is the only renewable resource which is enough for accommodate the future demand of the human society on energy (Peterson et al., 2008; Zhang et al., 2013) and chemicals (Gallezot, 2011; Tong et al., 2010). Another advantage of biomass utilization is green, since the CO₂ evolved during the utilization processes is then consumed through photosynthesis of plants in their growth.

As a major component of woody plants, lignin is the second most abundant natural polymer (just after cellulose), and is

* Corresponding author. Tel.: +86 22 27405613; fax: +86 22 27405243.
  E-mail address: ydli@tju.edu.cn (Y. Li).

produced from the wood-pulp or sugarcane milling industry largely as a waste-product. Lignin is a complex and irregular macromolecule mainly consisting of three monolignols, guaiacyl, syringyl and p-hydroxyphenyl propane, through connectings of various ether and carbon–carbon bonds, such as β-O-4, α-O-4, β-β, β-5, 5-5 links (Huber et al., 2006; Zakzeski et al., 2010). Lignin is currently mostly used as a boiler fuel to provide heat and power, i.e. unselective oxidation to carbon dioxide. This results in the massive waste of the resource as well as pollution of the environment. Lignin conversion to chemicals or bio-oil fuel is an attractive route and a number of processes have been intensively explored. The approaches, including cracking, hydrolysis, reduction and oxidation, have been reviewed (Yaman, 2004; Zakzeski et al., 2010). Because of the special phenyl propanol structure, much attention has been focused on the production of phenols (Amen-Chen et al., 2001; Bu et al., 2014; Kleinert and Barth, 2008; Ma et al., 2014b; Singh et al., 2014; Zakzeski et al., 2012), cycloalkanes (Yan et al., 2008), and polyols (Mahmood et al., 2013). Mixed oxide catalysts have been demonstrated to be active in the conversion of lignin or wood (Barta et al., 2010, 2014; Huang et al., 2014; Matson et al., 2011; Warner et al., 2014). Over a Cu-based oxide catalyst in supercritical methanol at 320 °C without addition of H_2, pine flour was converted to 9.1 wt% C2–C6 higher alcohols and ethers, 4.0 wt% C9–C12 substituted cyclohexyl alcohols and ethers components (Matson et al., 2011). At lower temperature, 140–220 °C, and in the presence of H_2, the same catalyst was demonstrated to convert organosolv lignin into catechols with a high yield up to 64 wt% (Barta et al., 2014). In supercritical ethanol using a $CuMgAlO_x$ catalyst, Kraft lignin conversion was examined, and a yield of monomeric aromatics of 23 wt% without char formation was reported at 300 °C under nitrogen atmosphere (Huang et al., 2014).

Molybdenum-based catalyst plays an important role in industry and has been used in biomass conversion reactions. Spruce enzymatic hydrolysis of lignin to phenols and hydrocarbon chemicals was investigated over a sulfided NiMoP/γ-Al_2O_3 catalyst and the principal role of the catalyst was supposed to be the rapid stabilization of the primary products of lignin decomposition preventing their condensation to high molecular weight products (Horáček et al., 2012). With Mo as a promoter, the activity of the reduced Mo–Ni/γ-Al_2O_3 catalyst was evaluated in the upgrading of raw bio-oil from the vacuum pyrolysis of pine sawdust (Xu et al., 2009). Molybdenum nitride (Mo_2N) was reported to be active in the hydrodeoxygenation (HDO) of 2-methoxyphenol, a common lignin model compound (Sepúlveda et al., 2011). Other molybdenum compounds, MoO_3, MoO_2, MoS_2 and MoP were reported to be active for the HDO of 4-methylphenol (Whiffen and Smith, 2010). Recently, we reported the complete ethanolysis of Kraft lignin over an α-$MoC_{1−x}$/AC catalyst in supercritical ethanol to give value-added chemicals (Ma et al., 2014a). High yield, up to 1.64 g/g lignin, of the products consisting of C6–C10 esters, alcohols, arenes, phenols, and benzyl alcohols was obtained at 280 °C.

In this work, the major objective was to evaluate the activity of an alumina supported molybdenum catalyst in converting Kraft lignin to high valued chemicals. The reduction temperature was found important for the activity and selectivity. The catalyst design and the key process factors were also discussed.

2. Methods

2.1. Materials

The Kraft lignin was purchased from Sigma–Aldrich (product number 471003). The elemental contents are 49.5 wt% C, 4.71 wt% H, 0.15 wt% N and 2.80 wt% S, while the ash content is 19.4 wt% (Ma et al., 2014b). Analytical grade chemicals and solvents, including guaiacol, phenol, o-cresol, ammonium molybdate ($(NH_4)_6Mo_7O_{24}·4H_2O$) and ethanol were purchased from Tianjin Guangfu Technology Development Co. Ltd. These materials were directly used as received. The alumina support was kindly provided by CNOOC Tianjin Chemical Research & Design Institute. The water used was provided by an Ulupure ultrapure water purification system (UPH-1-10).

2.2. Catalyst preparation and characterization

The supported molybdenum catalyst was prepared with an impregnation technique and with Mo loading of 30 wt%. Briefly, 2.37 g $(NH_4)_6Mo_7O_{24}·4H_2O$ was dissolved in 3.60 g ammonia water (12.9 wt%). The solution was used to impregnate 3.00 g alumina with the incipient wetness method. The samples were dried at 120 °C for 10 h, then ground and sieved to particles of 40–60 mesh. The reduction was carried out in flowing H_2 (210 mL/min, STP). The temperature was heated from 30 to 350 °C at a rate of 2 °C/min, then from 350 to 500 °C at a rate of 0.5 °C/min, and finally the temperature was increased to the prescribed temperature at a rate of 1 °C/min and held at that temperature for 120 min. The catalyst samples were denoted as X-Mo/Al_2O_3 in the context (X, the reduction temperature). For characterization, the fresh sample was passivated in a flow of 0.5% O_2/N_2 gas (320 mL/min, STP) for 4 h at room temperature before direct exposure to air.

H_2-temperature programmed reduction (TPR) was conducted on a TPDRO1100 apparatus (Thermo-Finnigan). A gas mixture consisting of H_2 (5% v/v) and N_2 was used as the reductant at a flow rate of 20 mL/min (STP). The temperature was increased from 30 to 900 °C at a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were measured with a powder diffractometer (Bruker AXS D8-S4), using the Cu-Kα radiation and operating at 40 kV and 40 mA in the range of 2θ from 10° to 80° with a scan rate of 8°/min. Nitrogen adsorption-desorption isotherms were obtained at −196 °C with a Quantachrome Autosorb-1 equipment. Prior to the measurement, the samples were degassed under vacuum at 250 °C for 6 h. Specific surface areas (S_{BET}) of the samples were obtained with the BET method based on the adsorption isotherm branch at relative pressures (P/P_0) ranging from 0.05 to 0.30, and a value of 0.162 nm^2 for the cross-sectional area of N_2 molecule was used. The total pore volume was derived from the adsorption amount at a relative pressure of 0.99. Pore size distribution was determined with the Barrett–Joyner–Halenda (BJH) method.

2.3. Lignin conversion experiment

The lignin conversion experiment was carried out in a hastelloy batch reactor (Parr 4566) equipped with a temperature controller (Parr 4848) for 6 h at 280 °C in supercritical ethanol and the condition was similar to that reported in papers (Ma et al., 2014a,b; Yang et al., 2013). The reactor was loaded with 1.0 g Kraft lignin, 0.5 g fresh catalyst and 100 mL ethanol. Then the reactor was fixed and sealed, and the initial pressure was set 0 MPa after purging with high-purity N_2 for three times. The reactor was heated to the desired temperature and remained for 6 h. The reactor was stirred with a fixed stirring rate of 400 rpm. After stopping the reaction and cooling to room temperature, the pressure was released and the reactor was opened. After filtration, the products were obtained.

2.4. Product analysis

The liquid phase product was analyzed qualitatively and quantitatively with an Agilent 6890-5973 GC–MS and an Agilent 6890 GC with a FID detector, respectively. The analysis method was