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Production of phenols from catalytic conversion of lignin over a tungsten phosphide catalyst

Xiaolei Ma, Ye Tian, Wenyue Hao, Rui Ma, 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, School of Chemical Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT

Production of phenols from alkaline lignin over a tungsten phosphide catalyst in a hot compressed water–ethanol mixed solvent is examined. The small molecular products mainly consist of five phenols, i.e. 2-methoxy-phenol (guaiacol), 2-methoxy-4-methyl-phenol, 2-methoxy-4-ethyl-phenol, 2-methoxy-4-acetyl-phenol and 2-methoxy-4-propyl-phenol. The activated carbon supported catalyst gives the highest overall phenols yield, 67.0 mg/g lignin, while the catalysts with other supports exhibit much lower overall yield. Ni and Fe doping of the tungsten phosphide improve phenols selectivity but lower the overall phenols yield. In addition, the result of MALDI-TOF analysis indicates that a longer reaction time leads to the formation of polymers with molecular weights of *m/z* 701–1040 due to the re-polymerization reactions. Therefore, the yield of the monophenols decreases with the increase of the reaction time.

1. Introduction

Due to the reduced reserve and the increased utilization of fossil fuels, such as coal, crude oil and natural gas, a great research interest has been focused on the exploration of alternative energy resources in recent years [1,2]. Furthermore, the greenhouse gases, CO_2 as the most important one, emission from the combustion of fossil fuels also become a great concern. New technologies of converting biomass into value-added chemicals and fuels are of practical meaning to relieve the huge pressure on energy and environmental needs. The growth of plants catches and fixes CO_2 thus mitigates the concern of global warming. Lignocellulose is the most abundant sort of biomass as it is the major component of all the plant cell wall contributing structural and mechanical integrity of plants. The estimated annual production rate of lignocellulose of the global biosphere is about 20 billion metric tons, which is potentially enough for the supply of energy and chemicals to the human society. Lignocellulose is mainly composed of cellulose, lignin and hemicellulose. Recently, transforming components of lignocellulose into bio-fuels or more value-added chemicals through enzymatic and catalytic routes becomes a dynamic research field worldwide [3–6]. Lignin utilization is more challenging which is isolated with a large volume in the wood-pulp or milling industry but only utilized as a low heating value fuel [7].

Different from cellulose, which is a polymer of monosaccharide, lignin is a complex and irregular macromolecular material, mainly constituted with three monolignols, i.e., guaiacyl, syringyl and p-hydroxyphenyl propanes. These units are randomly connected with various ether bonds and carbon–carbon bonds, such as β–O–4, 5–5 and 4–O–5 bond (Fig. 1) [3]. Due to its special composition, lignin is ideally suitable to be depolymerized into phenolic monomers for the production of phenols or other aromatic compounds, alleviating the current production pressure of these compounds from petroleum industry. During the past decade, various lignin conversion methods aiming at getting chemicals and bio-oil have been explored [8–17]. However, the common problems existing are the enormous diversity of the products and the low yield of the monomer phenols, normally lower than 5 wt%, even though under harsh reaction conditions [16,17].

Transition metal phosphides have good hydroprocessing performance and are often reported to be sulphur-resistant [18–20]. However, recent work mainly focuses on the preparation and characterization of tungsten phosphide (WP) [21–24]. WP has been used as catalyst in cellulose degradation [25] and guaiacol hydrodeoxygenation [26]. Here we report the direct catalytic decomposition of alkaline lignin into phenols over a WP catalyst in hot-compressed water–ethanol system. Furthermore, the activity of WP is also compared with the Ni and Fe doped-tungsten

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

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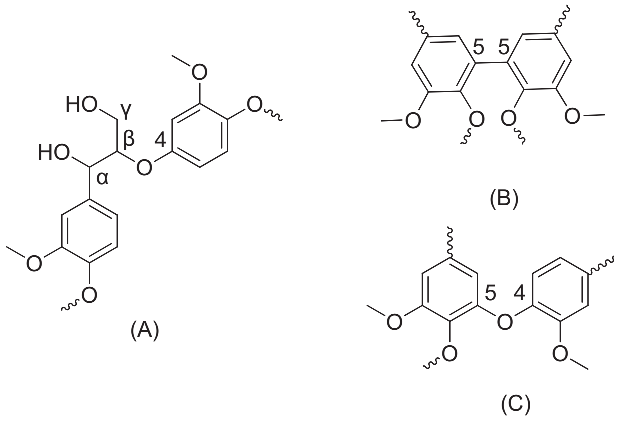

Fig. 1. Common linkage motifs in lignin.

phosphide catalysts. The reaction mechanism of lignin conversion to phenols is also discussed.

2. Materials and methods

2.1. Materials

The alkaline lignin (AL) used in this work was purchased from Sigma–Aldrich Co. (product number 471003) and was used directly. The provided average molecular weight of the AL is 1.0×10^4 (M_n, number-average molecular weight) and 6.0×10^4 (M_w, weight-average molecular weight) respectively. Table 1 gives its elemental content obtained with an Elementar system (Vario Micro cube). The ash content measured after ashing in air at 973 K for 6 h is 19.4 wt%. Analytical grade chemicals and solvents, including guaiacol, catechol, phenol, diammonium hydrogen phosphate, nickel nitrate, iron nitrate, dichloromethane and ethanol were purchased from Tianjin Guangfu Technology Development Co. Ltd. Ammonium meta-tungstate (analytical grade) was obtained from Sinopharm Chemical Reagent Co. Ltd. These materials were directly used as received. Commercial silicon oxide (SiO_2, Qingdao Marine Chemical Industry Co. Ltd., China) was used as the support of catalyst. The activated carbon (AC) with a surface area of 851 m^2/g (measured by Quantachrome Autosorb-1) was got from Norit Co. Ltd, the Netherlands and was made from peat. To purify the AC, mainly decrease the amount of metal element, the AC was refluxed with 30 wt% HNO_3 at 353 K for 5 h and then was washed for ten times by deionized water until detected to be neutral. The AC was finally dried at 353 K over night before being used as catalyst support. The water used was provided by an Ultrapure water purification system (UPH-1-10).

2.2. Catalyst preparation

Unsupported tungsten phosphide was prepared from tungsten phosphate precursor as reported in literature [21]. A mixture of 8.1 g (4.3 mmol) ammonium meta-tungstate $(NH_4)_6W_7O_{24}{\cdot}6H_2O$ and 4.0 g (30.3 mmol) diammonium hydrogen phosphate $(NH_4)_2HPO_4$ was dissolved in 30 mL of deionized water. A white solid was obtained after evaporation of the water. The material was calcined in air at 773 K for 4 h. Subsequently, the calcined solid was reduced in a quartz tube (internal diameter 10 mm) under flowing H_2 (40 mL/min, STP) with heating from room temperature to 573 K at a rate of 10 K/min, then from 573 K to 923 K at a rate of 1 K/min and held at 923 K for 150 min. After that the material was cooled to room temperature under the flowing H_2 stream. Supported tungsten phosphide, with the W loading 20 wt%, was prepared with an impregnation technique. Briefly, solution of the precursors was prepared by dissolving 0.8 g (0.4 mmol) $(NH_4)_6W_7O_{24}{\cdot}6H_2O$ and 0.4 g (2.8 mmol) $(NH_4)_2HPO_4$ in corresponding amount of deionized water, and the solution was used to impregnate 2.0 g SiO_2 support by the incipient wetness method. The obtained samples were dried and calcined at 773 K for 4 h, then ground and sieved to particles of 40/60 mesh. The calcined solid was reduced to phosphide in flowing H_2 (40 mL/min, STP) with heating from room temperature to 623 K at a rate of 5.5 K/min, and then from 623 K to 1123 K at a rate of 1 K/min and finally held at 1123 K for 60 min. For the WP/AC sample, the same solution was used to impregnate 2.0 g treated AC support. After drying and calcining under flowing N_2 stream (40 mL/min, STP) at 773 K for 4 h, the precursor was reduced under the same condition prescribed for the SiO_2 supported sample. Doped tungsten phosphides (with dopants loading of 2 wt%) were prepared by adding dopant $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ in impregnation step. During the impregnation, ammonia water (10 wt%) was used instead of deionized water.

Table 1
Elemental contents of the alkaline lignin.

Element	C	H	N	S
Content/wt%	49.5	4.71	0.150	2.80

A W_2C/AC sample was also prepared through a carbothermal hydrogen reduction (CHR) method in the absence of CH_4 [27,28]. In brief, AC was incipient wetness impregnated with an aqueous solutions of $(NH_4)_6W_7O_{24}{\cdot}6H_2O$. After drying and calcining under flowing N_2, the catalyst was finally carburized in H_2 with heating in ramp. The heating procedure was the same as that used for the preparation of WP/AC sample but without introduction of phosphorus.

The fresh catalyst was used in the lignin catalytic degradation experiment. For the characterization of the sample, the material was passivated in a flow of 0.5 vol% O_2/N_2 gas (320 mL/min, STP) for 4 h at room temperature before directly exposing to air.

2.3. Characterization of catalysts

The x-ray diffraction (XRD) patterns of the passivated materials were recorded on a powder diffractometer (Bruker AXS D8-S4), using a Cu-Kα radiation source, operated at 40 kV and 40 mA, with a scanning rate of 8°/min in a 2θ range from 15 to 80°. Nitrogen adsorption/desorption isotherms were obtained at 77 K using a Quantachrome Autosorb-1 instrument. Surface areas of the samples (S_{BET}) were obtained using the BET method based on the adsorption isotherms in a relative pressure (P/P_0) range from 0.05 to 0.30. A value of 0.162 nm^2 of 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. Prior to the measurements, samples were treated under vacuum at 523 K for 6 h.

2.4. Lignin conversion experiments

The lignin conversion experiments were carried out in a stainless steel stirred tank reactor (Parr 3560) controlled by a temperature controller (Parr 4842) similar to that reported in literature [12,13]. The reactor was loaded with alkaline lignin (1.0 g), fresh catalyst (0.3 g) and a mixture of water and ethanol solvent (volume ratio 1/1, total 100 mL). Then the reactor was fixed and sealed, pressurized to 2.0 MPa with H_2 after purged with N_2 and H_2 for three times. The reactor was heated by an electrical furnace to the desired temperature 553 K and remained for 2 h. During the reaction the reactor was stirred by a mechanical stirrer set at 400 rpm. The reaction time reported in this work does not contain the time