



Zirconia-supported 12-tungstophosphoric acid: Characterization and catalytic behavior in degradation of alkali lignin



Xiaole Liu, Gaofeng Zhao, Shixue Ren*, Guizhen Fang, Zhijun Chen, Shujun Li

Material Science and Engineering College, Key Laboratory of Bio-based Material Science and Technology Ministry of Education, Northeast Forestry University, Harbin, 150040, PR China

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ABSTRACT

Degradation of alkali lignin (AL) is important for practical applications of this valuable natural resource. 12-Tungstophosphoric acid (TPA), supported on materials with a high surface area, has been shown to be an effective catalyst for the degradation of AL. This complex catalyst is, however, relatively unstable and there are a limited number of suitable supporting materials. To overcome these problems, we prepared ZrO₂-supported TPA and demonstrated that this is an effective catalyst for the degradation of AL. Catalysts with different TPA loadings (10–40 wt%) were prepared using different calcinations temperatures (200–500 °C). The catalysts were characterized by X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FESEM), and surface area measurements. Catalyst loaded with 20% TPA and prepared at 200 °C demonstrated the highest catalytic efficiency when the catalyst-to-lignin ratio was 1:8. Under these conditions, total hydroxyl groups and phenolic hydroxyl groups increased by 203.9% and 148.4%, respectively. The catalyst could be reused at least three times, without significant loss of activity. This method thus represents a green and effective alternative for the degradation of AL into valuable small molecules.

Synopsis

The selective degradation of alkali lignin structure into smaller molecular units is the major challenge for converting it to value-added chemicals.

1. Introduction

Alkali lignin (AL), which is made up of aromatic hydrocarbon-containing units, is one of the most important natural carbon sources (Xie et al., 2016; Arturi et al., 2017). Generally, industrial AL has an irregular, randomly cross-linked structure, which does not have well-defined physical and chemical properties. This means that AL is unsuitable for many practical applications and, to address this problem, lignin is frequently degraded to provide more useful small molecules (Erdocia et al., 2015). The main strategy for degradation is cleavage of the ether linkages present in the lignin structure (Yoshikawa et al., 2014) and many different catalysts and reaction conditions have been tested in order to optimize this process. Acid-catalyzed, base-catalyzed, metal-catalyzed, ionic liquid-assisted and supercritical fluid-assisted reactions have all been used for the chemical degradation of AL (Chatel

and Rogers, 2016), with the acid-catalyzed method being one of the most effective.

Present, considerable efforts are being made to find efficient, sustainable, recyclable and environmentally friendly solid acid catalysts to serve as substitutes for the currently used homogeneous Brønsted and Lewis acids. Zeolites (Chen et al., 2016; Mullen and Boateng, 2010), polyoxometalates (Gregorio et al., 2016) and metal oxides (Zhang et al., 2015a) have all been tested as catalysts and 12-tungstophosphoric acid (TPA) has been identified as unique material that functions as both an acid and a redox catalyst (Pope and Müller, 2001). The Keggin structure of TPA not only has high acidic strength, relatively high thermal stability and a low oxidation potential but also has strong Brønsted acid characteristics. TPA is a stronger acid than conventional solid acids, such as zeolites and mixed oxides (Jalil et al., 2003).

TPA and its derivatives have been shown to readily degrade cellulose and lignin, giving useful intermediates by cleavage of ether bonds and double bonds, together with other fragmentations (Liu et al., 2017; Gromov et al., 2016). Shen et al. (2009) found that Industrial AL has been catalytically degraded by Keggin-HnXW₁₂O₄₀ (n = 3, X = P, n = 4, X = Si). The total amount of hydroxyl groups and the amount of phenolic hydroxyl groups in the AL after degradation was determined

* Corresponding author.

E-mail addresses: liuxiaole1990@163.com (X. Liu), zgf1993@yeah.net (G. Zhao), renshixue@nefu.edu.cn (S. Ren), fanggz_0@163.com (G. Fang), chenzhijun@nefu.edu.cn (Z. Chen), lishujun@nefu.edu.cn (S. Li).

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by potentiometric titration and UV spectrophotometry. Since the number of active functional groups after degradation was almost 3-fold higher than in AL, this provided a new way to improve the utility of lignin. Shimizu (Shimizu et al., 2009) found that heteropoly acids ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) were more effective than inorganic acids ($HClO_4$, H_2SO_4 and H_3PO_4) for the catalytic conversion of cellobiose and cellulose and increased the yield of reducing sugars ($H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > HClO_4 > H_2SO_4 > H_3PO_4$).

TPA is unsuitable for large scale use as a homogeneous catalyst since it is difficult to recover and recycle (Patel and Singh, 2014). When the solid acid is used as a catalyst, the low specific surface area, porosity of the bulk heteropoly acid and partial salt formation greatly reduce catalytic performance. This problem can be largely overcome by anchoring the solid catalyst to a suitable support that has a high specific surface area (Frattini et al., 2017; Singh and Patel, 2014). Immobilization of TPA on an acidic or near neutral carrier material can maximize both the surface area of the TPA and its strongly protonic acid properties, leading to highly reactive systems. However, because of the weak anchoring of the heteropoly acid onto the surface of the carrier, leaching is inevitable and the catalyst will be deactivated after several uses.

The surface of ZrO_2 is typically covered with hydroxyl species that are able to coordinate with active components and a number of groups have used the amphoteric characteristics of ZrO_2 to improve the performance of TPA (Escobar et al., 2015). Compared with acidic or neutral carriers, the weakly basic surface of ZrO_2 interacts strongly with TPA and thus, to a certain extent, reduces dissolution of immobilized TPA by the liquid phase. The successful development of solid acids is expected to completely solve the problem of catalyst regeneration and reuse.

In the present work, we have prepared a TPA/ ZrO_2 catalyst and investigated its ability to degrade AL. The structure and properties of TPA/ ZrO_2 were characterized by N_2 physisorption, X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy and field-emission scanning electron microscopy (FESEM). The degradation products were analyzed by FT-IR spectroscopy, gel permeation chromatography (GPC) and ^{13}C NMR techniques, and optimum degradation conditions were investigated. The effect of catalyst loading, calcination temperature and amount of TPA/ ZrO_2 on the degradation of AL were evaluated using the total amount of hydroxyl groups, the amount of phenolic hydroxyl groups and the molecular mass as indexes.

2. Materials and methods

2.1. Preparation of catalysts

The zirconia support was prepared using the sol-gel technique. Briefly, aqueous ammonia (10 M) was added dropwise to zirconyl chloride solution (0.2 M), to a final pH of 8. The precipitate was filtered and washed with aqueous ammonia (pH = 8) until it was free from chloride ions, as determined by the silver nitrate test. The gel particulate was air-dried at 120°C for 12 h. The product was then ground to a powder and dried for a further 12 h.

The TPA/ ZrO_2 composites were prepared using a modified wet impregnation method. Catalysts with different TPA loadings (10, 20, 30 and 40 wt%) were prepared by using different concentrations of TPA in ethanol. For each reaction, a mixture of zirconia support and TPA solution in ethanol (4 mL of ethanol solution per g of zirconia support) was stirred under reflux for 12 h. Excess ethanol was removed at 78°C under vacuum. The resulting solid materials were dried at 120°C for 24 h and ground to fine powders. The final products were then calcined at 200°C, 300°C, 400°C or 500°C for 4 h. The TPA/ ZrO_2 catalysts are denoted as xTPA/ ZrO_2 -t, where x represents the wt% of TPA and t refers to the calcination temperature.

2.2. Lignin preparation

The AL used in these reactions was prepared from black liquor dry matter (Shandong Tralin Paper Co. Ltd., Liaocheng, China), using the acid-precipitation method (Zhang et al., 2015b). Black liquor dry matter was dissolved in distilled water (mass ratio of lignin/distilled water, 1:9) and the solution was allowed to stand for 12–24 h. Insoluble material was removed by filtration and the filtrate was treated with 2 M hydrochloric acid to pH 4. The reaction mixture was allowed to stand for 12 h and then filtered. The filter cake was washed with distilled water to neutral and dried at 45°C under vacuum (0.08 MPa) for 48 h in a vacuum drying oven.

2.3. AL using TPA/ ZrO_2

AL decomposition reactions were carried out in a round bottomed flask, equipped with a reflux condenser and air stirrer. The flask was charged with AL (1.0 g) and ethanol/water (2:1 v/v, 30 mL) and placed in a water bath at 60°C. The contents were then stirred for 15–20 min. The TPA/ ZrO_2 catalyst was added and the mixture was stirred for 6 h. After cooling to room temperature, the catalyst was removed by filtration and washed with distilled water. The combined filtrates were evaporated using a rotary evaporator and the residue was dried under vacuum at 45°C for 24–48 h to give catalytically degraded lignin.

2.4. Characterization of the catalysts

The specific surface area, pore volume and pore size distribution of the catalysts were determined using an ASAP 2020 automatic physisorption system (Micromeritics Instrument Corp., Norcross, GA, USA). The specific surface area was calculated using the BET equation and the pore size distribution was calculated using the BJH equivalent cylindrical model. The samples were vacuum dried at 120°C for 10 h before the tests and the N_2 desorption isotherm was measured at $-196^\circ C$.

XRD measurements of the catalyst powders were recorded using a D/max-2200VPS diffractometer (Rigaku). Cu K-alpha radiation ($\lambda = 1.5418 \text{ \AA}$) was used, with a 2θ step of 0.04° and an integration time of 1 s/step for 2θ between 5° and 60° , recorded using a Tensor 27 FT-IR spectrometer (Bruker). Transmittance measurements were carried out using 1 wt% KBr discs and spectra were recorded at room temperature over the wavelength range $400\text{--}4000 \text{ cm}^{-1}$. The spectral resolution of the spectrometer was 4 cm^{-1} . FESEM images were obtained using a JCM-5000 scanning electron microscope (Jeol). Samples were plated with a layer of gold before testing.

2.5. Characterization of reaction products

The total amount of hydroxyl species in the lignin was measured using the acetylation-hydrolysis method (Zhang et al., 2014a). Lignin (0.10 g) was dissolved in acetylation reagent (purified pyridine/acetic anhydride/dioxane (1:1:1, v/v/v), 1.50 g) and the solution was held at 50 °C for 24–48 h. Acetylation reagent with no added lignin was used as a blank. Acetone (5 mL) was added and the solution was accurately diluted to 100 mL with distilled water. An aliquot (5 mL) of this solution was titrated with sodium hydroxide (0.1 M), using phenolphthalein as the indicator. Hydroxyl content was calculated using the following equations:

$$[OH](\%) = [(m \div m_0 \times b_0 - b) \times 1.7] \div A \times 100 \quad (1)$$

$$[OH](\text{mmol/g}) = [OH](\%) \times 1 \div 17 \times 1000 \quad (2)$$

where [OH] (%) is the total hydroxyl content (wt%) of the lignin; [OH] (mmol/g) is the total hydroxyl content (mmol/g) of the lignin; m and m_0 are the masses (mg) of acetylation reagent in the sample and blank, respectively; b and b_0 are the volumes (mL) of sodium hydroxide solution in the sample and blank, respectively; 1.7 g/L is the hydroxyl

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