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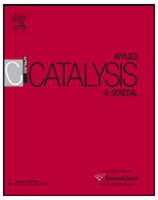

Catalytic decomposition of 4-phenoxyphenol to aromatics over Pd/$XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA ($X$ = 10, 20, 30, 40, and 50 wt%) catalysts

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ABSTRACT

Activated carbon aerogel (ACA) was prepared by a chemical activation of carbon aerogel using phosphoric acid (H_3PO_4). A series of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-impregnated activated carbon aerogels ($XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA) were prepared with a variation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content (X) in order to provide acid sites to ACA. Palladium catalysts were then supported on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-impregnated activated carbon aerogel (Pd/$XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, X = 10, 20, 30, 40, and 50 wt%) by an incipient wetness impregnation method for use in the decomposition of 4-phenoxyphenol to aromatics. 4-Phenoxyphenol was used as a lignin model compound for representing 4—O—5 linkage of lignin. Cyclohexanol, benzene, and phenol were mainly produced by the decomposition of 4-phenoxyphenol. Conversion of 4-phenoxyphenol and total yield for main products (cyclohexanol, benzene, and phenol) were closely related to the acidity of Pd/$XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA. Conversion of 4-phenoxyphenol and total yield for main products increased with increasing acidity of Pd/$XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA. Among the catalysts tested, Pd/$20Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA with the largest acidity showed the highest conversion of 4-phenoxyphenol and total yield for main products. Conversion of 4-phenoxyphenol and total yield for main products over Pd/$20Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA were much higher than those over palladium catalyst supported on commercial activated carbon (Pd/AC) and palladium catalyst supported on activated carbon aerogel (Pd/ACA).

1. Introduction

Carbon dioxide from burning of fossil fuels has been considered as a contributor to global warming. Furthermore, fossil fuels such as coal and crude oil are not sustainable [1–3]. Biomass has attracted much attention as an environmentally friendly and renewable energy source, because biofuels can reduce the dependence on fossil fuel and the emission of carbon dioxide [4].

Corn sugar and vegetable oil, which are known as first generation biofuels, are environmentally friendly, but feedstocks for first generation biofuels are limited and compete with food resource [5,6]. However, second generation biofuels derived from lignocellulosic feedstocks do not compete with food resource. Lignocellulose is typically composed of three main components: cellulose, hemicellulose, and lignin. Lignin produced by delignification process in the pulp industries is mainly burned as a low value fuel for power generation [7,8]. Therefore, decomposition of lignin to aromatics becomes as an advantageous technology for producing aromatics as biofuels, because lignin is the richest source of aromatics in nature [9,10].

Many attempts have been made on the catalytic decomposition of lignin to aromatics, because thermal cracking of lignin requires high temperature (over 450 °C) and pressure (over 100 atm) for considerable performance [11–14]. Liquid acid such as H_3PO_4 and solid acid such as cesium-exchanged heteropolyacid ($Cs_xH_{3.0-x}PW_{12}O_{40}$, x = 2.0–3.0) are known as promising catalysts for the decomposition of lignin to aromatics [15–17]. Novel metal catalysts supported on carbon (Pd/C, Pt/C, and Rh/C) also show a considerable performance for selective decomposition of C—O bond in lignin [18,19].

Dimeric lignin model compounds for representing C—O and C—C bonds in lignin have been used as a lignin feedstock due to the complex structure of lignin [20–22]. In particular, dimeric chemical compounds containing C—O bond such as β—O—4, α—O—5, and 4—O—5 have been used as lignin model compounds, because C—O bond is abundant linkage type in the lignin. Among various lignin model compounds, 4-phenoxyphenol has been widely employed as a lignin model compound for representing 4—O—5 bond in lignin [23,24].

Carbon aerogel (CA) [25–29] and activated carbon aerogel (ACA) [30–35] have been employed as catalyst support, electrochemical

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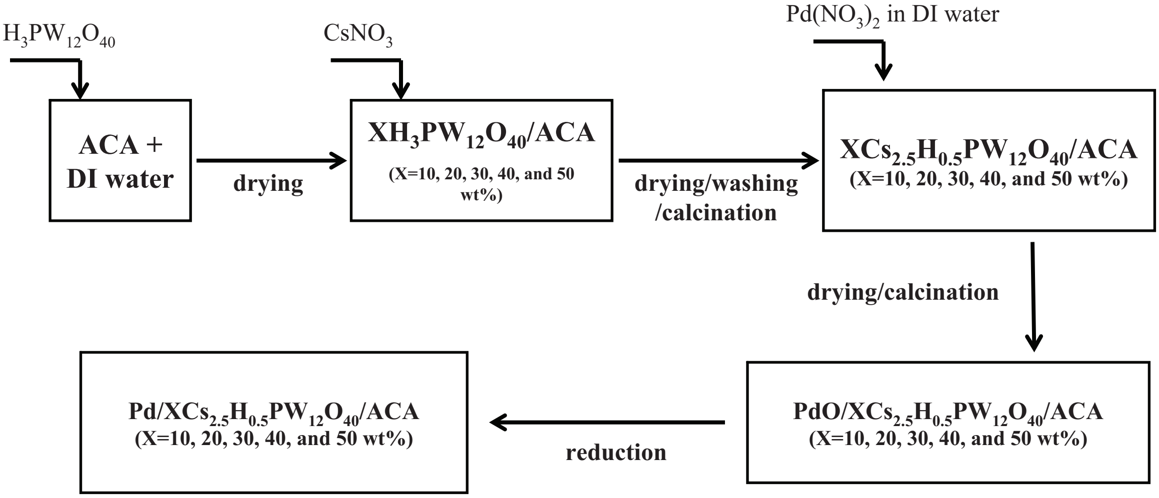

Fig. 1. Schematic procedures for the preparation of $XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA and $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA.

capacitor, and adsorbent, because CA and ACA provide both micropores and mesopores. Palladium catalyst supported on carbon aerogel (Pd/CA) [36] and palladium catalyst supported on activated carbon aerogel (Pd/ACA) [37] have been used for the decomposition of C—O bond in the lignin to take advantage of porous nature of CA and ACA.

Heteropolyacids (HPAs) are inorganic acids. Acid strength of HPAs is stronger than that of conventional solid acids [38–42]. HPA salts with K^+, Cs^+, and $NH_4{}^+$ cations have high surface area and porous structure by forming a tertiary structure [38,39]. It is known that surface acidity of cation-exchanged insoluble HPAs is different depending on cation content [38,39]. For example, surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0–3.0) shows a volcano-shaped trend with respect to cesium content within X = 2.0–3.0, and shows maximum value when X is 2.5 [40–42].

In this work, ACA was prepared by a chemical activation of CA with phosphoric acid (H_3PO_4). In order to provide acid sites to ACA, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was impregnated on ACA with a variation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content ($XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, X = 10, 20, 30, 40, and 50 wt%). Palladium catalysts supported on $XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA ($Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA) were then prepared by an incipient wetness impregnation method, and they were applied to the decomposition of 4-phenoxyphenol to aromatics. 4-Phenoxyphenol was chosen as a lignin model compound for representing 4—O—5 bond in lignin. For comparison, palladium catalyst supported on commercial activated carbon (Pd/AC) and Pd/ACA were also employed for the decomposition of 4-phenoxyphenol to aromatics. The effect of acidity of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA on the catalytic performance in the decomposition of 4-phenoxyphenol was investigated.

2. Experimental

2.1. Preparation of carbon aerogel (CA) and activated carbon aerogel (ACA)

CA and ACA were prepared according to the method in the literatures [27,36]. Carbon aerogel was prepared by a sol–gel polymerization of resorcinol and formaldehyde. 25.9 g of resorcinol ($C_6H_6O_2$, Sigma–Aldrich, 99%) was dissolved in 60.0 ml of DI water. Aqueous resorcinol was mixed with sodium carbonate (0.05 g) (a base catalyst) to accelerate dehydrogenation of resorcinol. After stirring the solution for a few minutes, 14.1 g of formaldehyde (H_2CO, Sigma–Aldrich, 37 wt% in H_2O) was added slowly into the solution to form a sol. Molar ratio of resorcinol (R) with respect to formaldehyde (F) was fixed at 1:2 (R/F = 1/2). R/C (resorcinol/catalyst) ratio was fixed at 500. The resulting sol was cured in a vial to produce resorcinol–formaldehyde (RF) gel at 80 °C for 24 h. Solvent exchange was performed with acetone at 50 °C for two days. Residual solvent was replaced with fresh acetone every 3 h to remove water thoroughly from the pore of RF wet gel. Ambient drying was then done at room temperature and 50 °C for one day. CA was finally obtained by carbonization of RF gel at 500 °C for 1 h.

Activated carbon aerogel was prepared by a chemical activation of carbon aerogel with phosphoric acid (H_3PO_4). 2 g of phosphoric acid (H_3PO_4) was dissolved in 10 ml of DI water and 2 g of carbon aerogel was dispersed into an aqueous solution of phosphoric acid. After stirring the solution for 1 h, the solid was dried at 110 °C for 3 h. The mixture of phosphoric acid and carbon aerogel was heated to react at 800 °C for 1 h under N_2 stream to obtain activated carbon aerogel. Phosphoric acid in activated carbon aerogel was washed off using DI water till the pH value of solution reached ca. 7. The residual solid was finally dried at 110 °C for 5 h to obtain ACA.

2.2. Preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacid impregnated on activated carbon aerogel ($XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA)

In order to provide acid sites to ACA, cesium-exchanged $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacid was impregnated on ACA with a variation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content ($XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, X = 10, 20, 30, 40, and 50 wt%). Fig. 1 shows the schematic procedures for the preparation of $XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA. A known amount of $H_3PW_{12}O_{40}$ (Sigma–Aldrich, 99.995%) was impregnated onto 1 g of activated carbon aerogel ($XH_3PW_{12}O_{40}$/ACA, X = 10, 20, 30, 40, and 50 wt%) by an incipient wetness impregnation method, and it was dried overnight at 80 °C. A known amount of cesium nitrate ($CsNO_3$, Sigma–Aldrich, 99%) was dissolved in 10 ml of DI water. 1 g of $XH_3PW_{12}O_{40}$/ACA was then dispersed into the solution with constant stirring, and the mixture was stirred for 3 h. After filtering and washing a solid product with DI water, the solid was dried overnight at 80 °C. The solid was finally calcined at 300 °C for 3 h to obtain $XCs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA ($X$ = 10, 20, 30, 40, and 50 wt%).