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Catalytic decomposition of 1,3-diphenoxybenzene to monomeric cyclic compounds over palladium catalysts supported on acidic activated carbon aerogels

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ABSTRACT

Activated carbon aerogel (ACA) was prepared by a chemical activation of carbon aerogel using phosphoric acid (H_3PO_4). Activated carbon aerogel bearing sulfonic acid (ACA-SO_3H), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-impregnated activated carbon aerogel ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA), and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-impregnated activated carbon aerogel bearing sulfonic acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$) were prepared in order to provide acid sites to ACA. Palladium catalysts were then supported on ACA, ACA-SO_3H, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$ by an incipient wetness impregnation method. The prepared Pd/ACA, Pd/ACA-SO_3H, Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, and Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$ catalysts were applied to the decomposition of 1,3-diphenoxybenzene. 1,3-Diphenoxybenzene was used as a trimeric lignin model compound for representing C-O bond in lignin. Cyclohexanol, benzene, and phenol were mainly produced by the decomposition of 1,3-diphenoxybenzene. 4-Phenoxyphenol was also produced as an intermediate by the decomposition of 1,3-diphenoxybenzene. Conversion of 1,3-diphenoxybenzene and total yield for main products (cyclohexanol, benzene, and phenol) increased with increasing acidity of the catalysts. Among the catalysts tested, Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$ with the largest acidity showed the highest conversion of 1,3-diphenoxybenzene and total yield for main products. Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$ also served as a stable and reusable catalyst in the decomposition of 1,3-diphenoxybenzene.

1. Introduction

First generation biofuels derived from corn sugar and vegetable oil are environmentally friendly, but feedstocks for first generation biofuels are limited and compete with food resource [1,2]. However, second generation biofuels derived from lignocellulosic feedstocks do not compete with food resource. Lignocellulosic is mainly composed of three components; cellulose, hemicellulose, and lignin. Among these components, lignin is a biopolymer synthesized by polymerization of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin produced by delignification process in the pulp industries is burned as a low value fuel for power generation [3,4]. Therefore, decomposition of lignin to aromatics becomes as an advantageous technology for producing aromatics as biofuels and chemicals, because lignin is the richest source of aromatics in nature [5].

One-step decomposition of lignin such as thermal cracking and hydrogenolysis of lignin over Ni-Mo and zeolite catalysts requires high temperature (over 450 °C) and pressure (over 100 atm) for considerable performance [6,7]. On the other hand, two-step decomposition of lignin has attracted as a promising technology for producing monomeric aromatics, because yields for aromatics via two-step decomposition of lignin are higher than those via one-step decomposition of lignin at low temperature and pressure [8,9]. In the two-step decomposition, lignin is partially depolymerized over base catalysts such as NaOH for producing oligomeric lignin units, and subsequently, monomeric aromatics are produced by catalytic cleavage of C-O bond in oligomeric lignin units.

Catalytic decomposition of lignin to aromatics has received much attention as a key technology for valorization of lignocellulosic biomass [9–17]. Liquid acids such as H_3PO_4 and solid acids 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 [12–15]. Novel metal catalysts supported on carbon (Pd/C, Pt/C, and Rh/C) [9] and novel metal catalysts supported on acidic activated carbon aerogel (ACA) (Pd/ACA-SO_3H [16] and Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA [17]) also showed considerable performance for selective decomposition of C-O bond in lignin.

Lignin model compounds for representing C—O and C—C bonds in lignin have been used as a lignin feedstock due to the

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complex structure of lignin [18–20]. In particular, chemical compounds containing aromatics linked by C—O bonds 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, phenethylphenyl ether, benzylphenyl ether, and 4-phenoxyphenol have been widely employed as a lignin model compound for representing β-O-4, α-O-5, and 4-O-5 bonds in lignin, respectively [21,22]. In addition, chemical compounds containing more than three aromatics linked by C—O bond have been used as an oligomeric lignin model compound [23].

Carbon aerogel (CA) [24–28] and activated carbon aerogel (ACA) [29–34] have been employed as catalyst supports, electrochemical capacitors, and adsorbents due to their porous nature. Pore structure of activated carbon aerogel can be controlled by changing activation conditions such as activation agent, activation temperature, and activation time. Heteropolyacids (HPAs) are inorganic acids. Acid strength of HPAs is stronger than that of conventional solid acids [35–38]. HPA salts with K^+, Cs^+, and NH_4^+ cations have high surface area and porous structure by forming a tertiary structure [36,37]. It is known that acidity of cesium-exchanged insoluble HPAs is different depending on cesium content [35,36].

In this work, carbon aerogel (CA) was prepared by a R-F (resorcinol-formaldehyde) method [26,35], and subsequently, CA was activated by H_3PO_4 to obtain an activated carbon aerogel. Activated carbon aerogel (ACA) containing acid sites were prepared by sulfonation of ACA (ACA-SO_3H) and by impregnation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ onto ACA ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA). $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was also impregnated on ACA-SO_3H to form $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$. Palladium catalysts supported on ACA, ACA-SO_3H, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$ were then prepared by an incipient wetness impregnation method, and they were applied to the decomposition of 1,3-diphenoxybenzene. 1,3-Diphenoxybenzene was chosen as a trimeric lignin model compound for representing C-O bond in lignin. Three aromatics are linked by two C—O bonds in 1,3-diphenoxybenzene.

2. Experimental

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

Carbon aerogel (CA) and activated carbon aerogel (ACA) were prepared according to the method in the literatures [26,35]. Carbon aerogel was prepared by a sol–gel polymerization of resorcinol and formaldehyde. 25.9 g of resorcinol ($C_6H_6O_2$, Sigma–Aldrich) was dissolved in 60 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) was slowly added 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 at 80 °C for 24 h to produce resorcinol-formaldehyde (RF) gel. 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 from the pore of RF wet gel. Ambient drying was then done at room temperature and 50 °C for one day. Carbon aerogel (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) [35]. 2 g of phosphoric acid (H_3PO_4) was dissolved in 10 ml of DI water, and 2 g of carbon aerogel was then dispersed into an aqueous solution of phosphoric acid. After stirring the mixture 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 nitrogen stream to obtain activated carbon aerogel. Phosphoric acid in the 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 activated carbon aerogel (ACA).

2.2. Preparation of ACA-SO_3H

In order to provide acid sites to ACA, activated carbon aerogel bearing sulfonic acid group (ACA-SO_3H) was prepared by sulfonation of activated carbon aerogel (ACA) [16]. Fig. 1 shows the schematic procedure for the preparation of ACA-SO_3H. 1 g of activated carbon aerogel was dispersed into 100 ml of H_2SO_4 solution (10 M). After stirring the mixture for 10 h under nitrogen stream, the solid was filtered and washed with DI water at 70 °C. The residual solid was dried at 110 °C for 5 h to obtain activated carbon aerogel bearing sulfonic acid group (ACA-SO_3H).

2.3. Preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA

To provide acid sites to ACA, cesium-exchanged $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacid was impregnated on ACA [17]. Fig. 1 also shows the schematic procedure for the preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA. 15 wt% of $H_3PW_{12}O_{40}$ (Sigma–Aldrich, 99.995%) was impregnated onto 1 g of activated carbon aerogel ($H_3PW_{12}O_{40}$/ACA) 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 $H_3PW_{12}O_{40}$/ACA was then dispersed into the aqueous solution containing cesium salt with constant stirring 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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA.

2.4. Preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$

Cesium-exchanged $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacid was impregnated on ACA-SO_3H to form $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$. Fig. 1 also shows the schematic procedure for the preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$. 15 wt% of $H_3PW_{12}O_{40}$ (Sigma–Aldrich) was impregnated onto 1 g of ACA-SO_3H ($H_3PW_{12}O_{40}$/ACA-SO_3H) by an incipient wetness impregnation method, and then it was dried overnight at 80 °C. A known amount of cesium nitrate ($CsNO_3$, Sigma–Aldrich) was separately dissolved in 10 ml of DI water. 1 g of $H_3PW_{12}O_{40}$/ACA-SO_3H was then dispersed into the cesium-containing solution with constant stirring 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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$.

2.5. Preparation of palladium catalysts supported on ACA, ACA-SO_3H, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$

5 wt% of palladium catalyst was supported on ACA, ACA-SO_3H, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$ by an incipient wetness impregnation method. The supported palladium catalysts were dried at 80 °C for 3 h, and they were calcined at 250 °C for 5 h. The supported catalysts were reduced with a mixed stream of hydrogen (5 cc/min) and nitrogen (30 cc/min) at 120 °C for 6 h to obtain Pd/ACA, Pd/ACA-SO_3H, Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA, and Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ACA-$SO_3H$.