Applied Catalysis A: General 437–438 (2012) 112–119

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

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

Hai Woong Park, Ung Gi Hong, Yoon Jae Lee, Jung Ho Choi, In Kyu Song*

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea

ARTICLE INFO

Article history:
Received 26 April 2012
Received in revised form 1 June 2012
Accepted 16 June 2012
Available online 26 June 2012

Keywords:
Heteropolyacid-impregnated activated carbon aerogel
Pd catalyst
Lignin
C—O bond
4-Phenoxyphenol

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

* Corresponding author. Tel.: +82 2 880 9227; fax: +82 2 889 7415.
E-mail address: inksong@snu.ac.kr (I.K. Song).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.06.024