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# Decomposition of 4-phenoxyphenol to aromatics over palladium catalyst supported on activated carbon aerogel

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### ABSTRACT

Carbon aerogel (CA) was prepared by a sol-gel polymerization of resorcinol and formaldehyde, and a series of activated carbon aerogels (ACA-H<sub>3</sub>PO<sub>4</sub>-*X*, *X* = 0, 0.5, 1.0, 2.0, and 3.0) were prepared by a chemical activation using different amount of phosphoric acid (*X* represented weight ratio of H<sub>3</sub>PO<sub>4</sub> with respect to CA). Palladium catalysts were then supported on activated carbon aerogels (Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X*, *X* = 0, 0.5, 1.0, 2.0, and 3.0) 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 average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X*. Conversion of 4-phenoxyphenol and total yield for main products increased with decreasing average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X*. Among the catalysts tested, Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 with the smallest average palladium particle size showed the highest conversion of 4-phenoxyphenol and total yield for main products over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 were much higher than those over palladium catalyst supported on commercial activated carbon (Pd/AC).

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### 1. Introduction

Biomass has attracted attention as a renewable energy source due to the depletion of fossil fuel [1–4]. Lignocellulose is typically composed of three main components; cellulose, hemicellulose, and lignin. Lignin produced by delignification process in the pulp industries is burned as a low value fuel for power generation [5–7]. Lignin is an amorphous polymer produced by polymerization of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Aromatic compounds in the lignin are mainly linked by C–O and C–C bonds. Decomposition of lignin to aromatic compounds has been conducted by thermal cracking and catalytic decomposition processes [8,9].

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 [10–13]. Hydrocracking of lignin over zeolite, Co–Mo/Al<sub>2</sub>O<sub>3</sub>, and Ni–Mo/Al<sub>2</sub>O<sub>3</sub> cleaves C–O bond and relatively weak C–C bond in lignin inner units [14,15]. Selective cleavage of C–O bond in lignin such as  $\beta$ -O-4,  $\alpha$ -O-4, and 4-O-5 bonds are known to be an advantageous technology for the decomposition of lignin to aromatics [16]. Cesium-exchanged heteropolyacid (Cs<sub>x</sub>H<sub>3.0-x</sub>PW<sub>12</sub>O<sub>40</sub>, X=2.0-3.0) is known to be an efficient catalyst for selective decomposition of C–O bond in lignin model compound containing  $\beta$ -O-4 and  $\alpha$ -O-4 bonds [17,18]. Novel metal catalysts supported on activated carbon (Pd/C, Pt/C, and Rh/C) also showed a considerable performance for selective decomposition of C–O bond in lignin. [19,20].

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 [21–23]. Therefore, dimeric chemical compounds containing C–O bond such as  $\beta$ -O-4,  $\alpha$ -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 [24,25].

Carbon aerogel has received much attention as catalyst support, electrochemical capacitor, and adsorbent, because of its porous nature [26–30]. Carbon aerogel has a network structure of primary carbon particles, providing micropore and mesopore. Micropore is related to the intra-particle structure, while mesopore and macropore are produced by the inter-particle structure. Pore structure of

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Fig. 1. Preparation of carbon aerogel and activated carbon aerogel.

carbon aerogel can be controlled by activation treatment of carbon aerogel. Activation of carbon aerogel by KOH,  $ZnCl_2$ , steam, and  $CO_2$  increases surface area and pore volume of carbon aerogel due to the formation of micropore and mesopore on carbon aerogel [31–37].

In this work, carbon aerogel (CA) was prepared by a sol–gel polymerization of resorcinol and formaldehyde, and subsequently, it was activated using different amount of  $H_3PO_4$  (ACA- $H_3PO_4$ -X, X (weight ratio of  $H_3PO_4$  with respected to CA)=0, 0.5, 1.0, 2.0, and 3.0) for use as a catalyst support. Palladium catalysts supported on activated carbon aerogel (Pd/ACA- $H_3PO_4$ -X, X=0, 0.5, 1.0, 2.0, and 3.0) were prepared by an incipient wetness impregnation method, and 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) was also employed for the decomposition of 4-phenoxyphenol to aromatics. This is the first example reporting the catalytic performance of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X for the decomposition of lignin model compound to aromatics.

### 2. Experimental

# 2.1. Preparation of carbon aerogel and activated carbon aerogel (ACA-H<sub>3</sub>PO<sub>4</sub>-X)

Carbon aerogel and activated carbon aerogel (ACA) were prepared as presented in Fig. 1. Carbon aerogel was prepared by a sol-gel polymerization of resorcinol and formaldehyde according to the method in literature [30]. 25.9 g of resorcinol ( $C_6H_6O_2$ , Sigma-Aldrich) 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, 14.1g of formaldehyde (H<sub>2</sub>CO, Sigma-Aldrich) was added slowly into the solution to form a sol. Molar ratio of resorcinol with respect to formaldehyde 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. Carbon aerogel 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<sub>3</sub>PO<sub>4</sub>). The weight ratio (X) of H<sub>3</sub>PO<sub>4</sub> as an activation agent with respect to carbon aerogel was fixed at 0, 0.5, 1.0, 2.0, and 3.0. A known amount of H<sub>3</sub>PO<sub>4</sub> was dissolved in 10 ml of DI water, and subsequently, carbon aerogel (1 g) was dispersed into an aqueous solution of H<sub>3</sub>PO<sub>4</sub>. After stirring the mixture for 1 h, the solid was recovered and dried at 110 °C for 3 h. The resulting solid was allowed to react at 800 °C for 1 h under N<sub>2</sub> stream. The activated carbon aerogel containing phosphoric acid was washed with DI water till the pH value of solution reached ca. 7. The resulting material was then dried at 110 °C for 5 h to obtain activated carbon aerogel (ACA- $H_3PO_4$ -X, X = 0, 0.5, 1.0, 2.0, and 3.0). For comparison, commercial activated carbon activated by phosphoric acid (AC-H<sub>3</sub>PO<sub>4</sub>-1.0) was prepared by a chemical activation of commercial activated carbon (AC: MSP20, Kanshai) with phosphoric acid.

2.2. Preparation of palladium catalyst supported on activated carbon aerogel ( $Pd/ACA-H_3PO_4-X$ )

5 wt% of palladium catalyst was supported on activated carbon aerogel (ACA-H<sub>3</sub>PO<sub>4</sub>-*X*, *X*=0, 0.5, 1.0, 2.0, and 3.0) by an incipient wetness impregnation method. Palladium nitrate (Pd(NO<sub>3</sub>)<sub>2</sub>, Sigma–Aldrich) as a palladium precursor was dissolved in DI water, and it was then introduced into the pores of ACA-H<sub>3</sub>PO<sub>4</sub>-*X* (*X*=0, 0.5, 1.0, 2.0, and 3.0). 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-H<sub>3</sub>PO<sub>4</sub>-*X* (*X*=0, 0.5, 1.0, 2.0, and 3.0). For comparison, 5 wt% palladium catalysts supported on AC-H<sub>3</sub>PO<sub>4</sub>-1.0 (Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0) and commercial activated carbon (Pd/AC, AC: MSP20, Kanshai) were also prepared by an incipient wetness impregnation method.

### 2.3. Characterization

Textural properties of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* (X = 0, 0.5, 1.0, 2.0, and 3.0) catalysts were determined by nitrogen adsorption–desorption isotherm measurements (ASAP 2010, Micromeritics). Surface morphology and palladium dispersion of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* catalysts were investigated by transmission electron microscopy (TEM, Jeol, JXA-8900R). Crystalline states of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* were determined by XRD (D-MA2500-PC, Rigaku) measurements using Cu K $\alpha$  radiation operated at 50 kV and 100 mA. Average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* catalysts was calculated using the Debye–Scherrer equation.

### 2.4. Decomposition of 4-phenoxyphenol

4-phenoxyphenol Decomposition of  $(C_6H_5OC_6H_4OH,$ Sigma–Aldrich) over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0) and Pd/AC catalysts was carried out in an autoclave reactor under hydrogen atmosphere. 9 ml of hexadecane (Sigma-Aldrich) (a solvent) and 0.01 g of catalyst were charged into the reactor. 0.2g of 4-phenoxyphenol was then added into the reactor. The catalytic reaction was performed at 200 °C and 10 atm (H<sub>2</sub>) for 1 h with agitation speed of 100 rpm. Reaction products were analyzed with a gas chromatograph (Younglin, ACME 6100) equipped with DB-5 column and flame ionization detector. Conversion of 4-phenoxyphenol and selectivity for product (cyclohexanol, benzene, and phenol) were calculated by following equations. Yield for product (cyclohexanol, benzene, and phenol) was calculated by multiplying conversion of 4-phenoxyphenol and corresponding product selectivity.

Conversion of 4-phenoxyphenol

$$= \frac{\text{moles of 4-phenoxyphenol reacted}}{\text{moles of 4-phenoxyphenol supplied}}$$
(1)

Selectivity for product (cyclohexanol, benzene, or phenol)

$$= \frac{\text{moles of cyclohexanol, benzene, or phenol formed}}{\text{moles of 4-phenoxyphenol reacted}}$$
(2)

(3)



Fig. 2. N2 adsorption-desorption isotherms of Pd/ACA-H3PO4-X.

Total selectivity for main products

= Total moles of cyclohexanol, benzene, and phenol formed moles of 4-phenoxyphenol reacted

Total yield for main products

= (Conversion of 4-phenoxyphenol)

 $\times$ (Total selectivity for main products) (4)

### 3. Results and discussion

## 3.1. Characterization of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X = 0, 0.5, 1.0, 2.0, and 3.0)

Textural properties of  $Pd/ACA-H_3PO_4-X$  (X=0, 05 1.0, 2.0, and 3.0) catalysts were examined by nitrogen adsorption-desorption isotherm measurements. Fig. 2 shows the N<sub>2</sub> adsorption-desorption isotherms of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X catalysts. All the samples showed type-IV isotherm with type-H2 hysteresis loop. This indicates that Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X still retained porous structure even after the activation of carbon aerogel with  $H_3PO_4$ . Surface area ( $S_{total}$ ,  $S_{meso}$ , and  $S_{micro}$ ), ratio of mesopore surface area with respect to micropore surface area  $(S_{\text{meso}}/S_{\text{micro}})$ , and average pore size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0) are summarized in Table 1. Surface area  $(S_{total})$ of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X increased from  $640 \text{ m}^2/\text{g}$  (X=0) to  $1169 \text{ m}^2/\text{g}$ (X=3.0) with increasing X (weight ratio of H<sub>3</sub>PO<sub>4</sub> with respect to CA), because micro surface area ( $S_{micro}$ ) of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X increased with increasing X from  $284 \text{ m}^2/\text{g}$  (X=0) to  $778 \text{ m}^2/\text{g}$ (X=3.0). This result implies that textural structure of carbon aerogel was changed upon chemical activation with phosphoric acid, because carbon aerogel was partially burned off in the presence of phosphoric acid. As a result, micropore and mesopore were created during the activation process. Micropore was increased with increasing the amount of phosphoric acid. However,

#### Table 1

Textural properties of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X = 0, 0.5, 1.0, 2.0, and 3.0).

	•				
nsity (A.U.)	Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -3.0				
	Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -2.0				
	Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -1.0				
Inte	Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -0.5				
	Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -0				
l	10 20 30 40 50 60 70 80				
	2 Theta (Degree)				

Fig. 3. XRD patterns of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X reduced at 120 °C for 6 h.

 Table 2

 Average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0).

Catalysts	TEM <sup>a</sup> (nm)	XRD <sup>b</sup> (nm)
Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -0	17.8	20.2
Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -0.5	16.9	19.7
Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -1.0	9.4	11.5
Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -2.0	13.4	14.8
Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -3.0	16.1	18.2

<sup>a</sup> Measured from TEM image.

<sup>b</sup> Calulated by the Debye-Scherrer equation.

mesopore surface area ( $S_{meso}$ ) and ratio of mesopore surface area with respect to micropore surface area ( $S_{meso}/S_{micro}$ ) showed maximum values ( $492 \text{ m}^2/\text{g}$  and 1.48, respectively) at X=1.0. Average pore size calculated by the BJH desorption curve increased in the order of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-3.0 (3.3 nm) < Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-2.0 (3.7 nm) < Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-0 (3.9 nm) < Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-0.5 (4.5 nm) < Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 (6.7 nm).

Successful impregnation of palladium metal on ACA-H<sub>3</sub>PO<sub>4</sub>-*X* (*X*=0, 0.5, 1.0, 2.0, and 3.0) was confirmed by XRD analysis, as shown Fig. 3. Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* exhibited characteristic XRD peaks at 39.8°, 46.3°, and 68.1°. This result indicates that metallic palladium was well formed after reduction process employed in this work. Characteristic carbon aerogel peak was also observed at 23.5°. This result indicates that the structure of carbon aerogel was still maintained even after the activation of carbon aerogel with H<sub>3</sub>PO<sub>4</sub>.

Fig. 4 shows the TEM images of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0) catalysts. Carbon particles in Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X were observed to form an interconnecting network structure with non-uniform textural porosity. Average palladium particle sizes of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X calculated using the Debye–Scherrer equation and measured from TEM images are listed in Table 2. Average palladium particle size calculated using the Debye–Scherrer equation decreased in order of Pd/ACA-H<sub>3</sub>

	X in Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -X				
	$\overline{X=0}$	X=0.5	X=1.0	X=2.0	X=3.0
Surface area $(S_{total})$ (m <sup>2</sup> /g)	640	682	824	972	1169
Micro surface area $(S_{\text{micro}})(m^2/g)$	284	301	332	593	778
Meso surface area $(S_{meso})$ (m <sup>2</sup> /g)	356	381	492	379	391
S <sub>meso</sub> /S <sub>micro</sub>	1.25	1.27	1.48	0.72	0.50
Average pore size (nm)	3.9	4.5	6.7	3.7	3.3



Fig. 4. TEM images of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X: (a) Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-0, (b) Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-0.5, (c) Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0, (d) Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-2.0, and (e) Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-3.0.

 $PO_4-0$  (20.2 nm) > Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-0.5 (19.7 nm) > Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-3.0  $(18.2 \text{ nm}) > Pd/ACA-H_3PO_4-2.0 (14.8 \text{ nm}) > Pd/ACA-H_3PO_4-1.0$ (11.5 nm). This trend was well consistent with the trend of average palladium particle size measured from TEM image. Among the palladium catalysts supported on ACA-H<sub>3</sub>PO<sub>4</sub>-X (X = 0, 0.5, 1.0,2.0, and 3.0), palladium supported on ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 was most finely dispersed on activated carbon aerogel. Average particle size of supported metal catalysts is affected by many factors such as preparation condition, the amount of metal loading, pore structure, and physical-chemical properties of support [38]. It is expected that pore structure may affect the formation of different metal size on carbon, because the same preparation method and metal loading were imposed in all the catalysts. It has been accepted that finely dispersed metal particle supported on carbon can be easily obtained with mesoporous carbon material, because mesopore of porous carbon serves as an individual nanoscale reactor or a barrier for metal aggregation [38]. On the contrary, aggregated metal particle will be formed with microporous carbon material, because metal cannot be easily introduced into micropore of carbon. Therefore, average pore size of carbon and ratio of mesopore surface area with respect to micropore surface area (S<sub>meso</sub>/S<sub>micro</sub>) play key roles in determining metal dispersion [38]. In our supported catalyst system, micropore of palladium catalyst supported on activated carbon aerogel (Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X, X = 0, 0.5, 1.0. 2.0, and 3.0) increased with increasing the amount of phosphoric acid as listed Table 1. Formation of mesopore of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X showed the maximum at X = 1.0, because mesopore of activated carbon aerogel was converted into micropore when X>2.0. Therefore,  $Pd/ACA-H_3PO_4-1.0$  with the largest average pore size (6.7 nm) and the highest  $S_{\text{meso}}/S_{\text{micro}}$  (1.48) retained most finely dispersed palladium, because mesoporosity of ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 served as an individual nanoscale reactor or a barrier for metal aggregation. On the contrary, microporosity of ACA-H<sub>3</sub>PO<sub>4</sub>-2.0 and ACA-H<sub>3</sub>PO<sub>4</sub>-3.0 may affect the formation of agglomerated metal on carbon, because metal cannot be easily introduced into micropore of carbon.

ICP-AES analysis (Shimadz, ICP-1000 IV) revealed that phosphoric acid did not remain in the final catalyst (Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X), because phosphoric acid used as a chemical activation agent was removed during the activation and washing steps.

## 3.2. Catalytic performance in the decomposition of 4-phenoxyphenol to aromatics

As preliminary experiments, cesium-exchanged heteropolyacid catalyst ( $Cs_xH_{3.0-x}PW_{12}O_{40}$ , X=2.0–3.0) and palladium catalyst supported on cesium-exchanged heteropolyacid  $(Pd/Cs_{x}H_{3,0-x}PW_{12}O_{40}, X=2.0-3.0)$ , which were highly active for the decomposition of benzyl phenyl ether (a model compound containing  $\alpha$ -O-4 bond in lignin) and phenethyl phenyl ether (a model compound containing  $\beta$ -O-4 bond in lignin) [17,18], were tested in the decomposition of 4-phenoxyphenol. However, these catalysts showed very low catalytic performance in the decomposition of 4-phenoxyphenol (a compound containing 4-O-5 bond in lignin). These results are well consistent with the previous study [39] reporting that activation energy for the decomposition of 4-0-5 bond in lignin inner unit is much higher than that for the decomposition of  $\beta$ -O-4 and  $\alpha$ -O-4 bonds. Therefore, many attempts have been made to find suitable catalysts for the decomposition of 4-phenoxyphenol, and finally, we found that novel metal catalyst supported on carbon showed a considerable catalytic performance in the decomposition of 4-phenoxyphenol.

Fig. 5 shows the scheme for the decomposition of 4phenoxyphenol to aromatics. Phenol is produced by the cleavage



Fig. 5. Scheme for cleavage of 4-O-5 bond in 4-phenoxyphenol.

Tabl	e 3
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Catalytic performance of  $Pd/ACA-H_3PO_4-X$  in the decomposition of 4-phenoxyphenol.

V-20
A=3.0
42.9
85.6
40.9
28.4
16.3
36.7
17.5
12.2
7.0

<sup>a</sup> Calculated by Eq. (3).

<sup>b</sup> Calculated by Eq. (4).

of C–O bond in the 4-phenoxyphenol [25]. According to the previous study [40], phenol is then hydrogenated to cyclohexenol as an intermediate, and it is further hydrogenated to cyclohexanol over palladium catalyst. Phenol is also directly converted to benzene by hydrogenolysis. In our reaction system, aromatic compounds such as phenol, benzene, and cyclohexanol were mainly produced by the decomposition of 4-phenoxypheol over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* (*X*=0, 0.5, 1.0, 2.0, and 3.0). Light hydrocarbons ( $C_2$ – $C_6$ ) and alcohols were produced as by-products in the decomposition of 4-phenoxyphenol. Main products and by-products produced by the decomposition of 4-phenoxyphenol over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* were identified by GC–MS (6890N GC, Agilent) equipped with mass selective detector (5975 MSD, Agilent).

Catalytic performance of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0) in the decomposition of 4-phenoxyphenol performed at 200 °C and 10 atm for 1 h is listed in Table 3. Conversion of 4-phenoxyphenol over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0) was in the range 37.4–62.4%. Total selectivity for main products (cyclohexanol, benzene, and phenol) and total yield for main products were in the range of 76.7–87.4% and 28.7–49.9%, respectively. Yield for cyclohexanol (15.2–24.1%) was higher than that for benzene (9.1–18.8%) and phenol (4.4–7.0%). The above results indicate that palladium catalyst supported on activated carbon aerogel (Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X, X=0, 0.5, 1.0, 2.0, and 3.0) served as an efficient catalyst in the decomposition of 4-phenoxyphenol to aromatics.

### 3.3. Effect of X in Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X on catalytic performance

Conversion of 4-phenoxyphenol and total yield for main products (cyclohexanol, bezene, and phenol) plotted as a function of X in Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X are shown in Fig. 6(a). Conversion of 4phenoxyphenol showed a volcano-shaped curve with respect to X. Total yield for main products also showed a volcano-shaped curve with respect to X. Among the catalysts tested,  $Pd/ACA-H_3PO_4-1.0$  showed the best catalytic performance in terms of conversion of 4-phenoxyphel (62.4%) and total yield for main products (49.9%).

Fig. 6(b) shows the yield for cyclohexanol, benzene, and phenol plotted as a function of X in Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. Yields for cyclohexanol and benzene showed volcano-shaped curves with respect to X in Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. However, yield for phenol was almost constant with regard to X. Among the catalyst tested, Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 showed the highest yield for cyclohexanol (24.1%) and benzene (18.8%).

# 3.4. Correlation between average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X and catalytic performance in the decomposition of 4-phenoxyphenol

Fig. 7 shows the correlation between conversion of 4phenoxyphenol over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* and average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* (X=0, 0.5, 1.0, 2.0, and 3.0). Average palladium particle sizes of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* were calculated using the Debye–Scherrer equation (Table 2). The correlation shows that conversion of 4-phenoxyphenol over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X* is closely related to the average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X*. Conversion of 4-phenoxyphenol increased with decreasing average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-*X*. Among the catalysts tested, Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 with the smallest average palladium particle size showed the highest conversion of 4phenoxyphenol. This result was well consistent with the previous works [38,41] reporting that the catalytic performance increased with decreasing metal particle size of supported catalysts because small metal particle provided high metal surface area.

Fig. 8 shows the correlation between total yield for main products (cyclohexanol, benzene, and phenol) over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X and average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. The



**Fig. 6.** Catalytic performance of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X in the decomposition of 4-phenoxyphenol plotted as a function of X. Reaction condition: temperature = 200 °C, pressure = 10 atm (H<sub>2</sub>), time = 1 h.



**Fig. 7.** Correlation between conversion of 4-phenoxyphenol over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X and average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. Average palladium particle sizes were calculated by the Debye–Scherrer equation (Table 2). Reaction condition: temperature =  $200 \degree$ C, pressure =  $10 \arg (H_2)$ , time = 1 h.



**Fig. 8.** Correlation between total yield for main products over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X and average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. Average palladium particle sizes were calculated by the Debye–Scherrer equation (Table 2). Reaction condition: temperature =  $200 \,^{\circ}$ C, pressure =  $10 \, \text{atm} (H_2)$ , time =  $1 \, \text{h}$ .

correlation shows that total yield for main products over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X is also closely related to the average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. Total yield for main products increased with decreasing average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. Among the catalysts tested, Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 with the smallest average palladium particle size showed the highest total yield for main products. Thus, the average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X played an important role in determining the catalytic performance in the decomposition of 4-phenoxyphenol to aromatics.



**Fig. 9.** Comparison of catalytic performance between  $Pd/ACA-H_3PO_4-1.0$ , Pd/AC, and  $Pd/AC-H_3PO_4-1.0$  catalysts in the decomposition of 4-phenoxyphenol. Reaction condition: temperature = 200 °C, pressure = 10 atm (H<sub>2</sub>), time = 1 h.

## 3.5. Catalytic performance of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0, Pd/AC and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 in the decomposition of 4-phenoxyphenol

For comparison, palladium catalysts supported on commercial activated carbon (Pd/AC) and commercial activated carbon activated by phosphoric acid (Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0) were prepared by an incipient wetness impregnation method. Textural properties and average palladium particle size of Pd/AC and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 were almost the same, as listed in Table 4. Surface area  $(824 \text{ m}^2/\text{g})$  and micro surface area  $(332 \text{ m}^2/\text{g})$  of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 were smaller than those of Pd/AC ( $1832 \text{ m}^2/\text{g}$  and  $1604 \text{ m}^2/\text{g}$ , respectively) and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 (1991 m<sup>2</sup>/g and 1748 m<sup>2</sup>/g, respectively). However, mesopore surface area (492 m<sup>2</sup>/g), ratio of mesopore surface area with respect to micropore surface area (1.48), and average pore size (6.7 nm) of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 were larger than those of Pd/AC (228 m<sup>2</sup>/g, 0.14, and 1.3 nm, respectively) and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 (243  $m^2/g$ , 0.14, and 1.2 nm, respectively), because mesopore was dominant in Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0. Average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 (11.5 nm) was smaller than that of Pd/AC (28.1 nm) and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 (28.7 nm) due to large average pore size and high  $S_{meso}/S_{micro}$  of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0.

Fig. 9 shows the catalytic performance of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0, Pd/AC, and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 catalysts in the decomposition of 4-phenoxyphenol. Catalytic performance of Pd/AC and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 catalysts was almost the same, due to similar textural properties and palladium particle size of Pd/AC and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 catalysts. However, conversion of 4-phenoxyphenol (62.4%) and total yield for main products (49.9%) over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 were much higher than those over Pd/AC (40.5% and 13.7%, respectively) and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0 (42.1% and 14.4%, respectively). This result also indicates that average palladium particle size supported on carbon played an important role in determining the catalytic performance in the decomposition of 4-phenoxyphenol. It can be

### Table 4

Textural properties and average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0, Pd/AC, and Pd/AC-H<sub>3</sub>PO<sub>4</sub>-1.0.

	Pd/ACA-H <sub>3</sub> PO <sub>4</sub> -1.0	Pd/AC	Pd/AC-H <sub>3</sub> PO <sub>4</sub> -1.0
Surface area $(S_{total}) (m^2/g)$	824	1832	1991
Micro surface area $(S_{micro})$ (m <sup>2</sup> /g)	332	1604	1748
Meso surface area $(S_{meso})$ (m <sup>2</sup> /g)	492	228	243
$S_{\rm meso}/S_{\rm micro}$	1.48	0.14	0.14
Average pore size (nm)	6.7	1.3	1.2
Average palladium particle size <sup>a</sup> (nm)	11.5	28.1	28.7

<sup>a</sup> Calulated by the Debye-Scherrer equation.

summarized that  $Pd/ACA-H_3PO_4-1.0$  catalyst was more efficient than Pd/AC and  $Pd/AC-H_3PO_4-1.0$  catalysts in the decomposition 4-phenoxyphenol to aromatics.

### 4. Conclusions

Carbon aerogel was activated using different amount H<sub>3</sub>PO<sub>4</sub> (ACA-H<sub>3</sub>PO<sub>4</sub>-X, X = 0, 0.5, 1.0, 2.0, and 3.0). Palladium catalyst supported on activated carbon aerogel ( $Pd/ACA-H_3PO_4-X$ , X=0, 0.5, 1.0, 2.0, and 3.0) were prepared by an incipient wetness impregnation method, and were applied to the decomposition of lignin model compound. 4-Phenoxyphenol was used as a dimeric lignin model compound for representing 4-O-5 bond in lignin. Conversion of 4-phenoxyphenol and total yield for main products (cyclohexanol, benzene, and phenol) over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0) were in the range of 37.4-62.4% and 28.7-49.9%, respectively. Among the main products produced by the decomposition of 4-phenoxyphenol, yield for cyclohexanol (15.2-24.1%) was much higher than that for benzene (9.1-18.8%) and phenol (4.4-7.0%). Conversion of 4-phenoxyphenol and total yield for main products were closely related to the average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X (X=0, 0.5, 1.0, 2.0, and 3.0). Conversion of 4-phenoxyphenol and total yield for main products increased with decreasing average palladium particle size of Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-X. Among the catalysts tested, Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 with the smallest average palladium particle size showed the highest conversion of 4phenoxyphenol (62.4%) and total yield for main products (49.9%). Conversion of 4-phenoxyphenol and total yield for main product over Pd/ACA-H<sub>3</sub>PO<sub>4</sub>-1.0 were much higher than those over palladium catalyst supported on commercial activated carbon (Pd/AC). It is concluded that  $Pd/ACA-H_3PO_4-X$  (X=0, 0.5, 1.0, 2.0, and 3.0) was an efficient catalyst in the decomposition of 4-phenoxyphenol to aromatics, and average palladium particle size of the catalysts played an important role in determining the catalytic performance.

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