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Catalytic decomposition of 4-phenoxyphenol over Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA (activated carbon aerogel)-SO₃H (X = 10-30 wt%) catalysts



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ABSTRACT

Activated carbon aerogel (ACA) bearing sulfonic acid group (ACA-SO₃H) was prepared by a sulfonation of activated carbon aerogel, and subsequently, Cs2.5H0.5PW12O40 was impregnated on ACA-SO3H and 30 wt%). Palladium catalysts were then supported on $XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ by an incipient wetness impregnation method. The prepared Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts were applied to the decomposition of 4-phenoxyphenol. 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. Acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts played an important role in the decomposition of 4-phenoxyphenol. Conversion of 4-phenoxyphenol and total yield for main products (cyclohexanol, benzene, and phenol) increased with increasing acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. Among the catalysts tested, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H 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/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H were much higher than those over palladium catalyst supported on activated carbon aerogel (Pd/ACA) and palladium catalyst supported on activated carbon aerogel bearing sulfonic acid group (Pd/ACA-SO₃H). Furthermore, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalyst was stable and reusable in the decomposition of 4-phenoxyphenol.

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1. Introduction

Fossil fuels such as coal and crude oil are not sustainable. Furthermore, carbon dioxide from burning of fossil fuels has been considered as a contributor to global warming [1,2]. Therefore, conversion of biomass to liquid fuels and chemicals has attracted much attention as an environmentally benign process, because biomass can reduce the dependence on fossil fuel and the emission of carbon dioxide [3].

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 [4,5]. On the other hand, second generation biofuels derived from lignocellulosic feedstocks do not compete with food resource. Lignin produced by delignification process in the pulp industries is burned as a low value fuel for power generation [6,7]. Aromatics such as coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol in lignin are mainly linked by C—O and C—C bonds. 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 [8,9].

Catalytic decomposition of lignin has received much attention as a key technology for valorization of lignocellulosic biomass, because thermal cracking of lignin requires high temperature (over 450 °C) and pressure (over 100 atm) for considerable performance [10–12]. Liquid acids such as H₃PO₄ 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 [13–15]. Novel metal catalysts supported on carbon (Pd/C, Pt/C, and Rh/C) [16,17] and novel metal catalysts supported on acidic activated carbon aerogel (ACA) (Pd/ACA-SO₃H [18] and Pd/Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA [19]) also showed considerable performance for selective decomposition of C–O bond in lignin.

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

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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 capacitor, and adsorbent due to its porous nature. Pore structure of activated carbon aerogel can be controlled by changing activation conditions such as activation agent, activation temperature, and activation time. Palladium catalyst supported on carbon aerogel (Pd/CA) and palladium catalyst supported on activated carbon aerogel (Pd/ACA) [36] have been used for the decomposition of C–O bond in the lignin to take advantage of mesoporous nature of CA and ACA.

Heteropolyacids (HPAs) are inorganic acids. Acid strength of HPAs is stronger than that of conventional solid acids [37–39]. HPA salts with K⁺, Cs⁺, and NH₄⁺ cations have high surface area and porous structure by forming a tertiary structure [38,39]. It is known that acidity of cesium-exchanged insoluble HPAs is different depending on cesium content [37,38].

In this work, activated carbon aerogel (ACA) bearing sulfonic acid group (ACA-SO₃H) was prepared by a sulfonation of ACA with H_2SO_4 , and subsequently, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was impregnated on ACA-SO₃H to form $XCs_{2.5}H_{0.5}PW_{12}O_{40}$ /ACA-SO₃H with a variation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content (X = 10, 15, 20, 25, and 30 wt%). Palladium catalysts supported on $XCs_{2.5}H_{0.5}PW_{12}O_{40}$ /ACA-SO₃H (Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H) were then prepared by an incipient wetness impregnation method, and they were applied to the decomposition of 4-phenoxyphenol. 4-Phenoxyphenol was chosen as a lignin model compound for representing 4-O-5 bond in lignin. For comparison, palladium catalyst supported on activated carbon aerogel (Pd/ACA) and palladium catalyst supported on activated carbon aerogel bearing sulfonic acid group (Pd/ACA-SO₃H) were also employed for the decomposition of 4-phenoxyphenol.

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 [27,36]. Carbon aerogel was prepared by a sol-gel polymerization of resorcinol and formaldehyde. 25.9 g of resorcinol (C₆H₆O₂, 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 (H₂CO, 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 2 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 1 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) . 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 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-SO₃H

In order to provide acid sites to ACA, activated carbon aerogel bearing sulfonic acid group (ACA-SO₃H) was prepared by sulfonation of activated carbon aerogel (ACA). Fig. 1 shows the schematic procedure for the preparation of activated carbon aerogel bearing sulfonic acid group (ACA-SO₃H). 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-SO₃H)

2.3. Preparation of $XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X = 10, 15, 20, 25, and 30 wt%)

Cesium-exchanged Cs2.5H0.5PW12O40 heteropolyacid was impregnated on ACA-SO₃H to form XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H with a variation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content (X=10, 15, 20, 25, and 30 wt%). Fig. 1 also shows the schematic procedures for the preparation of XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. A known amount of H₃PW₁₂O₄₀ (Sigma-Aldrich) was impregnated onto 1 g of ACA-SO₃H (XH₃PW₁₂O₄₀/ACA-SO₃H, X = 10, 15, 20, 25, and 30 wt%) by an incipient wetness impregnation method, and then it was dried overnight at 80 °C. A known amount of cesium nitrate (CsNO₃, Sigma-Aldrich) was separately dissolved in 10 ml of DI water. 1 g of XH₃PW₁₂O₄₀/ACA-SO₃H 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 $XCs_{25}H_{05}PW_{12}O_{40}/ACA-SO_{3}H$ (X = 10, 15, 20, 25, and 30 wt%).

2.4. Preparation of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X = 10, 15, 20, 25, and 30 wt%)

The schematic procedures for the preparation of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) catalysts are also shown in Fig. 1. 5 wt% of palladium catalyst was supported on XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) 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 cm³/min) and nitrogen (30 cm³/min) at 120 °C for 6 h to obtain Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%). For comparison, palladium catalyst supported on activated carbon aerogel bearing sulfonic acid (Pd/ACA-SO₃H) [18] were also prepared by an incipient wetness impregnation method.

2.5. Characterization

Textural properties of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%) catalysts were determined by nitrogen adsorption–desorption isotherm measurements (Micromeritic, ASAP 2010). Crystalline states of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H were determined by XRD (Rigaku, D-MA2500-PC) measurements



Fig. 1. Schematic procedures for the preparation of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X = 10, 15, 20, 25, and 30 wt%).

using Cu-K α radiation operated at 50 kV and 100 mA. Surface morphology and palladium dispersion of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts were investigated by TEM (Jeol, JXA-8900R). Chemical compositions of the catalysts were measured by ICP-AES (Shimadzu, ICPS-7500) and CHNS (LECO, US/CHNS-932) analyses.

NH₃-TPD experiment (BEL Japan, BELCAT-B) was carried out in order to measure the acidity of the catalyst. 0.04 g of each catalyst charged into the TPD apparatus was pretreated at 350 °C for 1 h with a stream of helium (50 ml/min). A mixed stream of ammonia (2.5 ml/min) and helium (47.5 ml/min) was then introduced into the reactor at 35 °C for 30 min in order to saturate acid sites of the catalyst with ammonia. Physisorbed ammonia was removed at 100 °C for 1 h under a flow of helium (50 ml/min). After cooling the catalyst, furnace temperature was increased from 35 °C to 700 °C at a heating rate of 5 °C/min under a flow of helium (30 ml/min). The desorbed ammonia was detected using a TCD.

2.6. Decomposition of 4-phenoxyphenol

4-phenoxyphenol Decomposition of $(C_6H_5OC_6H_4OH)$ Sigma–Aldrich) over $Pd/XCs_2 {}_5H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X=10, 15, 20, 25, and 30 wt%), Pd/ACA, and Pd/ACA-SO₃H 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. 0.2 g of 4-phenoxyphenol was then added into the reactor. The catalytic reaction was performed at 200 $^{\circ}$ C and 10 atm (H₂) 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 FID. Main products and by-products produced by the decomposition of 4-phenoxyphenol over Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H were identified by GC-MS (Agilent, 6890 N GC) equipped with mass selective detector (Agilent, 5975 MSD). Conversion of 4-phenoxyphenol and selectivity for product (cyclohexanol, benzene, and phenol) were calculated by the following equations. Yield for product (cyclohexanol, benzene, and phenol) was calculated by multiplying conversion of 4-phenoxyphenol and corresponding product selectivity.



Fig. 2. N₂ adsorption–desorption isotherms of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H: (a) Pd/10Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (b) Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (c) Pd/20Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (d) Pd/25Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, and (e) Pd/30Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. The adsorption data for (a)–(e) were offset vertically by 0, 150, 300, 450, and 600 (STP)/g, respectively.

3. Results and discussion

3.1. Characterization of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%)

Textural properties of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) catalysts were examined by nitrogen adsorption–desorption isotherm measurements. Fig. 2 shows the N₂ adsorption–desorption isotherms of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts. All the samples showed type-IV isotherm with type H2 hysteresis loop. This result indicates that Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H still retained a porous structure even after the sulfonation of ACA and the

$Conversion of 4-phenoxyphenol = \frac{moles of 4-phenoxyphenol reacted}{moles of 4-phenoxyphenol supplied}$	(1)
Selectivity for product (cyclohexanol, benzene, or phenol) = $\frac{\text{moles of cyclohexanol, benzene, or phenol formed}}{\text{moles of 4-phenoxyphenol reacted}}$	(2)
Total selectivity for main products = Total moles of cyclohexanol, benzene, and phenol formed moles of 4-phenoxyphenol reacted	(3)
Total yield for main products = (Conversion of 4-phenoxyphenol) \times (Total selectivity for main products)	(4)



Fig. 3. XRD patterns of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (*X*=10, 15, 20, 25, and 30 wt%).

subsequent impregnation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ onto ACA-SO₃H. Surface area and average pore size of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H are summarized in Table 1. Surface area of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H decreased from 1075 m²/g (X = 10 wt%) to 948 m²/g (X = 30 wt%) with increasing X (Cs_{2.5}H_{0.5}PW₁₂O₄₀ content) due to the impregnation of Cs_{2.5}H_{0.5}PW₁₂O₄₀ onto ACA-SO₃H. Average pore size of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀ onto ACA-SO₃H. Average pore size of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H was in the range of 4.6–4.8 nm. XRD patterns of Cs_{2.5}H_{0.5}PW₁₂O₄₀ and Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%)

Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%) are shown in Fig. 3. Diffraction peaks for Cs_{2.5}H_{0.5}PW₁₂O₄₀ were not observed in the Pd/10Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H and Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts due to fine dispersion of Cs_{2.5}H_{0.5}PW₁₂O₄₀ onto ACA-SO₃H. However, Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 20, 25, and 30 wt%) catalysts exhibited diffraction peaks for Cs_{2.5}H_{0.5}PW₁₂O₄₀ due to excess impregnation of Cs_{2.5}H_{0.5}PW₁₂O₄₀ onto ACA-SO₃H. This was well supported by the fact that diffraction peak intensity for Cs_{2.5}H_{0.5}PW₁₂O₄₀ increased with increasing X in the Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 20-30 wt%). Successful impregnation of palladium metal on XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%) was also confirmed by XRD patterns, as shown in Fig. 3. Average palladium particle size of the



Fig. 5. NH₃-TPD profiles of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%).

catalysts calculated by the Debye–Scherrer equation was in the range of 10.2–10.7 nm, as listed in Table 1.

Fig. 4 shows the TEM images of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) catalysts. Palladium metal on *X*Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (*X*=10, 15, 20, 25, and 30 wt%) was observed by TEM image as a dark spot. Palladium metal size of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) measured by TEM images was in the range of 5-15 nm, in good agreement with XRD result (Fig. 3 and Table 1). On the other hand, Cs_{2.5}H_{0.5}PW₁₂O₄₀ heteropolyacid (gray area) was not observed in the Pd/10Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA- SO_3H and $Pd/15Cs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ catalysts due to fine dispersion of Cs_{2.5}H_{0.5}PW₁₂O₄₀ onto ACA-SO₃H. However, Cs_{2.5}H_{0.5}PW₁₂O₄₀ heteropolyacid (gray area) was clearly observed in the $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X=20, 25, and 30 wt%) catalysts due to excess impregnation of Cs2.5H0.5PW12O40. This result was well consistent with XRD patterns of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (Fig. 3).

Fig. 5 shows the NH₃-TPD profiles of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) catalysts. Two desorption peaks were observed at around 170 °C and 560 °C. Acidity of the catalysts measured from NH₃-TPD peak area is summarized in Table 1. Acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts was in the range of



Fig. 4. TEM images of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H: (a) Pd/10Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (b) Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (c) Pd/20Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (d) Pd/25Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, (e) Pd/30Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H.

Table	1
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Surface area, average pore size, average palladium particle size, and acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%).

	Pd/XCs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /ACA-SO ₃ H				
	X=10	<i>X</i> =15	X=20	X=25	X=30
Surface area (m ² /g)	1075	1002	988	965	948
Average pore size ^a (nm)	4.7	4.8	4.6	4.6	4.7
Average palladium particle size ^b (nm)	10.7	10.3	10.2	10.7	10.4
Acidity ^c (µmol-NH ₃ /g)	189	258	246	211	194

^a Calculated by the BJH desorption branch.

^b Calculated by the Debye–Scherrer equation.

^c Determined by NH₃-TPD.

175–258 μ mol-NH₃/g. Acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts showed a volcano-shaped trend with respect to X (Cs_{2.5}H_{0.5}PW₁₂O₄₀ contents). Among the catalyst tested, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalyst showed the largest acidity due to fine dispersion of Cs_{2.5}H_{0.5}PW₁₂O₄₀ onto ACA-SO₃H, as evidenced by XRD and TEM analyses.

Sulfur content of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H determined by CHNS analysis was in the range of 0.88–0.92 wt%, as listed in Table 2. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content in the Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) catalysts determined by ICP-AES analysis is also listed in Table 2. The measured $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content in the Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H was smaller than the theoretical value. This result indicates that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ located on the outer surface of ACA-SO₃H was removed during the washing step. Palladium content of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H was in good agreement with the designed value (Table 2).

3.2. Catalytic performance of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ in the decomposition of 4-phenoxyphenol

Fig. 6 shows the scheme for the decomposition of 4-phenoxyphenol. Phenol is produced by the cleavage of C–O bond in the 4-phenoxyphenol [25]. According to the previous study [18,19], phenol is then hydrogenated to 2-cyclohexen-1-ol 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, phenol, benzene, and cyclohexanol were mainly produced by the decomposition of 4-phenoxypheol over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_{3}H$ (X=10, 15, 20, 25, and 30 wt%). Light hydrocarbons (C2–C6) and alcohols were produced as by-products in the decomposition of 4-phenoxyphenol (32.5–56.2%).

Catalytic performance of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%) 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/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X = 10, 15, 20, 25, and 30 wt%) was in the range 82.1–94.8%. Total selectivity for main products (cyclohexanol, benzene, and phenol) and total yield for main products were in the range of 53.3–71.2% and 43.8–67.5%, respectively. The above results indicate that Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H



Fig. 6. Scheme for the cleavage of 4-O-5 bond in 4-phenoxyphenol.

(X = 10, 15, 20, 25, and 30 wt%) served as an efficient catalyst in the decomposition of 4-phenoxyphenol.

3.3. Effect of X on the catalytic performance of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H

Fig. 7 shows the conversion of 4-phenoxyphenol, total selectivity for main products, and total yield for main products plotted as a function of X in the $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$. Conversion of 4-phenoxyphenol 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, $Pd/15Cs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ showed the best catalytic performance in terms of conversion of 4-phenoxyphel (94.8%) and total yield for main products (67.5%).

Yields for cyclohexanol, benzene, and phenol plotted as a function of *X* in the Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H are shown in Fig. 8. Yields for cyclohexanol and benzene showed volcano-shaped curves with respect to *X* in the Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. However, yield for phenol (1.3–2.2%) was almost constant with regard to *X*. Among the catalyst tested, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H showed the highest yields for cyclohexanol (31.2%) and benzene (35.0%).

3.4. Correlation between acidity of

 $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ and catalytic performance in the decomposition of 4-phenoxyphenol

Fig. 9 shows the correlation between conversion of 4-phenoxyphenol over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X=10, 15, 20, 25, and 30 wt%) and acidity of the



Fig. 7. Catalytic performance of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H (X = 10, 15, 20, 25, and 30 wt%) in the decomposition of 4-phenoxyphenol plotted as a function of$ *X*. Reaction conditions: temperature = 200 °C, pressure = 10 atm (H₂), time = 1 h.

Sulfur.	CS25H05PW12O40.	and Pd contents of Po	1/XCs2 5 H0 5 PW 12 O40	$ACA-SO_2H(X=10)$	15, 20, 25, and 30 wt%).
Junui,	C32.5110.51 V 12 C40,	, und i a contento oi i c	1/10/02/01/0.51	1101100311(11 10	13, 20, 23, and 30 webb).

Catalyst	Sulfur content (wt%) ^a	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ content (wt%)		Ifur content (wt%) ^a $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content (wt%)Pd content (wt%)		
		Theoretical	Measured ^b	Theoretical	Measured ^b	
Pd/10Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /ACA-SO ₃ H	0.88	10	8.2	5	4.9	
Pd/15Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /ACA-SO ₃ H	0.91	15	13.8	5	4.8	
Pd/20Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /ACA-SO ₃ H	0.87	20	17.4	5	4.9	
Pd/25Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /ACA-SO ₃ H	0.92	25	22.3	5	5.0	
$Pd/30Cs_{2.5}H_{0.5}PW_{12}O_{40}/ACA\text{-}SO_{3}H$	0.89	30	26.8	5	4.8	

^a Determined by CHNS analysis.

^b Determined by ICP-AES analysis.

Table 3

Catalytic performance of	Pd/XCs _{2.5} H _{0.5} PW	$_{2}O_{40}/ACA-SO_{3}H(X=1)$), 15, 20, 25, and 30 wt%	in the decomposition of	4-phenoxyphenol.
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	$Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$				
	X=10	X=15	X=20	X=25	X=30
Conversion (%)	82.1	94.8	88.3	87.9	84.0
Toal selectivity for main products ^a (%)	53.3	71.2	61.6	58.9	56.2
Cyclohexanol (%)	27.2	32.9	32.6	31.0	28.3
Benzene (%)	24.1	36.9	27.0	25.4	25.3
Phenol (%)	2.0	1.4	2.0	2.5	2.6
Total yield for main products ^b (%)	43.8	67.5	54.4	51.8	47.2
Cyclohexanol (%)	22.3	31.2	28.8	27.3	23.8
Benzene (%)	19.8	35.0	23.8	22.3	21.3
Phenol (%)	1.7	1.3	1.7	2.2	2.2

^a Calculated by Eq. (3).

^b Calculated by Eq. (4).

catalysts determined from NH₃-TPD measurement (Table 1). The correlation shows that conversion of 4-phenoxyphenol over Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H was closely related to the acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. Conversion of 4-phenoxyphenol increased with increasing acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. Among the catalysts tested, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H with the largest acidity showed the highest conversion of 4-phenoxyphenol.

Fig. 10 shows the correlation between total yield for main products over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (X = 10, 15, 20, 25, and 30 wt%) and acidity of the catalysts. The correlation shows that total yield for main products over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ was

also closely related to the acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. Total yield for main products increased with increasing acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H. Among the catalysts tested, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H with the largest acidity showed the highest total yield for main products. This result was well consistent with the previous work [37] reporting that the catalytic performance was increased with increasing acidity of the supported catalyst. Thus, acidity of Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H played an important role in determining the catalytic performance in the decomposition of 4-phenoxyphenol.



Fig. 8. Yields for cyclohexanol, benzene, and phenol produced by the decomposition of 4-phenoxyphenol over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ (*X* = 10, 15, 20, 25, and 30 wt%). Reaction conditions: temperature = 200 °C, pressure = 10 atm (H₂), time = 1 h.



Fig. 9. A correlation between conversion of 4-phenoxyphenol over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ and acidity of the catalysts. Acidity of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ was taken from Table 1. Reaction conditions: temperature = 200 °C, pressure = 10 atm (H₂), time = 1 h.



Fig. 10. A correlation between total yield for main products over $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ and acidity of the catalysts. Acidity of $Pd/XCs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ was taken from Table 1. Reaction conditions: temperature = 200 °C, pressure = 10 atm (H₂), time = 1 h.

3.5. Comparison of catalytic performance of Pd/ACA, Pd/ACA-SO₃H, and Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H in the decomposition of 4-phenoxyphenol

For comparison, palladium catalyst supported on activated carbon aerogel (Pd/ACA) and palladium catalyst supported on activated carbon aerogel bearing sulfonic acid (Pd/ACA-SO₃H) were prepared by an incipient wetness impregnation method [16,18]. Surface area of $Pd/15Cs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_{3}H$ (1002 m²/g) was much higher than that of Pd/ACA (824 m²/g) and Pd/ACA- SO_3H (743 m²/g), as listed in Table 4. However, average pore size of Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (4.8 nm) was smaller than that of Pd/ACA (6.7 nm) and Pd/ACA-SO₃H (6.9 nm). Average palladium particle size of Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H, Pd/ACA-SO₃H, and Pd/ACA was in the range of 10.3-10.7 nm with no great difference. Acidity of Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (258 µmol-NH₃/g) measured by NH₃-TPD was much larger than that of Pd/ACA (34 µmol-NH₃/g) and Pd/ACA-SO₃H (79 µmol- NH_3/g) due to the impregnation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ onto ACA-SO₃H.

Fig. 11 compares the catalytic performance of Pd/ACA, Pd/ACA-SO₃H, and Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts in the decomposition of 4-phenoxyphenol. Conversion of 4phenoxyphenol (71.9%) and total yield for main products (61.0%) over Pd/ACA-SO₃H were much higher than those over Pd/ACA (62.4% and 49.9%, respectively) due to the acidity of Pd/ACA-SO₃H derived from sulfonic acid. However, conversion of 4-phenoxyphenol (94.8%) and total yield for main products

Table 4

Surface area, average pore size, avera Pd/ACA, Pd/ACA-SO ₃ H, and Pd/15Cs _{2.5} H	ge palladium j 1 _{0.5} PW ₁₂ O ₄₀ /AC	A-SO ₃ H.	D
Pd/ACA	Pd/ACA-SO ₃ H	Pd/15Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /	

	-		ACA-SO ₃ H
Surface area (m ² /g)	824	743	1002
Average pore size ^a (nm)	6.7	6.9	4.8
Average palladium particle size ^b (nm)	10.7	10.7	10.3
Acidity ^c (μ mol-NH ₃ /g)	34	79	258

^a Calculated by the BJH desorption branch.

^b Calculated by the Debye–Scherrer equation.

^c Determined by NH₃-TPD.



Fig. 11. Comparison of catalytic performance between Pd/ACA, Pd/ACA-SO₃H, and Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalysts in the decomposition of 4-phenoxyphenol. Reaction conditions: temperature = $200 \degree$ C, pressure = $10 \arg (H_2)$, time = 1 h.

(67.5%) over Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H were much higher than those over Pd/ACA-SO₃H (71.9% and 61.0%, respectively) due to the large acidity of Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H derived from the impregnation of Cs_{2.5}H_{0.5}PW₁₂O₄₀. In summary, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalyst was more efficient than Pd/ACA and Pd/ACA-SO₃H catalysts in the decomposition of 4-phenoxyphenol due to its large acidity.

3.6. Stability and reusability of Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalyst

To investigate the stability and reproducibility of the catalyst, recycle test for the decomposition of 4-phenoxyphenol over Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalyst was performed three times (Fig. 12). Fig. 12 shows that conversion of 4-phenoxyphenol (94.8–93.6%) and total yield for main products (67.5–66.5%) of fresh and spent catalysts were almost constant with regard to recycle run. Furthermore, no significant Pd leaching was detected by ICP-AES analysis after each run. This result shows that



Fig. 12. Result for the decomposition of 4-phenoxyphenol over $Pd/15Cs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_3H$ catalyst with respect to recycle run. Reaction conditions: temperature = 200 °C, pressure = 10 atm (H₂), time = 1 h.

Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H catalyst served as a stable and reusable catalyst in the decomposition of 4-phenoxyphenol.

4. Conclusions

Activated carbon aerogel (ACA) bearing sulfonic acid (ACA-SO₃H) was prepared by a sulfonation of activated carbon aerogel using H₂SO₄, and subsequently, Cs_{2.5}H_{0.5}PW₁₂O₄₀ was impregnated onto ACA-SO₃H to form XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA- SO_3H with a variation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ content (X = 10, 15, 20, 25, and 30 wt%). Palladium catalysts supported on XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H were then prepared by an incipient wetness impregnation method, and they were applied to the decomposition of 4-phenoxyphenol. Conversion of 4phenoxyphenol and total yield for main products (cyclohexanol, benzene, and phenol) over Pd/XCs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H (X=10, 15, 20, 25, and 30 wt%) were in the range of 82.1–94.8% and 43.8-67.5%, respectively. Conversion of 4-phenoxyphenol and total yield for main products were closely related to the acidity of the catalysts. Conversion of 4-phenoxyphenol and total yield for main products increased with increasing acidity of the catalysts. Among the catalysts tested, Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H with the largest acidity showed the highest conversion of 4phenoxyphenol (94.8%) and total yield for main products (67.5%). Conversion of 4-phenoxyphenol and total yield for main product over Pd/15Cs_{2.5}H_{0.5}PW₁₂O₄₀/ACA-SO₃H were much higher than those over palladium catalyst supported on activated carbon aerogel (Pd/ACA) and palladium catalyst supported on activated carbon aerogel bearing sulfonic acid (Pd/ACA-SO₃H). It was also found that $Pd/15Cs_{2.5}H_{0.5}PW_{12}O_{40}/ACA-SO_{3}H$ (X = 10, 15, 20, 25, and 30 wt%) was an efficient and reusable catalyst in the decomposition of 4phenoxyphenol. It is concluded that acidity of the catalysts played an important role in determining the catalytic performance in the decomposition of 4-phenoxyphenol.

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References

[1] H.R. Bungav, Science 218 (1982) 643-646.

- [2] N. Savage, Nature 474 (2011) 9-11.
- [3] M.F. Demirbas, Appl. Energy 86 (2009) 151-161.
- [4] J.H. Clark, J. Chem. Technol. Biotechnol. 82 (2007) 603-609.
- [5] S.N. Naik, V.V. Goud, P.K. Rout, A.K. Dalai, Renew. Sustain. Energy Rev. 14 (2010) 578-597.
- [6] A.-C. Carlos, H. Pakdel, C. Roy, Bioresour. Technol. 79 (2001) 277-299.
- H.H. Nimz, R. Casten, Holz Roh Werkst 44 (1986) 207-212. [7]
- [8] A. Oasmaa, R. Alen, Bioresour. Technol. 45 (1993) 189-194.
- [9] M. Kleinert, T. Barth, Energy Fuels 22 (2008) 1371-1379.
- C. Amen-Chen, H. Pakdel, C. Roy, Bioresour. Technol. 79 (2001) 277-299. [10]
- [11] D.C. Elliott, Energy Fuels 21 (2007) 1792-1815.
- [12] R.W. Thring, J. Breau, Fuel 75 (1996) 795-800. [13] D.V. Evtuguin, A.I.D. Daniel, A.J.D. Silvestre, F.M.L. Amad, C.P. Neto, J. Mol. Catal.
- A: Chem. 154 (2000) 217-224. [14] A. Cyr, F. Chilts, P. Jeanson, A. Martel, L. Brossard, J. Lessard, H. Menard, Can. J.
- Chem. 78 (2000) 307-315.
- [15] H.W. Park, S. Park, D.R. Park, J.H. Choi, I.K. Song, Korean J. Chem. Eng. 28 (2010) 1177-1180.
- [16] H.W. Park, S. Park, D.R. Park, J.H. Choi, I.K. Song, Catal. Commun. 12 (2010) 1-4. N. Yan, C. Zhao, P.J. Dyson, C. Wang, L.-T. Liu, Y. Kou, ChemSusChem 1 (2008)
- 626-629
- [18] H.W. Park, U.G. Hong, Y.J. Lee, I.K. Song, Catal. Commun. 20 (2012) 89-93
- [19] H.W. Park, U.G. Hong, Y.J. Lee, J.H. Choi, I.K. Song, Appl. Catal. A: Gen. 437-438 (2012) 112-119.
- [20] M.T. Klein, P.S. Virk, Ind. Eng. Chem. Fundam. 22 (1983) 35-45.
- [21] P.F. Britt, M.K. Kidder, A.C. Buchanan, Energy Fuels 21 (2007) 3102-3108
- [22] P.F. Britt, A.C. Buchanan, E.A. Malcolm, J. Org. Chem. 60 (1995) 6523-6536
- [23] B. Mahdavi, A. Lafrance, A. Martel, J. Lessard, H. Menard, J. Appl. Electrochem. 27 (1997) 605-611.
- [24] P. Dabo, A. Cyr, J. Lessard, L. Brossard, H. Menard, Can. J. Chem. 77 (1999) 1225-1229.
- [25] B. Fang, L. Binder, J. Power Sources 163 (2006) 616-622.
- [26] C. Moreno-Castilla, F.J. Maldonado-Hodar, Carbon 43 (2005) 455-465.
- [27] Y.J. Lee, J.C. Jung, S. Park, J.G. Seo, S.-H. Baeck, J.R. Yoon, J. Yi, I.K. Song, Curr. Appl. Phys. 11 (2011) 1-5.
- Y.J. Lee, J.C. Jung, S. Park, J.G. Seo, S.-H. Baeck, J.R. Yoon, J. Yi, I.K. Song, Korean J. [28] Chem, Eng. 28 (2011) 492-496.
- [29] Y.J. Lee, J.C. Jung, J. Yi, S.-H. Baeck, J.R. Yoon, I.K. Song, Curr. Appl. Phys. 10 (2010) 682-686.
- [30] Y. Hanzawa, K. Kaneko, Langmuir 12 (1996) 6167-6169.
- [31] K. Kohler, R.G. Heidenreich, I.G.E. Krauter, I. Pietsch, Chem, Eur. I. 8 (2002) 622-631.
- [32] C. Schmit, H. Probstle, J. Fricke, J. Non-Cryst, Solids 285 (2001) 277-282.
- [33] S.K. Ling, H.Y. Tian, S. Wang, T. Rufford, Z.H. Zhu, C.E. Buckley, J. Colloid Interface Sci. 357 (2011) 157-162.
- A. Namane, A. Mekarzia, K. Benrachedi, N. Belhaneche-Bensemra, A. Hellal, I. [34] Hazard. Mater. B 119 (2005) 189-194.
- [35] S. Zhang, R. Fu, D. Wu, W. Xu, W. Ye, Q. Ye, Z. Chen, Carbon 42 (2004) 3209–3216.
- [36] H.W. Park, U.G. Hong, Y.J. Lee, I.K. Song, Appl. Catal. A: Gen. 409 (2011) 167–173.
- S. Park, S.H. Lee, S.H. Song, D.R. Park, S.-H. Baeck, T.J. Kim, Y.M. Chung, S.H. Oh, [37] I.K. Song, Catal. Commun. 10 (2009) 391–394. [38] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113–252.
- H. Lee, J.C. Jung, H. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, S.Y. Kim, I.K. Song, [39] Korean J. Chem. Eng. 26 (2009) 994-998.