

Catalytic decomposition of benzyl phenyl ether to aromatics over cesium-exchanged heteropolyacid catalyst

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Abstract—Cesium-exchanged $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($X=2.0-3.0$) heteropolyacid catalysts were prepared and applied to the decomposition of benzyl phenyl ether to aromatics. Benzyl phenyl ether was chosen as a lignin model compound for representing $\alpha\text{-O-4}$ bond in lignin. Phenol, benzene, and toluene were mainly produced by the decomposition of benzyl phenyl ether. Conversion of benzyl phenyl ether and total yield for main products (phenol, benzene, and toluene) were closely related to the surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($X=2.0-3.0$) heteropolyacid catalyst. Conversion of benzyl phenyl ether and total yield for main products increased with increasing surface acidity of the catalyst. Among the catalysts tested, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ with the largest surface acidity showed the highest conversion of benzyl phenyl ether and total yield for main products.

Key words: Heteropolyacid, Lignin, C-O Bond, Benzyl Phenyl Ether

INTRODUCTION

Biomass has received attention as a renewable energy source due to the depletion of fossil fuel [1]. Among various biomasses, lignocellulose has attracted much attention as a valuable biomass because it does not compete with the food source. 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 [2]. Decomposition of lignin to aromatic compounds has been conducted by thermal cracking and catalytic decomposition processes [3-5].

Catalytic decomposition of lignin has been considered as a key technology for lignin valorization, because thermal cracking of lignin requires high temperature (over 450 °C) and pressure (over 100 atm) for considerable performance [6,7]. Hydrocracking of lignin over zeolite, Co-Mo/ Al_2O_3 , and Ni-No/ Al_2O_3 cleaves C-O bond and relatively weak C-C bond in lignin inner unit [8-12]. Catalytic performance of zeolite such as H-ZSM-5 in the decomposition of lignin strongly depends on the structure and acid property of the catalyst. Other catalysts examined for lignin decomposition include $\text{Fe}_2\text{O}_3\text{-S}/\text{Al}_2\text{O}_3\text{-S}$, $\text{NiO-MoO}_3/\text{Al}_2\text{O}_3$, and $\text{MoO}_3/\text{TiO}_2\text{-S}$ catalysts [13]. Selective cleavage of C-O bond in lignin over novel metal catalysts supported on carbon (Pd/C, Ru/C, and Rh/C) is also known to be an advantageous technology [14].

Heteropolyacids (HPAs) are inorganic acids whose strength is stronger than that of conventional solid acids [15-20]. HPA salts with K^+ , Cs^+ , and NH_4^+ cations have high surface area and porous structure by forming a tertiary structure [21,22]. It is known that surface acidity of cation-exchanged HPAs varies depending on cation content. Surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($X=2.0-3.0$) shows a volcano-shaped curve with respect to cesium content within the range

of $X=2.0-3.0$, and shows maximum value when X is 2.5 [16-18].

Dimeric lignin model compounds for representing C-O and C-C bonds in lignin have been generally used as a lignin feedstock due to the complex and various structure of lignin [23,24]. Dimeric chemical compounds containing $\alpha\text{-O-4}$, $\beta\text{-O-4}$, and 4-O-5 bonds are usually used as lignin model compounds, because C-O bond in lignin is in the range of 55-75%. Among lignin model compounds, benzyl phenyl ether has been usually employed for representing $\alpha\text{-O-4}$ bond in lignin [5,25].

In this work, cesium-exchanged $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ heteropolyacid catalysts were prepared with a variation of cesium content ($X=2.0, 2.3, 2.5, 2.8$, and 3.0) and applied to the decomposition of benzyl phenyl ether to aromatics. Benzyl phenyl ether was chosen as a lignin model compound for representing $\alpha\text{-O-4}$ bond in lignin. Correlations between catalytic performance and surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ were then established and discussed. The catalytic performance of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was also compared to that of Raney nickel catalyst. This is the first example reporting the catalytic performance of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ for the decomposition of lignin model compound containing $\alpha\text{-O-4}$ bond.

EXPERIMENTAL

1. Catalyst Preparation

Cesium-exchanged $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($X=2.0-3.0$) heteropolyacid catalysts were prepared according to the reported method [17,22]. Commercially available $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Sigma-Aldrich) was thermally treated at 300 °C for 2 h for precise quantification, prior to the preparation of cesium-exchanged heteropolyacid catalysts. A set of cesium-exchanged $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ heteropolyacid catalysts were prepared by an ion exchange method with a variation of cesium content ($X=2.0, 2.3, 2.5, 2.8$ and 3.0). Known amount of cesium nitrate (CsNO_3 , Sigma-Aldrich) was dissolved in distilled water. The solution was added dropwise into an aqueous solution con-

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taining $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with constant stirring. The resulting solution was then slowly heated at 60 °C for 12 h to obtain a solid. The solid product was dried overnight at 70 °C and was calcined at 300 °C for 2 h to yield $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($x=2.0, 2.3, 2.5, 2.8$, and 3.0).

2. Decomposition of Benzyl Phenyl Ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$

Decomposition of benzyl phenyl ether over cesium-exchanged $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($x=2.0, 2.3, 2.5, 2.8$, and 3.0) heteropolyacid catalysts was carried out in an autoclave reactor under nitrogen atmosphere. 1,2,3,4-Tetrahydronaphthalene (Sigma-Aldrich) was used as a solvent for benzyl phenyl ether and as a hydrogen donor in the decomposition of benzyl phenyl ether. 24.5 ml of 1,2,3,4-tetrahydronaphthalene and 0.5 ml (2.7×10^{-3} mol) of benzyl phenyl ether (Sigma-Aldrich) were charged into the reactor. 0.025 g of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($x=2.0, 2.3, 2.5, 2.8$, and 3.0) or Raney nickel catalyst (Sigma-Aldrich) was then added into the reactor. The catalytic decomposition of benzyl phenyl ether was performed at 200 °C and 10 atm (N_2) 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 (60 m \times 0.32 mm \times 1.0 μm) and flame ionization detector. Column temperature was increased from 50 °C to 270 °C at a heating rate of 15 °C/min under a flow of nitrogen (2.5 ml/min). Conversion of benzyl phenyl ether and selectivity for product (phenol, benzene, or toluene) were calculated on the basis of carbon balance. Yield for product (phenol, benzene, or toluene) was calculated by multiplying conversion of benzyl phenyl ether and corresponding product selectivity.

Conversion of benzyl phenyl ether

$$= \frac{\text{moles of benzyl phenyl ether reacted}}{\text{moles of benzyl phenyl ether supplied}} \quad (1)$$

Selectivity for product (phenol, benzene, or toluene)

$$= \frac{\text{moles of phenol, benzene, or toluene formed}}{\text{moles of benzyl phenyl ether reacted}} \quad (2)$$

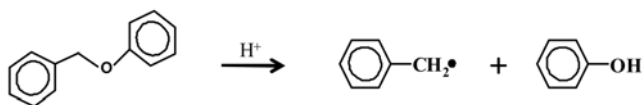
Total selectivity for main products

$$= \frac{\text{total moles of phenol, benzene, and toluene formed}}{\text{moles of benzyl phenyl ether reacted}} \quad (3)$$

Total yield for main products = (Conversion of benzyl phenyl ether)

$$\times (\text{Total selectivity for main products}) \quad (4)$$

Primary reaction



Secondary reaction

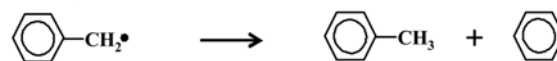


Fig. 1. Scheme for cleavage of α -O-4 bond in benzyl phenyl ether.

RESULTS AND DISCUSSION

1. Catalytic Performance in the Decomposition of Benzyl Phenyl Ether

Fig. 1 shows the scheme for cleavage of α -O-4 bond in benzyl phenyl ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ catalysts. Phenol and toluene radical are produced by the primary cleavage of α -O-4 bond in benzyl phenyl ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ catalysts. Toluene radical is then further converted to benzene and toluene through the secondary reaction. As shown Fig. 1, phenol, benzene, and toluene are mainly produced by the decomposition of benzyl phenyl ether.

Catalytic performance of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($x=2.0, 2.3, 2.5, 2.8$, and 3.0) in the decomposition of benzyl phenyl ether performed at 200 °C and 10 atm for 1 h is listed in Table 1. Conversion of benzyl phenyl ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ was in the range of 51.2–73.8%. Total selectivity for main products (phenol, benzene, and toluene) and total yield for main products were in the range of 50.3–55.5% and 25.7–40.9%, respectively. Selectivity for phenol (42.2–44.9%) was much higher than that for benzene (4.7–8.0%) and toluene (2.6–3.4%), because benzene and toluene were produced by secondary reaction of toluene radical. Selectivity for by-products such as light hydrocarbons (C_2 – C_7) and alcohols was in the range of 44.5–49.7%. Yield for phenol (21.6–33.1%) was much higher than that for benzene (2.4–5.9%) and toluene (1.7–2.1%). The above results indicate that cesium-exchanged $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ serves as an efficient acid catalyst in the decomposition of benzyl phenyl ether to aromatics.

2. Effect of Cesium Content on the Catalytic Performance

Conversion of benzyl phenyl ether, total selectivity for main products (phenol, benzene, and toluene), and total yield for main prod-

Table 1. Catalytic performance of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ in the decomposition of benzyl phenyl ether

	X in $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ ($x=2.0$ –3.0)				
	X=2.0	X=2.3	X=2.5	X=2.8	X=3.0
Conversion (%)	59.6	65.6	73.8	67.1	51.2
Total selectivity for main products ^a (%)	51.9	53.7	55.5	51.7	50.3
Phenol (%)	43.6	44.4	44.9	42.7	42.2
Benzene (%)	5.5	6.2	8.0	5.9	4.7
Toluene (%)	2.8	3.1	2.6	3.1	3.4
Total yield for main products ^b (%)	31.0	35.2	40.9	34.7	25.7
Phenol (%)	26.0	29.1	33.1	28.6	21.6
Benzene (%)	3.3	4.1	5.9	4.0	2.4
Toluene (%)	1.7	2.0	1.9	2.1	1.7

^aCalculated by Eq. (3)

^bCalculated by Eq. (4)

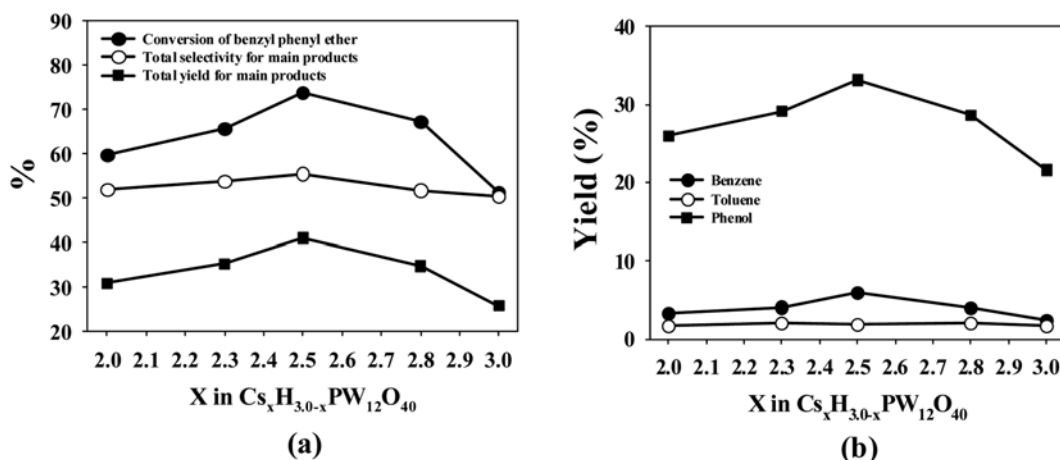


Fig. 2. (a) Catalytic performance of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ in the decomposition of benzyl phenyl ether, and (b) yields for phenol, benzene, and toluene plotted as a function of cesium content in $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. Reaction condition: Temperature=200 °C, Pressure=10 atm (N_2), Time=1 h.

ucts plotted as a function of cesium content in $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ are shown in Fig. 2(a). Conversion of benzyl phenyl ether showed a volcano-shaped curve with respect to cesium content. Total selectivity for main products was almost constant with respect to cesium content. As a consequence, total yield for main products showed a volcano-shaped curve with respect to cesium content. Among the catalysts tested, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ showed the best catalytic performance in terms of conversion of benzyl phenyl ether (73.8%) and total yield for main products (40.9%).

Fig. 2(b) shows the yields for phenol, benzene, and toluene plotted as a function of cesium content in $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. Yields for phenol and benzene showed volcano-shaped curves with respect to cesium content. However, yield for toluene (1.7–2.1%) was almost constant with regard to cesium content. Among the catalysts tested, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ showed the highest yields for phenol (33.1%) and benzene (5.9%).

3. Effect of Surface Acidity on the Catalytic Performance

Fig. 3(a) shows the correlation between conversion of benzyl phe-

nyl ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ and surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. Surface acidity data were taken from literature [18]. The correlation shows that conversion of benzyl phenyl ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ is closely related to the surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. Conversion of benzyl phenyl ether increased with increasing surface acidity of the catalyst. Among the catalysts tested, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ with the largest surface acidity showed the highest conversion of benzyl phenyl ether.

Fig. 3(b) shows the correlation between total yield for main products (phenol, benzene, and toluene) over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ and surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. The correlation shows that total yield for the main products is also closely related to the surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. Total yield for main products increased with increasing surface acidity of the catalyst. Among the catalyst tested, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ with the largest surface acidity showed the highest total yield for main products. Thus, surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ played an important role in determining the catalytic performance in the decomposition of benzyl phenyl ether to aromatics.

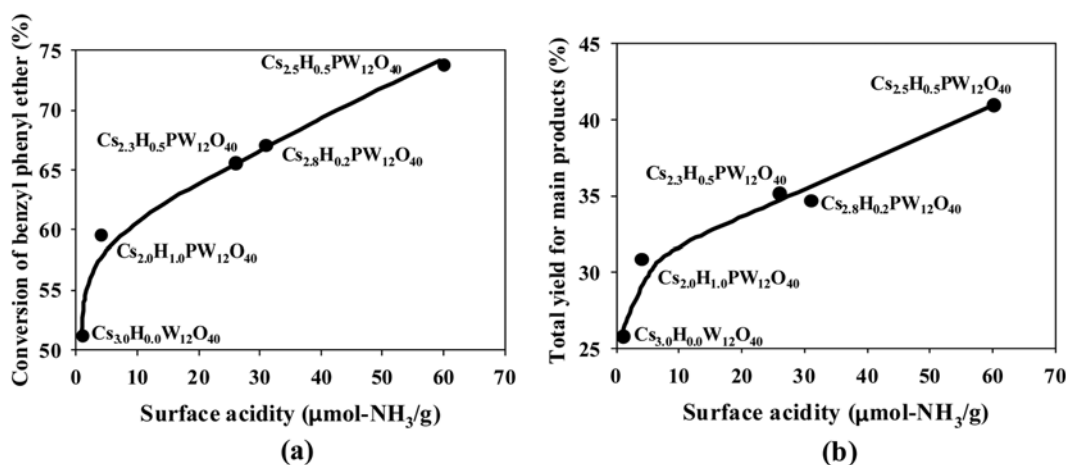


Fig. 3. (a) Correlation between conversion of benzyl phenyl ether over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ and surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$, and (b) correlation between total yield for main products (phenol, benzene, and toluene) over $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$ and surface acidity of $\text{Cs}_x\text{H}_{3.0-x}\text{PW}_{12}\text{O}_{40}$. Surface acidity data were taken from the literature [18]. Reaction condition: Temperature=200 °C, Pressure=10 atm (N_2), Time=1 h.

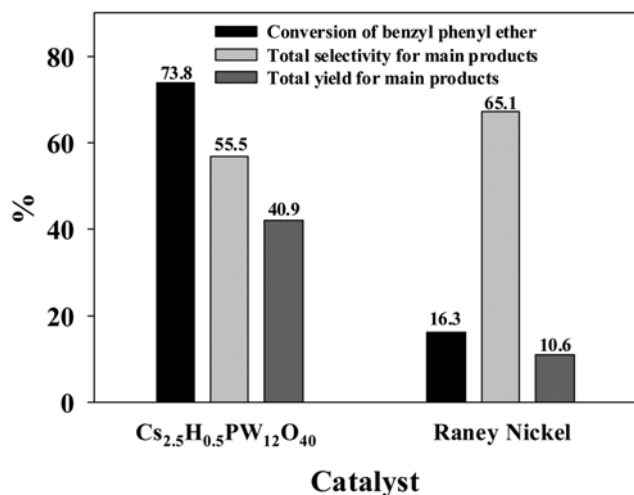


Fig. 4. Comparison of catalytic performance between Cs_{2.5}H_{0.5}PW₁₂O₄₀ and Raney nickel catalysts in the decomposition of benzyl phenyl ether. Reaction condition: Temperature=200 °C, Pressure=10 atm (N₂), Time=1 h.

4. Comparison of Catalytic Performance between Cs_{2.5}H_{0.5}PW₁₂O₄₀ Catalyst and Raney Nickel Catalyst in the Decomposition of Benzyl Phenyl Ether

Raney nickel is a well known catalyst for the decomposition of lignin [11]. Fig. 4 shows the comparison of catalytic performance between Cs_{2.5}H_{0.5}PW₁₂O₄₀ catalyst and Raney nickel catalyst in the decomposition of benzyl phenyl ether. Conversion of benzyl phenyl ether (73.8%) and total yield for main products (40.9%) over Cs_{2.5}H_{0.5}PW₁₂O₄₀ were much higher than those over Raney nickel catalyst (16.3% and 10.6%, respectively). Therefore, we come to conclude that Cs_{2.5}H_{0.5}PW₁₂O₄₀ catalyst is more efficient than Raney nickel catalyst in the decomposition of benzyl phenyl ether to aromatics.

CONCLUSIONS

Cesium-exchanged Cs_xH_{3.0-x}PW₁₂O₄₀ (X=2.0, 2.3, 2.5, 2.8, and 3.0) catalyst were prepared and applied to the decomposition of lignin model compound. Benzyl phenyl ether was employed as a dimeric lignin model compound for representing α-O-4 bond in lignin. Conversion of benzyl phenyl ether and total yield for main products (phenol, benzene, and toluene) over Cs_xH_{3.0-x}PW₁₂O₄₀ were in the range of 51.2-73.8% and 25.7-40.9%, respectively. Among the main products produced by the decomposition of benzyl phenyl ether, yield for phenol (21.6-33.1%) was much higher than that for benzene (2.4-5.9%) and toluene (1.7-2.1%). Conversion of benzyl phenyl ether and total yield for main products were closely related to the surface acidity of Cs_xH_{3.0-x}PW₁₂O₄₀. Conversion of benzyl phenyl ether and total yield for main products increased with increasing surface acidity of the catalyst. Among the catalysts tested, Cs_{2.5}H_{0.5}PW₁₂O₄₀ with largest surface acidity showed the highest conversion of benzyl phenyl ether and total yield for main products. It is concluded that cesium-exchanged Cs_xH_{3.0-x}PW₁₂O₄₀ was an efficient

catalyst in the decomposition of benzyl phenyl ether to aromatics and surface acidity of the catalyst played an important role in determining the catalytic performance.

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