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$Cs_x H_{3.0-x} PW_{12}O_{40}$ (X = 2.0–3.0) Heteropolyacid Nano-Catalysts for Catalytic Decomposition of 2,3-Dihydrobenzofuran to Aromatics

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Cesium-exchanged $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) heteropolyacid nanocatalysts were prepared, and they were applied to the catalytic decomposition of lignin model compound to aromatics. Successful formation of cesium-exchanged $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0-3.0) catalysts was confirmed by FT-IR, ICP-AES, and XRD measurements. 2,3-Dihydrobenzofuran was employed as a lignin model compound for representing β -5 bond in lignin. Phenol, ethylbenzene, and 2-ethylphenol were mainly produced by the catalytic decomposition of 2,3-dihydrobenzofuran. Conversion of 2,3-dihydrobenzofuran and total yield for main products (phenol, ethylbenzene, and 2-ethylphenol) were closely related to the surface acidity of $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0-3.0) catalysts. Conversion of 2,3-dihydrobenzofuran and total yield for main products increased with increasing surface acidity of the catalysts. Among the catalysts tested, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts served as an important factor determining the catalytic performance in the decomposition of 2,3-dihydrobenzofuran to aromatics.

Keywords: Lignin, 2,3-Dihydrobenzofuran, Heteropolyacid Catalyst, Aromatics, Decomposition.

1. INTRODUCTION

As one of the most significant renewable resources, biomass has attracted much attention to reduce carbon dioxide emission and global dependency on fossil fuels.¹ In particular, lignin has received continuous attention as a valuable biomass, because it does not compete with food resources.^{2,3} In addition, lignin, which is an amorphous polymer comprising aromatic compounds, is regarded as the richest source of aromatics in nature.^{4,5} Therefore, decomposition of lignin to aromatics becomes as an advantageous technology for producing aromatics as biofuels.

Catalytic decomposition of lignin has attracted significant interest as a promising technology for the production of aromatic compounds, because polymeric lignin is thermally stable.^{6,7} Conventional catalytic process for the production of aromatic compounds is based on cleavage of C—O bond over acid catalysts such as HCl and HI.⁸

However, these mineral acids involve many drawbacks in an environmental point of view, because their corrosive and homogeneous properties cause corrosion of reaction system and disposable problem. Other catalysts examined for lignin decomposition include Mo- or W- based sulfides supported on alumina.^{9–12} Hydrocracking over these catalysts requires severe reaction conditions such as high temperature and high pressure. For effective decomposition of lignin, therefore, it is necessary to develop an environmental benign catalyst that can give high catalytic activity and stable performance under mild reaction conditions.

It has been reported that acid strength of heteropolyacids (HPAs) is stronger than that of conventional solid acids.^{13, 14} For this reason, HPAs have been widely utilized as solid acid nano-catalysts in several acid-catalyzed reactions.^{13–17} HPAs salt with K⁺, Cs⁺, and NH₄⁺ cations have high surface area and porous structure by forming a tertiary structure.¹³ It is well known that surface acidity of cation-exchanged HPAs varies depending

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on cation content. For example, surface acidity of $Cs_x H_{3.0-x} PW_{12}O_{40}$ (X = 2.0-3.0) shows a volcano-shaped trend with respect to cesium content within the range of X = 2.0-3.0.^{13, 14, 16}

Due to the complex structure of lignin,¹⁸ studies on lignin decomposition have been simplified by employing lignin model compounds rather than lignin itself.^{5, 18} Among various lignin model compounds, 2,3dihydrobenzofuran has been widely used as a model compound for representing β -5 bond in lignin.^{7, 18}

In this work, cesium-exchanged $Cs_xH_{3,0-x}PW_{12}O_{40}$ nano-catalysts were prepared with a variation of cesium content (X = 2.0, 2.3, 2.5, 2.8, and 3.0), and they were applied to the catalytic decomposition of 2,3-dihydrobenzofuran (a lignin model compound) to aromatics. Correlations between catalytic performance and surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) nano-catalysts were then established and discussed.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

Cesium-exchanged $Cs_xH_{3-x}PW_{12}O_{40}$ (X = 2.0–3.0) heteropolyacid nano-catalysts were prepared according to the method reported in the literatures.^{13, 16} Commercially available H₃PW₁₂O₄₀ (Sigma-Aldrich) was thermally treated at 300 °C for 2 h for precise quantification, prior to the preparation of cesium-exchanged heteropolyacid nanocatalysts. A series of cesium-exchanged heteropolyacid nano-catalysts ($Cs_x H_{3,0-x} PW_{12}O_{40}$) 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). A known amount of cesium nitrate (CsNO₃, Sigma-Aldrich) was dissolved in distillated water. The solution was added dropwise into an aqueous solution containing $H_3PW_{12}O_{40}$ 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 then it was calcined at 300 °C for 2 h to yield $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) catalysts.

2.2. Catalyst Characterization

Successful formation of cesium-exchanged $Cs_{x}H_{3-x}PW_{12}O_{40}$ (X = 2.0–3.0) nano-catalysts was confirmed by FT-IR (Nicolet, Nicolet 6700) measurements. Chemical compositions of constituent elements in the $Cs_x H_{3.0-x} PW_{12} O_{40}$ (X = 2.0-3.0) catalysts were determined by ICP-AES (Shimadzu, ICP-1000IV) analyses. Crystalline phases of the catalysts were investigated by XRD (Rigaku, D-MAX2500-PC) measurements using Cu-K α radiation ($\lambda = 1.541$ Å) operated at 40 kV and 20 mA. Crystal size and morphology of the catalysts were examined by SEM (Jeol, JSM-6700F). All the catalysts were thermally treated at 300 °C in a stream of nitrogen prior to characterization and catalytic reaction.

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2.3. Catalytic Decomposition of 2,3-Dihydrobenzofuran

Decomposition of 2,3-dihydrobenzofuran over cesiumexchanged $Cs_x H_{3.0-x} PW_{12}O_{40}$ (X = 2.0-3.0) nanocatalysts was carried out in a stainless steel autoclave reactor (25 ml) under nitrogen atmosphere. Tetralin (Sigma-Aldrich) was used as a solvent for 2,3dihydrobenzofuran (Sigma-Aldrich) and as a hydrogen donor in the decomposition of 2,3-dihydrobenzofuran. 0.05 g of $Cs_r H_{3,0-r} PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) and a mixture of 2,3-dihydrobenzofuran (1 ml), tetralin (15 ml), and hexadecane (1 ml, an internal standard) were charged into the reactor at room temperature. The reactor was purged with nitrogen several times in order to remove air. The reactor was then heated to reaction temperature (250 °C). The reaction was carried out for 1 h at nitrogen pressure of 30 bar in order to prevent vaporization of reaction mixture. After 1 h-reaction, reaction products were sampled and analyzed using a gas chromatograph (Younglin, YL6100 GC-FID) equipped with a capillary column (Agilent, DB-5MS, 60 m \times 0.320 mm). Conversion of 2,3-dihydrobenzofuran and selectivity for product (phenol, ethylbenzene or 2-ethylphenol) were calculated according to the following equations on the basis of mole balance. Yield for product (phenol, ethylbenzene or 2-ethylphenol) was calculated by multiplying conversion of 2,3-dihydrobenzofuran and corresponding product selectivity. For comparison, commercial HZSM-5 (Zeolvst International, Si/Al = 50) was also employed for the decomposition of 2,3-dihydrobenzofuran.

Conversion of 2,3-dihydrobenzofuran

$$= \frac{\text{moles of 2,3-dihydrobenzofuran reacted}}{\text{moles of 2,3-dihydrobenzofuran supplied}}$$
(1)

Selectivity for product

(phenol, ethylbenzene or 2-ethylphenol)

= moles of phenol, ethylbenzene or 2-ethylphenol formed

 \cdot (moles of 2,3-dihydrobenzofuran reacted)⁻¹ (2)

Total selectivity for main products

- = Total moles of phenol, ethylbenzene or
 - and 2-ethylphenol formed
 - \cdot (moles of 2,3-dihydrobenzofuran reacted)⁻¹ (3)

Total yield for main products

= (Conversion of 2,3-dihydrobenzofuran)

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

3. RESULTS AND DISCUSSION

3.1. Catalysts Characterization

Successful formation of $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0–3.0) heteropolyacid (HPA) catalysts was confirmed by FT-IR



Figure 1. FT-IR spectra of $Cs_x H_{3.0-x} PW_{12}O_{40}$ (X = 2.0–3.0) catalysts.

analyses, which provided information about the maintenance of heteropolyacid structure.¹³ FT-IR spectra of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts are shown in Figure 1. The structure of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts could be identified by four characteristic IR bands appearing in the range of 700–1200 cm⁻¹. The four characteristic IR bands of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts appeared at 1080 cm⁻¹ (P–O), 985 cm⁻¹ (W=O), 890 cm⁻¹ (inter-octahedral W–O–W), and 810 cm⁻¹ (intra-octahedral W–O–W), in good agreement with the characteristic IR bands of $H_3PW_{12}O_{40}$. This result was well consistent with the previous work,¹⁹ indicating successful formation of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) heteropolyacid catalysts.

Successful formation of $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0-3.0) catalysts was further confirmed by ICP-AES analyses. Chemical compositions of cesium, phosphorous, and tungsten in the $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0-3.0) catalysts determined by ICP-AES analyses are summarized in Table I. The measured Cs:P:W ratios in the $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0-3.0) catalysts were in good agreement with the theoretical values.

In order to examine the crystalline phase of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) heteropolyacid catalysts, XRD measurements were carried out. Figure 2 shows the XRD patterns of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts. It was observed that $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts exhibited the same diffraction patterns corresponding to cubic phase of *Pn3m* crystalline structure, indicating that the crystalline structure of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) was not

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Table I. Chemical compositions of cesium, phosphorous, and tungsten in the $Cs_xH_{3,0-x}PW_{12}O_{40}$ (*X* = 2.0–3.0) catalysts determined by ICP-AES analyses.

Catalyst	Ratio of Cs:P:W			
	Theoretical value	Measured value		
$\overline{Cs_{20}H_{10}PW_{12}O_{40}}$	2.0:1.0:12.0	1.9:1.0:12.0		
$Cs_{2,3}H_{0,7}PW_{1,2}O_{40}$	2.3:1.0:12.0	2.3:1.0:12.0		
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	2.5:1.0:12.0	2.5:1.0:12.0		
$Cs_{2.8}H_{0.2}PW_{12}O_{40}$	2.8:1.0:12.0	2.8:1.0:12.0		
Cs _{3.0} PW ₁₂ O ₄₀	3.0:1.0:12.0	3.0:1.0:12.0		

changed. This result was in good agreement with the precious work,^{20, 21} indicating successful formation of $Cs_x H_{3.0-x} PW_{12}O_{40}$ (*X* = 2.0–3.0) heteropolyacid catalysts.

Crystal size and morphology of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts were examined by SEM analyses. Figure 3 shows the SEM images of $Cs_xH_{3,0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts and their crystal size distribution. It was observed that crystallites of cesium-exchanged heteropolyacid catalysts were composed of elementary particles, which were agglomerated in large-spherical particles within the range of 30–260 nm. Crystal size of heteropolyacids increased with increasing cesium content (X). This result was well consistent with the previous reports.^{22, 23}

3.2. Catalytic Performance in the Decomposition of 2,3-Dihydrobenzofuran

Cleavage of dihydrofuran ring in the 2,3dihydrobenzofuran over acid catalysts mainly produces 2-ethylphenol.⁸ Figure 4 shows that 2-ethylphenol is produced by the primary cleavage of β -5 bond in the 2,3dihydrobenzofuran over Cs_xH_{3.0-x}PW₁₂O₄₀. 2-Ethylphenol is further converted to phenol and ethylbenzene through the secondary reaction over the catalysts. As shown in Figure 4, aromatic compounds such as phenol,



Figure 2. XRD patterns of $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0–3.0) catalysts.

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Figure 3. SEM images of $Cs_x H_{3,0-x} PW_{12}O_{40}$ (X = 2.0–3.0) catalysts and their crystal size distribution.

ethylbenzene, and 2-ethylphenol are mainly produced in the decomposition of 2,3-dihydrobenzofuran.

Catalytic performance of $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) in the decomposition of 2,3dihydrobenzofuran performed at 250 °C and 30 bar for 1 h is listed in Table II. Conversion of 2,3-dihydrobenzofuran over $Cs_xH_{3.0-x}PW_{12}O_{40}$ was in the range of 23.5–62.2%. Selectivity for 2-ethylphenol (40.2–45.2%) was much higher than that for phenol (15.5–20.2%) and ethylbenzene



Figure 4. Scheme for the decomposition of 2,3-dihydrobenzofuran over $Cs_{x}H_{3,0-x}PW_{12}O_{40}$.

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(2.3–4.7%), because phenol and ethylbenzene were produced by the secondary reaction of 2-ethylphenol. Among the secondary products, selectivity for phenol (15.5–20.2%) was higher than that for ethylbenzene (2.3–4.7%). Selectivity for by-products such as light hydrocarbons (C_2 – C_8) and alcohols was in the range of 30.3–37.3%.

Yield for 2-ethylphenol (10.4–28.1%) was much higher than that for phenol (3.7–12.6%) and ethylbenzene (0.9– 2.7%). Yield for phenol (3.7–12.6%) was higher than that for ethylbenzene (0.9–2.7%). Total selectivity for main products (phenol, ethylbenzene, and 2-ethylphenol) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ was in the range of 62.7– 69.7%. Total yield for main products (phenol, ethylbenzene, and 2-ethylphenol) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ was in the range of 15.2–43.4%. Among the catalysts tested, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst showed the best catalytic performance in terms of conversion of 2,3-dihydrobenzofuran and total yield for main products (Table II).

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Catalytic Decomposition of 2,3-Dihydrobenzofuran

Table II. Catalytic performance of $Cs_x H_{3,0-x}PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) in the decomposition of 2,3-dihydrobenzofuran performed at 250 °C and 30 bar for 1 h.

	X in $Cs_x H_{3.0-x} PW_{12}O_{40}$ (X = 2.0–3.0)				
	X = 2.0	X = 2.3	X = 2.5	X = 2.8	X = 3.0
Conversion (%)	37.7	52.4	62.2	58.4	23.5
Total selectivity for main products ^{<i>a</i>} (%)	63.0	65.6	69.7	62.7	64.6
Phenol (%)	16.3	17.2	20.2	20.0	15.5
Ethylbenzene (%)	2.3	3.4	4.3	2.5	4.7
2-Ethylphenol (%)	44.4	45.0	45.2	40.2	44.4
Total yield for main products ^{b} (%)	23.7	33.4	43.4	36.7	15.2
Phenol (%)	6.1	9.0	12.6	11.7	3.7
Ethylbenzene (%)	0.9	1.8	2.7	1.5	1.1
2-Ethylphenol (%)	16.7	23.6	28.1	23.5	10.4

Notes: ^a Calculated by Eq. (3); ^bCalculated by Eq. (4).

3.3. Effect of Cesium Content on the Catalytic Performance

Figure 5 shows the catalytic performance of $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts in the decomposition of 2,3-dihydrobenzofuran plotted as a function of cesium content. Conversion of 2,3-dihydrobenzofuran showed a volcano-shaped curve with respect to cesium content. Total yield for main products also showed a volcano-shaped curve with respect to cesium content. Among the catalysts tested, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst showed the best catalytic performance in terms of conversion of 2,3-dihydrobenzofuran and total yield for main products.

Figure 6 shows the yields for phenol, ethylbenzene, and 2-ethylphenol plotted as a function of cesium content. Yields for phenol, ethylbenzene, and 2-ethylphenol showed volcano-shaped curves with respect to cesium content. Among the catalysts tested, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst showed the best catalytic performance in terms of yields for phenol, ethylbenzene, and 2-ethtylphenol.



Figure 5. Catalytic performance of $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts in the decomposition of 2,3-dihydrobenzofuran plotted as a function of cesium content.



Figure 6. Yields for phenol, ethylbenzene, and 2-ethylphenol plotted as a function of cesium content.

As mentioned above, yield for 2-ethylphenol was much higher than that for phenol and ethylbenzene.

3.4. Effect of Surface Acidity on the Catalytic Performance

Figure 7(a) shows the correlation between conversion of 2,3-dihydrobenzofuran over $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts and surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts. Surface acidity data of $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts were taken from a literature.²⁴ Conversion of 2,3-dihydrobenzofuran increased with increasing surface acidity of cesium-exchanged heteropolyacid (HPA) catalysts. This result clearly shows that conversion of 2,3-dihydrobenzofuran is closely related to the surface acidity of the catalysts. Among the catalysts examined, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst with the largest surface acidity showed the highest conversion of 2,3-dihydrobenzofuran.

Figure 7(b) shows the correlation between total yield for main products (phenol, ethylbenzene, and 2-ethylphenol) over $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts and surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts. Total yield for main products increased with increasing surface acidity of the catalysts. This result also shows that total yield for main products is closely related to the surface acidity of the catalysts. Thus, cesium-exchanged $Cs_xH_{3,0-x}PW_{12}O_{40}$ heteropolyacid nano-catalysts served as an efficient acid catalyst in the decomposition of 2,3-dihydrobenzofuran to aromatics. It is concluded that surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$ heteropolyacid nano-catalysts played an important role in determining the catalytic performance in the decomposition of 2,3-dihydrobenzofuran.

3.5. Comparison of Catalytic Performance Between Cs_{2.5}H_{0.5}PW₁₂O₄₀ Catalyst and HZSM-5 Catalyst in the Decomposition of 2,3-Dihydrobenzofuran

In order to compare the performance of acid catalysis, commercial HZSM-5 was employed as a catalyst

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Figure 7. Correlations (a) between conversion of 2,3-dihydrobenzofuran over $Cs_xH_{3,0-x}PW_{12}O_{40}$ and surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$, and (b) between total yield for main products (phenol, ehtylbenzene, and 2-ethylphenol) over $Cs_xH_{3,0-x}PW_{12}O_{40}$ and surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$. Surface acidity data were taken from a literature.²⁸



Figure 8. Comparison of catalytic performance between $Cs_{2,5}H_{0,5}PW_{12}O_{40}$ and HZSM-5 in the decomposition of 2,3-dihydrobenzofuran.

for the decomposition of 2,3-dihydrobenzofuran. Figure 8 shows the comparison of catalytic performance between $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and HZSM-5 in the decomposition of 2,3-dihydrobenzofuran at the reaction conditions. Conversion of 2,3-dihydrobenzofuran over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (62.2%) was much higher than that over HZSM-5 (38.2%). Total yield for main products over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst (43.4%) was much higher than that over HZSM-5 catalyst (25.0%). Thus, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was more efficient than HZSM-5 in the decomposition of 2,3-dihydrobenzofuran to aromatics.

4. CONCLUSIONS

Catalytic decomposition of lignin model compound to aromatics was carried out over cesium-exchanged $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) heteropolyacid nano-catalysts. Successful formation of cesium-exchanged $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0-3.0) catalysts was confirmed by FT-IR, ICP-AES, and XRD

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measurements. 2,3-Dihydrobenzofuran was used as a lignin model compound for representing β -5 bond in lignin. Conversion of 2,3-dihydrobenzofuran and total yield for main products (phenol, ethylbenzene, and 2-ethylphenol) over $Cs_x H_{3.0-x} PW_{12}O_{40}$ (X = 2.0–3.0) catalysts were in the range of 23.5-62.2% and 15.2-43.4%, respectively. Conversion of 2,3-dihydrobenzofuran and total yield for main products were closely related to the surface acidity of $Cs_xH_{3,0-x}PW_{12}O_{40}$ catalysts. Among the catalysts tested, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst with the largest surface acidity showed the highest conversion of 2,3-dihydrobenzofuran and total yield for main products. It is concluded that surface acidity of $Cs_rH_{3,0-r}PW_{12}O_{40}$ catalysts played an important role in determining the catalytic performance in the decomposition of 2,3-dihydrobenzofuran to aromatics.

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