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Decomposition of phenethyl phenyl ether to aromatics over $Cs_xH_{3.0-x}PW_{12}O_{40}$ ($X = 2.0–3.0$) heteropolyacid catalysts

Hai Woong Park, Sunyoung Park, Dong Ryul Park, Jung Ho Choi, In Kyu Song *

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

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ABSTRACT

Cesium-exchanged $Cs_xH_{3.0-x}PW_{12}O_{40}$ heteropolyacids were prepared with a variation of cesium content ($X = 2.0–3.0$) and were applied to the decomposition of phenethyl phenyl ether to aromatics. Phenethyl phenyl ether was used as a lignin model compound for representing β-O-4 linkage of lignin. Phenol, benzene, toluene, and ethylbenzene were mainly produced by the decomposition of phenethyl phenyl ether. Conversion of phenethyl phenyl ether and total yield for main products increased with increasing surface acidity of the catalyst. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with the largest surface acidity showed the highest conversion of phenethyl phenyl ether and the highest total yield for main products.

1. Introduction

Lignin has been generally produced by the delignification process in the pulp and paper processes and burned for power generation [1,2]. Biorefinery process has provided resource of lignin because lignin is simultaneously produced as a by-product of biorefinery process [3]. Lignin has attracted much attention as an aromatic resource because lignin is an amorphous polymer linked by aromatic compounds [4–6]. Recently, researches on the decomposition of lignin for production of aromatic compounds have been widely conducted due to the depletion of fossil fuels.

Catalytic decomposition of lignin has attracted much attention as a key technology for production of aromatic compounds because polymeric lignin is thermally stable [7,8]. H-ZSM-5 has been used for cleavage of β-O-4 bond and relatively weak C–C bond in the lignin inner unit. The catalytic performance of H-ZSM-5 in the decomposition of lignin strongly depends on the structure and acid property of the catalyst [9]. Other catalysts examined for lignin decomposition include sulfided Co–Mo/Al_2O_3, Ni–W/Al_2O_3, and Ni–Mo/Al_2O_3 catalysts [10–13], Fe_2O_3–S/Al_2O_3–S, NiO–MoO_3/Al_2O_3, and MoO_3/TiO_2–S catalysts [14], and Raney Ni, Pd/C, Rh/C, Rh/Al_2O_3, Ru/C, and Ru/Al_2O_3 catalysts [15]. Hydrocracking of lignin by these catalysts requires relatively high temperature (over 400 °C) and high pressure (50–100 atm).

Heteropolyacids (HPAs) are inorganic acids. Acid strength of HPAs is stronger than that of conventional solid acids [16–19]. HPA salts with K^+, Cs^+, and NH_4^+ cations have high surface area and porous structure by forming a tertiary structure [17,19]. It is known that surface acidity of cation-exchanged HPAs is varied depending on cation content. Surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$ ($X = 2.0–3.0$) 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 [18–22].

Dimeric lignin model compounds have been generally used as a lignin feedstock for research on lignin decomposition due to the complex and various structure of lignin [23,24]. Among various model compounds, phenethyl phenyl ether has been widely used as a lignin model compound for representing β-O-4 bond that is dominant linkage in the lignin [25–29].

In this work, cesium-exchanged $Cs_xH_{3.0-x}PW_{12}O_{40}$ heteropolyacid catalysts were prepared with a variation of cesium content ($X = 2.0$, 2.3, 2.5, 2.8, and 3.0), and were applied to the decomposition of phenethyl phenyl ether (a lignin model compound) to aromatics. Correlations between catalytic performance and surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$ were then established and discussed. This is the first example reporting the catalytic performance of $Cs_xH_{3.0-x}PW_{12}O_{40}$ catalyst for the decomposition of lignin model compound to aromatics.

2. Experimental

2.1. Catalyst preparation

$Cs_xH_{3.0-x}PW_{12}O_{40}$ catalysts were prepared according to the reported method [19,22]. Commercially available $H_3PW_{12}O_{40}$ (Sigma-Aldrich) was thermally treated at 300 °C for 2 h for precise quantification, prior to the preparation of cesium-exchanged heteropolyacid catalysts. A series of cesium-exchanged heteropolyacid catalysts ($Cs_xH_{3.0-x}PW_{12}O_{40}$) were prepared by an ion exchange method with

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

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a variation of cesium content (X = 2.0, 2.3, 2.5, 2.8, and 3.0). A known amount of cesium nitrate ($CsNO_3$, Sigma-Aldrich) was dissolved in distilled 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 $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0, 2.3, 2.5, 2.8, and 3.0) catalysts. Cesium content in $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0 − 3.0) catalysts was confirmed by ICP-AES analysis (Shimadz, ICP-1000 IV).

2.2. Decomposition of phenethyl phenyl ether over $Cs_xH_{3.0-x}PW_{12}O_{40}$

Decomposition of phenethyl phenyl ether over cesium-exchanged $Cs_xH_{3.0-x}PW_{12}O_{40}$ heteropolyacid catalysts was carried out in an autoclave reactor under nitrogen atmosphere. 1,2,3,4-Tetrahydronaphthalene was used as a solvent for phenethyl phenyl ether and as a hydrogen donor in the decomposition of phenethyl phenyl ether. 24.5 ml of 1,2,3,4-tetrahydronaphthalene (Sigma-Aldrich) and 0.5 ml of phenethyl phenyl ether (Frinton Laboratory) were charged into the reactor. 0.025 g of $Cs_xH_{3.0-x}PW_{12}O_{40}$ (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 reaction was performed at 200 °C and 10 atm 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 phenethyl phenyl ether and selectivity for product (phenol, benzene, toluene, or ethylbenzene) were calculated on the basis of carbon balance. Yield for product (phenol, benzene, toluene, or ethylbenzene) was calculated by multiplying conversion of phenethyl phenyl ether and corresponding product selectivity.

Conversion of phenethyl phenyl ether

$$= \frac{\text{moles of phenethyl phenyl ether reacted}}{\text{moles of phenethyl phenyl ether supplied}} \tag{1}$$

Selectivity for product (phenol, benzene, toluene, or ethylbenzene)

$$= \frac{\text{moles of phenol, benzene, toluene, or ethylbenzene formed}}{\text{moles of phenethyl phenyl ether reacted}} \tag{2}$$

Total selectivity for main products

$$= \frac{\text{Total moles of phenol, benzene, toluene, and ethylbenzene formed}}{\text{moles of phenethyl phenyl ether reacted}} \tag{3}$$

Total yield for main products

$$= (\text{Conversion of phenethyl phenyl ether}) \times (\text{Total selectivity for main products}) \tag{4}$$

3. Results and discussion

3.1. Catalytic performance in the decomposition of phenethyl phenyl ether

Fig. 1 shows that phenol and styrene are produced by the primary cleavage of β-O-4 linkage in the phenethyl phenyl ether over $Cs_xH_{3.0-x}PW_{12}O_{40}$ catalysts. Styrene is then further converted to benzene, toluene, and ethylbenzene through the secondary reaction over the catalyst. As shown in Fig. 1, aromatic compounds such as phenol, benzene, toluene, and ethylbenzene are mainly produced in the decomposition of phenethyl phenyl ether.

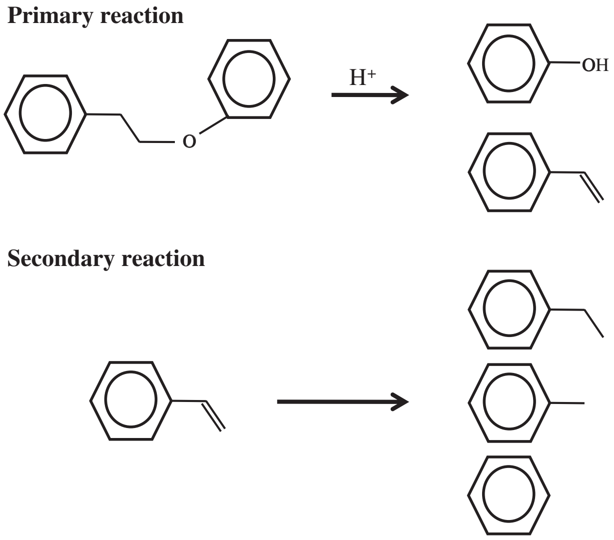

Fig. 1. Scheme for the decomposition of phenethyl phenyl ether over $Cs_xH_{3.0-x}PW_{12}O_{40}$.

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 phenethyl phenyl ether performed at 200 °C and 10 atm for 1 h is listed in Table 1. Conversion of phenethyl phenyl ether over $Cs_xH_{3.0-x}PW_{12}O_{40}$ was in the range of 31.2–68.1%. Selectivity for phenol (40.7–51.3%) was much higher than that for benzene, toluene, and ethylbenzene, because benzene, toluene, and ethylbenzene were produced by secondary reaction of styrene. Among the products produced by secondary reaction, selectivity for ethylbenzene (17.6–19.2%) was a little higher than that for benzene (9.3–16.7%). Selectivity for by-products such as light hydrocarbons (C_2–C_7) and alcohols was in the range of 16.7–26.0%.

Because selectivity for phenol was higher than that for benzene, toluene, and ethylbenzene, yield for phenol (16.0–30.2%) was much higher than that for benzene, toluene, and ethylbenzene. Yield for ethylbenzene (6.0–12.3%) was a little higher than that for benzene (2.9–11.4%). Total selectivity for main products (phenol, benzene, toluene, and ethylbenzene) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ was in the range of 74.0–83.3%. Total yield for main products (phenol, benzene, toluene, and ethylbenzene) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ was in the range of 25.4–54.9%. 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 phenethyl phenyl ether and total yield for main products (Table 1).

Table 1
Catalytic performance of $Cs_xH_{3.0-x}PW_{12}O_{40}$ in the decomposition of phenethyl phenyl ether.

	X in $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0–3.0)					
	X = 1.5 [c]	X = 2.0	X = 2.3	X = 2.5	X = 2.8	X = 3.0
Conversion (%)	51.1	56.9	59.8	68.1	61.8	31.2
Total selectivity for main products [a] (%)	70.8	74.0	77.9	80.4	83.3	81.3
Phenol (%)	39.7	40.7	43.6	44.3	47.3	51.3
Benzene (%)	13.1	14.0	14.8	16.7	15.7	9.3
Toluene (%)	1.6	1.7	1.6	1.4	1.6	1.5
Ethylbenzene (%)	16.4	17.6	17.9	18.0	18.7	19.2
Total yield for main products [b] (%)	36.2	42.2	46.7	54.9	51.4	25.4
Phenol (%)	20.3	23.2	26.1	30.2	29.2	16.0
Benzene (%)	6.7	8.0	8.9	11.4	9.7	2.9
Toluene (%)	0.8	1.0	1.0	1.0	1.0	0.5
Ethylbenzene (%)	8.4	10.0	10.7	12.3	11.5	6.0

[a] Calculated by Eq. (3).
[b] Calculated by Eq. (4).
[c] Conducted for comparison.

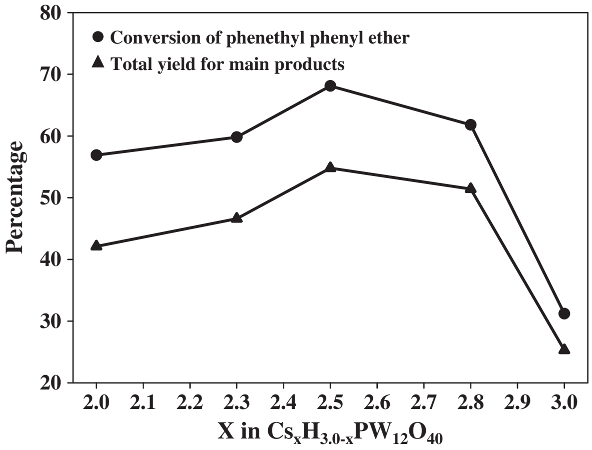

Fig. 2. Catalytic performance of $Cs_xH_{3.0-x}PW_{12}O_{40}$ in the decomposition of phenethyl phenyl ether plotted as a function of cesium content in $Cs_xH_{3.0-x}PW_{12}O_{40}$. Reaction condition: Temperature = 200 °C, Pressure = 10 bar (N_2), Time = 1 h.

3.2. Effect of cesium content on the catalytic performance

Fig. 2 shows the catalytic performance of $Cs_xH_{3.0-x}PW_{12}O_{40}$ in the decomposition of phenethyl phenyl ether plotted as a function of cesium content in $Cs_xH_{3.0-x}PW_{12}O_{40}$. Conversion of phenethyl phenyl ether 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, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed the best catalytic performance in terms of conversion of phenethyl phenyl ether and total yield for main products.

Fig. 3 shows the yields for phenol, benzene, and ethylbenzene plotted as a function of cesium content in $Cs_xH_{3.0-x}PW_{12}O_{40}$. Yields for phenol, benzene, and ethylbenzene 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, benzene, and ethylbenzene. As mentioned earlier, yield for phenol was much higher than that for ethylbenzene or benzene.

3.3. Effect of surface acidity on the catalytic performance

Fig. 4a shows the correlation between conversion of phenethyl phenyl ether 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 [19]. The correlation clearly shows that conversion of phenethyl phenyl ether is closely related to the surface acidity of the catalyst. Conversion of phenethyl phenyl ether increased with increasing surface acidity of the catalyst. Among the tested catalysts, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst with the largest surface acidity showed the highest conversion of phenethyl phenyl ether.

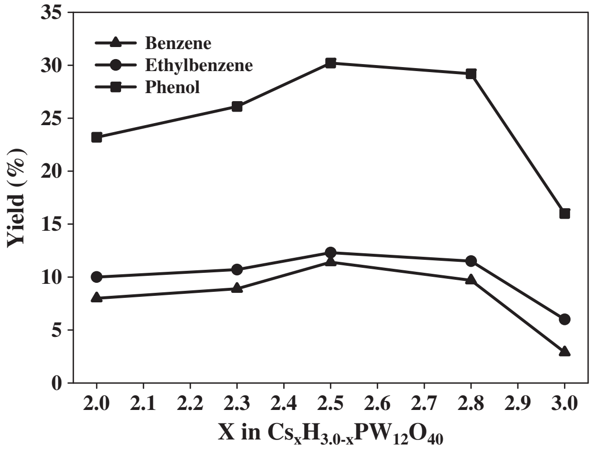

Fig. 3. Yields for phenol, benzene, and ethylbenzene plotted as a function of cesium content in $Cs_xH_{3.0-x}PW_{12}O_{40}$. Reaction condition: Temperature = 200 °C, Pressure = 10 - bar (N_2), Time = 1 h.

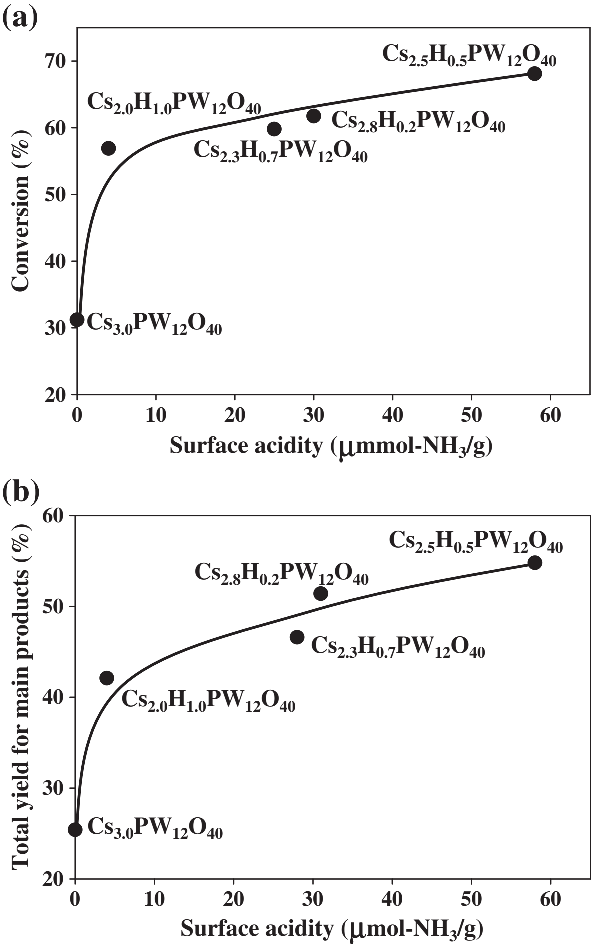

Fig. 4. Correlations (a) between conversion of phenethyl phenyl ether over $Cs_xH_{3.0-x}PW_{12}O_{40}$ and surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$, and (b) between total yield for main products (phenol, benzene, toluene, and ethylbenzene) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ and surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$. Surface acidity data were taken from a literature [19]. Reaction condition: Temperature = 200 °C, Pressure = 10 bar (N_2), Time = 1 h.

Fig. 4b shows the correlation between total yield for main products (phenol, benzene, toluene, and ethylbenzene) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ and surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$. The correlation shows that total yield for main products is also closely related to the surface acidity of the catalyst. Total yield for main products increased with increasing surface acidity of the catalyst. It is concluded that cesium-exchanged $Cs_xH_{3.0-x}PW_{12}O_{40}$ heteropolyacid catalysts served as an efficient acid catalyst in the decomposition of phenethyl phenyl ether to aromatics. Surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$ played an important role in determining the catalytic performance in the decomposition of phenethyl phenyl ether.

Catalytic performance of $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ in the decomposition of phenethyl phenyl ether is also listed in Table 1 for comparison purpose. Conversion of phenethyl phenyl ether (51.1%) and total yield for main products (36.2%) over $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ were higher than those over $Cs_{3.0}PW_{12}O_{40}$ (31.2% and 25.4%, respectively) but were lower than those over $Cs_{2.0}H_{1.0}PW_{12}O_{40}$ (56.9% and 42.2%, respectively). Judging from the fact that surface acidity of $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ (2 μmol-NH_3/g-cat) was higher than that of $Cs_{3.0}PW_{12}O_{40}$ (1 μmol-NH_3/g-cat) but was lower than that of $Cs_{2.0}H_{1.0}PW_{12}O_{40}$ (5 μmol-NH_3/g-cat) [19], it can also be

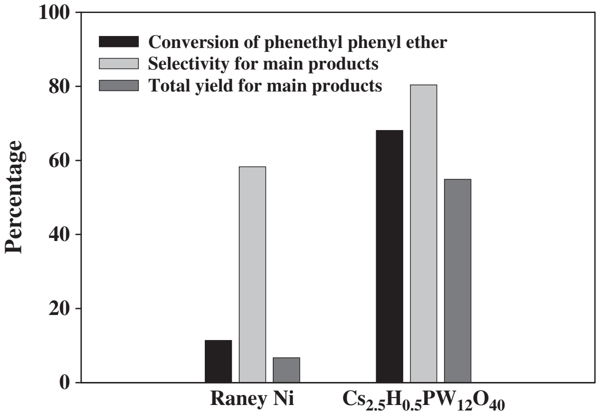

Fig. 5. Catalytic performance in the decomposition of phenethyl phenyl ether over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst and Raney Nickel catalyst. Reaction condition: Temperature = 200 °C, Pressure = 10 bar (N_2), Time = 1 h.

concluded that surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$ played an important role in determining the catalytic performance in the target reaction.

3.4. Comparison of catalytic performance between $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst and Raney Nickel catalyst in the decomposition of phenethyl phenyl ether

Raney Nickel catalyst is a well known catalyst for lignin decomposition [15]. Fig. 5 compares the catalytic performance between $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst and Raney Nickel catalyst in the decomposition of phenethyl phenyl ether. Conversion of phenethyl phenyl ether over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (68.1%) was much higher than that over Raney Nickel catalyst (11.4%). Total yield for main products produced by the acid catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (54.9%) was much higher than that produced by Raney Nickel catalyst (6.7%). It is concluded that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was more efficient than Raney Nickel catalyst in the decomposition of phenethyl phenyl ether.

4. Conclusions

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 phenethyl phenyl ether to aromatics was studied in this work. Conversion of phenethyl phenyl ether and total yield for main products (phenol, benzene, toluene, and ethylbenzene) over $Cs_xH_{3.0-x}PW_{12}O_{40}$ (X = 2.0–3.0) was in the range of 31.2–68.1% and 25.4–54.9%, respectively. Conversion of phenethyl phenyl ether 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, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with the largest surface acidity showed the highest conversion of phenethyl phenyl ether and total yield for main products. It is concluded that surface acidity of $Cs_xH_{3.0-x}PW_{12}O_{40}$ played an important role in determining the catalytic performance in the decomposition of phenethyl phenyl ether.

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