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Lignin Depolymerization into Aromatic Monomers
Using Supported Metal Catalysts in Supercritical WaterAritomo YAMAGUCHI^{†1)*}, Naoki MIMURA^{†1)}, Atsushi SEGAWA^{†2)}, Hitoshi MAZAKI^{†2)}, and Osamu SATO^{†1)}^{†1)} Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST),
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Lignin is a potentially useful source of aromatic monomers. Depolymerization of organosolv-lignin into aromatic monomers was investigated over charcoal-supported palladium, platinum, rhodium, or ruthenium catalyst (Pd/C, Pt/C, Rh/C, and Ru/C) in supercritical water (658–688 K) for reaction times of 0.5–3 h. Ru/C showed no catalytic activity for lignin depolymerization into aromatic monomers, but did catalyze conversion of lignin into gaseous products such as methane and carbon dioxide. In contrast, Pd/C, Pt/C, and Rh/C showed catalytic activity for lignin depolymerization into aromatic monomers. Yield of aromatic monomers decreased in the order Pd/C > Rh/C > Pt/C at 673 K and 1 h. Pd/C showed higher selectivity for phenolic aromatic monomers than Rh/C and Pt/C. Investigation of the activity of Pd/C at 673 K over time (0.5–3 h) found the highest yield of aromatic monomers (12.7 %) was obtained at 2 h.

KeywordsLignin depolymerization, Aromatic monomer, Supercritical water, Supported metal catalyst,
Organosolv-lignin**1. Introduction**

Conversion and utilization of lignocellulosic biomass, which consists of cellulose, hemicellulose and lignin, has high potential for reducing carbon dioxide emissions and establishing a sustainable society^{1)–3)}. Cellulose and hemicellulose are polysaccharides that can be converted into valuable products and fuels^{4)–10)}. Lignin is a three-dimensional polymer consisting of aromatic monomers cross-linked *via* C–O–C and C–C bonds, so conversion of lignin into valuable aromatic products is important to achieve carbon-efficient use of lignocellulosic biomass. Lignin can be converted into aromatic products by depolymerization^{11)–14)} but generally results in a wide range of aromatic monomers^{15)–29)}. Such mixtures of products must be separated or upgraded to homogeneous products before commercial use. For example, depolymerization of lignin into simple phenolic monomers as achieved with a two-step process of depolymerization in water/butanol solution at 573 K for 2 h followed by catalytic cracking using a CeO₂–ZrO₂–Al₂O₃–FeO_x catalyst at 673 K for 2 h, resulting in about 19 % yield of aromatic monomers^{30)–32)}. In this man-

uscript, we report lignin depolymerization into simple phenolic monomers by a one-step simple procedure.

Previously, we reported the cleavage of bonds between aromatic monomers in lignin model compounds *via* a one-step process using supported metal catalysts (palladium, platinum, and rhodium) and supercritical water (673 K), which did not require the addition of hydrogen gas and so prevented aromatic hydrogenation^{33),34)}. We predicted the yields of aromatic monomers from lignin using supported metal catalysts in supercritical water based on our previously reported data on the bond cleavage reactions of lignin model compounds, along with published data regarding the percentages of various linkage types in lignin derived from softwood and hardwood biomass³⁵⁾. We also investigated the direct conversion of lignocellulosic biomass, Japanese cedar, into aromatic monomers with a maximum yield of 19 %³⁶⁾ and reported the two-step conversion of lignocellulosic biomass, bagasse, using Pt/C for converting the cellulose, hemicellulose, and lignin in lignocellulosic biomass into useful chemicals³⁷⁾. The yield of monomeric aromatics was 40 %.

The present study investigated the conversion of organosolv-lignin, which is generally a low-denaturation lignin, using our one-step process to achieve depolymerization of organosolv-lignin, and obtained a maximum yield of aromatic monomers of 12.7 % using a

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supported palladium catalyst.

2. Experimental

2.1. Materials

Charcoal-supported palladium, platinum, rhodium, and ruthenium catalysts (Pd/C, Pt/C, Rh/C, and Ru/C, with 5 wt% metal loading) were purchased from Wako Pure Chemical Industries, Ltd. Lignin (organosolv-lignin powder) was purchased from Aldrich and used without further purification.

2.2. Characterization

The dispersion of metal particles was defined as the fraction of metallic atoms present on the surface, which was measured by adsorbed hydrogen at 313 K in a volumetric unit (Quantachrome, Autosorb-1). Saturation monolayer uptakes were estimated by extrapolating isotherms to zero pressure. Samples were pretreated in flowing H₂ at 643 K for 0.5 h and evacuated at 643 K for 0.5 h to remove chemisorbed hydrogen. X-ray diffraction (XRD) patterns of the catalysts were recorded using a Rigaku SmartLab with Cu K α radiation (λ = 0.15406 nm) using 30 mA current and 40 kV voltage with a 2θ step size of 0.02°.

2.3. Reaction Procedure

Depolymerization of lignin was performed using a stainless steel (Japanese Industrial Standard: SUS316) tube (inner volume, 6.0 cm³) as the batch reactor. Catalyst (0.15 g), lignin (0.10 g), and water (3.0 g) were loaded into the reactor. The reactor was purged with argon gas and then submerged into a molten-salt bath (KNO₃-NaNO₃) heated to the reaction temperature (typically 673 K) for the reaction time (typically 1 h). The partial pressure of water under typical reaction conditions was 37.1 MPa in the supercritical phase. After the reaction was complete, the reactor was submerged in a water bath to cool to ambient temperature. Gaseous products were collected using a glass syringe and analyzed by gas chromatography (GC-8A, Shimadzu Corp.) using a ShinCarbon ST column (Shinwa Chemical Industries Ltd.) and a thermal conductivity detector. Liquid and solid products were recovered from the reactor with tetrahydrofuran and filtered to separate the tetrahydrofuran-insoluble solid fraction from the tetrahydrofuran-soluble fraction. Products dissolved in the tetrahydrofuran solution were quantitatively analyzed using a gas chromatograph (HP-6890, Agilent) equipped with a flame ionization detector and a DB-WAX capillary column (Agilent). The molecular weight distributions of products in the tetrahydrofuran solution were determined by a gel permeation chromatograph (GPC, Shimadzu) with a refractive index detector and a UV-Vis detector (λ = 254 nm) equipped with GPC columns (KF801 and KF803 L, Shimadzu). Standard calibration was performed with polystyrene standards (average molecular weight range 492–21600 g

mol⁻¹), 2-phenethyl phenyl ether (molecular weight 198.3 g mol⁻¹), and bibenzyl (molecular weight 182.3 g mol⁻¹). The amount of solid product (char plus unreacted lignin) was estimated by subtracting the weight of the catalyst loaded in the reactor from the weight of the tetrahydrofuran-insoluble solid fraction. Product yield based on carbon and gas composition was defined as follows:

$$\text{Product yield(\%)} = \frac{(\text{moles of carbon in product})}{(\text{moles of carbon in lignin sample}) \times 100} \quad (1)$$

$$\text{Gas composition(\%)} = \frac{(\text{moles of gas product})}{(\text{sum of moles in gas product}) \times 100} \quad (2)$$

3. Results and Discussion

3.1. Lignin Depolymerization in Supercritical Water at 673 K

The molecular formula of the lignin used in this study was C_{42.39}H_{45.46}O_{12.15}, as determined by ultimate CHNS analyzer (Perkin-Elmer, model 2400). The molecular weight was between 1000 and 1500, as determined by GPC (Waters, GPC150C plus)³⁸. The metal dispersions of the catalysts Pd/C, Pt/C, Rh/C, and Ru/C were 11, 21, 19, and 43 %, respectively, based on hydrogen adsorption, indicating that metal particles were dispersed on the carbon support surfaces.

Previously, we reported that supercritical water (673 K) and supported metal catalysts can be used to cleave the β -O-4 and 4-O-5 linkages in lignin model compounds^{33,34}. This study used the same reaction conditions to examine depolymerization of organosolv-lignin (**Fig. 1** and **Table 1**). Aromatic monomers (*e.g.*, benzene, toluene, phenol, cresol, and ethylphenol) were obtained both with and without catalyst (**Fig. 1**). Aromatic monomer yield decreased in the order Pd/C (10.7 %) > Rh/C (7.8 %) > Pt/C (6.4 %) > no catalyst (1.9 %) > Ru/C (1.8 %), indicating that Pd/C, Pt/C, and Rh/C, but not Ru/C, had catalytic activity for lignin depolymerization in supercritical water. The yields of aromatic monomer from the organosolv-lignin were lower than those from the lignocellulosic biomass, Japanese cedar (*ca.* 17 %) [34], indicating that the preparation method of lignin was important for conversion. The lower yields from organosolv-lignin might depend on the denaturation of lignin during extraction in organic solvent.

Previously, we investigated the conversion of lignin to gas products over Pd/C, Pt/C, Rh/C, and Ru/C in supercritical water at 673 K^{39–42}. We concluded that lignin was converted to gas products *via* two steps involving lignin decomposition to alkylphenols and formaldehyde *via* hydrolysis, followed by conversion of the alkylphenols and formaldehyde to methane, carbon dioxide, and hydrogen over the supported metal catalyst. In the absence of catalyst, the alkylphenols and

formaldehyde repolymerized to form solid char. In the present study, Pt/C, Rh/C, and Pd/C showed low catalytic activity for conversion of lignin to gas products (Table 1), and suppressed repolymerization of alkylphenols and formaldehyde to a solid, resulting in the formation of aromatic products.

Lignin consists of aromatic monomers with methoxy and phenolic hydroxyl groups, so the products of lignin depolymerization tend to be phenolic monomers^{15)~28)}. In the present study, the yields of phenolic monomers obtained were 8.8, 3.6, and 1.6 % using Pd/C, Rh/C, and Pt/C, so 82, 46, and 25 % of the total aromatic monomers were phenolic monomers, respectively. Phenolic compounds were preferentially obtained from lignin over Pd/C catalyst in supercritical water, whereas aromatic compounds without phenolic groups were preferentially obtained from lignin over Pt/C catalyst. Previously, we checked the stability of methoxy and

phenolic hydroxyl groups over Pd/C and Pt/C in supercritical water using anisole and phenol as model compounds³⁴⁾. Anisole was converted to phenol and benzene, indicating that the methoxy group was either decomposed or converted into a phenol group. In addition, most of the phenol was recovered from the reaction in the presence of Pd/C, whereas part of the phenol was converted to benzene by hydrodeoxygenation in the presence of Pt/C, suggesting that phenolic hydroxyl groups are removed by Pt/C. These results explain why the aromatic monomers obtained in the present study did not have methoxy groups, and why phenolic aromatic monomers were preferentially obtained in the presence of Pd/C and non-phenolic aromatic monomers were preferentially obtained in the presence of Pt/C.

The gas and solid yields obtained at 673 K are shown in Table 1, together with the percentage composition of the gas product determined by gas chromatography and the gravimetric method. For example, aromatic monomer (10.7 %), gas (17.9 %), and solid (8.5 wt%) were obtained using Pd/C. The material balance was less than 100 %, but the other products could not be identified, probably because lignin was depolymerized into aromatic oligomers with two or three aromatic rings that were soluble in tetrahydrofuran. The molecular weight distributions of products in the tetrahydrofuran solution were estimated by GPC analysis (Fig. 2). The retention time of tetrahydrofuran solution after lignin depolymerization was longer than that of organosolv-lignin, indicating that the molecular weight of lignin had decreased after the reaction. Peaks with number average molecular weights of 267, 156, 109, and 95 were observed in the tetrahydrofuran solution from lignin depolymerization using Pd/C, indicating the presence of aromatic oligomers with two or three aromatic rings in the product solution.

The catalysts Pt/C, Rh/C, and Pd/C were characterized before and after the reaction by XRD (Fig. 3). The sharp diffraction peak at 40.1 degree due to Pd(111) was observed in the XRD pattern of the Pd/C catalyst before the reaction, and the mean crystalline size was 24.2 nm from the Scherrer equation. The crystalline size in the Pd/C catalyst did not change significantly after the reaction (24.3 nm). Conversely, the crystalline size of Pt (2.5 nm before the reaction) in Pt/C

Fig. 1 Yields of Aromatic Monomers from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm^{-3}) for 1 h at 673 K with or without Supported Metal Catalyst

Table 1 Gas Yield and Composition, and Solid Yield (including unreacted lignin), from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm^{-3}) for 1 h at 673 K with or without Supported Metal Catalyst

Catalyst	Gas yield [%]	Gas composition [%]				Solid yield [wt%]
		H ₂	CH ₄	CO ₂	C ₂ H ₆	
Pd/C	17.9	21.0	13.3	62.2	3.6	8.5
Pt/C	25.5	9.4	24.3	63.0	3.3	10.9
Rh/C	29.1	6.0	36.6	55.0	2.3	5.3
Ru/C	73.5	5.8	44.7	48.8	0.8	0.0
None	8.2	7.0	33.7	57.2	2.1	26.1

Fig. 2 Time Course of UV Intensity by GPC Analysis for (a) Organosolv-lignin Dissolved in Tetrahydrofuran and (b) Tetrahydrofuran Solution from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm^{-3}) for 1 h at 673 K with Pd/C

Fig. 3 XRD Patterns for Fresh Catalysts, (a) Pt/C, (c) Rh/C, and (e) Pd/C before Reaction and Used Catalysts, (b) Pt/C, (d) Rh/C, and (f) Pd/C after the Repeated Reactions in Fig. 1

increased to 3.3 nm after the reaction. A diffraction peak at around 41 degree due to Rh(111) was not observed clearly in Rh/C before the reaction, but a broad peak at around 41 degree was observed in Rh/C after the reaction, indicating that the Rh metal species had also aggregated slightly.

3.2. Lignin Depolymerization in Supercritical Water at Different Temperatures

Lignin depolymerization was examined at higher and lower temperature than that used in the previous experiment. Aromatic monomers such as benzene, toluene, phenol, cresol, and ethylphenol, were obtained from lignin using the Pd/C, Pt/C, Rh/C, and Ru/C catalysts in supercritical water at 658 K for 1 h (Fig. 4). Aromatic monomer yield with Pd/C (6.9 %) or Rh/C (6.3 %) was lower at 658 K than at 673 K. The aromatic monomer

Fig. 4 Yields of Aromatic Monomers from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm^{-3}) for 1 h at 658 K with or without Supported Metal Catalyst

yield with Pt/C (6.7 %) at 658 K was comparable with that obtained at 673 K. In contrast, the aromatic monomer yield with Ru/C (3.3 %) at 658 K was higher than at 673 K, suggesting that the activity of Ru/C for conversion of aromatic monomers to gas products was lower at 658 K than at 673 K. The gas yield obtained for each of the catalysts was lower at 658 K than at 673 K (Table 2).

Total aromatic monomer yield using Pd/C (10.2 %) or Rh/C (6.7 %) was slightly lower at 688 K than at 673 K (Fig. 5). The gas yields obtained with Pd/C and Rh/C at 688 K (Table 3) were slightly higher than those obtained at 673 K, indicating greater conversion of the aromatic monomers to gas products at higher temperature. The aromatic monomer yield obtained with Pt/C (7.7 %) was slightly higher than that obtained at 673 K. Pd/C catalyst provided the best yield (10.7 %) of aromatic monomers at 673 K.

3.3. Lignin Depolymerization in Supercritical Water as a Function of Reaction Time

Lignin depolymerization using Pd/C or no catalyst at 673 K was investigated as a function of reaction time (0.5–3 h; Fig. 6). Total aromatic monomer yield without catalyst was less than 2.1 % even at 3 h. In contrast, total aromatic monomer yield using Pd/C increased with reaction time up to 2 h (12.7 %) and then decreased slightly at 3 h (11.3 %), indicating that Pd/C has high catalytic activity for lignin depolymerization.

The yields of gas products such as methane, hydrogen, and carbon dioxide were 15.0, 18.5, 20.1, and 21.9 % at 0.5, 1, 2, and 3 h, respectively. The decrease in aromatic monomer yield at reaction times from 2 to 3 h might be caused by conversion of aromatic monomer to gas products. The yields of phenol and cresol were 5.8 % and 2.7 %, respectively, at 2 h. In contrast to previous studies in which many aromatic compounds were obtained^{15)–28)}, in the present study phenol accounted for almost half of the aromatic monomer yield obtained using Pd/C. Previously, we checked the stability of the ethyl group over Pd/C in supercritical water at 673 K using ethylbenzene as a model compound³³⁾. Toluene and benzene were obtained from ethylbenzene, indicating that Pd/C catalyzed the cleavage of the C–C bond. Thus, phenol and cresol were mainly obtained from lignin depolymerization using Pd/C.

We also investigated the reusability of the Pd/C catalyst for lignin depolymerization in supercritical water at 673 K. The catalyst was separated from the liquid product by filtration after each reaction, and dried at 393 K overnight in air. The yield of aromatic monomers using Pd/C decreased with longer reaction times (Fig. 7), indicating that the Pd/C catalyst deactivated during the reaction. Pd metal particles did not aggregate during the reaction based on the XRD patterns (Fig. 3). Therefore, catalyst deactivation might result from carbon precipitation on the Pd surface after the reaction. We will consider methods of catalyst regeneration in the future.

4. Conclusion

Charcoal-supported catalysts (Pd/C, Pt/C, Rh/C, and Ru/C) were used to depolymerize lignin in supercritical water. Ru/C catalyzed conversion of lignin into gas

Fig. 5 Yields of Aromatic Monomers from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm⁻³) for 1 h at 688 K with or without Supported Metal Catalyst

Table 2 Gas Yield and Composition, and Solid Yield (including unreacted lignin), from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm⁻³) for 1 h at 658 K with or without Supported Metal Catalyst

Catalyst	Gas yield [%]	Gas composition [%]				Solid yield [wt%]
		H ₂	CH ₄	CO ₂	C ₂ H ₆	
Pd/C	16.9	21.8	12.4	64.2	1.6	8.6
Pt/C	24.6	8.0	23.7	64.8	3.5	13.0
Rh/C	20.3	6.5	33.9	57.3	2.3	6.7
Ru/C	48.9	6.2	40.3	51.8	1.6	0.0
None	5.9	4.5	28.6	65.3	1.6	28.4

Table 3 Gas Yield and Composition, and Solid Yield (including unreacted lignin), from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm⁻³) for 1 h at 688 K with or without Supported Metal Catalyst

Catalyst	Gas yield [%]	Gas composition [%]				Solid yield [wt%]
		H ₂	CH ₄	CO ₂	C ₂ H ₆	
Pd/C	18.2	22.9	13.9	59.9	3.3	8.9
Pt/C	26.0	8.7	25.0	62.4	3.8	12.9
Rh/C	31.7	5.9	39.6	52.2	2.3	3.2
Ru/C	78.1	5.7	45.8	47.9	0.6	0.0
None	8.6	13.6	29.5	54.8	2.1	24.2

Fig. 6 Yields of Aromatic Monomers from Lignin Depolymerization in Supercritical Water (density, 0.5 g cm^{-3}) at 673 K with Pd/C (a) or without Catalyst (b) as a Function of Reaction Time

products, whereas Pd/C, Pt/C, and Rh/C catalyzed depolymerization of lignin into aromatic monomers. Aromatic monomer yields at 673 K and 1 h decreased in the order Pd/C > Rh/C > Pt/C. The maximum yield of aromatic monomers (12.7 %) was obtained with Pd/C at 673 K for 2 h.

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Fig. 7 Lignin Depolymerization to Aromatic Monomers Using Recycled Pd/C in Supercritical Water for 1 h at 673 K and Water Density 0.5 g cm^{-3}

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要 旨

担持金属触媒を用いた超臨界水中でのリグニン解重合反応による芳香族モノマーへの変換

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リグニンは有用な芳香族化合物の供給源として期待される。我々は、活性炭担持パラジウム、白金、ロジウム、およびルテニウム触媒 (Pd/C, Pt/C, Rh/C および Ru/C) を用いて超臨界水中 (658 ~ 688 K) にて反応時間 0.5 ~ 3 時間で、オルガノソルブリグニンの解重合反応による芳香族モノマーへの変換を検討した。Ru/C 触媒は、リグニン解重合反応による芳香族モノマー製造には活性を示さず、メタンや二酸化炭素などのガス生成物への変換に活性を示した。一方で、Pd/C, Pt/C および Rh/

C 触媒は、リグニン解重合反応による芳香族モノマー製造に活性を示した。673 K にて反応時間 1 時間では、Pd/C > Rh/C > Pt/C の順で芳香族化合物モノマー収率が高かった。Pd/C 触媒では、Rh/C や Pt/C を用いたときよりもフェノール系芳香族モノマーの選択性が高かった。Pd/C 触媒を用いて 673 K にて経時変化を検討したところ、反応時間 2 時間で芳香族モノマーの最高収率 12.7 % が得られた。