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Noguchi, Ibuki

Ichihashi, Yuichi

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Selective Synthesis of Hydroquinone via the Liquid-phase Oxidation of Benzene over Cu(II)-2,2'-bipyridine Complexes in a Slug Flow Reactor

Ibuki Noguchi[†1] and Yuichi Ichihashi*[†1],[†2]

[†1] Dept. of Chemical Science and Engineering, Graduate School of Engineering, Kobe University,
Rokkodai, Nada-ku, Kobe 657-8501, JAPAN
[†2] Research Center for Membrane and Film Technology, Kobe University, Rokkodai, Nada-ku, Kobe 657-8501, JAPAN

The liquid-phase oxidation of benzene using Cu(II)-2,2'-bipyridine complexes as catalysts and molecular oxygen as oxidants has been investigated. The reaction activity of three types of catalysts with one, two, and three bipyridine molecules coordinated to Cu(II) ions was compared in a batch reactor, and [Cu(bipy)Cl$_2$] with coordination of one bipyridine molecule obtained the highest yield of hydroquinone. The coordination structure of the complexes and ease of ligand desorption are speculated to have influenced the reaction activity. The reactor was changed from a batch reactor to a slug flow reactor to investigate the effect of different reactors on the reaction. The results indicate that the reaction in the slug flow reactor obtained a hydroquinone yield that was 5.7 times higher than that in the batch reactor. The formation of the slug flow is assumed to have continuously supplied oxygen to the liquid phase efficiently, which improved the hydroquinone yield.

1. Introduction

The selective oxidation of hydrocarbons is a useful synthetic method for high-value chemical raw materials and pharmaceuticals; however, it is challenging to achieve. High temperatures lead to complete oxidation and the formation of CO_2 and tar-like substances. Conversely, despite complete oxidation being suppressed to negligible levels at room temperature, partial oxidation does not proceed. Therefore, a suitable catalyst for selective hydrocarbon oxidation under mild conditions must be developed.

Dixon and Norman achieved the first direct oxidation of benzene in the liquid phase in the 1960s using iron(II) sulfate–H_2O_2, also known as Fenton's reagent[1]; H_2O_2 has also been used as an oxidant in other studies[2]~[9]. However, H_2O_2 is expensive and difficult to handle under high pressures and other conditions; therefore, it is unsuitable for commercialization. Fleszar et al. used molecular oxygen as an oxidant, which is inexpensive and easy to handle[10]. Subsequently, researchers synthesized phenol via the direct oxidation of benzene using molecular oxygen as the oxidant on various catalysts in the presence of a reducing reagent[11]~[13].

We previously synthesized phenol via the one-step oxidation of benzene in the presence of metal complex catalysts such as copper and vanadium, molecular oxygen as the oxidant, and L-ascorbic acid and zinc powder as the reducing agents[14]~[19]. However, this synthesis may generate byproducts such as hydroquinone, catechol, and benzoquinone[20]. Among these products, hydroquinone has applications as a reducing agent in photographic development, polymerization inhibitor in polymer synthesis, brightening agent, automobile fuel, and an antioxidant in rubber and food[21]. This suggests that the selective synthesis of hydroquinone via the oxidation of benzene is extremely useful.

In this study, we achieved the selective synthesis of hydroquinone via the liquid-phase oxidation of benzene using molecular oxygen as the oxidant. In this regard, different Cu(II)-2,2'-bipyridine complexes, which effectively catalyze the one-step oxidation of benzene and other aromatics into quinones[22]~[24], were used as catalysts. The reaction conditions for the mild and efficient synthesis of hydroquinone were investigated using an autoclave and a closed-type reactor. In addition, the reactor was changed from an autoclave to a slug flow reactor to improve hydroquinone formation. Slug flow is an alternating and intermittent flow of two partially miscible phases and can be achieved over a wide
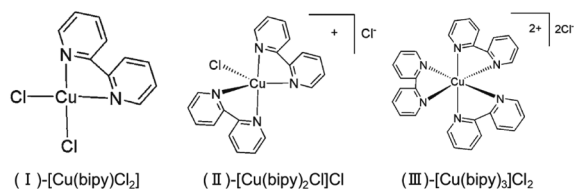
Fig. 1　Structures of the Three As-synthesized Cu(II)-2,2'-bipyridine Complexes

range of micro-to-millimeter flow scales[25]. The formation of a slug flow increases the interfacial area between the gas and liquid phases and leads to the formation of a circulating flow inside the slug; both these factors promote the mass transfer between the two phases. In this reaction, mass transfer of oxygen forming gas-phase slag to the liquid-phase side is important. Specifically, this is the dissolution of oxygen into the solution. The amount of dissolved oxygen is estimated to increase as the gas-liquid interfacial area increases. In addition, the internal circulation flow helps renew the surface concentration of the slug. Therefore, the difference between the interface and equilibrium concentrations, which is the driving force of the mass transfer, is maintained, and mass transfer between the two phases is facilitated. Furthermore, because oxygen is continuously supplied, oxygen consumed during the reaction can be easily compensated. Therefore, oxygen continues to dissolve efficiently in the liquid phase owing to the formation of the slug flow. Several studies have demonstrated that introducing a slug flow promoted the mass transfer between the two phases and improved the reaction efficiency[26)~30)]. Overall, using the slug flow reactor is expected to improve the efficiency of hydroquinone formation in this reaction.

2. Experimental

2. 1. Catalyst Preparation
2. 1. 1. Reagents
Nacalai special-grade copper(II) chloride, 2,2'-bipyridine, and ethanol were purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and used to prepare the catalysts.
2. 1. 2. Preparation of Cu(II)-2,2'-bipyridine Complexes
Three Cu(II)-2,2'-bipyridine complexes with different ligands, namely [Cu(bipy)Cl₂], [Cu(bipy)₂Cl]Cl, and [Cu(bipy)₃]Cl₂, were prepared (**Fig. 1**). Briefly, 1 mmol of CuCl₂ was dissolved in 3 mL of ethanol; this solution was named Solution A. Subsequently, 1 mmol of 2,2'-bipyridine was dissolved in 5 mL of ethanol; this solution was named Solution B. Solution A was added to Solution B while continuously stirring. After the appearance of a precipitate, the mixture was stirred for another 10 min. Subsequently, 8 mL of the

mixture of Solutions A and B was separated into 2 mL portions and allowed to dry spontaneously for 1 d into a crystal solid of [Cu(bipy)Cl₂]. The same procedure was followed for the preparation of [Cu(bipy)₂Cl]Cl and [Cu(bipy)₃]Cl₂ with 2 and 3 equiv. of 2,2'-bipyridine in Solution B, respectively.

2. 2. Characterization
Ultraviolet-visible (UV-vis) spectra were measured in acetonitrile using V-650CA (JASCO Corp., Tokyo, Japan).

The coordination states of the three Cu(II)-2,2'-bipyridine complexes were investigated using X-ray absorption fine structure (XAFS) measurements (SPring-8 BL14B2, Hyogo, Japan). The XAFS spectra near the Cu K-edge were measured at room temperature using the transmission method, and analyzed using the REX2000 software (Rigaku Corp., Tokyo, Japan). The spectra of CuO, Cu₂O, Cu foil, and Cu(II) phthalocyanine (CuPc) were used as the reference standards for curve fitting.

2. 3. Liquid Phase Oxidation
2. 3. 1. Reagents
Nacalai special-grade benzene, phenol, L-ascorbic acid, acetic acid, and acetonitrile were used. O₂ gas was purchased from K. K. Kobe Oxygen (Hyogo, Japan).
2. 3. 2. Oxidation of Benzene Using the Autoclave
Four different solvent mixtures of 2.5 mL each (Solvents 1, 2, 3, and 4) were used in the reaction. The compositional ratios (acetonitrile : water : acetic acid) of the four solvent mixtures were as follows for Solvents 1-4, respectively: 4 : 0 : 1, 3 : 1 : 1, 2 : 2 : 1, and 1 : 3 : 1. The catalyst (0.1 mmol), benzene (0.25 mL), and L-ascorbic acid (2.8 mmol) were added to a glass pressure-resistant autoclave (Büchiglasuster, Uster, Switzerland). The reaction was performed in an O₂ atmosphere (0.0-0.6 MPa) at temperatures ranging between 293 K and 343 K for 1-5 h under continuous stirring using a magnetic stirrer. The products were analyzed via gas chromatography (GC; GC-2014, Shimadzu Corp, Kyoto, Japan). A mixture of Nacalai special-grade toluene (0.5 vol%) and acetonitrile was used as the internal standard, which was added to the solution after the reaction.
2. 3. 3. Oxidation of Phenol Using the Autoclave
Phenol oxidation was also conducted via the same process as benzene oxidation using the [Cu(bipy)Cl₂] complex catalyst (0.1 mmol), phenol (0.22 mL), and Solvent 1 (2.5 mL) for 1-5 h. The reaction temperature was 323 K and the oxygen pressure was 0.3 MPa. The products were analyzed via GC, as indicated in Section **2. 3. 2.**
2. 3. 4. Oxidation of Benzene Using the Slug Flow Reactor
A schematic of the slug flow reactor, which is a closed circulation system, is shown in **Fig. 2**. [Cu(bipy)-
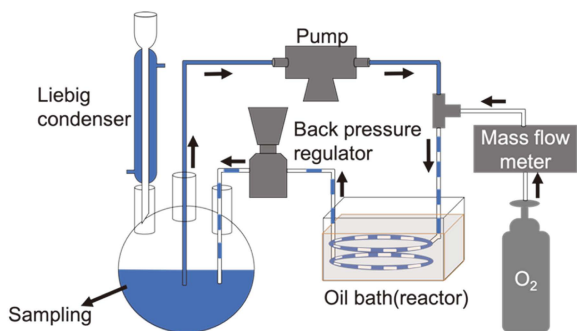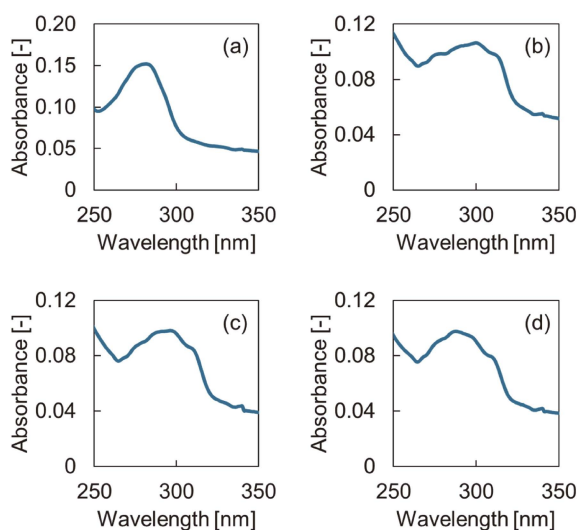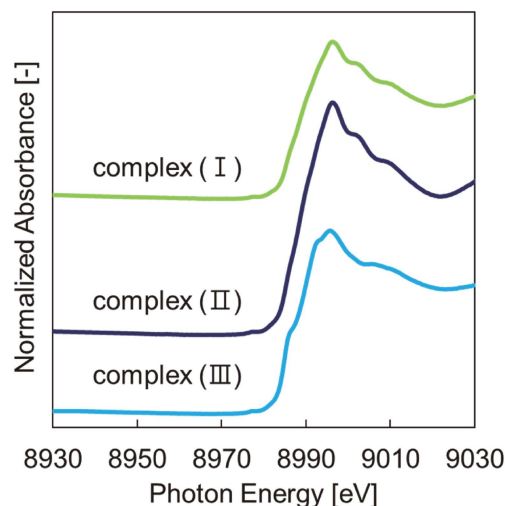
Fig. 2 Schematic of the Slug Flow Reactor

Fig. 4 Cu K-edge X-ray Absorption Near Edge Spectroscopy Spectra of the Cu(II)-2,2'-bipyridine Complexes: (I)-[Cu(bipy)Cl$_2$], (II)-[Cu(bipy)$_2$Cl]Cl, and (III)-[Cu(bipy)$_3$]Cl$_2$

Fig. 3 UV-bis Spectra of (a) 2,2'-Bipyridine, (b) [Cu(bipy)Cl$_2$], (c) Cu(bipy)$_2$Cl]Cl, and (d) [Cu(bipy)$_3$]Cl$_2$ in Acetonitrile
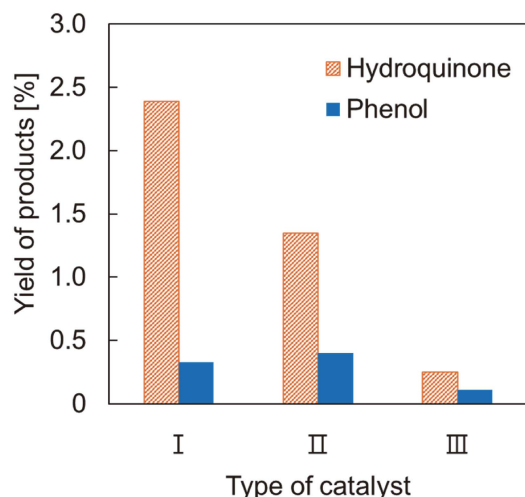
3. Results and Discussion

3. 1. Characterization of Each Synthesized Cu(II)-2,2'-bipyridine Complex

UV-vis spectra were measured for 2,2'-bipyridine and the three complexes synthesized (**Fig. 3**). In acetonitrile, 2,2'-bipyridine demonstrated an absorption peak at 280 nm. However, this peak was not observed for any other sample, suggesting that nearly all bipyridines were coordinated to Cu.

Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra were acquired to confirm the Cu-centered coordination structures of the three Cu(II)-2,2'-bipyridine complexes. The pre-edge peak at approximately 8977 eV, which was observed in all three complexes, corresponded to the 1s → 3d transition of Cu(II) (**Fig. 4**). The peak at approximately 8981 eV in the XANES spectra of CuO and Cu$_2$O, corresponding to the 1s → 4pπ transition of Cu(I) (Fig. S1), was not observed for all three complexes. In addition, the Cu(I) peak at 8977 eV, which suggests the presence of filled 3d orbitals, was not observed. These results confirm the divalent state of Cu in all three complexes.

The Fourier-transform EXAFS spectra of all three complexes were acquired to determine the radial distribution function (Fig. S2). [Cu(bipy)$_3$]Cl$_2$ exhibited the highest peak intensities, whereas [Cu(bipy)Cl$_2$] showed the lowest. This result correlates with the coordination number of 2,2'-bipyridine in each complex. Each peak in the first coordination sphere is attributed to Cu–N[31]. Furthermore, inverse Fourier-transform spectra were obtained using the radial distribution function, and the coordination number of Cu and interatomic distances around Cu were calculated using the nonlinear

Cl$_2$] was used as the catalyst, and a solvent mixture of acetonitrile : water : acetic acid with a ratio of 1 : 1 : 0.5-2 was used. Polytetrafluoroethylene tubing with a diameter of 1 mm and a three-way joint with an inner diameter of 2.4 mm were used to feed a mixed solution of the catalyst (2.0 mmol), the solvent (50 mL), benzene (5.0 mL), and L-ascorbic acid (11.2 mmol), as well as the O$_2$ gas, into the reactor. The length of the reactor in the section heated by the oil bath was 6.0 m, the slug linear velocity was 5.5 cm/s, the liquid slug length was 0.55 cm, and the gas slug length was 0.825 cm. The reaction gauge pressure was varied by squeezing the back pressure regulator. The inflow rates of the pump and O$_2$ were adjusted to maintain a constant slug linear velocity, liquid slug length, and gas slug length despite being under pressurization. Oxidation was performed for 4 h in a batch operation under a reaction gauge-pressure and temperature of 0.00-0.15 MPa and 325-345 K, respectively. The products were analyzed via GC, as indicated in Section **2. 3. 2.**

Reactor: batch reactor, catalysts: (I)-[Cu(bipy)Cl$_2$], (II)-[Cu(bipy)$_2$Cl]-Cl, and (III)-[Cu(bipy)$_3$]Cl$_2$, solvent: Solvent 1, reaction temperature: 323 K, oxygen pressure: 0.3 MPa, reaction time: 4 h.

Fig. 5　Product Yields of the Oxidation of Benzene over the Cu(II)-2,2'-bipyridine Complexes
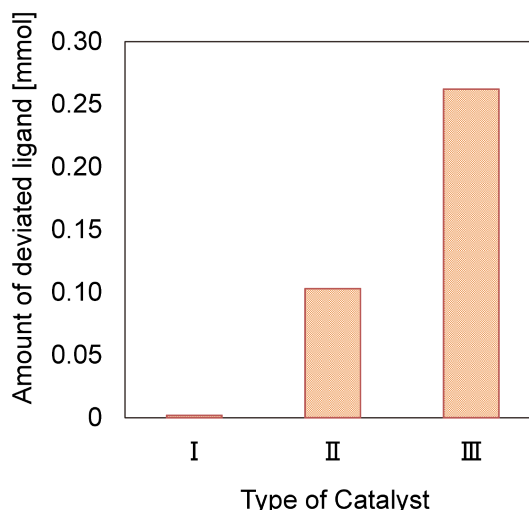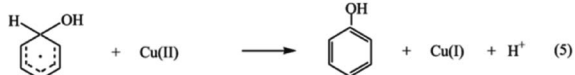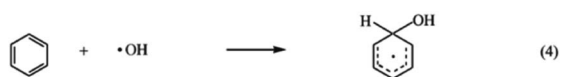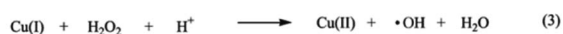

Reactor: batch reactor, catalysts: (I)-[Cu(bipy)Cl$_2$], (II)-[Cu(bipy)$_2$Cl]-Cl, and (III)-[Cu(bipy)$_3$]Cl$_2$, solvent: Solvent 1, reaction temperature: 323 K, oxygen pressure: 0.3 MPa, reaction time: 4 h.

Fig. 6　Amount of Deviated Ligand (2,2'-bipyridine) during the Oxidation of Benzene over the Cu(II)-2,2'-bipyridine Complexes

Scheme 1　Oxidation of Benzene to Phenol over the [Cu(bipy)Cl$_2$] Catalyst

least-squares method (Table S1). CuPc was used as the standard for curve fitting. In each complex, the coordination number of the N atoms around Cu was consistent with the structure shown in **Fig. 1**, and the bond length was nearly equal to that of Cu–N in the pyridine complex[32].

3. 2. Evaluation of the Catalytic Activities of Cu(II)-2,2'-bipyridine Complexes

The catalytic activities of all three complexes during the liquid-phase oxidation of benzene into hydroquinone were determined by conducting the reactions in an autoclave with Solvent 1 (**Fig. 5**). The yield of hydroquinone was higher than that of phenol with all catalysts. [Cu(bipy)Cl$_2$] obtained the highest yield of hydroquinone (2.39 %) among the catalysts. Furthermore,

the production of hydroquinone decreased with an increasing number of 2,2'-bipyridine molecules coordinated to Cu. This presumably occurred because the easiness of the electron transfer and coordination structure of the complexes have an influence on the reaction, which is supposed to proceed via the reduction of Cu(II) with L-ascorbic acid, the reducing agent (Eq. (1), **Scheme 1**)[15]. Therefore, the ease of electron transfer between L-ascorbic acid and Cu is suspected to have a significant effect on the reaction activity. For [Cu(bipy)$_3$]Cl$_2$, the oxidation state of Cu is stabilized by the three bipyridine molecules, and electron transfer is less likely to occur; however, because only one bipyridine is coordinated for [Cu(bipy)Cl$_2$], this effect is likely small, and the coordination positions around Cu are filled for [Cu(bipy)$_3$]Cl$_2$. Therefore, it is difficult for the oxidants or substrates to access Cu. In addition, the desorption of the ligand presumably contributed to the reduced hydroquinone yield. **Figure 6** shows the amount of 2,2'-bipyridine molecules present in the solution after the reaction with each catalyst. The reaction mixture with [Cu(bipy)Cl$_2$] contained the smallest amount of 2,2'-bipyridine after the completion of the reaction, unlike those of the other two catalysts. Conversely, the reaction mixture with [Cu(bipy)$_3$]Cl$_2$ contained 0.263 mmol of 2,2'-bipyridine ($\sim$ 87 % of the initial amount) after the reaction. This suggests that the greater the number of 2,2'-bipyridines coordinated to Cu, the weaker the coordination bond between the Cu and N atoms, which could lead to a desorption of the ligand. These are assumed to be the reasons for

the decrease in the oxidation reaction activity as the co-ordination number increases.

The phenol oxidation reaction was attempted to investigate the hydroquinone formation process from benzene. Figure S3 shows the time on stream of the hydroquinone yield for the benzene and phenol oxidation. For the benzene oxidation, hydroquinone was formed from the beginning of the reaction. Conversely, for the phenol oxidation, no hydroquinone was produced until 2 h after the beginning of the reaction, suggesting that there was an induction phase for the hydroquinone formation from phenol. If hydroquinone was formed only via the oxidation of phenol, then hydroquinone would not be formed during the initial stage of the reaction for the benzene oxidation. Therefore, it is assumed that a certain amount of the hydroquinone is formed directly from benzene without phenol. In addition, for the benzene oxidation, the rate of hydroquinone formation increased during the reaction, presumably because the phenol generated via benzene oxidation was oxidized to hydroquinone after the induction phase. Therefore, in this reaction, hydroquinone apparently formed directly from benzene and also via phenol through the sequential oxidation of benzene.

In this reaction, the gas-phase oxygen molecules dissolve in the liquid phase and react with the substrate; therefore, the amount of oxygen dissolved in the liquid phase can be used as a parameter to measure the catalytic activity. Thus, the effect of oxygen pressure on this reaction was investigated (**Fig. 7**). The yields of phenol and hydroquinone increased as the oxygen pressure increased from 0.0 to 0.3 MPa, but remained nearly unchanged at higher pressures, suggesting oxygen saturation at 0.3 MPa.

Table 1 presents the dependence of the reaction temperature on this reaction. At 293 K, neither phenol nor hydroquinone were formed. However, as the reaction temperature increased, the yields and selectivities of both products increased, with the highest phenol and hydroquinone yields and selectivities obtained at 323 K. Comparing the results at 303 K and 323 K, the significant increase in hydroquinone selectivity, despite the nearly unchanged phenol selectivity, can be attributed to the promotion of the sequential oxidation of benzene. Although the promotion of phenol formation is expected as the temperature increases, phenol is speculated to be readily oxidized to hydroquinone at 323 K. Consequently, phenol selectivity did not change significantly, whereas the hydroquinone selectivity was improved. At temperatures higher than 323 K, the yields and selectivities of both products decreased. Furthermore, benzene conversion considerably increased, whereas the carbon budget significantly decreased, suggesting that the formation of CO and CO_2 increased at higher temperatures. In addition, below 323 K, the progressively increasing conversion but gradually decreasing
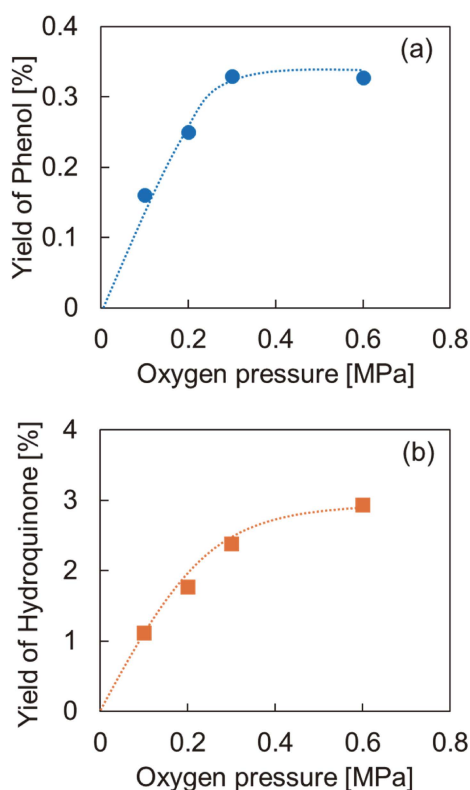
Reactor: batch reactor, solvent: Solvent 1, reaction temperature: 323 K, oxygen pressure: 0-0.6 MPa, reaction time: 4 h.

Fig. 7 Effect of Oxygen Pressure on the (a) Phenol and (b) Hydroquinone Yields from the Oxidation of Benzene over the [Cu(bipy)Cl2] Catalyst

Table 1 Dependence of the Reaction Temperature on the Oxidation of Benzene over the [Cu(bipy)Cl2] Catalyst

Temperature [K]	Product yield [%]		Product selectivity [%]		Conversion [%]	Carbon budget [%]
	Phenol	Hydroquinone	Phenol	Hydroquinone		
293	-	-	-	-	40.0	60.0
303	0.230	0.047	0.530	0.108	43.3	56.9
323	0.330	2.388	0.700	5.07	47.1	55.6
343	0.047	0.918	0.048	0.948	96.8	4.13

Reactor: batch reactor, solvent: Solvent 1, reaction temperature: 293-343 K, oxygen pressure: 0.3 MPa, reaction time: 4 h.

Table 2 Product Yields from the Oxidation of Benzene over the [Cu(bipy)Cl₂] Using Different Reactors at Atmospheric Pressure

Reactor	Product yield [%]	
	Phenol	Hydroquinone
Slug flow	0.751	-
Batch	-	-

Solvent: Solvent 3, reaction temperature: 325 K, oxygen pressure: 0 MPa, reaction time: 4 h.

Reactor: slug flow reactor, the solvent is a mixture of acetonitrile : water : acetic acid with a ratio of 1 : 1 : 0.5-2, reaction temperature: 325 K, oxygen pressure: 0 MPa, reaction time: 4 h.

Fig. 8 Effect of the Acetic Acid Concentration in the Solvent Mixture on the Oxidation of Benzene over the [Cu(bipy)Cl₂] Catalyst

carbon budgets as the reaction temperatures increased suggest the formation of uncollectable gaseous products. Therefore, the formation of byproducts was considered to be the major source for the decrease in phenol and hydroquinone yields at high temperatures.

The optimal solvent composition was determined. Solvent 1 was used as the solvent for the reaction in the autoclave; however, the solid raw materials, [Cu(bipy)Cl₂] and ʟ-ascorbic acid, did not dissolve in this solvent. Therefore, the use of Solvent 1 in the slug flow reactor might clog the pump and pressurizer. Notably, [Cu(bipy)Cl₂] is poorly soluble in water but easily soluble in acetonitrile, and ʟ-ascorbic acid is readily soluble in water but hardly soluble in acetonitrile. Therefore, we determined the optimal solvent composition for dissolving both [Cu(bipy)Cl₂] and ʟ-ascorbic acid. Four solvent mixtures of different compositions were prepared. Both [Cu(bipy)Cl₂] and ʟ-ascorbic acid were completely dissolved in Solvents 3 and 4. Subsequently, the liquid-phase oxidation of benzene was evaluated in the presence of each solvent mixture (Fig. S4). Higher yields of phenol were obtained with solvents containing a larger proportion of water, whereas hydroquinone yields varied slightly. This can be attributed to the following reasons. Because ʟ-ascorbic acid is readily dissolved in water, using a solvent with a large percentage of water increases the number of ʟ-ascorbic acid molecules interacting with the Cu species in the Cu(II)-2,2'-bipyridine complex, which promotes the reduction reaction of Cu(II) (Eq. (1), **Scheme 1**). This explains the higher yields of phenol obtained in the presence of Solvent 3. However, using Solvent 4, which has the highest proportion of water, led to lower phenol yields than that of Solvent 3. This can be explained by the occurrence of an equilibrium shift towards the left-hand side of Eq. (1) in the presence of excess water, which decelerates the reduction reaction of the Cu(II) species.

3. 3. Evaluation of the Effectiveness of the Slug Flow Reactor

First, the reaction in the presence of Solvent 3 was evaluated in both the autoclave and slug flow reactor under an oxygen pressure of 0 MPa (**Table 2**). Neither phenol nor hydroquinone was formed in the au-

toclave, whereas only phenol was formed in the slug flow reactor. The product was obtained only in the slug flow reactor presumably because the formation of the slug flow contributed to the increase in the gas-liquid interfacial area and the generation of the internal circulation flow, which accelerated the mass transfer of oxygen from the gas phase to the liquid phase. This suggests that the slug flow reactor enables an efficient supply of oxygen into the liquid phase and provides a sufficient amount of oxygen for the reaction to proceed even under a lower oxygen pressure. Furthermore, it is speculated that hydroquinone was not produced using the slug flow reactor because more hydroxyl radicals are required for the hydroquinone formation than that for the phenol formation. Therefore, more oxygen must be supplied to the liquid-phase side for hydroquinone to form. Despite the formation of the slug flow contributing to an efficient dissolution of oxygen, it is assumed that under low pressure conditions, the low amount of oxygen dissolved barely produced hydroquinone.
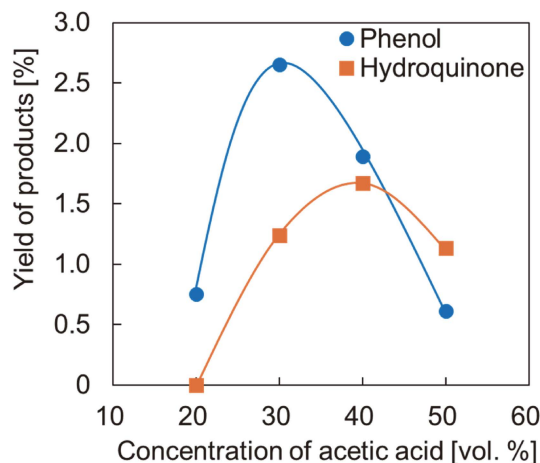
Subsequently, the concentration of acetic acid was increased in the solvent to increase the number of hydroxyl radicals produced, which are the key intermediates in the formation of hydroquinone. Because H_2O_2 is more stable in acidic solutions[33], higher concentrations of acetic acid would promote the generation of hydroxyl radicals (Eq. (3), **Scheme 1**). This was confirmed by the higher phenol and hydroquinone yields at higher acetic acid concentrations (**Fig. 8**). The maximum phenol yield was observed at a 30 vol% acetic acid concentration, whereas the maximum hydroquinone yield was obtained at a 40 vol% acetic acid con-

centration. However, both phenol and hydroquinone yields decreased at >40 vol% acetic acid concentrations. This may be because, in the presence of excess acetic acid, protons are not released from L-ascorbic acid (Eq. (1), **Scheme 1**). This could hinder the reduction of Cu(II) species and possibly, the benzenium ion intermediate, which is necessary for the production of phenol and hydroquinone (Eq. (5), **Scheme 1**).

Subsequently, the effect of the reaction temperature on the hydroquinone yield was investigated using a slug flow reactor (**Fig. 9**). At 325 K, the phenol yield was higher than that of hydroquinone; however, at higher temperatures, hydroquinone was selectively obtained. The maximum phenol and hydroquinone yields were observed at 340 K; however, as the temperature was increased to 345 K, the yields of both products decreased. This may be owing to the decrease in the solubility of oxygen as the reaction temperature increased. The benzene conversion and carbon budget did not change significantly with reaction temperature using the slug flow reactor. Therefore, the decrease in the solubility of oxygen, rather than the formation of byproducts, appeared to have a greater influence on the decrease in

phenol and hydroquinone yields at higher temperatures when the slug flow reactor was used.

To further improve the hydroquinone yield, the reaction was performed in both the autoclave and the slug flow reactor under the same conditions at higher oxygen pressures (**Table 3**). Compared to the results at the atmospheric pressure (an oxygen pressure of 0 MPa), both product yields increased; notably, the yield of hydroquinone increased dramatically. This may be owing to an increase in the amount of oxygen dissolved in the liquid phase due to pressurization. The reaction in the slug flow reactor obtained hydroquinone yields and selectivities that were approximately 5.7 times and 5.5 times higher than that in the autoclave, respectively. In addition, the improvement of the yield and selectivity was presumably caused by the efficient dissolution of oxygen into the liquid phase owing to the slug flow formation. The accelerated mass transfer of oxygen to the liquid phase and the easy replenishment of oxygen consumed via the reaction by the continuous supply of oxygen improved the activity for the benzene oxidation. In particular, this efficient dissolution of oxygen contributed to the promotion of the sequential oxidation of benzene, namely, the formation of hydroquinone from phenol, which is assumed to improve the hydroquinone selectivity. This result suggests that the increase in the amount of dissolved oxygen owing to pressurization and the efficient supply of oxygen through the formation of the slug flow improved the activity of hydroquinone formation in this reaction.

4. Conclusions

The liquid-phase oxidation of benzene was evaluated using three as-synthesized Cu(II)-2,2'-bipyridine complexes in an autoclave. Among the catalysts, [Cu(bipy)Cl$_2$] obtained the highest yield of hydroquinone (~ 2.4 %). Using the slug flow reactor, a hydroquinone yield of up to 8.6 % was achieved, which was better than that obtained using the autoclave under the same reaction conditions. The increase in the oxygen pressure dramatically promoted the formation of hydroquinone. Our findings demonstrate that the slug flow reactor is effective for the efficient synthesis of hydroquinone via the liquid-phase oxidation of benzene with
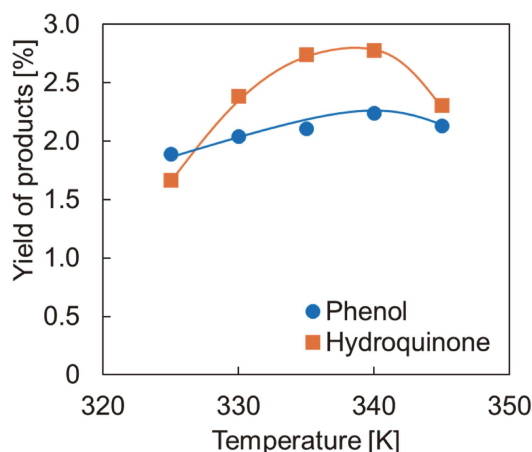
Reactor: slug flow reactor, the solvent is a mixture of acetonitrile : water : acetic acid with a ratio of 1 : 1 : 1.3, reaction temperature: 325-345 K, oxygen pressure: 0 MPa, reaction time: 4 h.

Fig. 9 Effect of Reaction Temperature on the Oxidation of Benzene over the [Cu(bipy)Cl$_2$] Catalyst

Table 3 Product Yields and Selectivities for the Oxidation of Benzene over the [Cu(bipy)-Cl$_2$] Catalyst Using Different Reactors at 0.15 MPa

Reactor	Product yield [%]		Product selectivity [%]	
	Phenol	Hydroquinone	Phenol	Hydroquinone
Slug flow	2.37	8.62	2.58	9.37
Batch	1.91	1.50	2.08	1.69

Solvent is a mixture of acetonitrile : water : acetic acid with a ratio of 1 : 1 : 1.3, reaction temperature: 340 K, oxygen pressure: 0.15 MPa, reaction time: 4 h.

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oxygen as the oxidant.

Supporting Information

Supplementary data associated with this article can be found in the online version at https://jstage.jst.go.jp/browse/jpi/-char/en (DOI: doi.org/10.1627/jpi.68.27).

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要　　旨

スラグ流反応器における Cu(II)-2,2'-ビピリジン錯体を用いた
ベンゼンの液相酸化によるヒドロキノンの選択的合成

野口　伊吹[†1]，市橋　祐一[†1),†2]

[†1] 神戸大学大学院工学研究科応用化学専攻，657-8501　神戸市灘区六甲台町1-1
[†2] 神戸大学先端膜工学研究センター，657-8501　神戸市灘区六甲台町1-1

Cu(II)-2,2'-ビピリジン錯体を触媒とし，分子状酸素を酸化剤とするベンゼンの液相酸化反応を検討した。回分反応器を用い，Cu(II) イオンにビピリジン分子が一つ，二つおよび三つ配位した3種の触媒で反応活性を比較した。ビピリジン分子が1分子配位した錯体触媒が最も高いヒドロキノン生成活性を示した。これには，錯体の配位構造や配位子の脱離のしやすさが影響を及ぼしていると推測された。次に，反応器の違いが反応活性に与える影響について検討するため，回分反応器からスラグ流反応器に変更した。結果，スラグ流反応器の方が回分反応器に比べ，約5.7倍のヒドロキノン収率を示した。スラグ流の形成によって酸素が液相に効率的に供給され続けたため，ヒドロキノンの収率が向上したものと推測された。

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