

Selective oxidation of phenol with hydrogen peroxide using two types of catalytic microreactor

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Abstract

Selective oxidation of phenol with hydrogen peroxide over titanium silicalite-1 (TS-1) was performed using two types of catalytic microreactor: a packed bed microreactor and a catalytic wall microreactor. The reaction rates were markedly faster in both microreactors than in flasks due to improvement of the contact efficiency between reactant and catalyst. However, using a packed bed microreactor, phenol conversion and yields of benzenediols decreased gradually with time course. Therefore, we developed a catalytic wall microreactor in which catalyst elements could be exchanged easily. Use of this new catalytic wall reactor suppressed catalyst deactivation. In addition, the regioselectivity of hydroxylation, *i.e.*, the molar ratio of *para*-diol (hydroquinone)/*ortho*-diol (catechol) changed remarkably. A higher degree of *para*-selectivity was achieved with the wall type reactor than the packed bed type reactor.

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1. Introduction

Selective oxidation is an important technology for transformation of chemical raw materials to useful chemical products. Especially, the use of heterogeneous catalysts is favorable from the viewpoint of environmental and economic considerations [1,2]. Heterogeneous catalysts facilitate the separation process, and permit reuse and recycling. However, oxidation with a solid catalyst is a problematic reaction. The majority of organic syntheses are reactions in liquid phase, especially in solution. For actual industrial applications, the use of a solid catalyst in liquid phase has been limited, because of the inferior productivity using conventional reactors. Oxidation reactions are rapid, but actual reaction times of selective oxidations are generally long. There are two reasons for this. First, the reaction rate of multiphase reactions is dependent on the slowest step among the processes, *e.g.*, mass transport from the bulk liquid to the liquid–solid interface, diffusion into the porous structure, *etc.* Furthermore, these reactions must be conducted under mild conditions, as it is necessary to control

the huge amounts of exothermic heat and to suppress undesirable over-oxidation reactions.

To overcome these problems, the application of microreactors has been examined. Microreactors have the potentials to save both cost and time in manufacturing and process development of specialty chemicals [3–5]. The characteristic dimensions are from the sub-micrometer to the sub-millimeter range. Such small characteristic dimensions and high surface-to-volume ratio greatly improve heat transfer performance. Furthermore, the concentration of reactant can be controlled precisely due to mass transport [6]. Some studies on homogeneous liquid phase selective oxidation processes using microreactor systems have been reported [7,8]. Microreactor processes have been shown to allow severe oxidation reactions to proceed safely. However, there have been a few reports on liquid phase reaction using heterogeneous catalytic microreactors [9]. As a rare example of liquid–solid phase reaction, Wan et al. investigated partial oxidation of alkene to epoxide with hydrogen peroxide (H_2O_2) over catalytic membranes in microchannels [10]. A titanium silicalite-1 (TS-1) zeolite catalyst was synthesized onto the microchannels, which markedly increased the contact efficiency between catalyst and reactants. However, the catalyst membranes were deactivated after the reaction [11]. The deactivated catalyst could not be regenerated by calcination.

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Conventional methods of catalyst immobilization onto microchannels (*e.g.*, coating on the walls of microchannels) make it difficult to exchange deactivated catalyst. Previously, we proposed the design concept of catalytic microreactors, *i.e.*, assembled type catalytic microreactors composed of catalyst elements and microchannel elements [12]. The catalyst elements are fabricated separately and installed inside the microchannel elements. We have prepared several catalytic microreactors according to this concept [13]. The use of assembly microreactors facilitates removal and replacement of the catalyst elements. In addition, by changing the catalyst elements, the catalytic microreactors could be applied to many types of reaction economically.

As a model reaction, we conducted selective oxidation of phenol (PH) with hydrogen peroxide (H_2O_2) in aqueous media over a Ti-containing zeolite catalyst, *i.e.*, titanium silicalite-1 (TS-1). Fig. 1 shows the scheme of PH oxidation with H_2O_2 over TS-1. The desired products are the benzenediols hydroquinone (HQ) and catechol (CA). However, many unexpected by-products were generated using conventional batch reactors. For example, benzoquinone (BQ) was produced by the consecutive reaction. In addition, the selectivity of benzenediols is known to be dependent on the reaction conditions, such as temperature, reactant concentration, solvent, *etc.*

The catalyst contributes markedly to the selectivity. In the hydroxylation of aromatics, the TS-1 catalyst developed by Enichem researchers in the 1980s [14] exhibited excellent reactivity and high efficiency for H_2O_2 utilization because of the unique Lewis acidity [15]. In addition, the pore structure and hydrophobic environment of active sites caused shape selectivity [2]. The regioselectivity of diols, *i.e.*, the molar ratio of *para*-diol (HQ) to *ortho*-diol (CA), has remarkable behavior [16]. The regioselectivity was dependent on reaction conditions, such as temperature, concentrations of reactants, kind of solvent, and crystal size of TS-1 catalyst. These phenomena were suggested to be due to differences in the active sites of TS-1 [17]. TS-1 was presumed to have two different active sites—the Ti site inside the zeolite pores and another on the external surface. The former is *para*-selective (HQ-rich), and the latter is *ortho*-selective (CA-rich).

In the present study, we developed versatile catalytic microreactors, and experimentally compared two types of catalytic microreactor, packed bed catalytic microreactors and

catalytic wall microreactors, to clarify their characteristics, including catalyst placement, distribution of reactant concentration, and the contact efficiency between reactant and catalyst. Furthermore, we attempted to control the selectivity of multiple reaction systems.

2. Experimental section

2.1. Materials and preparation of catalyst

Hydrogen peroxide (H_2O_2) in 30.0–35.5 wt.% aqueous solution was used (Wako Pure Chemicals Industries, Ltd., guaranteed grade without stabilizer). The concentrations of H_2O_2 were determined by redox titration before use. Titanium silicalite-1 catalyst was prepared by the following method [14]. A mixture of tetraethyl orthosilicate (TEOS), tetraethyl orthotitanate (TEOT), and tetrapropylammonium hydroxide (TPAOH) with a molar ratio TEOS/TEOT/TPAOH = 100/2/36 was stirred for 3 h at 60 °C. Then, the solution was placed into an autoclave with a Teflon inner cylinder and heated for 3 h at 175 °C with stirring. The crystals obtained were filtered, washed, and calcined for 6 h at 550 °C. Prepared powder catalyst was identified as TS-1 by infrared spectroscopy (JEOL Ltd., JIR-SPX60) and X-ray diffraction spectroscopy (Rigaku Corp., RAD3C) with a Cu K α source. The physical properties were also characterized, and Ti content was confirmed to be 2.3 wt.% and the specific surface area was 470 m²/g by the BET method. The results of secondary electron microscopy (JEOL Ltd., JSM-6700) indicated the crystal of TS-1 catalyst to be uniform size in the range of 50–100 nm.

2.2. Preparation of microreactors

For continuous selective oxidation reactions in a heterogeneous solid–liquid two-phase system, we adopted two different types of catalytic microreactor (Fig. 2): (a) packed bed microreactor and (b) catalytic wall microreactor. Solid catalyst was immobilized inside the microchannels under our basic concept of removable and exchangeable catalyst elements.

First, we prepared a packed bed microreactor (Fig. 2a). Packing the catalyst powder is the simplest method of catalyst immobilization, but this method is difficult to apply to the TS-1 catalyst. TS-1 catalyst powder is inherently too fine to filter. To

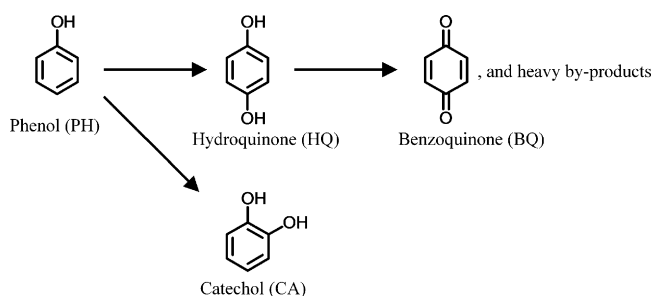


Fig. 1. Reaction scheme of phenol oxidation with hydrogen peroxide over TS-1 catalyst.

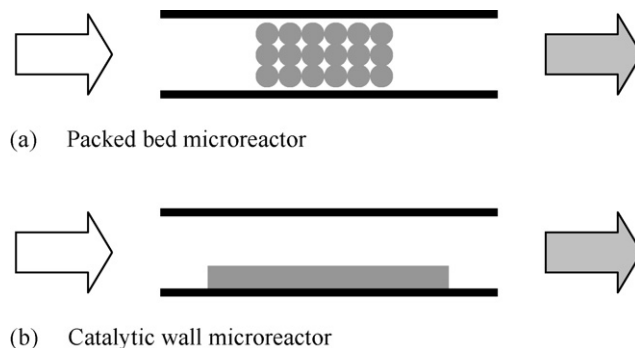


Fig. 2. Schematic drawings of the two types of catalytic microreactor.

avoid problems with solution feeding, TS-1 catalyst was granulated before packing. The powder was molded by compression (18 MPa, 3 min) and crushed. Following classification into particles of desired average sizes (100–150 μm) by sieving, obtained particles of TS-1 catalyst were packed into the reactor tubes with filters (pore diameter = 2 μm) on the ends. The experimental conditions using the prepared packed bed microreactors are summarized in Table 1. To create packed bed type reactors, we prepared several microtubes with different inner diameters. A smaller-scale channel would be better to emphasize the merits of microscaling, *e.g.*, to remove the reaction heat more effectively from the catalyst bed. However, it was impossible to pack catalyst particles inside the microtubes with inner diameters of several tens or hundreds of micrometers. Packing was made easier with diameter sizes greater than 1.0 mm. Therefore, we adopted millimeter-scale tubes (inner diameter = 1.0 mm or 2.0 mm) as packed bed reactors.

Next, we designed a new type of catalytic wall microreactor (Fig. 2b) as assembled type, as the packed microreactor has the disadvantage that it is restricted to a narrow operation range because of high pressure loss. The catalytic reactor consists of two plates made of stainless steel, a catalyst plate and a microchannel plate (Fig. 3). The microchannel plate (Fig. 3c) was fabricated mechanically. The cross-section of channels was rectangular, with the width of 1.00 mm. The channel height and length were changed optionally. In general, heterogeneous catalysts are obtained in powder form. Therefore, it is desirable that general powder catalysts can be adopted into these new catalytic microreactors without complicated processes. In this study, as TS-1 catalyst is a very fine powder, it was not necessary to use binder compounds, and the catalyst plate (Fig. 3b) was made by compressing the catalyst powder. The fine powder was molded into thin tablets inside a circular hollow (diameter = 32.0 mm, height = 500 μm) at the center of the plate. This catalyst plate can be disassembled into three pieces: a doughnut-shaped piece, a disk-shaped piece, and a lower cover piece. The hole of the doughnut-shaped piece over the lower cover piece was charged with the catalyst powder (catalyst weight = 0.35 g), and then the disk-shaped piece was placed on the powder as a drop lid (described in Fig. 4a). After compression (18 MPa, 3 min), the catalyst was fixed on the

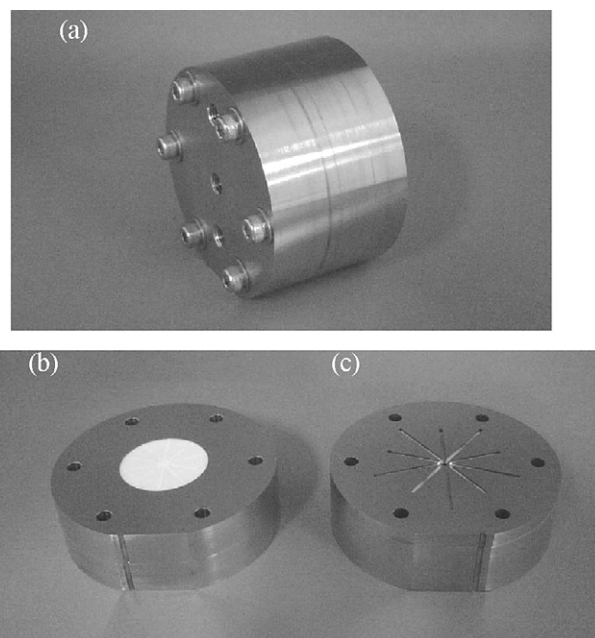


Fig. 3. Photographs of catalytic wall microreactor. (a) Assembled device; (b) catalyst plate (catalyst size = $\phi 32.0$ mm (diameter) \times 0.5 mm (thickness)); (c) microchannel plate (channel size = 0.8 mm (height) \times 1.0 mm (width) \times 16.0 mm (length), channel geometry = 10 straight channels in a radial pattern).

plate as a tablet shape. This new microreactor allows the catalyst tablet to be fabricated to a given size with good accuracy, because tablet is formed inside the microreactor to settle. The thickness of the catalyst tablet can be varied by changing the height of the disk-shaped piece (push-up bottom), if it is more than 500 μm to maintain the shape of film during assembling. The catalyst plate, in which the catalyst tablet was flipped with the doughnut and disk on the lower cover, was put together with the microchannel plate in a face-to-face manner, and compressed by six screws. A flow inlet and an outlet were set on the upper microchannel plate. Fig. 4b shows a schematic drawing of the cross-section. The catalyst film was placed at the bottom in the reactor, and the reactants were passed in a laminar flow on the upper space of the catalyst. The depth of the channel could be changed. As further applications, multi-plate type devices could be prepared, laying pairs of channel plates and catalyst plates alternately corresponding to various reaction

Table 1
Specifications of microreactors

Parameters	Packed bed microreactor	Catalytic wall microreactor
Material	Stainless steel or Teflon (PTFE)	Stainless steel
Cross-section shape of channel	Circle	Rectangle
Channel size (mm)	$\phi 1.00$ – $\phi 2.10$ (i.d.) 20.00–75.00 (bed length)	0.80 (height) 1.00 (width) 14.00–113.00 (length)
Empty volume (mL)	0.047–0.260	0.011–0.181 ^a
Void fraction	0.86	1.00 ^a
Catalyst weight (g)	0.02–0.11	0.35
Form of TS-1 catalyst	Particle (irregular shape)	Disk-shaped tablet
Catalyst size (mm)	0.10–0.15 (diameter)	$\phi 32.00$ (diameter), 0.50 (thickness)
Catalyst density (kg/m ³)	3.0×10^{-3}	3.0×10^{-3}

^a Neglecting the hollow volume of the catalyst plate.

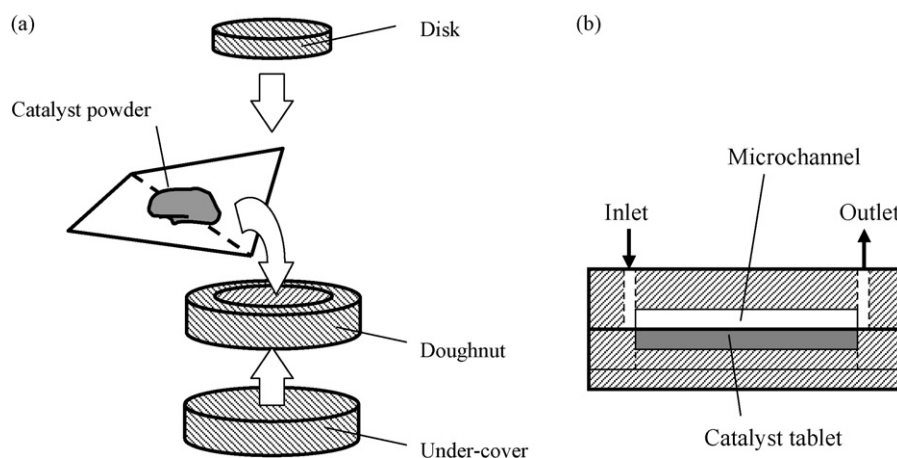


Fig. 4. Schematic drawings of catalytic wall microreactor. (a) Assembling diagram of catalytic plate; (b) cross-section view of assembled microreactor.

schemes. We checked the operability of the microreactor by visual inspection for several hours, and then confirmed that the feed of reaction solution (up to 10 mL/min) was possible without collapse of the catalyst tablet. Polishing the facing surface of these plates beforehand prevented reaction liquids from leaking out from the facing surface of two plates up to a pressure of 3 MPa at the same level as the maximum usable pressure of tube fittings in both microreactors.

Table 1 lists typical examples of catalytic wall microreactors as compared with packed bed microreactors. Although the reactor volumes are nearly equal, the amounts of catalyst in catalytic microreactors are larger than packed bed reactors. This is because there are only small fractions of catalyst surface area of tablet in contact with reaction solution and most of the catalyst is inaccessible to reactants. However, the poor utilization of catalyst in catalytic wall reactors would not matter so much if the catalyst can be recycled easily.

2.3. Selective oxidation of phenol

To examine the practical applicability of the two different types of catalytic microreactor described above, we conducted selective oxidation of phenol in aqueous H_2O_2 solution over TS-1 catalyst. PH was dissolved in distilled water and aqueous H_2O_2 solution premixed in a glass flask at a given concentration (PH = 0.16 mol/L and H_2O_2 = 0.29 mol/L). To avoid increases in temperature due to the exothermic reaction, the reactant concentrations were kept low. The reactant solution was fed continuously into the microreactor by a plunger pump (Shimadzu Corp., LC-20AD). The microreactor and a preheating tube (stainless steel, outer diameter = 1.58 mm, inner diameter = 1.0 mm, length = 1000 mm) connected to the inlet of the microreactor were heated in a temperature-controlled bath (Tokyo Rikakikai Co. Ltd., NTT-2000) at 60 °C. The reaction mixture from the outlet of the microreactor was collected into glass vials, and diluted immediately with distilled water. Samples of the product were analyzed by high performance liquid chromatography (Shimadzu Corp., LC-VP) with an ODS column (Shimpack CLC-ODS). Reaction products were identified by comparison with authentic samples.

The amounts of PH, HQ, CA, and BQ were quantified relative to internal standard. The concentrations of H_2O_2 were determined by high performance liquid chromatography simultaneously. The reliability was cross-checked by titration of 0.1 mol/L cerium (IV) tetraammonium sulfate solution, and iodometry (titration of 0.1 mol/L sodium thiosulfate solution into the mixture of sample solution and saturated potassium iodide solution). Conversion, yield, and selectivity were calculated based on the starting amount of phenol. We checked the inertness of constituent materials of both reactors by feeding the reactant solution into the microreactor without TS-1 catalyst.

3. Results and discussion

3.1. Selection of microchannel type

The proposed microreactor has the advantage that it is possible to select various microchannels flexibly for a given reaction. First, we examined the appropriate microchannels for phenol oxidation. Some types of microchannel were prepared to increase the catalyst surface contact area. The simplest was linear in shape. First, we prepared multichannel plates in which the flow pass was split into a number of channels, as shown in Fig. 3c. However, this multichannel type required special attention in the assembly process. Even a slight defect on the catalyst tablet caused the reproducibility of the reaction results to be poor, because the stream was biased in proportion to the flow resistance of each channel. On the other hand, the vortical pathway is one of the most efficient shapes to gain a larger surface area of a catalyst with a single channel. However, channeling occurred when the vortical pathway was close to the neighboring path (e.g., channel width = 1 mm and barrier width = 1 mm). To make a stable stream of reaction solution in the microchannel, it was necessary for the channel barriers to be of sufficient width. Fig. 5 shows an excellent microchannel plate (barrier width = 5–7 mm). The surface area ratio of catalytic wall in contact with the reaction channel ($1.13 \times 10^{-4} \text{ m}^2$) to one side of the catalyst tablet ($8.04 \times 10^{-4} \text{ m}^2$) is 0.14. We mainly used this improved



Fig. 5. Photograph of the microchannel plate used in reaction experiments (channel size = 0.8 mm (height) \times 1.0 mm (width) \times 113.0 mm (length), channel geometry = vortex).

channel geometry for the oxidation reaction experiments performed in this study.

3.2. Oxidation using a packed bed catalytic microreactor

First, we used a packed bed microreactor with TS-1 catalyst particles (sieved to 100–150 μm) in a tubular reactor (inner diameter = 2.0 mm, bed length = 20.0 mm). The reaction was conducted at 60 $^{\circ}\text{C}$ with an initial $\text{H}_2\text{O}_2/\text{PH}$ molar ratio of 1.8. Mainly HQ, CA, and unreacted PH were detected from the outlet of the microreactor. As a consecutive by-product, traces of benzoquinone were detected. Table 2 summarizes the reaction results. The conversion of phenol was increased markedly in a short residence time, compared with the use of a batch reactor (50 mL glass round-bottomed flask) and TS-1 catalyst powder (catalyst weight = 20 mg). This was due to the marked improvement in contact efficiency between reactant and catalyst. In addition, the narrow residence time distribution, which is the major advantage of continuous processes, suppressed the generation of consecutive side reactions (over-oxidation, etc.). This is found by the small yields of BQ that is major product in batch reactor.

However, the phenol conversion and the yields of benzenediols decreased gradually with time. Fig. 6 shows

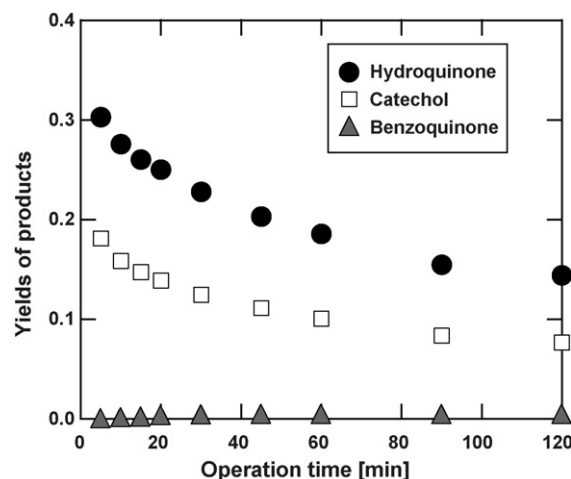


Fig. 6. Yields of products against operation time using a packed bed micro-reactor (residence time = 0.5 min).

the time course of yields of products using a packed bed microreactor (residence time = 0.5 min). As the operation time increased to 2 h, the yields of benzenediols decreased to approximately half those at 10 min after the beginning of the process. These phenomena were in agreement with the results reported by Wan et al. [11]. It was assumed that the catalyst was deactivated by fouling due to heavy by-products. In oxidation of phenols, oligomers are generated easily by oxidative coupling. Indeed, tar-like by-products were observed on the TS-1 catalyst. After the reaction operation, TS-1 catalyst particles removed from the microreactor were dark brown in color.

To confirm the assumptions regarding deactivation, regeneration of the deactivated catalyst was tested. After reaction for 2 h, aqueous H_2O_2 solution was fed into the microreactor at 60 $^{\circ}\text{C}$ for 4 h (residence time = 1.0 min). The catalyst activity recovered (phenol conversion = 0.828) up to the initial activity (conversion = 0.893). The slight deterioration of activity was considered due to leaching of Ti atoms from active sites [2]. In a preliminary examination in which H_2O_2 solution was fed into the catalytic microreactor before the reaction, the reaction activity did not change. Catalytically active species of TS-1 catalyst are known to be present in the framework of silicalite-1 (MFI structure) and to show solvent resistance to most polar

Table 2
Comparison of reactivities between batch reactor and packed bed microreactor

Reactor	Residence time (min)	PH conversion	Yields of products		
			HQ	CA	BQ
Microreactor (packed bed)	0.1 ^a	0.136	0.086	0.047	0.002
Microreactor (packed bed)	0.5 ^a	0.436	0.276	0.159	0.001
Microreactor (packed bed)	1.0 ^a	0.893	0.568	0.325	0.001
Batch reactor (flask)	60	0.026	0.016	0.010	0.000
Batch reactor (flask) [16] ^b	60	0.199	0.056	0.048	0.080
Batch reactor (flask) [16] ^b	300	0.371	0.176	0.085	0.047

^a The value of empty volume divided by flow rate was defined as the hydrodynamic residence time without correction by void fraction. These reaction solutions were sampled at 10 min from start of the reaction operation.

^b Experimental data are from Ref. [16]. A large amount of TS-1 catalyst (50 mg) was used.

solvents, including aqueous H_2O_2 [18]. The reactive Ti content of the catalyst was thought to decrease during the course of repeating the redox cycle.

3.3. Oxidation using a catalytic wall microreactor

Next, hydroxylation of phenol was performed using a catalytic wall microreactor, to control the reactant concentration on the TS-1 catalyst surface by strict laminar flow [19]. Using this catalytic wall type microreactor when the mass diffusion is the rate-determining process, heterogeneous distribution of reactant concentration in the direction perpendicular to the flow will be achieved. We compared the reactor performance of the wall type reactor with that of the packed bed type microreactor. The former is expected to react slowly and strictly, and the latter is aimed at reacting fast and uniformly.

Table 3 lists the yields of benzenediols obtained using a catalytic wall microreactor (channel shape = vortex, channel height = 0.8 mm) in contrast to those using a packed bed microreactor. HQ and CA were generated as the main reaction products. The residence time was controlled in the range of 0.1–2.0 min by changing the pump flow rate. The conversion and product yields were increased monotonically with residence time. Fig. 7 shows the changes in yields of HQ, CA, and BQ with phenol conversion using the catalytic wall microreactor. The objective yields of benzenediols varied linearly with conversion of PH. The mass balance in each sampling was more than 95%. These observations clearly showed that the consecutive reactions are suppressed as compared with those using batch reactors. However, the reaction rate on the reactor volume basis was somewhat lower than that of the packed bed microreactor, because the probability of contact between reactant and catalyst is lower in the case of the wall type reactor. Part of the reactant passes through on the far side of catalytic wall without coming across the catalyst. To investigate the effect of the surface area of the catalyst wall, channel length was changed (length = 14.0 mm, geometry = straight). The reaction data were arranged as a function of residence time based on the catalyst surface area $\tau_A = \tau(A/V_c)$, where τ represents the mean residence time, A is the surface area, and V_c is the empty volume of the microchannel (Fig. 8). The plots from two wall type microreactors, which have different reaction volumes, were collinear. These results support the conclusion that this reaction does not progress in bulk solution but on the surface of the catalyst. In addition, these indicated that the catalyst surface area in contact with the vortical channel

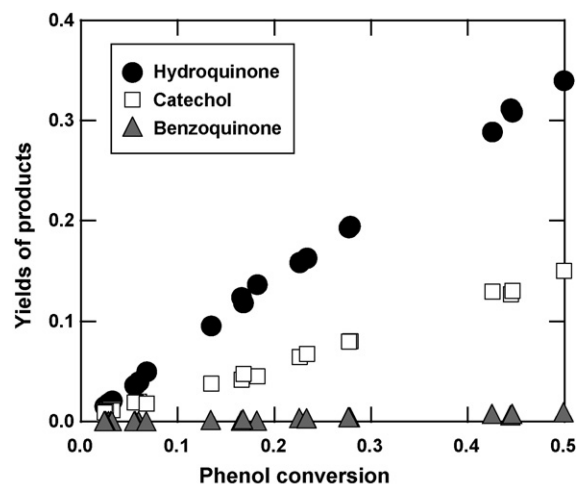


Fig. 7. Product yields of phenol oxidation using a catalytic wall microreactor.

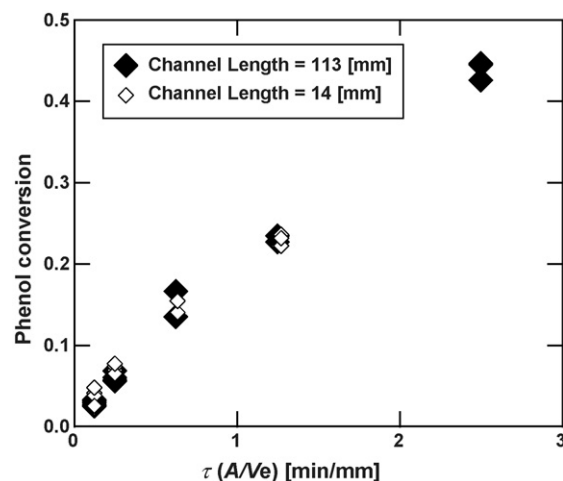


Fig. 8. Changes in conversion of phenol with residence time based on surface area.

(length = 113.0 mm) is almost accessible without channeling between the vortical pathway.

Fig. 9 shows the yields of products with a lapse time of reaction using the catalytic wall microreactor. In earlier stages, the yields increased, and the value at 30 min after the start of the reaction did not decrease even after 2 h. Except for the early transitional period, catalytic wall microreactors provided stable operation and good reproducibility. It seems that the catalyst deactivation is suppressed using the catalytic wall microreactor.

Table 3

Comparison of reactivities between packed bed microreactor and catalytic wall microreactor after 2 h

Reactor	Residence time (min)	PH conversion	Yields of products		
			HQ	CA	BQ
Microreactor (packed bed)	0.1 ^a	0.060	0.038	0.020	0.001
Microreactor (packed bed)	0.5 ^a	0.225	0.144	0.077	0.005
Microreactor (packed bed)	1.0 ^a	0.478	0.306	0.165	0.008
Microreactor (wall)	1.0 ^a	0.234	0.163	0.068	0.003
Microreactor (wall)	2.0 ^a	0.446	0.308	0.131	0.007

^a The reaction solutions were sampled at 120 min from start of the reaction operation.

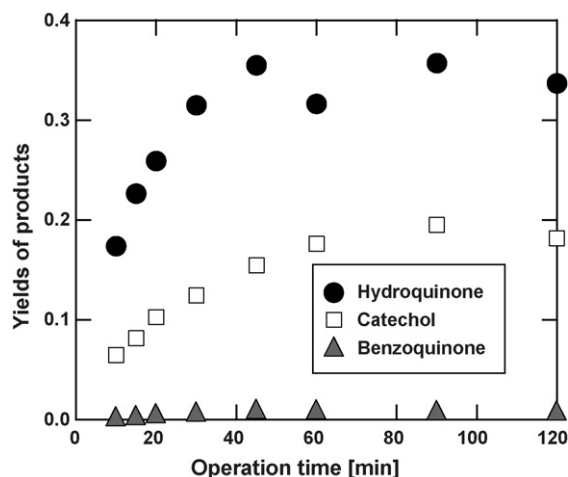


Fig. 9. Yields of products against operation time using a catalytic wall microreactor (residence time = 2.0 min).

This is attributed to the following two possible reasons: larger amount of catalyst, or smaller accumulation of deactivating materials. With use packed bed type microreactors (Fig. 6), catalyst deactivation was significantly progressed by deposits of oligomers inside the zeolite pores. The catalytic wall type is superior to the packed bed type from the viewpoint of operability including low pressure loss and easy catalyst replaceability. The used catalyst was removable easily by poking the catalyst tablet in the center of the doughnut-shape piece. After calcination and powdering, the recovered powder catalyst could be reused over again.

3.4. Comparison of selectivity between two types of microreactor

Next, we directed our attention to product selectivity, *i.e.*, the regioselectivity of hydroxylation estimated from the values of product molar ratio of *para*-/*ortho*-diol. The mole ratios of hydroquinone to catechol are plotted as a function of phenol conversion in Fig. 10. The wall type of microreactor gave higher *para*-selectivity than the packed bed type. Here, we clarified that this regioselectivity can be changed depending on the type of catalyst placement.

Selectivity was decreased slightly with PH conversion. Using the catalytic wall type microreactor, the ratio of HQ/CA was in the range of 2.2–2.5. On the other hand, using the packed bed catalyst type microreactor, the ratio changed in the range of 1.7–1.9. As mentioned in Section 1, regioselectivity is dependent on the reaction conditions, such as the concentrations of reactants. From the drastic change of regioselectivity, it was considered that the wall type microreactor would make it possible to make the specific distribution of reactant concentration by the slow diffusion process, particularly near the catalyst wall. In addition, the regioselectivity might be controlled by changing the size and geometry of microchannels inside the catalytic wall reactor. On the other hand, in the case of packed bed reactor, the reactant concentrations around the catalyst particles are supposed to be nearly equal to those in

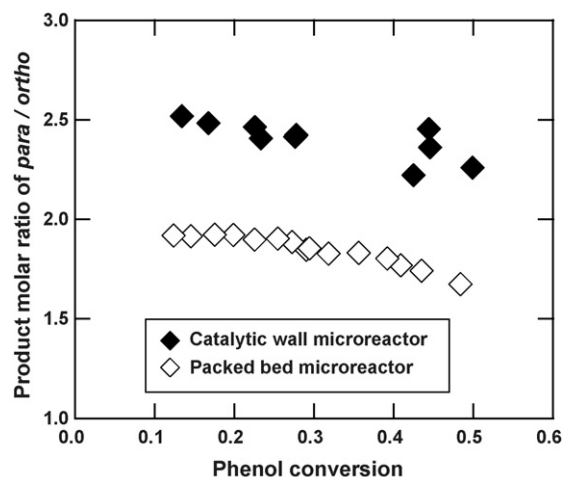


Fig. 10. Changes in the ratio of HQ/CA.

bulk solution because of the short diffusion length. Indeed, the regioselectivity was not so much changed by the variation of microchannels. The packed bed reactors with different inner diameters (1.0 mm, 2.0 mm, or 2.1 mm) and different bed lengths (20.0 mm, 50.0 mm, or 75.0 mm) yielded similar regioselectivity.

Finally, we investigated at the efficiency of H_2O_2 consumption, defined as the mole ratio of consumed phenol to consumed H_2O_2 . The efficiencies using the two types of microreactor are shown in Fig. 11 as a function of PH conversion. Using a packed bed catalyst type microreactor, the efficiency of H_2O_2 was almost 1, *i.e.*, H_2O_2 reacted with PH stoichiometrically. On the other hand, using a catalytic wall type microreactor, H_2O_2 efficiency was low in the range of 0.5–0.6. In this type of microreactor, it is possible that H_2O_2 was wasted on side reactions, such as decomposition of H_2O_2 . We also consider the suppression of deactivation of the catalyst in the catalytic wall type microreactor as due to H_2O_2 being wasted in the decomposition of oligomers that would cause fouling at the active site of the catalyst.

The phenol oxidation rate is controlled by both phenol and H_2O_2 concentrations. The reactions to CA and HQ occurred

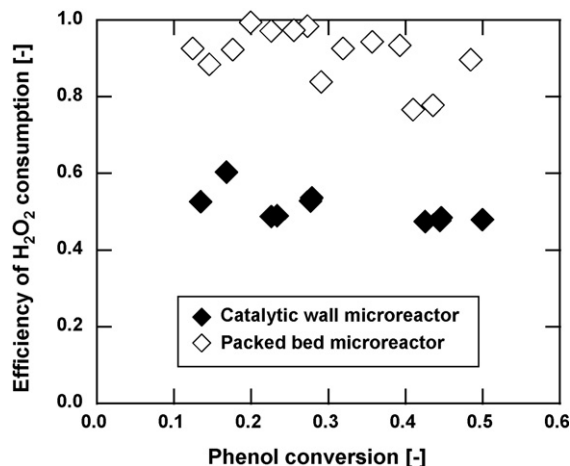


Fig. 11. Consumption efficiency of H_2O_2 .

preferentially at the surface and in the micropores of the catalyst, respectively [16,17]. Following this mechanism, the above experimental results suggested that the reaction in the micropores proceeds favorably in the catalytic wall microreactor. The mass diffusion resistance of the stagnant layer around the catalyst is comparable to that of micropores in the wall type microreactor because of laminar flow. Due to the decrease in the contribution of the slow diffusion inside the micropores, the catalytic wall type microreactor was able to use the active sites there effectively. In contrast, the flow was disordered by random collision with the catalyst particles in the packed type reactor. Therefore, the diffusion length outside the zeolite pores was small. That is, the reaction rate is controlled by diffusion in the stagnant layer on the catalyst surface in the wall type microreactor. In addition, the balance between H_2O_2 and phenol concentration at the surface and inside the catalyst is changed judging from the H_2O_2 consumption. These reaction conditions were thought to bring about the high yield of HQ by reacting selectively with phenol inside the micropores of the catalyst. To clarify this assumption, we plan to examine the effects of parameters such as channel height, *etc.* in the near future. Apart from the mechanism, it was found that the catalytic wall type microreactor provides the possibility of controlling selectivity without catalysis deactivation.

4. Conclusions

We developed two catalytic microreactors differing in method of immobilization: a packed bed catalytic microreactor and a catalytic wall microreactor. The former was developed to improve the contact efficiency, while the latter was designed to control the distribution of reactant concentration. Comparison of the results of H_2O_2 oxidation of phenol using each reactor indicated that the packed bed type was useful for acceleration of the reaction rate, while the catalytic wall type was effective for extension of the catalyst life. In addition, it was clarified that the regioselectivity of benzenediols could change depending on the reactor type differing in catalyst layout on the microchannels. Thus, the proposed catalytic wall type microreactor provides

easy control of regioselectivity and the active state of the catalyst surface.

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