

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 (H₂O₂) 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

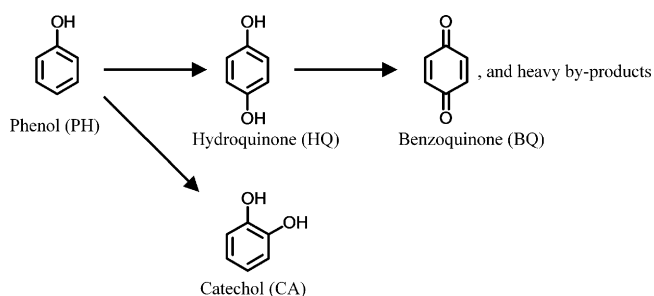


Fig. 1. Reaction scheme of phenol oxidation with hydrogen peroxide over TS-1 catalyst.

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 $K\alpha$ source. The physical properties were also characterized, and Ti content was confirmed to be 2.3 wt.% and the specific surface area was 470 m^2/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

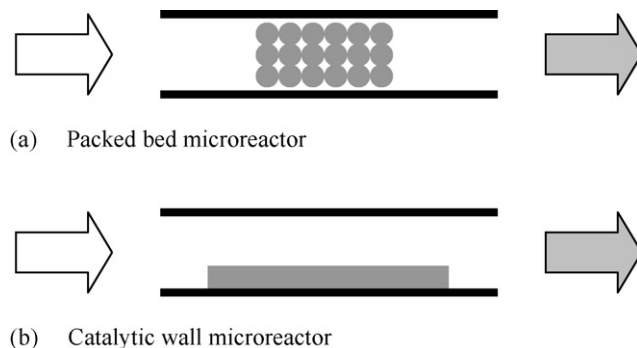


Fig. 2. Schematic drawings of the two types of catalytic microreactor.

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