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Ceramic hollow fiber membrane distributor for heterogeneous catalysis: Effects of membrane structure and operating conditions

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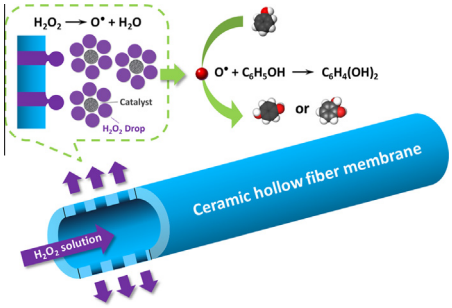
HIGHLIGHTS

- Ceramic hollow fiber membrane distributor is proposed for reactant dispersion.
- Membrane distributors with small pore size show higher product selectivity.
- Proper gradient in the pore structure promotes the membrane dispersion.
- Increase of reactant flow rate and/or stirring rate improves the reaction selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

A ceramic hollow fiber membrane distributor was proposed for the micro-scale distribution of reactants in heterogeneous catalytic reaction. To evaluate the feasibility and the performance of the ceramic hollow fiber membrane based reactant distribution, phenol hydroxylation with hydrogen peroxide (H_2O_2) over TS-1 solid catalysts was selected as a model reaction. The effects of membrane structural parameters of ceramic hollow fiber membrane on the micro-scale distribution and the reaction selectivity were studied in detail. The influence of operation conditions such as hydrogen peroxide flow rate, stirring rate and phenol/H_2O_2 molar ratio on the membrane distribution process was discussed. The ceramic hollow fiber membrane with small pore size and proper gradient in the pore structure was demonstrated to have a promotion effect on the reaction selectivity, which indicated its ability to generate uniform droplets in micro-scale. In addition, the increase of H_2O_2 flow rate and/or stirring rate can result in an improvement of reaction selectivity. Because of its controllable structure, high chemical stability and high packing density, the ceramic hollow fiber membrane distributor has potential for widespread applications in heterogenous catalysis.

1. Introduction

Heterogeneous catalysis has become a key technology used in the petrochemical, fine chemical and pharmaceutical industries [1,2]. For heterogeneous catalysis concerning nano/micro-sized solid catalysts, the inorganic membrane reactor, combining the catalytic reaction and membrane separation, has advantages that retains the catalysts in situ and makes the reaction process continuous [3–5]. Catalysts in the membrane reactor are mainly classified into three types: immobilized onto the substrate [6–8], packed on the membrane surface [9,10] and suspended in the reaction mixture [11]. Our previous studies [12–14] reported the ceramic membrane reactor had an impressive performance in catalytic reactions such as phenol hydroxylation and acetone ammoximation. Owing to the introduction of ceramic membranes, both reaction conversion and product selectivity distinctly improved while almost no weight loss of catalyst particles could be observed.

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The membrane function in the reactor is not only to selectively separate the solid catalysts from reaction mixture, but also can serve to control the addition of reactants to the reaction mixture [15,16]. Luo and coworkers [17–19] developed a membrane dispersion microreactor with a microfiltration membrane as the dispersion media which exhibited excellent micro-mixing performance in homogeneous and heterogeneous precipitation reactions for the preparation of nanoparticles. They found the microfiltration membrane was critical for assuring its high performance.

In liquid–solid catalytic reaction, one important factor for the promotion of mass transfer and reaction selectivity is the effective contact area between liquid reactants and solid catalysts [20]. Recently, for the purpose of increasing the liquid–solid interfacial contact area, tubular porous ceramic membranes were employed as the reactant distributor in heterogeneous catalytic reactions [14]. The porous ceramic membrane distributor could provide controllable and uniform distributed reactant in micro-scale size, meanwhile the controlled addition of reactants limited the side reactions and thereby enhanced the product selectivity. Although the experimental results showed several remarkable characteristics of porous ceramic membrane based distribution process, the effects of membrane structure and operation conditions on the micro-scale distribution were still not clearly illustrated.

Membrane morphology control is a great challenge because many preparation factors can solely or jointly affect the formation of membrane structures. Li and coworkers [21–25] developed a well-designed phase inversion/sintering process coupled with an optimal spinning suspension for obtaining inorganic hollow fiber membranes with desired membrane morphology. Due to its high surface area/volume ratios (500–9000 m^2/m^3) and high thermal, chemical and mechanical stability, the ceramic hollow fiber membrane has showed potential applications in catalytic membrane reactors and membrane contactors [26]. However, to date, the utilization of the ceramic hollow fiber membrane distributor in heterogeneous catalytic reaction has been seldom reported.

In this paper, the ceramic hollow fiber membrane was used as a reactant distributor to achieve the micro-scale distribution of reactants in heterogeneous catalysis. To evaluate the feasibility and the performance of the ceramic hollow fiber membrane distributor, catalytic hydroxylation of phenol with hydrogen peroxide on TS-1 catalyst was selected as a model reaction. Dihydroxybenzene (DHB), including hydroquinone (HQ) and catechol (CA), are widely used as antioxidants, medicines, perfumes, polymerization inhibitors, and for organic synthesis, etc. Phenol hydroxylation with H_2O_2 over the TS-1 catalyst for DHB production is considered as a promising production process for its remarkable advantages such as mild reaction condition, superior shape-selective oxidation capability as well as simple and environmentally friendly process [27,28]. The effect of structural parameters of ceramic hollow fiber membrane on the micro-scale distribution and the reaction selectivity was studied. Further, the influence of operation conditions such as the H_2O_2 flow rate, the stirring rate and the phenol/H_2O_2 molar ratio on the phenol hydroxylation reaction was investigated.

2. Experimental section

2.1. Materials

Phenol and hydroquinone were purchased from Shantou Xilong Chemical Co., Ltd. (China). Catechol was provided by the Shanghai Sansi Reagent Co., Ltd. (China), and 30% H_2O_2 solution was supplied by the Sinopharm Chemical Reagent Co., Ltd. (China). The above materials were of analytical grade. Methanol (>chromatography grade) was supplied by the Yuwang Group (China). TS-1 catalyst (average particle size, 200 nm; specific surface area, 408 $m^2\ g^{-1}$; Si/Ti molar ratio, 59) was provided by Baling Petrochemical Company (China). All water used in this work was self-prepared deionized water and had an electrical conductivity below 12 $\mu s\ cm^{-1}$.

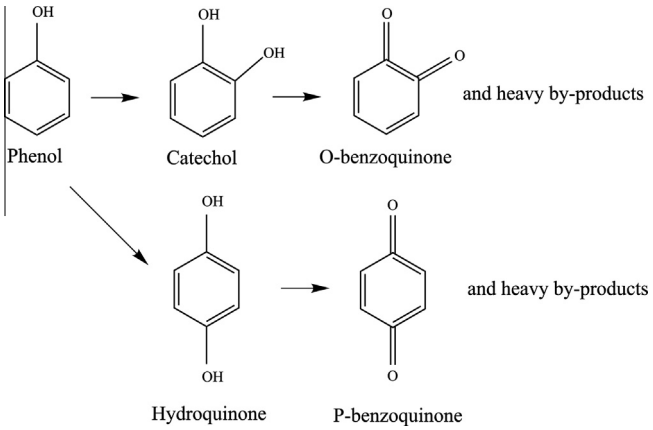
2.2. Fabrication of ceramic hollow fiber membranes

The ceramic hollow fiber membranes were prepared according to the method reported in the literature [21,22]. The varied microstructural characteristics of membrane were controlled by using different bore fluid composition [24,29]. The required quantity of aluminum powder, polyvinylpyrrolidone (PVP) and *N*-methyl-2-pyrrolidone (NMP) were taken in a stainless bottle, while a stirrer at a given speed was used to ensure that all the aluminum powders are dispersed uniformly in the suspended solution. After that, polyethersulfone (PES) was added into the suspension solution slowly. The result polymer solution was degassed at room temperature. Then the spinning dope was extruded by a variable flow pump through the spinneret into water with the air gap of 150 mm. Finally, the prepared precursor was dried at 373 K for 12 h and then calcined at a high temperature to form the ceramic hollow fiber membrane. The pore size distribution of ceramic hollow fiber membranes was measured by a modified bubble-point method [30]. The ceramic hollow fiber membranes with pore size of 2.0, 1.0, 0.5, and 0.3 μm were used as the reactant distributor. Their length, outer diameter and inner diameter were approximately 50 mm, 2.1 mm and 1.0 mm, respectively.

2.3. Hydroxylation experiment

To investigate the effects of ceramic hollow fiber membrane structure and operating conditions on the heterogeneous catalysis, the phenol hydroxylation with hydrogen peroxide over TS-1 was taken as a model reaction. For phenol hydroxylation catalyzed by TS-1, as a typical catalytic reaction in solid–liquid system, the surface titanium peroxo compounds form with H_2O_2 and subsequently transfer the peroxidic oxygen to phenol [31,32]. However, some unexpected by-products such as benzoquinone would be generated because of the strong oxidizing properties of H_2O_2, resulting in the decrease of DHB selectivity, as depicted in Scheme 1.

A submerged ceramic membrane reactor system was constructed and is shown schematically in Fig. 1, which consists mainly of slurry stirred reactor, ceramic hollow fiber membrane module, feed system and heating system. The reactor was a transparent cylindrical tank with a working volume of 300 mL. The ceramic hollow fiber membrane was connected to the liquid feeding tube at one end, and the other end was sealed with glaze. A constant flow pump (Beijing Chuangxin Tongheng Science & Technology Co., Ltd., China) was employed to feed H_2O_2 into the phenol



Scheme 1. The hydroxylation of phenol with hydrogen peroxide over TS-1 catalyst.