Chemical Engineering Journal 155 (2009) 829–837

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A one-step conversion of benzene to phenol using MEMS-based Pd membrane microreactors

Shu-Ying Ye[a,*], Satoshi Hamakawa[a,**], Shuji Tanaka[b], Koichi Sato[a], Masayoshi Esashi[b], Fujio Mizukami[a]

[a] Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1, Nigatake, Miyagino-ku, Sendai 983-8511, Japan
[b] Department of Nanomechanics, Tohoku University, 6-6-01 Aza Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

ARTICLE INFO

Article history:
Received 16 April 2009
Received in revised form 31 August 2009
Accepted 4 September 2009

Keywords:
MEMS (micro-electro-mechanical system)
Microreactor
Pd membrane
Hydrogen permeation
Direct hydroxylation
Benzene
Phenol

ABSTRACT

We have developed an MEMS-based Pd membrane microreactor for one-step conversion of benzene to phenol, and also evaluated the H_2 permeation characteristics through the Pd membrane before the benzene hydroxylation experiments. The conversion of benzene, selectivity and yield of phenol were investigated by varying the operation conditions. The phenol yield of 20% and benzene conversion of 54% were obtained at a reaction temperature of 200 °C. The phenol and dihydric phenols dominated the distribution of products and the hydrogenation products of from benzene and phenol were absent in the MEMS-based Pd membrane microreactor, which was very different from the macrotubular Pd membrane reactors. The effect of H_2/O_2 ratio on products distribution has been investigated. From the comparison of reaction results with a macrotubular Pd membrane reactor, it is figured out that the Pd membrane microreactors fabricated by MEMS technology gave a higher reaction conversion and product yield.

1. Introduction

Phenol is an extremely important chemical in industry, which is widely used in the production of drugs, dyestuffs and synthetic resin. Phenol is primarily produced by the cumene process, in which benzene is converted via cumene to cumene hydroperoxide. This multi-step process accompanies high-energy consumption and a large amount of acetone as a by-product. To overcome these problems, direct hydroxylation of benzene to phenol using oxidant such as H_2O_2 and N_2O has been studied [1–8]. These oxidants are, however, too much expensive to apply to the commercial production.

The direct hydroxylation of benzene using mixture of O_2 and H_2 is another alternative and has been widely studied in the liquid and gas phase [9–12]. Benzene oxidation in the gas phase seems to be more practicable for industrial applications [12], because the use of solvents is avoided. Although a very high selectivity of phenol (>90%) had been reported by some researchers [12, and references there], the conversion of benzene was less than 2% and resulted that the yield of phenol was also less than 2%. Such a yield of phenol is inadequate for practical use. In addition, there is a serious risk of explosion when H_2 mixes with O_2.

Our research group reported that a tubular Pd membrane reactor (PdMR) [13–18], schematically shown in Fig. 1, promoted hydroxylation and hydrogenation. It should be noted that this type of membrane reactor attained the direct conversion of benzene to phenol (yield ~ 20%). Active hydrogen species, which appear onto the surface via the Pd membrane, can easily react with molecules of oxygen and form active species like HO* or HOO* radicals. Thus, the active species attack benzene, and hydroxylation occurs readily to form phenol. This system is quite simple and can eliminate the risk of explosion because the supplies of O_2 and H_2 are physically separated, but the tubular shape of the Pd membrane has some difficulties to stack them for mass production.

The developments of chemical process miniaturization have taken large strides in the past few decades due to the evolution of micro-electro-mechanical system (MEMS) technology. MEMS technology enables us to integrate reactors with other devices such as pressure transducers, flow controllers and temperature control apparatus to form micro-systems capable of analyzing or synthesizing chemicals [19,20]. More importantly, the miniaturizations of chemical reactors to a micro-scale leads to unique characteristics different from conventional macroreactors, such as low-energy consumption, high surface-to-volume ratio, short response times, good reaction controllability, better heat and mass transfer properties and uniform flow and temperature distributions. In fact, a

---

[*] Corresponding author. Current affiliation: MEMS CORE Co. Ltd. 3-11-1, Aketori, Izumi-ku, Sendai 981-3206, Japan. Tel.: +81 22 777 8717; fax: +81 22 777 8718.
[**] Corresponding author. Tel.: +81 22 237 5211; fax: +81 22 237 5226.
E-mail addresses: yeh@mems-core.com (S.-Y. Ye), hamakawa.s@aist.go.jp (S. Hamakawa).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.09.007

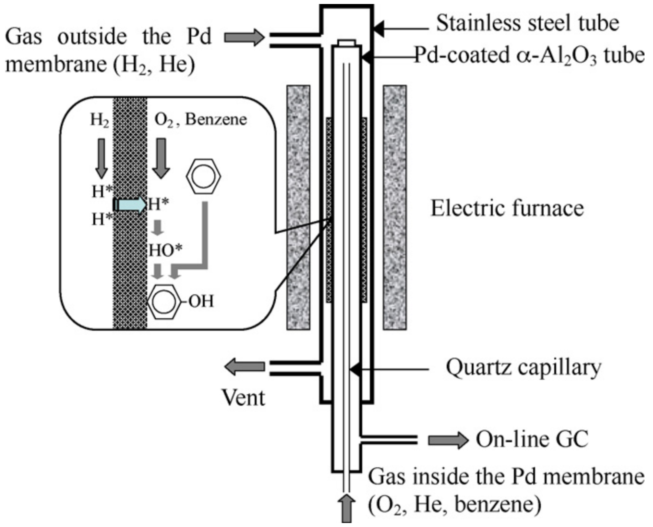

Fig. 1. Tubular PdMR for direct hydroxylation of aromatics and the working principle of the Pd membrane.

higher conversion and better product yield obtained in microreactors have been observed by some researchers [21–23]. Many fine chemical reactions of interest are constrained by unfavorable thermodynamics that could benefit from the membrane operation. Selective product removal could improve the product purity and achieve supra-equilibrium conversions [21–26]. Miniaturization also enhances the selectivity and permeation of the membrane compared to conventional membrane units [27–28].

We have developed a MEMS-based Pd membrane microreactor (PdMMR) [20] and applied it to the hydrogenation of 1-butene successfully. Since the PdMMR has a micro-dimension, the concentration of reactant gases is almost uniform on the surface of the membrane. Therefore, it is expected that the PdMMR promotes the hydroxylation of the benzene to phenol and increases the yield of phenol. Furthermore, the PdMMR has a possibility of scaling-up laboratory-level experiments directly to commercial production by stacking the same microreactors.

In this study, we demonstrated one-step conversion of benzene to phenol using the MEMS-based PdMMR for the first time. Prior to reaction experiment, we evaluated the gas permeation and permselectivity of the Pd membrane. The conversion, selectivity and yield of reactions were investigated by varying the operation conditions. Each test reaction was carried out and lasted up to 9 h. Results of reactions were compared with those of the macrotubular PdMRs [13–18].

2. Microreactor fabrication

The schematic structure of the MEMS-based PdMMR is shown in Fig. 2. It is composed of three layers: top glass cap, Si substrate and bottom glass cap. H_2 and reaction gas are supplied to the bottom and top side of the Pd membrane, respectively. Reaction products are obtained from the top side. The Pd membrane has a size of 5 mm × 5 mm. Oxidized porous silicon (PS) is served as a structural support for the Pd membrane. Under the oxidized PS support, micro-flow channels with a diameter of 100 μm are opened. A Pt/Ti micro-heater is formed on a Si_3N_4 insulation layer for heating the Pd membrane to improve H_2 permeability and prevent H_2 embrittlement. The oxidized PS ring is also formed around the Pd membrane for thermal isolation. The thermal isolation gap under the oxidized PS ring is 100 μm in width.

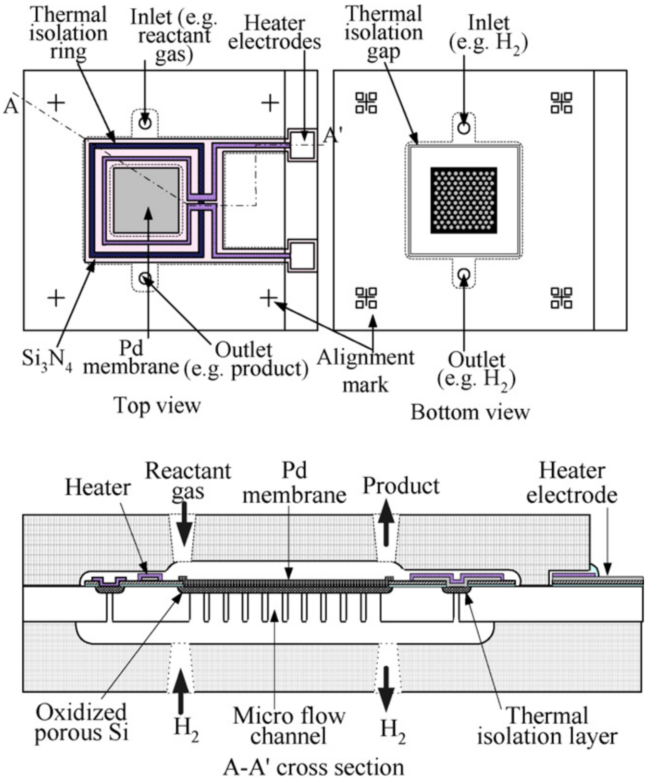

Fig. 2. Structure of MEMS-based PdMMR.

The fabrication process of the microreactor is shown in Fig. 3. The microreactor was fabricated from a 300 μm thick ⟨1 0 0⟩ p-type Si wafer polished on the double sides with resistivity of 0.01–0.02 Ω cm. The process started from coating the wafer with a 100-nm thick SiO_2 film and a 300-nm thick Si_3N_4 film by means of wet thermal oxidation and low pressure chemical vapor deposition (LPCVD), respectively. Then, the bilayer film of Si_3N_4/SiO_2, whose stress is compensated, was patterned by standard photolithography, followed by dry CF_4 plasma etching of Si_3N_4 and wet etching of SiO_2 using buffered oxide etch (BOE). In this step, the films of Si_3N_4 and SiO_2 on the backside were also removed.

Within the opened windows of the Si_3N_4/SiO_2 film, PS was formed by anodization in HF-ethanol (C_2H_5OH) electrolyte (HF (50%):C_2H_5OH:H_2O = 1:1:1 in volume). To generate a 30 μm thick PS layer, the anodizing time was 20 min with a current density of 30 mA/cm^2. Furthermore, the PS should be oxidized thermally to stop deep reactive ion etching (DRIE) in the step 7 of the process chart. Next, the Pt/Ti heater was formed around the PS area by sputtering and lift-off process. The ring design of the micro-heater allows a large area of the membrane to be heated. And then, the thermal isolation ring and the heater were covered with SiO_2 to prevent gas from permeating via the thermal isolation ring and to prevent synthesized product from being decomposed by Pt.

The Si substrate was etched from the backside by deep reactive ion etching (DRIE) to release the PS layer and make the flow channels of H_2. After the bottom glass cap was bonded to the Si substrate by anodic bonding technique, a 500-nm thick Pd film was deposited on the surface of the oxidized PS by controlling sputtering time at a substrate temperature of 200 °C. To improve H_2 permeation through the Pd membrane, we did not use any adhesion layer. The final step in the fabrication was to bond the top glass cap to the Si substrate. Both top and bottom cap are made of Pyrex glass and etched in HF (50%) solution to form micro-gas channels. Through holes served as gas inlets and outlets were fabricated by sandblasting from a nozzle. The size of the completed microreactor is 25 mm × 20 mm.