Catalysis Science & Technology

PAPER

Cite this: Catal. Sci. Technol., 2013, 3, 2380

Received 7th March 2013, Accepted 27th May 2013

DOI: 10.1039/c3cy00159h

www.rsc.org/catalysis

1 Introduction

Phenol is an important intermediate chemical in industry, which is widely used in the synthesis of drugs, polymers, petrochemicals and agrochemicals. Phenol is mainly produced by the multi-step cumene process with high energy consumption, low atom utilization and a large amount of acetone as the side product. The direct hydroxylation of benzene to phenol using clean oxidants like H_2O_2 and N_2O has therefore attracted more attention.¹⁻⁴ These oxidants are too expensive to be applied in commercial production, but considerable economic benefits could be gained if oxygen is used as oxidant agent. As a result, several direct routes have been proposed with examples using O_2 and H_2 over precious metal catalysts.^{5,6} The O_2 - H_2 system is green but still presents considerable challenges. The desired benzene conversion and phenol yield have not been achieved although a very high phenol selectivity (>90%) was

One-step hydroxylation of benzene to phenol *via* a Pd capillary membrane microreactor

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A novel Pd capillary membrane microreactor for one-step hydroxylation of benzene to phenol was synthesized and investigated to showcase the effectiveness of 'Niwa concept'. Reaction parameters including H_2/O_2 ratio and temperature were systematically studied for their effects on benzene conversion and phenol yield. A detailed examination of different membrane reactors, feed mode and long-term reaction stability was also conducted. Pd capillary membrane displayed good stability for low temperature separation and reaction due to the excellent anchorage of Pd layer into the porous α -alumina support. An optimum H_2/O_2 ratio was identified at 473 K with the benzene conversion of 19.6% and phenol yield of 18.1%. An increase in reaction temperature caused not only an increase in benzene conversion but also a decrease in phenol selectivity. A comparison between our work and the literature results was also made to discuss the feasibility of the membrane reactor concept. Experimental results proved that narrow flow channels and larger Pd membrane surface area-to-volume ratios provided more effective area of Pd interface and promoted the radial diffusion of reactants, enabling the reactive species more opportunities to react directly with benzene resulting in high benzene conversion.

reported. On the other hand, the operation is restricted by the flammability and the high cost of acid solvents.

A higher benzene conversion and phenol yield over the O2-H2 system has been achieved by the research group of AIST (Japan) who introduced a Pd membrane reactor, employing the surface of a dense Pd film on a porous support as the catalyst.⁷ In this novel reactor, the palladium membrane was used to separate and control the reaction between hydrogen and oxygen. The active hydrogen atom generated through the membrane reacted with oxygen to produce 'in situ' hydrogen peroxide and other active oxygen species (e.g., HOO[•] and HO[•]), which further reacted with the benzene to form phenol. A high phenol yield up to 23% with phenol selectivity of 77% were reported at moderate reaction temperature (473 K). Via the Pd membrane reactor, the direct contact of O2 and H2 can be avoided and the hazard of O2-H2 process is greatly reduced. Thus it becomes a safe, simple, clean and economical process.

It has been a decade since Niwa and co-workers proposed the Pd membrane reactor for one-step hydroxylation of benzene to phenol,^{7–10} however other researchers reported some difficulty in reproducing their results.^{11–17} Vulpescu *et al.* reported that the phenol yield was at a negligible level (as low as 0.16%) and stated that the membrane reactor concept was still far from

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commercial application.¹¹ Sayyar and Wakeman concluded that this process was uneconomical due to the low phenol productivity and selectivity.12 Shu and co-workers reported that the Pd membranes were almost inert (as low as 0.13%) for the reaction and this membrane concept was not effective for the benzene hydroxylation.¹³ Bortolotto and Dittmeyer investigated a novel 'double membrane reactor' with different membranes to distribute hydrogen and oxygen into the microchannels with total height of 2 mm.^{14,15} However, an undesirable benzene conversion (ca. 0.015%) was obtained. It should be noted that membrane deterioration was also observed when the reactions were prolonged in earlier works.⁷ So far, long-term reaction stability has seldom been reported although it is a key factor for practical application. Pd-zeolite composite membranes were attempted to improve the reaction performance by introducing a zeolite layer to the Pd membrane reactor. Pd-Sil-1 (silicalite-1) composite membrane was employed for direct hydroxylation of benzene to phenol.¹⁶ Although the stability of the Pd membrane reactor was improved, the benzene conversion was still too low (ca. 5%) to be considered practical. Previously we applied a novel bifunctional Pd-TS-1 composite membrane reactor to improve the Pd membrane stability by incorporating a TS-1 (titanium silicalite-1) zeolite which is an active catalyst for the selective oxidation of organics.¹⁷⁻²² It is possible to enhance the catalytic performance using Pd-TS-1 composite membrane reactor though the benzene conversion was remained low. Compared to the Pd-TS-1 membrane, Pd-TS-1p (mesopore TS-1) membrane exhibited better catalytic performance.¹⁷ A faster diffusion of reactants in mesoporous TS-1p layer led to higher benzene conversion in Pd-TS-1p (ca. 5.4%) as compared to Pd-TS-1 composite membrane (ca. 0.1%). When comparing the performance of tubular membrane reactors with different diameters,^{7-13,16,17,22} normally reactors with larger diameter membranes displayed lower benzene conversion due to the smaller area of Pd interface for reactions and slower radial diffusion of reactants resulting from the smaller membrane surface area-to-volume ratio. This may be an important reason for the lower reaction efficiency related to the larger diameter membrane. A similar phenomenon was also observed in our recent work that the benzene conversion and phenol yield were consistently lowered using a large diameter membrane with a small membrane surface area-to-volume ratio and indeed the use of a Pd capillary microreactor with a larger surface area-to-volume ratio improved the benzene conversion up to 19%.²² A higher benzene conversion of 54% and phenol yield of 20% were obtained using a 'real' microsystem fabricated by silicon-based MEMS technology.23 Miniaturization can lead to high membrane surface area-to-volume ratio and better mass transfer properties, thus resulting in better reaction performance.

In spite of these advantages, there is still a hot debate on the real effectiveness of this membrane concept to be applied in this reaction process. Consequently, it is still necessary to have more experimental results to illustrate the feasibility of the reaction concept. The aim of the present work was to investigate a novel Pd capillary membrane microreactor for direct hydroxylation of benzene to phenol. It is expected that the reaction performance could be improved due to the enhanced mass transfer rate along the radial direction by providing a large palladium membrane surface area-to-volume ratio. The reactor configuration and reaction conditions on benzene hydroxylation were systematically examined. Further more, the long-term stability of the Pd membrane, a key factor for the reaction, was demonstrated. Finally, a comparison with the literature results was given in details.

2 Experimental

2.1 Materials

The α -Al₂O₃ capillary tubes from Hyflux Ltd. have inner and outer diameters of 2.5 and 3.5 mm, respectively. The 75 mm long α -alumina tubes with a mean pore diameter of 800 nm were used for palladium deposition. The reagents for the synthesis of the Pd membranes including hydrazine (N₂H₄), tin chloride dehydrate (SnCl₂·2H₂O), Na₂EDTA·2H₂O (C₁₀H₁₄N₂Na₂O₈·2H₂O) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Palladium chloride (PdCl₂) was supplied by Shanghai Jiuling Chemical Co., Ltd.

2.2 Membrane preparation

The tubes were first cleaned by a series of sonication in ethanol and distilled water to remove dirt and contaminants, and dried in an oven overnight at 393 K. The tubes were then end-sealed with glass enamel and gave a 30 mm porous section for membrane deposition. A thin continuous palladium layer was deposited on the α -alumina tubes by electroless plating technique.²⁴ Prior to the deposition of palladium membrane, the tubes were first seeded by a sequential immersion in SnCl₂ and PdCl₂ solutions for 8-10 times until a perfectly activated layer with a dark-brown color was obtained. Each dipping lasted for 4 min and the support was rinsed with distilled water between both solutions. The activated α-alumina tube was then treated in a plating solution containing PdCl₂, EDTA·2Na, NH₃·H₂O and N₂H₄ at 318 K for 240 min to form a thin palladium layer on substrate. The membrane was rinsed with ethanol and distilled water before drying at 393 K. The microstructure and thickness of membrane were examined by KYKY-2800B and JEOL 6300F scanning electron microscopy at 20 kV accelerating voltage. The quantitative analysis of membrane was performed on a energy dispersive X-ray spectrometer (EDX) equipped with a SEM instrument. The permeation properties of the membrane were measured by hydrogen and nitrogen permeations in a home-made gas permeation unit.17 Nitrogen leak tests were first performed at room temperature and only leakfree membranes were used. The flux was measured at different feed pressures and temperatures using a soap-bubble flow meter.

2.3 Hydroxylation of benzene to phenol

The membrane reactor shown in Fig. 1 was used for the direct hydroxylation of benzene to phenol using hydrogen and oxygen as co-reactants. The Pd membranes were placed inside a stainless steel tube using graphite O-rings. The Pd membrane



Fig. 1 Schematic of direct hydroxylation of benzene to phenol using the Pd capillary membrane microreactor.

supported on porous α -alumina capillary tubes has a small tubular passage of 2.5 mm. The distance from the inner wall of the stainless reactor shell to the surface of the Pd membrane was designed at 500 microns to form a microchannel. Compared to large diameter membranes,^{11–13,16,17} a Pd membrane microreactor was formed. Fig. 2 describes the different flow configurations. In a typical operation mode as shown in Fig. 2a, benzene was fed to the membrane side together with oxygen by bubbling nitrogen carrier through a benzene saturator, while hydrogen flowed through the tube side was permeated through the membrane to the reaction zone. While in some cases, a different operation mode was adopted with hydrogen introduced to the outside of the membrane and a ternary mixture gas of benzene, oxygen and nitrogen flowing to the inside of the Pd membrane, as shown in Fig. 2b. The feed rates of the gases were regulated by mass flow controllers and the temperatures of the membrane module were adjusted by a temperatureprogrammable furnace. The feed rate of hydrogen, oxygen and benzene was fixed at 40, 1–20 and 0.61 ml min⁻¹, respectively. To investigate the effect of H₂/O₂ ratio (the amount of hydrogen transported through the membrane in relation to the

amount of oxygen fed to the reactor) on the product distribution, the H₂ permeation flux was kept constant by adjusting the pressure in the inlet and the feed rate of O₂ was varied. The hydrogen permeation rate under the reaction conditions was calculated by subtracting the hydrogen flow rate in the retentate side measured by a soap bubble flowmeter from the amount of hydrogen fed to the reactor.9 The gaseous mixture coming out of the reactor was analyzed by two online gas chromatographs (GC-7890T; GC-7890F). The organic products were analyzed by FID equipped with a 50 meters SE-30 capillary column, while inorganic products were analyzed by a thermal conductivity detector (TCD) with a 13X molecular sieve and a GDX molecular sieve packed columns. The benzene conversion (X_{BEN}) and phenol selectivity (S_{PHE}) based on the generated hydrocarbons were calculated according to the eqn (1) and (2). All gas lines from the furnace to the chromatograph were heated and temperature-controlled to avoid condensation of the products. The whole reactions in this study were performed by using the sole Pd membrane tube. In order to avoid the membrane damage by the rapid change of temperature, the reactor was kept at the reaction temperature with nitrogen



Fig. 2 Feed modes of reaction scheme with the Pd membrane reactor.

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flowing both trough the inside and outside of the membrane during the reactions.

$$X_{\rm BEN} = \frac{\rm MOL(reacted BEN)}{\rm MOLS\,(un-reacted BEN + generated hydrocarbons)} \times 100\%$$
(1)

$$S_{\rm PHE} = \frac{\rm MOL(PHE)}{\rm MOLS(PHE + generated other hydrocarbons)} \times 100\%$$
(2)

3 Results and discussion

3.1 Preparation of the Pd membrane on a capillary ceramic tube

Fig. 3 displays the SEM images of α -alumina support and deposited palladium membrane. It can be seen in Fig. 3a and b that the α -Al₂O₃ capillary tube has smooth surface and small pore size distribution. A mean pore diameter of 800 nm was measured, although larger pores were also observed from the micrograph (marked with blue rings). Fig. 3c and d are SEM images of the deposited Pd layer on the surface of the support. A 4–5 µm thick palladium layer with micron-sized grains was uniformly deposited on the support. Defects and pinholes were not observed during the SEM examination and the prepared membrane was impermeable to nitrogen at room temperature. The palladium was anchored directly on the capillary ceramic tube forming a strong adhesion.

Fig. 4 plots the energy dispersive X-ray spectrum (EDX) of surface and cross-section line scans for Pd capillary membrane.

Only palladium was detected by EDX surface line analysis (Fig. 4 inserted), demonstrating that a dense Pd membrane layer on the surface of the capillary ceramic tube was successfully deposited. The elemental profiles along the cross-section of the Pd membrane show three distinct regions rich in Al, O and Pd corresponding to the α -Al₂O₃ support and Pd membrane, respectively. The palladium signal is most intense near the surface where it coincides with the 5 µm thick layer and decreases as it approaches the alumina bulk. The plots of Pd and Al signals indicate that besides forming a thin layer on the surface, the Pd also penetrated deep into the porous alumina support through the pores. Better membrane stability with similar anchorage was obtained as reported in literatures.^{25,26}

The hydrogen flux and H_2/N_2 ideal selectivity are plotted in Fig. 5 and 6 as a function of temperature and trans-membrane pressure. The H_2 flux and H_2/N_2 ideal selectivity of the Pd membrane at 473 K were 0.08 mol m⁻² s⁻¹ and 379, respectively. Higher H_2 flux of 0.14 mol m⁻² s⁻¹ and H_2/N_2 selectivity of 1023 were obtained at 673 K. The low nitrogen permeance of the Pd membrane was less than 10^{-9} mol m⁻² s⁻¹ Pa⁻¹, suggesting low number of defects. Fig. 6 shows that the hydrogen fluxes increase linearly with $\Delta P^{0.5}$ in the working temperature range, which is consistent with Sievert's law.²⁷ The H_2 permeation and H_2/N_2 ideal selectivity are comparable to the literatures.^{9,10,28-31}

3.2 Direct hydroxylation of benzene to phenol

The direct hydroxylation of benzene to phenol on Pd capillary membrane reactor was performed at different feed mode, $\rm H_2/O_2$



Fig. 3 SEM images of (a and b) α -alumina tube and (c and d) deposited palladium membrane.



Fig. 4 EDX surface and cross-section line scans of the Pd capillary membrane.



Fig. 5 (a) Hydrogen flux and (b) ${\rm H_2/N_2}$ ideal selectivity of the Pd membranes at different temperatures.



3.2.1 H_2/O_2 ratio. The probable reaction pathways shown in Fig. 7 could be classified into three categories: hydrogenated products (*i.e.*, cyclohexane, cyclohexanone, *etc.*), oxidized products (*i.e.*, CO₂, H₂O) and hydroxylation products (*i.e.*, phenol and diphenol). The surface state of the Pd membrane should strongly depend on the atmospheric gas and the reaction was sensitive to the H₂/O₂ ratio.^{8,17,23} Some researchers have investigated the effects of H₂/O₂ ratio on the product distribution using flat Pd microreactor,^{14,15,23} however, to our knowledge, a detailed elaboration of the effect of H₂/O₂ ratio on the benzene hydroxylation reaction performance in tubular membrane reactor is not available in open literatures. Furthermore, the



Fig. 6 Hydrogen flux of the Pd membranes as a function of pressure at different temperatures.

correlation between the H_2/O_2 ratio and the product distribution may also be dependent on the different membrane reactors,^{8,14–17,23} especially for flat, tubular or capillary membrane geometries. Therefore, a number of experiments were carried out at 473 K with different H_2/O_2 ratio in order to determine their influence on reaction performance. In order to investigate the effect of H_2/O_2 ratio (the amount of hydrogen transported through the membrane in relation to the amount of oxygen fed to the reactor) on the product distribution, the H_2 permeation flux was kept constant by adjusting the pressure of H_2 in the inlet, while the feed rate of O_2 was varied to adjust the ratio of H_2 to O_2 from 1.5 to 10.



Fig. 7 Proposed reaction scheme for the direct hydroxylation of benzene to phenol over a Pd membrane reactor.

Fig. 8 shows the reaction performance as a function of H_2/O_2 ratio under mode 1 which benzene and oxygen reactants were fed into the membrane side and hydrogen was introduced into the inside of the membrane. The distribution of products was completely different at a H_2/O_2 ratio of 3.3 and 2.5. High H_2/O_2 ratio (>3.3) favored hydrogenation resulting in an increase in cyclohexanone, while low H_2/O_2 ratio (<2.5) led to the formation of carbon dioxide, which is the main oxidized product (Fig. 7). Note that other by-products were not observed except CO2 when H2/O2 ratio was below 2.0. The maximum benzene conversion of 19.6% and phenol yield of 18.1% were obtained at H₂/O₂ ratio of 4. The H₂/O₂ ratio strongly influenced the atmospheric conditions of the membrane reactor. When H_2/O_2 ratio was below 2.5, most of the generated active hydrogen atoms were consumed by oxygen and the unreacted oxygen remained in the reactor. Therefore, the palladium surface was under an oxidative atmosphere, in which H₂ complete oxidation was dominant. On the other hand, when the H_2/O_2 ratio was larger than 3.3, most of the oxygen reacted with permeated active hydrogen species. Thus, unreacted permeated hydrogen atoms recombined to form molecular hydrogen on the surface of the palladium layer and desorbed into the inside of the reactor. As a result, in this case, the reactor was under a reductive atmosphere, which is favored for hydrogenation. A similar dependency on the H_2/O_2 ratio was reported for the direct hydroxylation of methyl benzoate to methyl salicylate.³² It is clearly seen from the results that the concentration of hydrogen and oxygen in the reaction region is crucial for increasing the phenol yield and should be controlled in a proper range. More importantly, compared to the published results,^{11–13,16,17} a high benzene conversion and phenol yield were obtained in this work. The high reaction performance is believed to be due to the larger membrane surface area-to-volume ratio in the capillary membrane compared to the large diameter membrane by other researchers and our previous works.^{11-13,16,17} Indeed, the use of MEMSbased 'real' Pd microreactor with higher membrane surface area-to-volume ratio gave benzene conversion of up to 54% and phenol yield of 20%.²³ Miniaturization could significantly improve the surface area-to-volume ratio to contribute to a better reaction performance. The comparison of reaction data on mode 1 and mode 2 (Fig. 2) further confirms this hypothesis.



Fig. 8 Effect of H_2/O_2 ratio on the reaction properties (a: benzene conversion/ phenol yield; b: phenol and cyclohexanone selectivity) under mode 1.

For mode 1 shown in Fig. 2, the benzene and oxygen were fed to the membrane side and the hydrogen was fed from the support side. Under this condition, the distance from the outside surface of the membrane to the inner wall of the stainless steel reactor was only 0.5 mm. The volume of the reaction zone and Pd membrane surface area-to-volume was 188.4 mm³ and 1.75 mm⁻¹, respectively. While for mode 2, the benzene and oxygen were introduced into the inside of membrane tube and the hydrogen flow from outside of the membrane; in this case, the volume of the reaction zone and Pd membrane surface area-to-volume was 288.5 mm³ and



Fig. 9 Reaction properties of (a) benzene conversion, (b) phenol selectivity and (c) yield as a function of H_2/O_2 ratio under mode 2.

1.14 mm⁻¹, respectively. Compared to mode 1, the effective reaction zone was decreased for mode 2, which should result in a lower reaction activity. On the other hand, for mode-1, the benzene and oxygen reactants flowed along the surface of the membrane and most of the reactants could react with permeated active hydrogen species immediately, whereas, for mode-2, the benzene and oxygen reactants had to diffuse through the porous support layer from the tube side to reach the membrane interface to react with hydrogen. The larger reaction zone and the diffusion resistance across the support may jointly affect the contact opportunity between benzene, oxygen, and the permeated hydrogen for mode 2, which resulted in lower reaction performance and different optimum operation conditions. Compared to mode-1, mode-2 provided less area of Pd interface for reactions as part of the Pd membrane was blocked by the porous support. This may be another reason for the lower reaction efficiency from mode-2. The effect of less membrane area in mode-2 is also reflected by its lower hydrogen permeation flux value of 0.05 mol m^{-2} s⁻¹ at the transmembrane pressure of 160 kPa in contrast with the flux value of $0.07 \text{ mol m}^{-2} \text{ s}^{-1}$ when permeated from the membrane side. In another word, at similar operating and feeding conditions, mode-2 provided less hydrogen atoms, which in some sense also restricted the reactions. Indeed, the maximum benzene conversion and phenol yield decreased compared to mode-1, as shown in Fig. 9. The highest benzene conversion of 15.8% and phenol yield of 14.5% were obtained when H₂/O₂ ratio was 2.5 for mode-2. Although the optimum H_2/O_2 ratio for two modes

was different, the change trend was similar. The benzene conversion and phenol yield increased with increasing the H₂/O₂ ratio and reached a maximum and then decreased with H_2/O_2 ratio. Noteworthy is that the reaction volume of the Pd capillary membrane reactor was smaller than those from literatures^{11-13,16,17} even for mode-2 and a larger membrane surface area-to-volume ratio from the Pd capillary membrane reactor definitely led to high reaction activity. For a more in-depth understanding of this phenomenon, the difference in reactant transport path and the chance for reaction participation from two modes is schematically shown in Fig. 10. It is not difficult to understand that larger part of the reactants easily flow along the axial direction for the larger diameter Pd membrane (Fig. 10a) and only a smaller part of reactants diffuse along the radial direction to reach the membrane surface. Thus, there is a smaller quantity of reactants to reach the reaction region and react with active hydrogen atoms in larger diameter Pd membrane reactors,^{11–13,16,17} leading to lower catalytic activity. On the contrary, the Pd capillary membrane with smaller diameter could give the reactants more contact opportunity resulting in higher reaction performance (Fig. 10b).

3.2.2 Temperature. Fig. 5 and 6 show that the hydrogen permeation flux increases with temperature and should favor the hydrogenation reaction as shown in Fig. 11. Table 1 summarizes the results of the benzene hydroxylation at 423, 473, 523 and 573 K under mode 1 operation condition. With increasing the temperature, the phenol selectivity decreased,



Fig. 11 Effect of temperature on hydrogenation.



Fig. 10 Diffusion diagram of reactants on (a) large Pd membrane reactor and (b) Pd capillary membrane reactor.²²

				** 1	Phenol selectivity (%)	Products yield (%)		
Temperature (K)	conversion (%)	(kg per kg Pd per h)	H ₂ O/phenol molar ratio	conversion (%)		Phenol	Cyclohexane	Cyclohexanone
423	16.01	0.92	90	39.1	90.01	14.41	0.00	1.59
473	18.87	1.04	122	54.5	86.35	16.29	1.59	0.98
523	22.38	1.09	145	56.6	76.32	17.08	3.51	1.79
573	17.21	0.75	215	42.5	68.32	11.76	3.67	1.71
Note: the mass of	f Pd supported or	n capillary tube was 0.0	024 g.					

 Table 1
 Effect of reaction temperature on direct hydroxylation of benzene to phenol

although benzene conversion increased, probably due to the formation of hydrogenated products. The highest benzene conversion of 22.4% and phenol yield of 17.1% (1.09 kilograms per kilograms of catalyst per hour) were obtained at 523 K in this study. On the other hand, most of the hydrogenation products (i.e., cyclohexane and cyclohexanone) were also formed at 523 K. Here, the palladium acted as the catalyst not only for hydroxylation but also for hydrogenation and oxidation. High temperature enhanced the hydrogenation reaction and suppressed the selectivity of phenol. High temperature favors water production leading to lower hydrogen efficiency. The water generation rate was increased by 95% with increasing temperature from 423 to 573 K as high temperature would accelerate the decomposition of peroxide on palladium surfaces.³³ Despite the comparable phenol production rate was obtained at 473 and 523 K (1.04 versus 1.09 kilograms per kilograms of catalyst per hour), water generation rate was much lower at 473 K. With overall consideration, it is proper to choose 473 K as reaction temperature in terms of benzene conversion, phenol selectivity and hydrogen utilization for this reaction.

3.2.3 Stability. Although the stability of the Pd membrane reactor has been widely studied at high temperature (>600 K), the application at low temperature was limited because the pure palladium often suffers embrittlement at temperatures below 573 K.³⁴ A high risk of membrane failure at low temperature for benzene hydroxylation was observed by Niwa et al.7 and Shu et al.13 Fig. 12 and 13 show the results of long-term reaction of benzene hydroxylation at 473 K. The benzene conversion and phenol selectivity remained constant during the 140 h of reaction. On the other hand, during the entire reaction process, the cyclohexanone selectivity and yield were also constant. The significant deactivation was not observed during the series reactions. The hydrogen flux during the reaction was measured and plotted in Fig. 14. A flux of *ca.* 0.05 mol m^{-2} s⁻¹ was maintained at 473 K over the entire period. The hydrogen flux was also relatively constant before and after the reaction at different temperatures, as shown in Fig. 15. SEM analysis of the membrane before and after reaction (Fig. 16) did not reveal a significant change in morphology. The excellent stability of the Pd capillary membrane was due to the excellent anchorage of the Pd layer inside the α -alumina support (Fig. 4). Thus, the microstructure of the Pd membrane played an important role in reaction stability. These results indicated that the Pd capillary membrane was highly stable and exhibited good reaction performance.



Fig. 12 The catalytic stability of the palladium membrane supported on a hollow fiber ceramic tube at 473 K in terms of benzene conversion, phenol selectivity and yield.



Fig. 13 The catalytic stability of the palladium membrane supported on a hollow fiber ceramic tube at 473 K in terms of cyclohexanone selectivity and yield.

3.2.4 Comparison with published data. As mentioned earlier, the hot debate on the effectiveness of the Pd membrane reactor is still going on for the direct hydroxylation of benzene to phenol. Therefore, it is important to liaise with the literatures' results to shed some light on the feasibility of the membrane concept. The related reaction results are summarized in Tables 2–4 for comparison purpose. It is not difficulty to see from Table 2 that the reported catalytic performances vary

0.10



Fig. 14 Long-term operation for hydrogen permeation at 473 K and 160 kPa



Fig. 15 Hydrogen flux before and after hydroxylation reaction at different temperatures at 160 kPa.

greatly from different research groups. A higher benzene conversion and phenol yield were obtained on the Pd membrane reactor possessing both narrow flow channels and larger membrane surface area-to-volume ratio (Table 3). As illustrated in Fig. 10, the reactants transport not only in radial direction but also in axial direction. For the bigger diameter Pd membrane (Fig. 10a),^{11-13,16,17} larger part of benzene and oxygen reactants outflow the reactor and only a smaller part of reactants could diffuse along the radial direction to the reactive interface. As a result, only a small amount of reactants could participate in the reaction with active hydrogen atoms permeated from the opposite side; the unconsumed hydrogen atoms would recombine to molecular hydrogen, leading to lower hydrogen efficiency and benzene conversion. However, for the Pd capillary membrane, the narrow flow channel spurs more reactants to flow along the surface of the tube and reach the reactive interface and then react with active hydrogen species immediately (Fig. 10b). On the other hand, thin wall thickness of support will also be beneficial for the benzene and oxygen diffusion along the radial direction to the reaction zone, as shown in Fig. 10. The narrow flow channel and thin wall thickness may jointly enhance the radial diffusion of reactants, which further improve the contact opportunity of reactants with active hydrogen species. The permeated hydrogen species through the Pd capillary membrane could react with oxygen and benzene immediately, preventing the permeated hydrogen atoms to recombine on the Pd membrane. The availability of active species could be improved and a higher benzene conversion and phenol yield was obtained. Our recent work also proved that larger membrane surface area-to-volume ratio and small reaction volume gave the reactive species greater opportunity to react directly with benzene resulting in high benzene conversion by comparing three different Pd membrane reactors.²² The concentration and flow rate of reactants should also influence the catalytic activity. Table 3 gives the benzene feed rate and residence time on the different Pd membrane reactors.



Fig. 16 SEM images of the Pd membrane: (a and b) before and (c) after reaction.

Support			Reaction performance					
O.D. (mm)	I.D. (mm)	Wall thickness (mm)	Flow channel (mm)	Benzene conversion (%)	Phenol selectivity (%)	Phenol yield (%)	Long-term (h)	Ref.
2.0	1.6	0.2	1.6	13.25	85.3	11.3	10	7
2.0	1.6	0.2	_	2.11	94.8	2.0	_	7^a
2.0	1.5	0.25	1.5	25-30	~77	19-23	7	8
2.0	1.6	0.2	0.9	18	79	14.3	5	9^a
2.0	1.6	0.2	0.9	10	40	4	20	10^a
14.2	_	_	_	3.8	4.1	0.16	72-96	11
_	7 (3.2)	_	_	_	_	_	_	12
12.5	7.5	2.5	0.5-0.7	0.15	87	0.13	_	13
13	9	2	2-3	5.06	60.81	3.08	46	16
13	9	2	2-3	5.39	94.79	5.11	_	17
13	9	2	0.5	7.3	95	6.9	_	22
_	_	_	0.1	54	37	20	9	23^b
_	_	_	2	0.015	9.6	0.001	_	14^c
_	_	_	2	_	67	_	_	15^c
3.5	2.5	0.5	0.5	18.80	86.10	16.19	140	Mode 1^d
3.5	2.5	0.5	2.5	15.82	91.50	14.48	140	Mode 2^d

 a The reaction occurred at the back side of the Pd membrane. b Planar MEMS-based Pd membrane microreactor. c Planar microstructured membrane reactor with distributed dosing of H₂ and O₂ through Pd and Ag film. d This work.

Table 3 Comparison of the performance for the different Pd-based membranes

Pd membrane ^a				Reaction performance ^b									
O.D. (mm)	I.D. (mm)	L (mm)	Area (mm²)	Cross section area (mm ²)	Reaction volume (mm ³)	A/V (mm ⁻¹)	<i>Т</i> (°С)	Benzene feed rate (mL min ⁻¹)	Linear velocity (mm min ⁻¹)	Space velocity (mm min ⁻¹)	Residence time (min)	Benzene conversion (%)	Ref.
2.0	1.6	100	502.4	2.01	200.9	2.5	150	0.426	0.848	211.94	0.47	13.25	7
2.0	1.6	100	502.4	2.01	200.9	2.5	200	0.342	0.681	170.15	0.59	10-15	7
2.0	1.6	100	502.4	3.14	_	_	150	2.01	4.0	640.13	0.16	2.11	7 ^c
2.0	1.6	100	502.4	3.14	_	_	200	2.01	4.0	640.13	0.16	3.00	7 ^c
2.0	1.5	100	471.0	1.77	176.6	2.67	200	0.17	0.361	96.05	1.04	25-30	8
2.0	1.6	100	628.0	1.63	275.5	2.78	150	0.54	0.860	331.29	0.3	15.9	9 ^c
2.0	1.6	100	628.0	1.63	275.5	2.78	200	0.54	0.860	331.29	0.3	18.0	9 ^c
2.0	1.6	100	628.0	1.63	275.5	2.78	160	0.052	0.083	31.90	3.13	10	10^c
14.2	_	72	3210	162.02	5324.2	0.6	150	14.9	4.642	91.96	0.78	3.8	11^d
12.5	7.5	100	3925	10.01-14.12	2041-2901.4	1.4-1.9	150	0.16	0.041	11.33-15.98	6.26-8.83	0.15	13
12.5	7.5	100	3925	10.01-14.12	2041-2901.4	1.4-1.9	180	0.54	0.138	38.24-53.95	1.85 - 2.62	0.15	13
13	9	30	1224.6	150.72	2826-4521.6	0.3-0.4	200	1.06	0.866	7.03	4.27	4.26	17
_	_	_	4800	80	_	_	—	0.309	0.064	_	2-2.5	0.015	14
_	_	_	25	_	_	100	—	0.001	0.04	_	_	54	23
3.5	2.5	30	329.7	6.28	188.4	1.75	200	0.61	1.851	97.13	0.31	18.9	This work
3.5	2.5	30	329.7	9.62	288.5	1.14	200	0.61	1.851	63.41	0.47	15.8	This

^{*a*} Cross-section area are referred to the Pd membrane side, the reaction volume was the benzene fed to and the *A/V* was the membrane area/reaction volume. ^{*b*} Linear velocity was calculated by benzene feed rate/area of the Pd membrane, space velocity was calculated by benzene feed rate/cross section area and residence time was calculated by *L*/space velocity. ^{*c*} The reaction occurred at the back of the Pd membrane. ^{*d*} The flow channel was assumed to be 3 mm.

Table 4	Comparison of membrane	productivity and	l raw materia	Is efficiency of
different	Pd membranes			

Mass of Pd (g)	$T(^{\circ}C)$	Phenol (kg per kg Pd per h)	H ₂ O/phenol ratio	Hydrogen conversion (%)	Ref.
0.008	150	1.5	500	NR	7 and 8
0.077	150	0.1	120	6.8	11
0.02	150	$4.92 imes10^{-5}$	_	_	14
0.024	150	0.92	90	39.1	This work
0.024	200	1.04	122	54.5	This work

It should be noted that the benzene conversion was not completely dependent on the residence time of benzene reactant in the reactor. For the larger diameter Pd membrane,^{11,13,17} the residence time was much more than for the Pd capillary membrane. However, the large diameter Pd membrane exhibited lower catalytic performance. On the other hand, as one expect, slow benzene flow rate could result in better interface contact with active hydrogen species and lead to higher benzene conversion. However, the benzene conversion was not in accordance with

benzene linear velocity and space velocity as illustrated in Table 3. This is because the benzene and oxygen reactants are in favor of transverse diffusion along the ceramic tube as above explained. Thus, slow benzene flow rate could not lead to better interface contact with active hydrogen and result in lower benzene conversion for the larger diameter membrane. On the contrary, excellent interface contact and higher benzene conversion were obtained though the benzene flow rate was high for capillary membrane due to the small diameter. The difference should be the effective contact area between the reactants and active hydrogen species resulting from the different membrane surface area-to-volume ratio. Table 3 exhibits that the benzene conversion was correlating well with the membrane surface area-to-volume ratios. As a result, we believe that the effective area of the Pd interface should be key factors for the large difference in catalytic performances of tubular Pd membranes from different research groups. Indeed, the capillary membrane provided a larger membrane surface area-to-volume ratio than the large tubular Pd membranes, as shown in Table 3. Larger surface area-to-volume could provide more effective area of Pd interface, leading to higher catalytic activity. Actually, the use of a 'real' MEMS-based Pd planar microreactor possessing 100 µm wide microchannels and large surface-to-volume ratio of ca. 100 gave benzene conversion of up to 54% and phenol yield of 20%.²³ It can be concluded that the Pd capillary membrane with small diameter and large surface-to-volume ratio should give the reactants more opportunity to participate the reaction and of course result in better reactor performance.

It is worthwhile to compare the productivity normalized by the weight of Pd as its cost is an important factor to be considered in the reactor design and the results are shown in Table 4. At first sight, the results of Niwa^{7,8} in terms of phenol productivity are better than ours. However, the values of H₂O/phenol ratio presented in Table 4 display a lower production of water in our system compared to the Niwa case. Compared to the large tubular membrane,¹¹ the Pd capillary membrane exhibits better phenol productivity and material efficiency. This is maybe due to the faster response and the effective contact between reactants for the Pd capillary membrane resulting from the small dimensions and large surface-to-volume ratio.

Another positive aspect of the Pd capillary membrane is the long-term reaction stability. Membrane life is important as pure palladium usually suffers from hydrogen embrittlement at temperatures below ca. 573 K.³⁴ As can be seen from Table 2, most of the reaction time was controlled at less than 20 h from the literatures. Vulpescu and co-workers gave 72-96 h longterm stability, but the benzene conversion and phenol yield were only 3.8% and 0.16%, respectively.¹¹ The 'hot spot' of the Pd membrane was also observed in their work. The membrane deterioration was detected when the reaction was prolonged in Niwa's report.⁷ Leakage and damage of the membrane was also found in the work of Shu and co-workers.¹³ However, in this work, the Pd capillary membrane exhibited excellent long-term stability at least for 140 h maintaining high benzene conversion and phenol yield, which is contributed by the strong adhesion between the Pd membrane and the support.

Paper

4 Conclusions

A Pd capillary membrane microreactor was designed and synthesized for the direct hydroxylation of benzene to phenol. A crack-free thin palladium layer with ca. 4-5 µm thickness was successfully deposited on a porous capillary ceramic tube. This membrane showed high hydrogen permeability even at 473 K with selectivity of 379. The palladium layer penetrated deeply into the porous α -alumina support, but firmly anchored to the support. This gave the Pd capillary membrane good stability even at low temperatures. A constant benzene conversion and phenol yield were obtained during the entire 140 h run. The phenol production and side reactions (such as complete oxidation and hydrogenation) were competitive and affected by the H₂/O₂ ratio. The highest benzene conversion of 19.6% and phenol yield of 18.1% were achieved with the optimum H₂/O₂ ratio of 4 at 473 K. The conversion decreased under the conditions less or greater than the ratio of 4. An increase in the reaction temperature caused an increase in benzene conversion but a decrease in phenol selectivity.

An excellent long-term stability of the Pd capillary membrane with higher benzene conversion and phenol yield was obtained compared to literature results. We believe that the obvious difference of reaction performance was mainly due to the effective Pd interface area and reaction zone differences resulting from the membrane surface area-to-volume ratio in the large diameter membrane in previous works and capillary membrane used in this study.^{11–13,16,17} The experimental results show the advantage of the Pd membrane reactor concept for the direct hydroxylation of benzene to phenol. To ensure sufficient reactant contact and to reduce the dead-end volume are key factors for further improving the reaction performance. The main challenges would be to significantly increase the contact area and the opportunity of reactants to participate in the reaction.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (Grant No. 21276147 and 20673017), the Natural Science Foundation of Shandong Province (Grant No. ZR2012BQ003) and the Young Teacher Supporting Scheme of Shandong University of Technology.

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