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# Pd-silicalite-1 composite membrane reactor for direct hydroxylation of benzene to phenol

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#### ABSTRACT

Pd–Sil-1 composite membrane consisting of 5  $\mu$ m Pd membrane anchored by multi-leg protrusions to the 2  $\mu$ m Sil-1 intermediate support layer was prepared from Pd/Sil-1 co-seeds. The membrane displays good permeation flux and is stable for 2.5 weeks of permeation and reaction studies. The Pd–Sil-1 composite membrane was employed for direct hydroxylation of benzene to phenol. Reaction parameters including temperature and H<sub>2</sub>/O<sub>2</sub> molar feed ratio were investigated for their effects on benzene conversion, phenol yield, water generation and hydrogen efficiency.

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#### 1. Introduction

Phenol is an important intermediate in the synthesis of many important petrochemicals, agrochemicals, polymers and plastics. Phenol is commercially produced by indirect oxidation of benzene via cumene process [1]. The direct hydroxylation of benzene to phenol is an attractive route for cleaner production of phenol and has been demonstrated for a variety of oxidants including N<sub>2</sub>O [2,3], H<sub>2</sub>O<sub>2</sub> [4–7] and molecular oxygen [8]. The N<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub> are expensive and there is considerable economic motivation to develop industrially viable catalytic process based on O<sub>2</sub>. Pd–Cu/SiO<sub>2</sub> [9], Pt/V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> [10,11], Pd/Ti–silicalite [12], Pd–PMo<sub>12</sub>/SiO<sub>2</sub> [13], Pd/Pt/Nafion/SiO<sub>2</sub> and Pd/Pt/Amberlyst [14,15] were catalysts used for direct hydroxylation of benzene in a mixture of O<sub>2</sub> with H<sub>2</sub>. Hydrogen peroxide generated by the catalyst from reactions between oxygen and hydrogen is believed to be responsible for the conversion of benzene to phenol.

The one-step conversion of benzene to phenol was first reported by Niwa et al. [16] using a palladium membrane reactor. They postulated that the atomic hydrogen permeated across the palladium reacts with the molecular oxygen to generate "in situ  $H_2O_2$ " and other reactive species (i.e., HOO\* and HO\*) that react with benzene to form phenol [16–23]. They observed the reaction is sensitive to  $H_2/O_2$  feed ratio [18]. Nonselective oxidation and complete combustion occur under oxygen-rich condition [19,20], while hydrogenation is favored under hydrogen-rich conditions. Cyclohexane, cyclohexanone, carbon dioxide and water are the main reaction byproducts. Although the phenol yield was low, the process is safe, simple, clean and economical. Palladium membranes are widely studied for separation and reaction applications [24–34]. However, the cost of the membrane and its long-term performance remained an important issue. This work investigates a new Pd–Sil-1 composite membrane for direct hydroxylation of benzene to phenol. The high flux Pd membrane was anchored to the Sil-1 zeolite intermediate support layer by multi-legs Pd protrusions that penetrate through the interstices of the zeolite grains.

#### 2. Experimental

#### 2.1. Preparation of Pd-Sil-1 composite membrane

The Pd–Sil-1 composite membrane was prepared according to the method described in a prior work [35]. Porous alumina (ca. 3  $\mu$ m nominal diameter) purchased from Foshan Ceramics Research Institute of China with inner and outer diameters of 9 and 13 mm were cut into 75 mm long pieces. The outer wall of the tubes were polished with sand paper, washed with dilute HCl and NaOH, rinsed with deionized water and ethanol, and dried overnight in oven at 393 K. The tubes were then end-sealed with glass enamel, leaving a porous length of 30 mm for membrane deposition. The tube was dip-coated in a water seed solution containing 2 wt.% Sil-1 seed (150 nm diameter), 0.8 wt.% PdCl<sub>2</sub> and 20 wt.% poly(vinyl) alcohol (PVA, MW = 1750 g.mol<sup>-1</sup>). The Sil-1 seed was prepared according to the synthesis procedure published in a prior work

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[36,37]. A 2  $\mu$ m thick Sil-1 zeolite layer was deposited from a clear synthesis solution with molar composition of 40 SiO<sub>2</sub>: 5 TPA<sub>2</sub>O: 20,000 H<sub>2</sub>O [28,38–40]. Tetraethyl orthosilicate and tetrapropy-lammonium hydroxide were respectively the silica source and structure directing agent.

Prior to the deposition of palladium by electroless plating, the zeolite membrane tube was calcined in air at 823 K for 6 h before pretreating in flowing H<sub>2</sub> at 623 K for 3 h to convert Pd(II) to Pd<sup>0</sup> seeds. The palladium was deposited at 318 K from a plating solution containing 3.5 g/L PdCl<sub>2</sub> (99.9 wt.%), 30 g/L Na<sub>2</sub>EDTA(>99 wt.%), 101 ml/L NH<sub>4</sub>OH (15 M) and  $16 \text{ ml/LN}_2$ H<sub>4</sub> (1 M) [26,41,42]. The Pd–Sil-1 composite membrane was obtained by depositing a 5  $\mu$ m thick Pd by repeating the 120 min plating twice. The X-ray diffraction of the deposited Pd was taken at a grazing angle. The membrane was examined by scanning electron microscopy (KYKY-2800B) before and after reaction. X-ray diffraction of the Pd–Sil-1 composite membrane was obtained.

#### 2.2. Hydrogen permeation

Hydrogen and nitrogen permeations were measured in a homemade gas permeation unit. The membrane was sealed in the stainless steel module using graphite O-rings. The gases were fed to the module by electronic mass flow meters and the gas pressure was adjusted by back-pressure regulators. The temperature of the membrane module was monitored by a set of thermocouples and heated by a temperature-programmable furnace. The gas was fed to the annulus formed by the membrane tube and the shell module. The gas diffuses through the Pd membrane layer deposited on the outer wall of the alumina tube to the permeate-side kept at atmospheric pressure. The flux was measured for different feed pressures and permeation temperatures using a soap-bubble flow meter.

#### 2.3. Hydroxylation of benzene to phenol

A schematic drawing of the reactor set-up is shown in Fig. 1. The hydroxylation reaction was carried out in the reactor with a feed mixture of benzene, oxygen and nitrogen in the annulus and hydrogen permeating across the Pd membrane from the tubeside. Benzene is fed as vapor by bubbling 5 sccm N<sub>2</sub> through a benzene saturator kept at a temperature of 287 K. The benzene concentration in the feed was calculated from Antoine's equation and monitored by gas chromatograph. The reactor temperature was controlled by a furnace and all the gas lines were heated to prevent condensation. The composition of reactor outlet was analyzed by two on-line gas chromatographs (GC-7890T; GC-7890F). The organic products were analyzed by a GC equipped with flame ionization detector and 50 m SE-30 capillary column, while the inorganic components were detected using a GC equipped thermal conductivity detector and a 13× molecular sieve/GDX-502 molecular sieve packed columns.

#### 3. Results and discussion

#### 3.1. Preparation of Pd-silicalite-1 composite membrane

The scanning electron micrographs of the Pd–Sil-1 composite membrane are shown in Fig. 2a for the membrane surface and Fig. 2b for the membrane cross-section. Fig. 2a shows the palladium was deposited uniformly on the support and consists of micronsized grains. Defects and pinholes were not observed during the SEM examination and the prepared membrane was impermeable to nitrogen at room temperature tests. A 5- $\mu$ m thick Pd film was deposited on the Sil-1 layer (cf. inverted pyramidal structures in Fig. 2b). A closer examination reveals that palladium penetrated



**Fig. 1.** Apparatus used for hydroxylation of benzene. (1) On/off valve; (2) mass flow controller; (3) benzene container; (4) pressure gage; (5) stainless steel reactor; (6) glass enamel; (7) Pd-silicalite-1 membrane; (8) thermocouple; (9) furnace; (10) temperature controller; (11) needle valve; (12) bubble flowmeter; (13) three-way valve; (14) on-line gas chromatograph equipped with FID detector; (15) on-line gas chromatograph equipped with TCD detector.



Fig. 2. SEM images and schematic diagram of Pd-silicalite-1 composite membrane: (a) surface; (b) cross section; (c) schematic diagram.

the Sil-1 layer through gaps formed between neighboring zeolite crystals anchoring the Pd film to the support. X-ray diffraction of the Pd–Sil-1 membrane at a grazing angle shows only peaks belonging to Pd indicating that no major impurity is present in the deposited membrane.

The schematic drawing in Fig. 2c illustrates the structure of the Pd–Sil-1 composite membrane. The Pd/Sil-1 co-seeds deposited on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> seeded the growth of Sil-1. The Sil-1 grew from the seed layer following the contours of the underlying support and displayed random orientation. The gap between neighboring crystals can be controlled during seeding and zeolite regrowth [43]. Prior to palladium deposition by electroless plating, hydrogen treatment was performed to convert Pd(II) in the Pd/Sil-1 co-seeds to Pd<sup>0</sup> seeds. The palladium deposition was rapid and occurred mainly around the vicinities of gaps formed between intergrowing zeolites. The palladium deposition proceeds deep within the Pd<sup>0</sup>/Sil-1 co-seed layer before emerging on the surface layer forming the Pd protrusions that anchored the film to the support as shown in Fig. 2b.

#### 3.2. Hydrogen permeation of Pd-silicalite-1 composite membrane

The hydrogen permeation study of the Pd–Sil-1 composite membrane was carried out at temperatures and pressures similar to that of reaction. The hydrogen flux was plotted as a function of trans-membrane pressure drop in Fig. 3 for different temperatures. The plots show the H<sub>2</sub> flux varies linearly with the trans-membrane H<sub>2</sub> pressure difference and is taken to indicate that the surface processes were the rate-determining step rather than the bulk diffusion of H<sub>2</sub> through the Pd membrane [44,45]. However, it is also possible that the Sil-1 layer may contribute towards higher n value



Fig. 3. H<sub>2</sub> flux as a function of pressure difference at different temperatures.

[46–48]. The H<sub>2</sub> flux increases with temperature and activation energy of 8.3 kJ mol<sup>-1</sup> was obtained.

## 3.3. Benzene hydroxylation reaction in Pd–silicalite-1 composite membrane

The hydroxylation of benzene on Pd-silicalite-1 composite membrane was performed at different  $H_2/O_2$  molar feed ratio and temperature and their effect on benzene conversion, phenol yield, water generation and hydrogen efficiency were examined.

#### 3.3.1. $H_2/O_2$ molar feed ratio

Niwa et al. [16] proposed that the main advantage of Pd membrane reactor for benzene hydroxylation reaction is the generation of "in situ  $H_2O_2$ " and other reactive species on the membrane surface that catalyzes the reaction benzene to phenol. The reaction is sensitive to the  $H_2/O_2$  molar feed ratio [18] and the reaction results for Pd–Sil-1 (Fig. 4) shows an optimum phenol yield at  $H_2/O_2$  molar feed ratio of 3% and benzene conversion of 5% were obtained at this condition. Low  $H_2/O_2$  molar feed ratio led to combustion with production of carbon dioxide in addition to main cyclohexane and cyclohexanone byproducts, while high  $H_2/O_2$  molar feed ratio favored hydrogenation resulting in an increase in cyclohexane production at the expense of both phenol and cyclohexanone.

Hydrogen was not only consumed by the hydroxylation and hydrogenation reactions, but also by reaction with oxygen to produce water as shown in Fig. 5. This is responsible for the low hydrogen efficiency observed in prior works [16,18–20]. Water is produced by benzene hydroxylation,  $H_2/O_2$  reaction and combustion reactions. It is evident from the plots in Fig. 5 that water is



Fig. 4. Effect of H<sub>2</sub>/O<sub>2</sub> molar ratio on the reaction properties.



Fig. 5. Effect of  $H_2/O_2$  molar ratio on the  $H_2$  efficiency.



Fig. 6. Effect of temperature on hydrogenation of benzene to cyclohexane.

produced mainly by the  $H_2/O_2$  reaction in our reactor. We speculated that this is due to the higher hydrogen flux of the thinner Pd–Sil-1 composite membrane that made more hydrogen available for reaction. The lower phenol yield and benzene conversion are believed to be due to poorer mass transfer rate in the large diameter membrane compared to the capillary membrane used by Niwa et al. [16].

#### 3.3.2. Temperatures

Fig. 3 shows that  $H_2$  permeation flux increases with temperature and should favor the conversion of benzene to cyclohexane as shown in Fig. 6. The results of the benzene hydroxylation reaction at the temperatures of 423, 473 and 523 K are summarized in Table 1. The selectivity for cyclohexane increases with temperature as expected. The most cyclohexane product was obtained at 523 K corresponding to the lowest benzene conversion (2.1%) and phenol selectivity (27%). It is very probable that temperature affects the generation and reaction of reactive species (i.e., "in-situ  $H_2O_2$ , HOO\*, HO\*). Landon et al. [49] reported that high temperature accelerates the decomposition of peroxides on Pd surfaces. In addi-

#### Table 1

Effect of temperature on direct hydroxylation of benzene.



Fig. 7. Membrane stability: (a) long-term operation for hydrogen permeation at 473 K; (b)  $\rm H_2$  permeation flux before and after hydroxylation at different temperature.

tion, high temperature favors water production resulting in lower hydrogen efficiency. The highest benzene conversion (5.06%) and phenol selectivity (60.81%) were obtained at 473 K for this study.

#### 3.4. Stability of Pd-silicalite-1 composite membrane

The Pd–Sil-1 composite membrane was operated for 18 days; 13 days were spent in membrane stabilization and hydrogen permeation studies and 5 days were spent for the reaction studies reported in this work. The membrane was stable for membrane permeation from 423 to 773 K and display reproducible H<sub>2</sub> permeation over the entire period of study lasting 12 days. In addition, the Pd–Sil-1 composite membrane was able to survive 15 temperature cycles between 673 and 773 K lasting 18 h, followed by 15 pressure cycles between 20 and 100 kPa at 773 K lasting 12 h, and H<sub>2</sub>/N<sub>2</sub> gas exchange cycles of 240 h with 18 cycles at 623 K and 10 cycles at 473 K.

Often pure palladium membrane suffers embrittlement at temperatures below 573 K. Niwa et al. [16] and Shu et al. [22] both reported a high risk of membrane failure for low temperature hydroxylation reaction. Membrane life is therefore important for the application. Tests were carried out for the Pd–Sil-1 compos-

Temperature (K)	Conversion (%)	Yield (%)		Selectivity (%)		Water generation rate (mg/min)
	Benzene	Phenol	Phenol	Cyclohexane	Cyclohexanone	
423	4.91	1.95	39.63	14.95	45.40	20.1
473	5.06	3.08	60.81	15.17	24.02	22.5
523	2.15	0.59	27.41	36.23	36.36	27.4



**Fig. 8.** Catalytic stability for the Pd–silicalite-1 membrane in the reaction versus time on stream at 473 K.

ite membrane at 473 K and trans-membrane pressure difference of 100 kPa. The H<sub>2</sub> flux of the Pd–Sil-1 composite membrane was monitored over the 180 h and plotted in Fig. 7a. A flux of 0.075 mol m<sup>-2</sup> s<sup>-1</sup> was maintained over the entire period.

The Pd–Sil-1 composite membrane is also stable for the benzene hydroxylation reaction. The H<sub>2</sub> flux before and after the reaction was measured and plotted in Fig. 7b. A typical reaction as shown in Fig. 8 often lasted for 46 h and permeation results in Fig. 7b shows that the H<sub>2</sub> flux was relatively constant before and after the reaction. This indicates that the membrane was stable and no coking occurred during the reaction. SEM analysis of the membrane after reaction did not show significant change in membrane microstructure. Indeed, the reaction is stable as shown in Fig. 8. The benzene conversion and phenol yield remained constant at ca. 5% and 3%, respectively during the reaction at 473 K and H<sub>2</sub>/O<sub>2</sub> = 4.7. This indicates that hydrogen permeation across the membrane is constant during the reaction.

#### 4. Concluding remarks

A new Pd-Sil-1 composite membrane was prepared from Pd/Sil-1 co-seeds by first growing a Sil-1 zeolite to serve as intermediate support layer before depositing the palladium membrane. The palladium deposition occurred at the gaps formed between intergrowing zeolites and proceeds from deep within the Pd<sup>0</sup>/Sil-1 co-seed layer before emerging on the surface layer forming the Pd protrusions that anchored the film to the support. This gave the Pd-Sil-1 membrane good stability that can tolerate low temperature separation and reaction. The direct hydroxylation of benzene was conducted in the Pd-Sil-1 membrane reactor. An optimum  $H_2/O_2$  feed molar ratio was identified at reaction temperature of 473 K, but the benzene conversion and phenol yield remain low compared to literature report. We believe that this is mainly due to poorer mass transfer in the large diameter membrane used in this study compared to capillary membranes employed in prior works [16–20], and the higher hydrogen flux through the Pd–Sil-1 membrane that results in higher water production that could compete with adsorption sites on the membrane surface. Improvement in mass transfer rates could be achieved through miniaturization as demonstrated in the previous work by the authors [50–64].

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