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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 μm Pd membrane anchored by multi-leg protrusions to the 2 μm 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_2/O_2 molar feed ratio were investigated for their effects on benzene conversion, phenol yield, water generation and hydrogen efficiency.

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_2O [2,3], H_2O_2 [4–7] and molecular oxygen [8]. The N_2O or H_2O_2 are expensive and there is considerable economic motivation to develop industrially viable catalytic process based on O_2. Pd–Cu/SiO_2 [9], Pt/V_2O_5/SiO_2 [10,11], Pd/Ti–silicalite [12], Pd–PMo_{12}/SiO_2 [13], Pd/Pt/Nafion/SiO_2 and Pd/Pt/Amberlyst [14,15] were catalysts used for direct hydroxylation of benzene in a mixture of O_2 with H_2. 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 μm 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.% $PdCl_2$ and 20 wt.% poly(vinyl) alcohol (PVA, MW = 1750 g.mol^{-1}). The Sil-1 seed was prepared according to the synthesis procedure published in a prior work

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[36,37]. A 2 μm thick Sil-1 zeolite layer was deposited from a clear synthesis solution with molar composition of 40 SiO_2: 5 TPA_2O: 20,000 H_2O [28,38–40]. Tetraethyl orthosilicate and tetrapropylammonium 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_2 at 623 K for 3 h to convert Pd(II) to Pd^0 seeds. The palladium was deposited at 318 K from a plating solution containing 3.5 g/L $PdCl_2$ (99.9 wt.%), 30 g/L Na_2EDTA (>99 wt.%), 101 ml/L NH_4OH (15 M) and 16 ml/L N_2H_4 (1 M) [26,41,42]. The Pd–Sil-1 composite membrane was obtained by depositing a 5 μm 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 home-made 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 tube-side. Benzene is fed as vapor by bubbling 5 sccm N_2 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 micron-sized 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-μm thick Pd film was deposited on the Sil-1 layer (cf. inverted pyramidal structures in Fig. 2b). A closer examination reveals that palladium penetrated

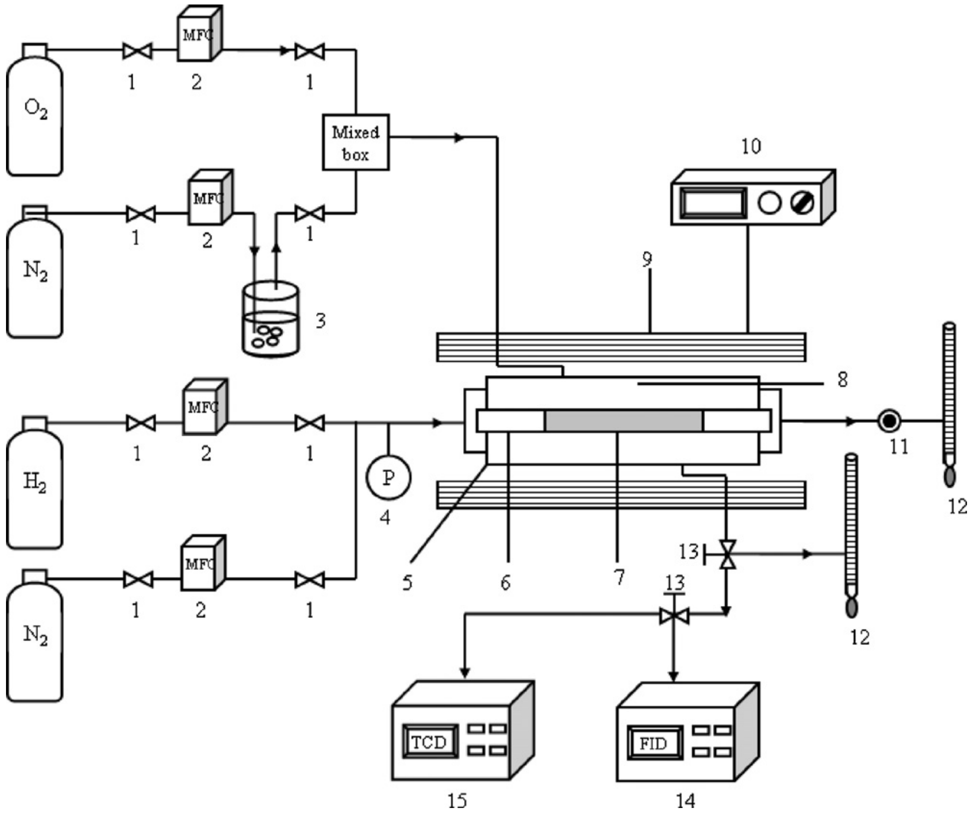

Fig. 1. Apparatus used for hydroxylation of benzene. (1) On/off valve; (2) mass flow controller; (3) benzene container; (4) pressure gage; (5) stainless steel reactor; (6) glass enamel; (7) Pd–silicalite-1 membrane; (8) thermocouple; (9) furnace; (10) temperature controller; (11) needle valve; (12) bubble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