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Structural changes of a Pd-based membrane during direct hydroxylation of benzene to phenol

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Abstract

The relationship between the chemical state and the catalytic activity of Pd was studied to improve direct hydroxylation by using a Pd membrane reactor. Pretreatment with oxygen or hydrogen at 473 K caused the surface of Pd to easily suffer from oxidation or reduction, respectively, but did not affect the hydroxylation activity. The surface state of Pd during the reaction could be divided into two major regions: the oxidized region near the gas entrance of the reactor, which favored complete oxidation, and the reduced region near the gas exit, which favored hydrogenation. These two surface states depended on the concentration of oxygen and hydrogen both inside and outside the membrane during the reaction. After the reaction or after both pretreatments, significant morphological changes of the membrane were not detected by SEM.

Keywords: Palladium membrane; Direct hydroxylation; Benzene; Phenol; Chemical state

1. Introduction

Direct hydroxylation of aromatic compounds, such as benzene to phenol, is an attractive catalysis process as an alternative to the current cumene process, which is a multi-step reaction system whose disadvantages include high-energy consumption and a large amount of acetone as a by-product. Although direct hydroxylation from benzene by using molecular oxygen has been widely investigated, high efficiency has not been achieved. One reason for this low efficiency is the high reactivity of phenol toward oxidation compared with benzene itself. Another reason is the difficulty in properly forming an active oxygen species for direct hydroxylation on a solid catalyst from molecular oxygen. In general, negatively charged oxygen species, such as O^{2-} formed on transition metal-supported catalysts, do not have sufficient activity for direct hydroxylation. To achieve the direct hydroxylation of aromatic compounds, a neutral oxygen species or radical oxygen species must function as the active species [1].

Attempts at efficient production of active oxygen species on a catalyst can be classified into three categories. The first category is reaction with oxidizing reagents such as N_2O and H_2O_2. For the last two decades, N_2O has been used as an effective oxidizing reagent. The high performance of N_2O over MFI zeolite and Fe-doped MFI-based catalysts has been widely reported [2–4]. The disadvantage of the use of N_2O is its high cost. Although H_2O_2 can also be used in direct hydroxylation by using vanadium oxide or titanium silicate-based catalysts [5–7], the cost of H_2O_2 is even higher than that of N_2O. The second category is activation of molecular oxygen by mixing with a proper reductant such as H_2. Reaction with a mixture of H_2 and O_2 over SiO_2-based catalysts has been achieved [8,9], although the yield of phenol is inadequate for practical use due to the restricted reaction condition imposed by the explosion limit of the H_2/O_2 mixture. Owing to this restriction, most studies have involved liquid phase, which limits the commercial application of this system. The third category is the application of H_2–O_2 fuel cell reactor systems to generate the active oxygen species on a membrane separator. The oxygen in

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these systems is activated by the permeated hydrogen from the electrolyte membrane. Otsuka et al. reported a high performance for hydroxylation in such a system by using Pd- or $SmCl_3$-coated carbon as the electrode catalyst [10,11].

For efficient generation of active oxygen species, we previously applied a Pd membrane reactor to the direct hydroxylation of aromatic compounds [12–14]. In this reactor, H_2 and a mixture of O_2 and benzene are separately supplied to both sides of the Pd membrane. The active oxygen species on Pd is reductively produced by the reaction with the active hydrogen species, which permeates into the Pd membrane from the opposite side. The adsorbed benzene on Pd reacts with the active oxygen species, and is thus directly converted into phenol. The advantages of this reactor include (i) no need for expensive oxidizing reagents, such as N_2O and H_2O_2, (ii) avoidance of the risk of explosion, because O_2 and H_2 are supplied separately rather supplied as a mixture, and (iii) efficient generation of dissociatively activated hydrogen species on the surface of Pd owing to the direct supply through the membrane. In a previous work, we reported the formation of phenol with a certain yield at a reaction temperature less than 473 K [12]. This Pd membrane reaction system is not limited to benzene, but also can be applied to the hydroxylation of toluene [12] and methyl benzoate [13]. In the reaction of methyl benzoate, the yield of methyl salicylate was ca. 4.7% at 413 K [13].

In this Pd membrane reaction system as a commercially available system, the stability of the membrane for long reaction is crucial. The application and stability of a Pd membrane reactor system at high temperature (>600 K) has been widely studied, e.g., hydrogenation removal combined with the dehydrogenation reaction [15,16] or partial oxidation or steam reforming of methane [17]. In contrast, the application of a Pd membrane at low temperature (<573 K) has been limited because two different palladium hydride phases with different unit cell sizes coexist below 566 K, causing Pd membranes to become brittle. Although direct hydroxylation at less than 473 K has been achieved, no significant deterioration of the Pd membrane was detected during a long reaction over 10 h [12]. During the direct hydroxylation reaction, however, the surface of Pd was exposed to oxygen and hydrogen species which permeated from the opposite side of the membrane. This exposure suggests that the stability, morphology, and chemical state of the Pd membrane might be affected by the reaction gas atmosphere.

In this study, for the construction of an efficient catalytic system, we investigated the stability and structural changes of a Pd membrane during the direct hydroxylation of benzene. First, the relationship between the catalytic activity and chemical state of the Pd surface was investigated, by determining the effect of various pretreatments on the chemical state of Pd. Second, the stability and morphological changes of the Pd membrane were studied. Results showed that although the nitrogen permeation slightly increased after the reaction, significant destruction of the Pd membrane was not detected during the reaction or after the pretreatments.

2. Experimental

2.1. Preparation of Pd membrane

A Pd membrane tube was prepared by depositing a Pd layer on a porous α-Al_2O_3 tube (2.0-mm o.d., 1.6-mm i.d., 0.15 μm average pore size, and 4.5 m^2/g specific surface area calculated by N_2 adsorption isotherm measured at 77 K) by using metallorganic chemical vapour deposition method with $Pd(COOCH_3)_2$. Pd was deposited on the outer wall of α-Al_2O_3 tube as a thin layer with approximately 1 μm thick along 100 mm. This preparation method for the Pd membrane tube was previously described [12–14]. The hydrogen permeance of the prepared samples ranged from 1.0×10^{-3} to 3.8×10^{-3} mol m^{-2} s^{-1} $Pa^{-0.5}$ at 573 K.

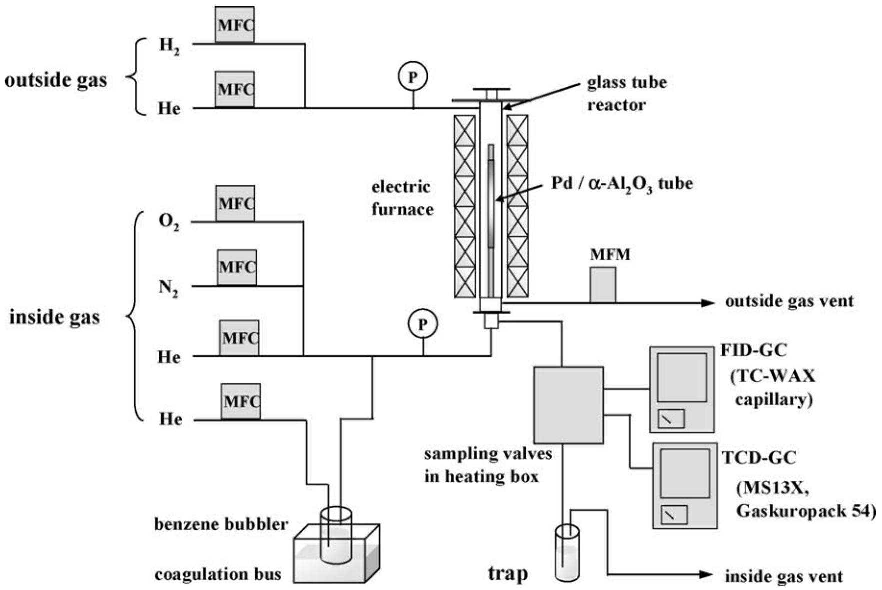

Fig. 1. Schematic of Pd membrane reactor for direct hydroxylation.

2.2. Reaction test of benzene hydroxylation

Direct hydroxylation was carried out by using a contentious flow type reactor schematically shown in Fig. 1. The Pd tube was placed in a 12-mm o.d. glass tube reactor. One end of the Pd tube was sealed and the opposite end was fixed in a 4-mm o.d. stainless steel tube by epoxy resin. A 0.7-mm o.d. quartz capillary tube was then inserted inside this Pd membrane tube. The inside gas was introduced to the inner surface of the Pd tube through this capillary.

In the typical reaction condition, the outside gas was H_2 and He, while the inside gas was a mixture of He, O_2, benzene, and N_2, which is an internal standard gas. Benzene was introduced with He through a gas bubbler cooled at 280 K. All of the gas flow rates were controlled by a mass flow controller as follows: 10 ml/min for H_2, 10 ml/min for He outside the Pd membrane, 2 ml/min for O_2, 2 ml/min for N_2, and 16 ml/min for He inside the Pd membrane. The molar ratio of H_2, O_2, and benzene was 5:1:0.026. The reaction temperature was maintained at 433 K by an electric furnace.

The reaction products were analyzed using two online gas chromatographs (GC: Shimadzu GC-14A); one was equipped with a thermal conductivity detector (TCD) and the other with a flame ionization detector (FID). Inorganic materials were analyzed by TCD-GC with a 13X molecular sieve and Gaskuropack 54 (GL Science) packed columns. Organic materials were analyzed by FID-GC with a TC-WAX capillary column (GL Science, 30 m).

Before the reaction, the Pd membrane was pretreated by H_2 or O_2 in the reactor (*in situ* pretreatment) at 473 K for 1 h. H_2 pretreatment was performed by permeating H_2 from outside to inside the membrane. The outside gas was a mixture of H_2 at 20 ml/min and He at 10 ml/min, while the inside sweep gas was He at 10 ml/min. O_2 pretreatment of the inside of the membrane was carried out using pure O_2 at 20 ml/min.

For the observation of the Pd surface after the reaction, some of reactions were performed at the outside surface of the membrane. In this case, the inside gas was diluted H_2, while the outside gas was diluted O_2 and benzene. The flow rates were the same as mentioned above. The permeated hydrogen species reacted with O_2 and benzene at the outside surface of Pd membrane.

Permeation measurements for a gas mixture of H_2 and N_2 were carried out before and after the reaction at 413 K by using the same reactor for the reaction. A gas mixture of equal amounts of H_2 and N_2, ranging from 10 to 70 ml/min at atmospheric pressure, was introduced to the outside of the Pd membrane, and the inside sweep gas was He at 20 ml/min. The amount of permeated gas was measured by using TCD-GC as described above.

Note that to prevent damage to the membrane, both sides of the Pd membrane were exposed to He during the heating of the membrane to the reaction temperature or pretreatment temperature.

2.3. Characterization of the Pd membrane

To observe the Pd surface of the series of samples during pretreatment, small pieces of fresh membrane samples were treated in H_2 flow or O_2 flow at 473 K for 1 h by using the quartz glass tube and electric furnace in a manner similar to *in situ* pretreatment as described in Section 2.2.

The chemical state of the Pd surface was measured by X-ray photoelectron spectroscopy (XPS) using a PHI-5600 spectrometer with MgKα (300 W) excitation. The Pd 3d lines were analyzed with a pass energy of 29.5 eV and step energy of 0.125 eV. The peak energies were corrected using the C 1s line of the adventitious carbon at 285.0 eV. The surface morphology of the Pt-coated Pd membrane was observed by using scanning electron microscopy (SEM, Hitachi Ltd., S-800).

3. Results and discussion

3.1. Effect of pretreatment of the Pd membrane for benzene hydroxylation

Fig. 2 shows the Pd 3d XPS spectra of the Pd membrane after the pretreatments. The peaks of fresh sample at 335.1 and 340.3 eV with spin orbital coupling (Pd $3d_{5/2}$ and Pd $3d_{3/2}$) were assigned to Pd^0 of Pd metal (Fig. 2a). O_2 pretreatment at 473 K for 1 h resulted in a cleaving of these two peaks (Fig. 2b). The new peaks at 336.1 and 343.1 eV were assigned to Pd^{2+}, indicating the formation of PdO at the surface of the Pd membrane. Since the electron inelastic mean free path excited by MgKα radiation (1253.6 eV) in Pd metal is below 2 nm [18], small particles or a thin layer of PdO were located in a very shallow region of the Pd membrane. H_2 pretreatment for 1 h at 473 K caused the peaks of Pd^{2+} to disappear (Fig. 2c). These

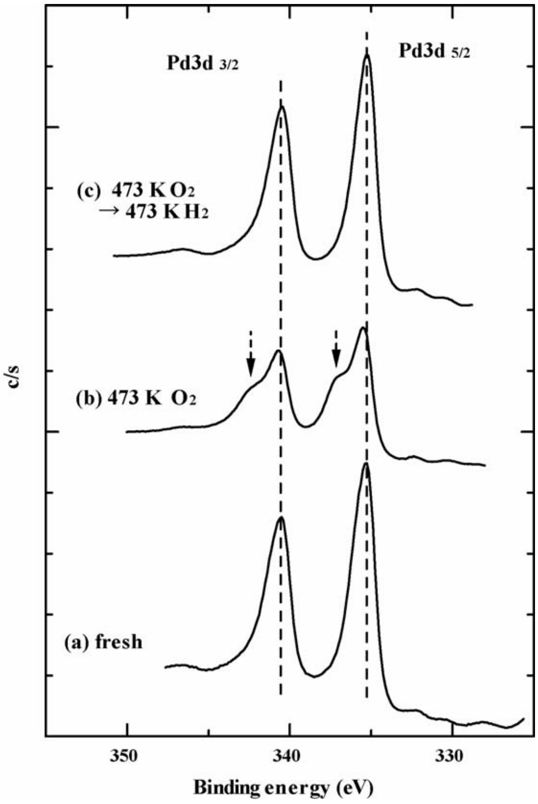

Fig. 2. Pd 3d XPS spectra of Pd membrane before and after pretreatment.

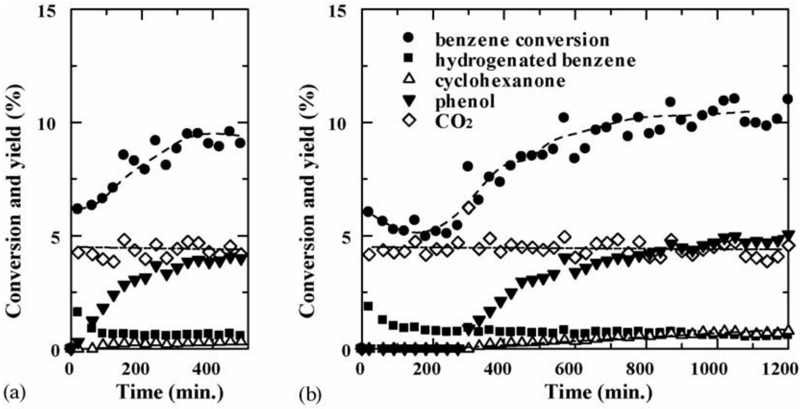

Fig. 3. Time course for benzene hydroxylation at 433 K after (a) H_2 pretreatment and (b) O_2 pretreatment.

changes suggest that the chemical state of the surface of the Pd membrane easily suffered from oxidation and reduction at 473 K.

Fig. 3a and b show the time course of benzene hydroxylation at 433 K after the H_2 and O_2 pretreatment, respectively, at 473 K. Under this reaction condition, the principle products were phenol, hydrogenated benzene (cyclohexane and partially hydrogenated benzene), cyclohexanone, and CO_2. CO was not detected in this reaction. Note that H_2O was produced by the reaction of oxygen and permeated hydrogen species. An induction period was observed after both pretreatments, although the duration of the induction period differed. After the H_2 pretreatment (Fig. 3a), the yield of CO_2 was relatively constant at 4.5% during 500 min of reaction, whereas that of phenol fluctuated. Just after the reaction started, phenol was not detected. However, it then appeared and increased rapidly, reaching ca. 4% at a reaction time of 300 min, and then remained constant. Cyclohexanone, which was formed by the hydrogenation of phenol, was confirmed with the production of phenol. In contrast to phenol, the yield of hydrogenated benzene group rapidly decreased, although a 2% yield was detected just after the reaction started. In the steady state, the conversion of benzene reached 10% and the phenol yield was 4%, the CO_2 yield was 4%, the hydrogenated benzene yield was 1%, and the cyclohexanone yield was 1%. After O_2 pretreatment (Fig. 3b), phenol was not detected during the first 300 min of reaction, whereas CO_2 and hydrogenated benzene were detected just after the reaction started. The phenol yield reached 4% at a reaction time of 800 min, and the products (benzene, hydrogenated benzene, and cyclohexanone) reached a constant yield. After the induction period, the catalytic activity reached a constant even after the different pretreatments (Fig. 3a and b), indicating that the conversion of benzene and selectivity of products were not affected by the difference in pretreatment. Since pretreatment can change the chemical state of the Pd surface as shown in Fig. 2b and c, these results suggest that the chemical state of Pd can be changed to the same state during the reaction.

In this reaction, both the active oxygen species and H_2O were simultaneously formed on the surface of Pd by the reaction of oxygen and permeated hydrogen species from the opposite side (1).

$$C_6H_6 + O_2 + H_2 \rightarrow C_6H_5OH + H_2O \qquad (1)$$

Our previously reported results about the hydroxylation of methyl benzoate suggest that oxidation and hydrogenation occur at different regions on the same membrane [13]. In the front region of the Pd membrane near the gas entrance, the oxygen concentration was relatively high compared with that of the permeated hydrogen species. This region, therefore, was under an oxidative condition, in which complete oxidation was dominant. Oxygen was completely consumed by reacting with permeated hydrogen at the halfway point within the membrane, because an H_2/O_2 ratio of 5, which was the reaction condition used here, is a hydrogen-excess condition for the formation of H_2O. In the rear region near the gas exit, permeated hydrogen species was recombined on Pd and then desorbed into the gas phase. This region accordingly became a reductive condition, causing the hydrogenation.

Judging from the above results, the Pd membrane also showed two different chemical states under the reaction condition: oxidized state in the front region, and reduced state in the rear region. This change in chemical state was due to the concentration of oxygen and hydrogen species during the reaction as suggested by the XPS measurements (Fig. 2). Note that direct hydroxylation of benzene might occur within a very limited region of the membrane in which the oxygen concentration is very low. In this study, this limited region was located between the oxidation and reduction regions. The reduction–oxidation cycle, therefore, might be related to the formation of active oxygen species.

Note that the induction period was affected by the reaction condition and the specific performance of the Pd membrane. In previous studies in which the reaction conditions differed from those of current study, steady activities were observed at 30 or 60 min of reaction time [12,14]. The proper reaction condition can therefore shorten the induction period.

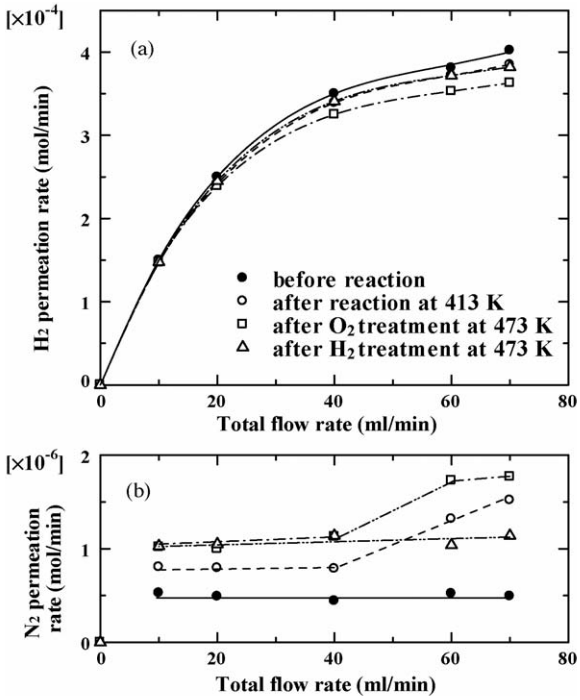

Fig. 4. Permeation rate of H_2 (a) and N_2 (b) at 413 K.

3.2. *Changes in Pd membrane during reaction and after pretreatment*

During the reaction and pretreatments, the chemical state of the Pd surface was changed between the oxide and metal. Thus, the effect of these changes on the stability and surface morphology of a Pd membrane was investigated. Fig. 4a and b show the measured permeation rate of H_2 and N_2, respectively, at 413 K before and after the reaction and pretreatments. The fresh sample showed the highest H_2 permeation and the lowest N_2 permeation, which did not depend on the flow rate. This independence suggests N_2 permeation occurred through pinholes in the Pd or connection (e.g., cracks) between the membrane and stainless steel tube. The ratio of the H_2 permeation rate to that of N_2 was over 700 at a total flow rate of 70 ml/min. After the 24 h reaction, the H_2 permeation rate slightly decreased, whereas the N_2 permeation rate increased. This increase in N_2 permeation suggests the formation of small pinholes or cracks. O_2 pretreatment at 473 K caused the decrease in H_2 permeation rate, which in turn was responsible for the formation of PdO on the surface of the membrane as revealed by XPS results (Fig. 2) [19]. H_2 pretreatment caused the recovery of H_2 permeation rate by the reduction of PdO. Although the N_2 permeation rate was increased by O_2 pretreatment, it was reduced by H_2 pretreatment. The difference in effect between the two pretreatments might be due to the change between Pd and PdO, which differ in crystal lattice size.

Fig. 5 shows SEM photographs of the Pd membrane before and after pretreatment and after the reaction. The fresh sample (Fig. 5a) showed small Pd grains less than 1 μm in diameter. No morphological changes were detected by SEM after either the H_2 or O_2 pretreatment (Fig. 5b and c, respectively). The Pd membrane after a reaction time of 24 h (Fig. 5d) showed no significant change at the outside of the membrane (the middle region of 10 cm membrane). Change in the chemical state of Pd was limited to a very shallow region of Pd, and thus could not be observed by SEM, although the increase in N_2 permeation was detected (Fig. 4). It is noted that direct hydroxylation over a Pd membrane simultaneously forms H_2O and an active oxygen

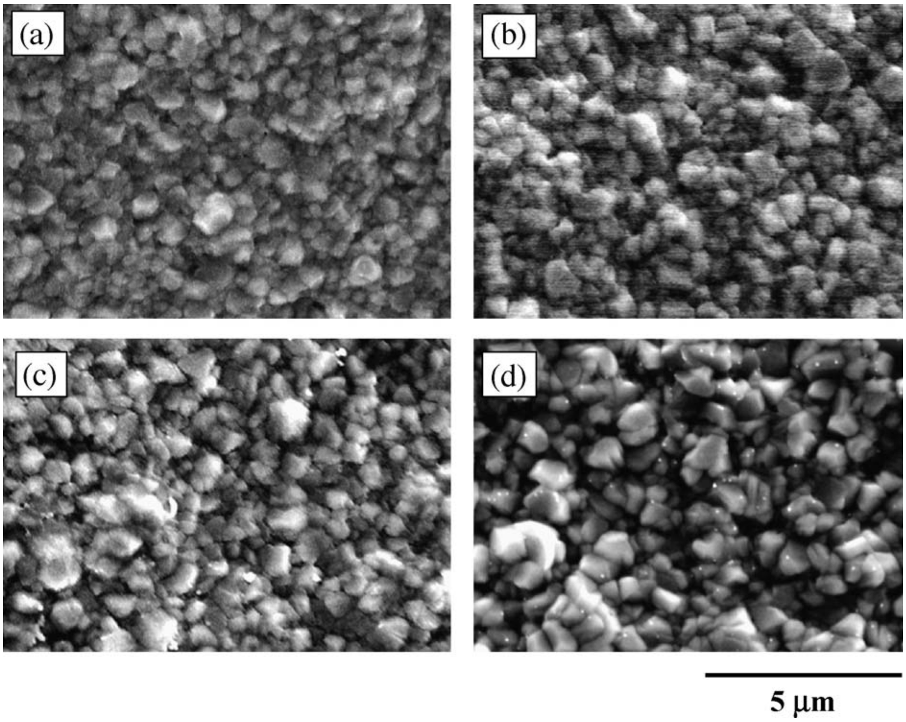

Fig. 5. SEM photographs of top view of Pd membrane: (a) fresh, (b) after O_2 pretreatment, (c) after H_2 pretreatment, and (d) after reaction for 24 h.

species. Lee et al. reported that H_2O induces formation of pinholes at 623 K [20]. Further study is needed on the pretreatment and effect of H_2O at low reaction temperature ($<$433 K) for lot of types of samples.

4. Conclusions

The relationship between the chemical state of Pd and catalytic activity was investigated in the direct hydroxylation of benzene to phenol by using a Pd membrane reactor. The chemical state of the surface of the Pd membrane was easily changed by pretreatment with oxygen or hydrogen at 473 K. These pretreatments, however, did not affect the hydroxylation activity. The surface chemical states of the Pd membrane depended on the concentration of oxygen and hydrogen during the reaction. Significant morphological changes in the surface of the membrane were not detected by SEM after the reaction or after either pretreatment.

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