Catalysis Today 156 (2010) 276–281

Contents lists available at ScienceDirect

Catalysis Today

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

Palladium-based bifunctional membrane reactor for one-step conversion of benzene to phenol and cyclohexanone

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ARTICLE INFO

Article history:
Available online 22 June 2010

Keywords:
Pd membrane
Direct hydroxylation
Benzene
Phenol
Cyclohexanone
Co-catalytic effect

ABSTRACT

On the one-step hydroxylation of benzene to phenol over a Pd membrane reactor, the bifunctional effects between Pd membrane and metal particles were investigated. In this reaction system, the active oxygen species are formed by the reaction with the permeated hydrogen and adsorbed oxygen over Pd membrane. The active oxygen species are reacted with benzene and directly converts into phenol. For improving this system, various active metals were loaded on the α-Al_2O_3 porous tube which was the substrate of the thin Pd membrane. The loading of noble metals resulted in the enhancement of the activity of side reactions, i.e., complete oxidation and hydrogenation, and a decrease in the hydroxylation activity. The negative effect on hydroxylation was due to the imbalance between the catalytic activities of highly dispersed noble metal particles and the Pd membrane, which has a relatively small surface area. In contrast, the loading of Cu suppressed complete oxidation and enhanced the hydroxylation activity. This effect was mainly due to the increase in the hydrogenation activity without significant acceleration of oxidation. In addition, the potential for the selective conversion of benzene to cyclohexanone by this reactor was discussed.

1. Introduction

Phenol and its derivatives, such as cyclohexanone, are valuable for chemical industries where they are used as intermediates of polymer. In industries, phenol is produced by the “cumene process” using cumene, an intermediate product obtained from benzene and propylene [1]. Although this process has been refined, it has two disadvantages: high energy consumption because of its multistep reaction and the vice production of acetone. The direct hydroxylation of benzene with molecular oxygen is an attractive alternative to current multistep reactions. The direct synthesis of phenol using molecular oxygen, however, does not yield satisfactory conversion and selectivity. The major problem is the difficulty in the proper generation of active oxygen species such as neutral or radical species and in suppressing consecutive oxidation due to the relatively high reactivity of phenol as compared to that of benzene.

In a previous study, our group has applied a Pd membrane reactor for the direct hydroxylation of benzene to phenol with relatively high performance [2]. In this reactor system, hydrogen and a mixture of oxygen and benzene are separately supplied to both sides of the Pd membrane (Fig. 1). Hydrogen molecules dissociatively adsorb on the surface of the Pd membrane and permeate into the membrane as dissociated hydrogen species by lattice diffusion. At the surface of the opposite side of the membrane, the permeated hydrogen species react with adsorbed oxygen and reductively produce active oxygen species, which can convert benzene into phenol. The reductive activation of oxygen by hydrogen has been widely studied and reported by several groups [3,4]. However, mixing the supplies of oxygen and hydrogen poses a risk of explosion, which limits reaction conditions. As a result of the limitation, the yield of phenol is inadequate for practical use. A membrane reactor can avoid the risk of explosion by separating the supplies of oxygen and hydrogen. In addition, all hydrogen species are efficiently supplied to the Pd surface as dissociatively activated species because of the lattice diffusion of dissociated hydrogen species into Pd. The membrane reaction system does not require expensive oxidizing reagents, e.g., N_2O, which shows good performance over Fe-MFI zeolite catalyst [5].

In a previous study, we investigated the direct hydroxylation on a Pd membrane reactor by studying the application of this membrane reactor for toluene and methyl benzoate [6,7], the H_2 permeation performance of the membrane [7], and the surface state and stability of the membrane during the reaction [8]. The results of the direct hydroxylation of methyl benzoate to methyl salicylate suggested that methyl salicylate was directly formed by this reactor, and geometric isomers of methyl salicylate were not detected,

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doi:10.1016/j.cattod.2010.04.045

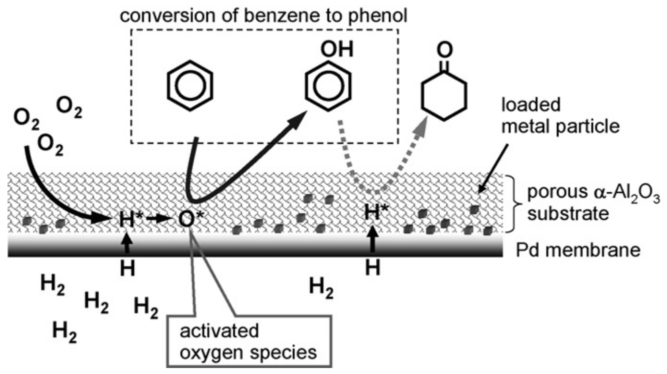


Fig. 1. Schematic illustration of one-step conversion of benzene to phenol and consecutive hydrogenation over metal-loaded Pd membrane reactor.

suggesting that this reaction did not proceed by the electrophilic reaction mechanism. As by-products, both hydrogenated products and oxygenated products were formed, suggesting that the catalytic activity was influenced by the concentration of hydrogen and oxygen.

In the current membrane reactor, the Pd membrane works as not only as a hydrogen separator but also a catalyst. The surface area of the Pd membrane is relatively small as compared to a common Pd-loaded catalyst in porous supports. A thin Pd metal membrane shows superior hydrogen permeation performance, but its catalytic activity for hydroxylation might not be optimized. In this study, for improving this membrane system, various active metals are loaded into the pores of the support tube of the Pd membrane, as shown in Fig. 1. Main aims of the study are to increase the Pd surface area by Pd loading and increase the co-catalytic effect between the loaded active metals and the Pd membrane. In addition, in order to determine the advantages of this reactor, subsequent hydrogenation of phenol to cyclohexanone is investigated.

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 (35-cm length, 2.0-mm OD, 1.6-mm ID, 0.15-μm average pore size, and 4.5-m^2/g specific surface area calculated from a N_2 adsorption isotherm measured at 77 K) by using the metalorganic chemical vapor deposition (CVD) method. Before the deposition of Pd, the outer surface of the tube was coated with glass paste to prevent gas permeation, except the middle part of tube that is the deposition region (10- or 3-cm length) of Pd. The glass paste was fixed by calcination in air at 1423 K. The CVD of Pd was performed in a stainless steel chamber equipped with an electric heater and rotary pumps. A thin layer of Pd, approximately 1-μm thick, was deposited by the sublimation of $Pd(COOCH_3)_2$ on the outer wall of the α-Al_2O_3 tube. This preparation method of the Pd membrane tube has been described in [2,6,7]. 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.

Bifunctional membranes were prepared by loading metal particles into the pores of the α-Al_2O_3 tube before the CVD treatment of Pd. Pd, Pt, Rh, Ru, Cu, and Fe were used as loading elements. Pd, Cu, and Fe were deposited by reductive deposition. In the case of Pd, the α-Al_2O_3 tube was dipped in 100 ml of $Pd(COOCH_3)_2$ chloroform solution (2.67×10^{-2} mol/l) for 10 min, dried at 383 K, and reduced in 100 ml of N_2H_2 aqueous solution (2 mol/l) for 10 min at room temperature. After washing the tube with water, it was dried at 383 K for 10 min. The entire process was repeated 10 times. For loading Cu and Fe, chloroform solutions of copper acetylacetonate and ferric acetylacetonate with the same concentration as that of the Pd solution were used, respectively. Pt, Rh, and Ru were deposited by the impregnation of the respective aqueous metal solution by dip coating for 10 min and drying at 383 K for 10 min. This cycle was repeated 10 times. For preparing the metal solutions, hexachloroplatinate (IV), rhodium (III) chloride, and ruthenium (III) chloride were used, respectively. The concentration of the solution was the same as that of the Pd solution. After the calcination at 673 K, the membranes were subjected to CVD treatment similar to that used in the case of the sole Pd membrane. Note that several numbers of membranes were prepared for reaction and characterization. These membranes were not completely the same because their substrates were different. The reaction results in this study are average performance.

The characterization of the metal particles loaded onto the α-Al_2O_3 tube was carried out before the CVD treatment of Pd by XRD (MAC Science MXP-18) with CuKα radiation and XPS (PHI ESCA5600) with MgKα radiation.

2.2. Reactor construction

The reaction was carried out by using a continuous flow type reactor at atmospheric pressure (Fig. 2). One end of the Pd membrane tube was sealed, and a stainless steel tube (OD 4.0 mm) was attached to the other end. It was placed inside a glass tube reactor whose outer diameter was 12 mm. A quartz capillary with an outer diameter of 0.7 mm was then inserted inside the Pd membrane tube. The inner gas, a mixture of He, O_2, benzene, and N_2, was supplied to the inner surface of the membrane through the capillary. Gas flow rates were controlled by a mass flow controller as follows: 2 ml/min for O_2, 2 ml/min for N_2, and 16 ml/min for He. Benzene was fed by using a microsyringe pump at a rate of 6.24 μl/h. N_2 was used as an internal standard gas for the calculation of the flow rate, because the total flow rate was not constant due to the permeation and reaction of hydrogen. The outer gas was a mixture of H_2 (10 ml/min) and He (10 ml/min). The molar ratio of H_2:O_2:benzene was 5:1:0.026. The permeation of hydrogen proceeds from the outside to the inside of the membrane tube. Hence, the reaction of benzene occurs at the inside of the membrane, the surface at which the metal particles are deposited. The reactor is heated up to a preset temperature, between 373 and 493 K, by using an electric furnace. All gas lines and sampling valves are also heated to prevent the condensation of products. For the confirmation of the reaction mechanism, oxidation (reaction of O_2 and benzene: 2 ml/min for O_2, O_2:benzene = 1:0.026 or 10 ml/min for O_2, O_2:benzene = 1:0.125) and hydrogenation (reaction of permeated H_2 and benzene: 10 ml/min for H_2, H_2:benzene = 5:0.026) at the inner surface of each membrane are investigated.

The hydrogenation of phenol over the Pd membrane (3-cm length) was also investigated. A 1 wt.% aqueous solution (0.2 ml/min) of phenol was introduced by using a microsyringe pump. The other reaction conditions were similar to those of the reaction of benzene (10 ml/min for H_2).

The products were analyzed using two online gas chromatographs, one equipped with a TCD detector (TCD-GC) and the other with an FID detector (FID-GC). The TCD-GC had packed columns (Molecular Sieve 13X, 2 m, and Gasukuropak 54, 2 m) for the analysis of inorganic gases, and the FID-GC had a TC-WAX capillary column (GL Science Inc., 30 m) for the analysis of organic compounds. Sampling was carried out several times under a given reaction condition, because the time course was observed [8]. The hydrogen permeation rate was calculated from the decrease in the gas flow rate of the outer gas, measured by using a flow meter.

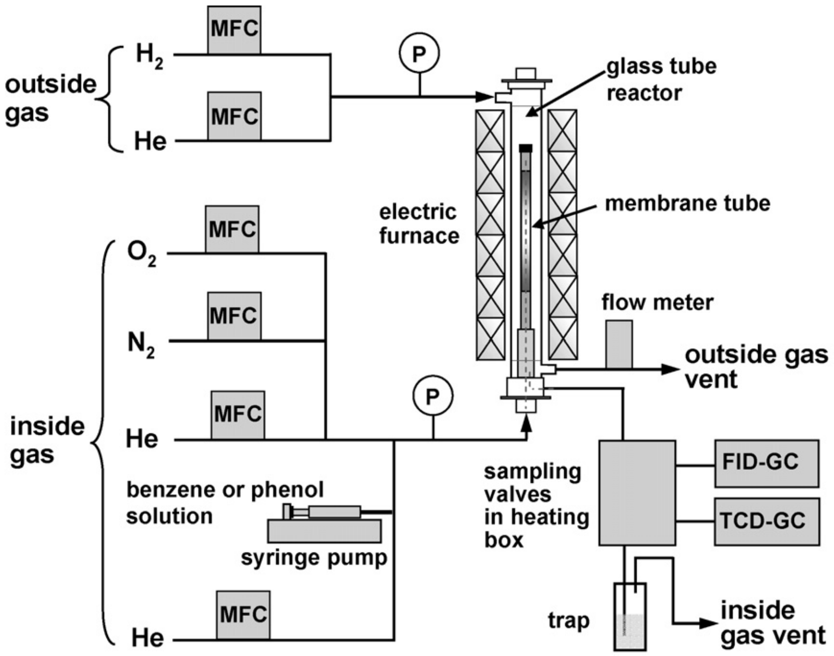


Fig. 2. Diagram of Pd based membrane reactor.

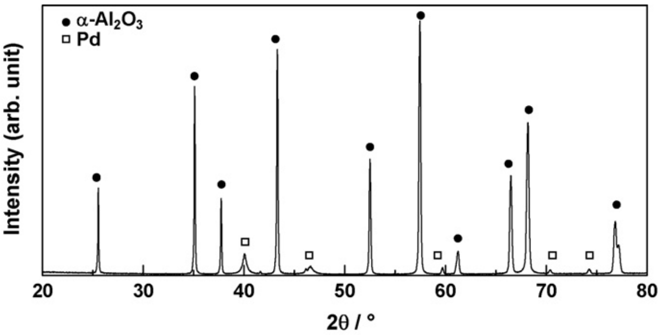


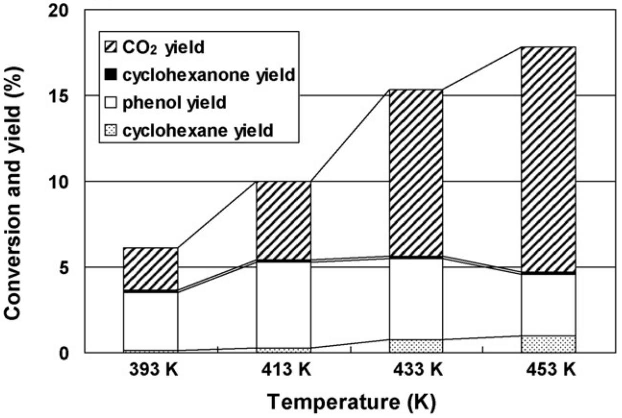
Fig. 3. XRD pattern of Pd-loaded α-Al_2O_3 tube before CVD treatment.

3. Results and discussion

3.1. Pd loading into pores of substrate

For increasing the valid surface area for hydroxylation, Pd particles were loaded into the pores of the α-Al_2O_3 substrate. Fig. 3 shows the XRD pattern of the Pd particles deposited on the α-Al_2O_3 substrate tube before the preparation of the Pd membrane by CVD treatment. Sharp peaks corresponding to α-Al_2O_3 and broad peaks corresponding to Pd metal were observed. The particle size of Pd was below 50 nm, as calculated from the FWHM of the XRD peaks. The color of the cross section of substrate tube was uniformly changed from white to black by loading of Pd. The surface Pd/Al ratio was 0.39 by XPS analysis, suggesting the Pd particles were not completely covered with the Al_2O_3 surface. These results indicated that almost Pd particles were highly dispersed in the pores of the α-Al_2O_3 tube. Fig. 4 exhibits the effect of reaction temperature on benzene hydroxylation over the Pd membrane and over the Pd-deposited Pd membrane (Pd–Pd membrane). In the former case, the major products were phenol, cyclohexanone, cyclohexane (with a negligibly small amount of partially hydrogenated benzene), and CO_2 (H_2O) under present reaction conditions (Fig. 4a). Cyclohexanone was produced by the consecutive hydrogenation of phenol. CO_2 was mainly formed by the oxidation of benzene. The yield of

(a) Pd membrane



(b) Pd-deposited -Pd membrane (Pd-Pd)

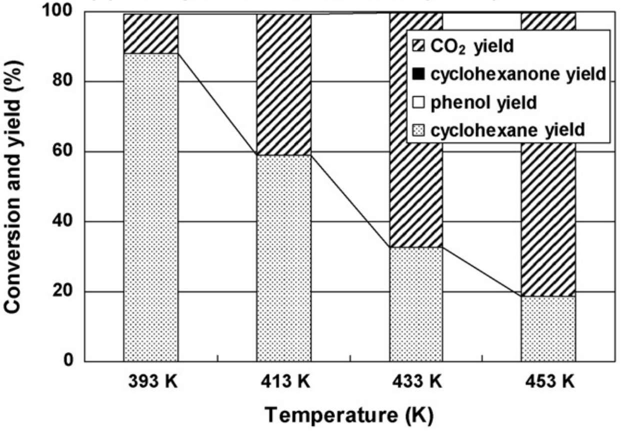


Fig. 4. Effect of reaction temperature on hydroxylation of benzene over (a) Pd membrane and (b) Pd-deposited Pd membrane (Pd–Pd).

Table 1
Effect of loadings noble metals into pores of α-Al_2O_3 tube on benzene hydroxylation at 413 K.

Membrane	Metal/Al molar ratio (XPS)	Benzene conv. (%)	Selectivity (%)			
			Cyclohexane	Phenol	Cyclohexanone	CO_2
Pd	–	10	3	49	2	46
Pt–Pd	0.04	99	24	0	0	76
Rh–Pd	0.20	63	89	0	0	11
Ru–Pd	0.05	37	92	0	0	8

other products was negligibly small. The conversion of benzene over the Pd/α-Al_2O_3 membrane was 7% at 393 K and increased with temperature. The yield of phenol was ca 4% at 393 K and increased to 5% at 413 K. Over 433 K, the yield decreased with increasing temperature. However, the yield of CO_2 increased with temperature. Thus, high temperature caused complete oxidation and a decrease in the yield of phenol. For enhancing the yield of phenol, the restriction of the complete oxidation is necessary.

At all temperatures, benzene conversion reached close to 100% due to the loading of Pd particles (Fig. 4b). However, only cyclohexane and CO_2 were obtained as products. The hydrogenation of phenol to cyclohexane mainly occurred at low temperatures, while complete oxidation was dominant at high temperatures. Although the loading of small Pd particles caused an increase in the Pd surface area, the loaded particles enhanced the hydrogenation and complete oxidation of benzene. However, the loaded particles did not show an obvious effect on hydroxylation. Note that most of Pd particles were highly dispersed in the pores of the substrate tube as described above. Hence, the catalytic reaction mainly occurred at the surface of Pd particles, which have a high surface area.

3.2. Loading of noble metals into pores of substrate

The co-catalytic effect between the Pd membrane and other metal particles in the pores of the substrate was investigated. Table 1 summarizes the effect of loading noble metals into the pores of the α-Al_2O_3 tube on benzene hydroxylation. XPS analysis revealed that the loaded metal particles did not completely cover the Al_2O_3 surface, but were dispersed on the surface, similar to the case of Pd particles explained in Section 3.1. As compared to the sole Pd membrane, the loading of noble metals into the pores of the substrate resulted in high benzene conversion in the order Pt > Rh > Ru. However, the products were limited to cyclohexane and CO_2, similar to the case of the Pd–Pd membrane (Fig. 4b).

Our previous study on the hydroxylation of methyl benzoate [6] suggested that hydroxylation and side reactions, i.e., oxidation and hydrogenation, occur at different regions of the same membrane. The complete oxidation takes place near the gas entrance region, which is oxygen rich. The concentration of oxygen gradually decreases along the membrane by the reaction of the permeated hydrogen and benzene. At the middle region, oxygen is completely consumed because the amount of hydrogen is larger than that of oxygen ($H_2/O_2 = 5$). From the middle region to gas exit region, hydrogen concentration gradually increases by desorption of the permeated hydrogen as hydrogen molecules. Hence, the hydrogenation favors the gas exit region. Hydroxylation occurs only in the central region of the membrane, where the oxygen concentration is low. These results suggest that the increase in the surface area due to the loading of noble metals did not lead to an increase in the surface area for hydroxylation.

It is noted that the exothermic heat might occur by the oxidation near the gas entrance region. In this reaction condition, it was mainly due to the water formation by the reaction of oxygen and the permeated hydrogen, because the flow rate of O_2 was higher than that of benzene (O_2:benzene = 1:0.026). The exothermic heat might enhance the complete oxidation which favors the high temperature over the Pd membrane as shown in Fig. 4a. Further investigation is need for the phenomenon. However, if the temperature gradient occurred, it did not affect the order of the benzene conversion among metal loaded membranes. The reaction site of oxygen and permeated hydrogen was limited at the surface of Pd membrane, because the permeated hydrogen species did not desorb under the oxygen rich condition. Hence, the influence of exothermic heat might be same for each membrane.

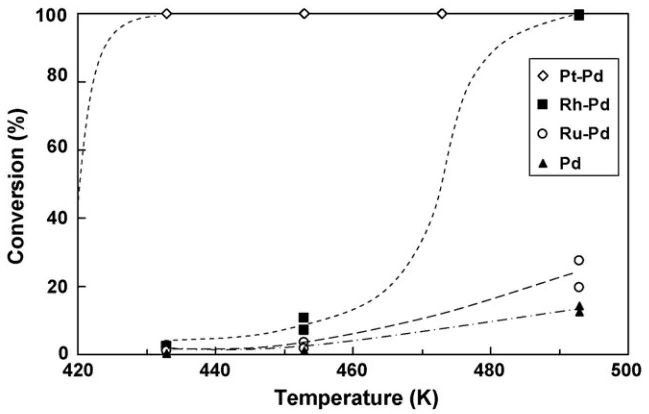


Fig. 5. Oxidation of benzene over noble-metal-loaded Pd membranes (O_2: 10 ml/min, O_2:benzene = 1:0.125).

In general, noble metals showed high catalytic performance for both oxidation and hydrogenation. Fig. 5 shows the result of benzene oxidation over noble-metal-loaded membranes. The products were CO_2 and H_2O. Although the amount of benzene in this reaction was 5 times higher than that in hydroxylation (Table 1), the Pt- or Rh-loaded membrane exhibited high performance in contrast to the sole Pd membrane. This can be attributed to the high activity of noble metals and the large surface area of metal particles dispersed on the surface of the substrate tube. The imbalance between the activities of the surface of the Pd membrane and the metal particles disturbs hydroxylation. If the interaction between the Pd membrane and the noble metals takes place, the imbalance due to the difference between the surface areas masks the co-catalytic effect. For example, benzene reacted with the oxygen on Pt particles rather than the active oxygen generated on the Pd surface. For the enhancement of the hydroxylation activity due to the co-catalytic effect, a balance between the activities of the Pd membrane surface and metal particles might be necessary.

3.3. Effect of Cu loading on hydroxylation

The loading of transition metals, such as Fe and Cu, showed different results as compared to noble metals (Table 2). The loading of Fe caused a decrease in benzene conversion and suppressed hydroxylation. In contrast, the loading of Cu caused an increase in benzene conversion and the selectivity of hydroxylation products, namely phenol and cyclohexanone, while the selectivity of CO_2 decreased to 18%. The loading amount of Cu was of the same

Table 2
Effect of loading transition metals into pores of α-Al_2O_3 tube on benzene hydroxylation at 413 K.

Membrane	Metal/Al molar ratio (XPS)	Benzene conv. (%)	Selectivity (%)			
			Cyclohexane	Phenol	Cyclohexanone	CO_2
Pd	–	10	3	49	2	46
Cu–Pd	0.08	18	9	49	24	18
Fe–Pd	15	8	18	0	0	82

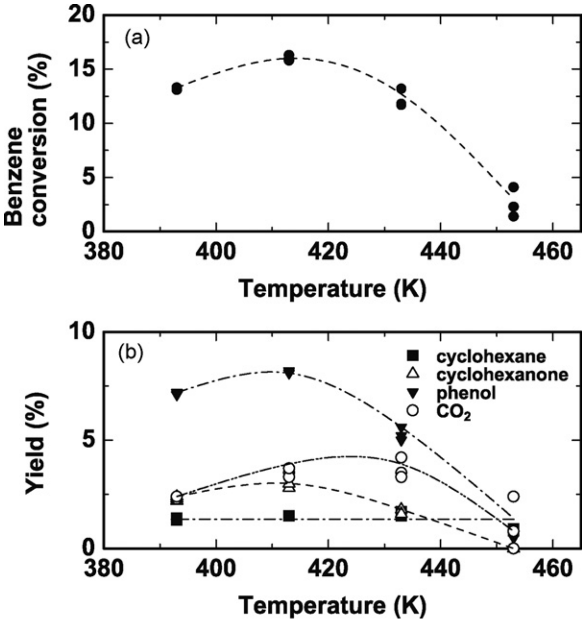


Fig. 6. Effect of reaction temperature on hydroxylation of benzene over Cu–Pd membrane: (a) conversion and (b) yield.

order as that of the noble metals (Table 1). The effect of reaction temperature over the Cu–Pd membrane is shown in Fig. 6. The maximum yield of phenol was observed at 413 K, which was same as that over the Pd membrane (Fig. 4a). However, the conversion of benzene and the yield of CO_2 decreased above 413 K, suggesting the restriction of complete oxidation at higher temperature ranges over the Cu–Pd membrane.

To confirm the catalytic activity of side reactions, the oxidation and hydrogenation of benzene were separately carried out over the Pd, Fe–Pd, and Cu–Pd membranes. The result of benzene oxidation is shown in Fig. 7a. The order of oxidation was Fe–Pd ≫ Cu–Pd ≈ Pd. In contrast to the noble-metal-loaded membranes, the loading of Cu did not significantly affect oxidation on the Fe–Pd and Cu–Pd membranes as compared to the sole Pd membrane. However, the oxidation activity over the Cu–Pd membrane increased with temperature in contrast to hydroxylation (Fig. 6). In the case of hydrogenation, the effect of Cu loading was evident. The order of the hydrogenation of benzene to cyclohexane was Cu–Pd ≫ Pd > Fe–Pd (Fig. 7b). These results suggested that the enhancement of the hydrogenation activity due to Cu loading suppressed the complete oxidation, which occurred near the gas entrance region, and enhanced the hydroxylation activity due to the co-catalytic effect. This enhancement was mainly due to the increase in the hydrogenation activity without significant acceleration of oxidation. That is, it is advisable to accelerate the hydrogenation activity without increasing the oxidation activity for increasing the hydroxylation activity. In the case of the noble-metal-loaded membrane, both oxidation and hydrogenation were enhanced, causing the acceleration of side reactions. In addition, in this reactor system, hydroxylation is highly influenced by the concentration of oxygen and hydrogen [8]. Hydroxylation occurs under the redox condition. In general, Cu works as a catalyst for the Fenton reaction to produce active oxidation species by the redox cycles. Hence, the co-catalytic effect of Cu might be effective in enhancing hydroxylation. The interaction between Pd and Cu was suitable for hydroxylation.

3.4. Conversion of phenol to cyclohexanone on Pd membrane reactor

One of the industrial utilization of phenol is the conversion to cyclohexanone for the synthesis of ε-caprolactam. In this Pd membrane reactor system, some amount of phenol is converted into cyclohexanone. In this reactor, near the gas exit region of Pd membrane is under hydrogen atmosphere, because oxygen is completely consumed at the region near the gas entrance. To confirm the catalytic activity for the conversion of phenol to cyclohexanone, the hydrogenation of phenol was carried out over the Pd membrane. Fig. 8 shows the results of phenol hydroxylation under the coexistence of vapor, because vapor was formed by the reaction of oxygen and permeated hydrogen during hydroxylation. The Pd membrane showed good performance for the selective conversion of cyclohexanone below 433 K under the coexistence of vapor. Thus, the hydrogenation activity effectively increased by loading metals into

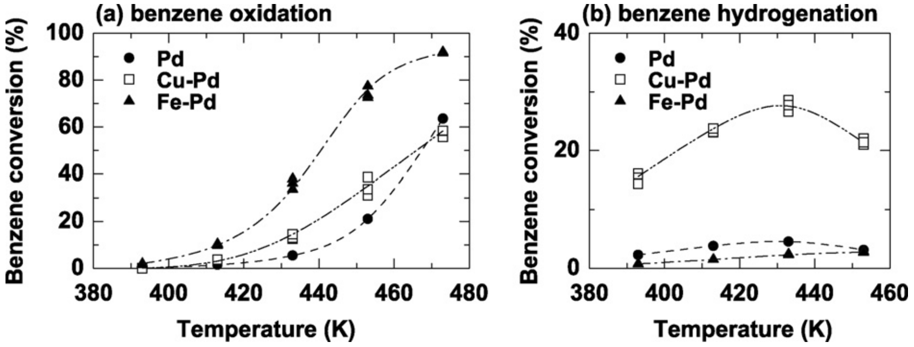


Fig. 7. Related reactions over transition-metal-loaded Pd membranes: (a) oxidation of benzene (O_2: 2 ml/min, O_2:benzene = 1:0.026) and (b) hydrogenation of benzene by permeated hydrogen (H_2: 10 ml/min, H_2:benzene = 5:0.026).

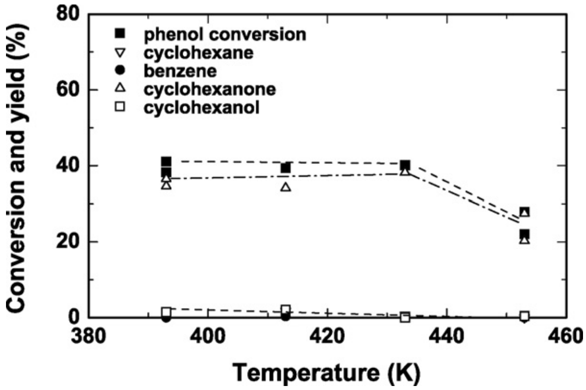


Fig. 8. Reaction of phenol and permeated hydrogen over length of 3 cm on Pd membrane (H_2: 10 ml/min, 1 wt.% phenol aqueous solution: 0.2 ml/min).

the pores of Pd membranes (Fig. 4b). Hence, proper loading of Pd particles near the gas exit region of the membrane might enhance the hydrogenation of phenol to cyclohexanone. This suggests that the selective conversion of benzene to cyclohexanone is performed by the sole reactor system.

4. Conclusion

The effect of loading metal particles into the pores of an α-Al_2O_3 substrate support tube on the one-step hydroxylation of benzene on a Pd membrane reactor was investigated. In this case, the Pd membrane worked not only as a hydrogen separator but also as a catalyst, which was not optimized for hydroxylation.

An increase in the surface area due to the loading of noble metal particles, such as Pd, Pt, and Rh, enhanced the activity of side reactions, i.e., complete oxidation and hydrogenation. This negative effect on hydroxylation was due to the imbalance between the catalytic activities of the noble metal particles and the Pd membrane, which has a relatively small surface area. In contrast, the loading of Cu enhanced the benzene conversion and hydroxylation activity by suppressing complete oxidation. This enhancement was mainly due to the increase in the hydrogenation activity without significant acceleration of oxidation. The interaction between Cu and Pd enhanced the hydroxylation activity.

In addition, this membrane system was found to be suitable for the selective hydrogenation of phenol to cyclohexanone. This shows that the appropriate combination of Pd membranes and active metals will enhance the hydrogenation activity for the selective conversion of benzene to cyclohexanone in a sole reactor system.

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