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Direct hydroxylation of aromatic compounds by a palladium membrane reactor

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Abstract

Direct hydroxylation of aromatic compounds was effectively achieved by using a newly developed Pd membrane reactor in which the Pd membrane is thin enough (ca. 1 μm) to allow permeation of hydrogen below 500 K. In this reactor, the active oxygen species is formed on the surface of Pd via the reaction between oxygen and permeated hydrogen from opposite sides of the membrane. Hydroxylation occurs on the surface of Pd via reaction of the aromatic compound and active oxygen. In the reaction of benzene at a reaction temperature of 423 K, the reactor achieved a benzene conversion of 15% and a phenol selectivity of 95%. An increase in reaction temperature, however, caused simultaneous hydrogenation. In the reaction of methyl benzoate, the reaction products were not only methyl salicylate, which is a hydroxylation product, but also numerous hydrogenation and oxidation compounds via side reactions. These side reactions were related to the gas balance between oxygen and hydrogen; oxygen-rich conditions caused complete oxidation, whereas oxygen-poor conditions (i.e., high amount of permeated hydrogen) induced high hydrogenation activity.

Keywords: Palladium membrane; Direct hydroxylation; Benzene; Phenol; Methyl benzoate

1. Introduction

Direct hydroxylation of aromatic compounds to manufacture valuable compounds, such as phenol, has been widely investigated. Direct conversion of benzene to phenol is an attractive alternative to the currently used cumene process, which is a multi-step reaction system whose disadvantage includes high-energy consumption and a large amount of acetone as a byproduct. Direct synthesis of phenol from benzene and oxygen requires the activation of C–H bonds in the aromatic ring and the subsequent insertion of oxygen. Most heterogeneous catalysts that contain transition metals, however, supply an oxygen species that has a negative charge, such as O^-, O^{2-} and $O_2{}^-$, all of which cause oxidation of benzene via the electrophilic reaction mechanism. If phenol is produced, the reactivity of phenol is higher than that of benzene, resulting in consecutive oxidation. To achieve direct hydroxylation of aromatic compounds, a neutral oxygen species or radical oxygen species, such as $HO^\bullet$ or $HOO^\bullet$, might work as the active species [1]. The efficient production of active oxygen species on a catalyst remains difficult. The methods for such production can be classified into three categories: (i) reaction with an oxidizing reagent, such as N_2O and H_2O_2, (ii) activation of oxygen by mixing with a reductant and (iii) utilization of a membrane reactor.

Since the 1980s, N_2O has been used as an oxidizing reagent. On the surface of a catalyst, N_2O is decomposed and can supply the active oxygen species, such as hydroxyl radicals or so-called "α-oxygen". In the first reported study involving N_2O as an oxidant, N_2O over a V_2O_5-SiO_2 catalyst achieved a benzene conversion of 11% and phenol selectivity of 45% [2]. Since then, H-ZSM-5 based catalysts have been a major research focus [3]. In a recent study, N_2O over a Fe-ZSM-5 catalyst at 623 K achieved a benzene

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conversion of 27% and a phenol selectivity of 99% [4]. The disadvantage of this method of using N_2O as the oxidizing reagent is the expensive supply cost of N_2O. A combination process that involves adipic acid synthesis from cyclohexanone to produce N_2O has been commercially attempted [5]. Although H_2O_2 is also available as an oxidizing reagent with vanadium oxide or TS-1 based catalysts [6–9], the supply cost of H_2O_2 is relatively expensive compared to that of N_2O.

Oxygen gas can be activated into a neutral oxygen species by mixing with a proper reductant, such as carbon oxide, aldehyde, alcohol or hydrogen. For example, hydrogen has been used over Pt/SiO_2, $Cu\text{-}Pt/SiO_2$ and $Pt\text{-}V_2O_5/SiO_2$ catalysts [10–13]. The yield of phenol, however, has been inadequate for practical use. In this system involving the activation of oxygen gas, the reaction condition is restricted by the explosion limit of the H_2/O_2 mixture. Therefore, most studies have been done using the liquid phase, which limits the commercial application of this system.

Membrane reactors are an effective method to produce active oxygen species. In the H_2–O_2 fuel cell system reactor reported by Otsuka et al. [14,15], the oxygen is activated by the permeated hydrogen from the electrolyte membrane. The reactor showed high performance by using Pd- or $SmCl_3$-coated carbon catalysts as the electrode catalyst. In this type of reactor, the oxidation can be controlled simply by using an electric power supply at the external circuit.

For a more effective supply of active oxygen species, we previously developed a Pd membrane reactor [16,17], schematically shown in Fig. 1. In this reactor, hydrogen and oxygen are separately supplied on opposite sides of the membrane. The active hydrogen species formed by the permeation from one side of the Pd membrane produces active oxygen species on the opposite side by reacting with oxygen gas. Then, the active oxygen species reacts with the adsorbed benzene on Pd and the benzene directly converts into phenol. The permeated hydrogen species in Pd is completely dissociated and activated, suggesting that the opposite surface of Pd is filled by the activated hydrogen species. It is effective for the production of active oxygen species, compared with effectiveness of mixing a supply of oxygen and hydrogen from the gas phase to the Pd surface. The advantages of using this Pd membrane reactor are that it does not need expensive oxidizing reagents and it eliminates the risk of explosion because the supplies of oxygen and hydrogen are physically separated.

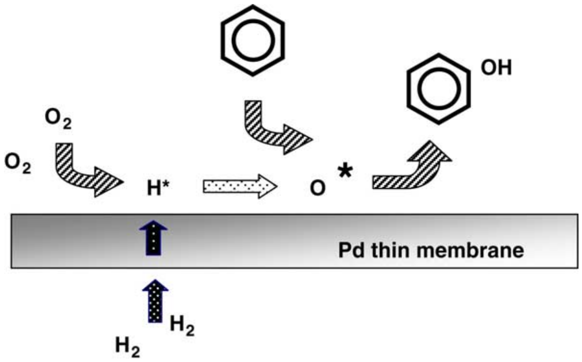

Fig. 1. Conceptual illustration of direct hydroxylation of benzene to phenol by using a Pd membrane reactor.

In this study, for the direct hydroxylation of aromatic compounds, we developed a Pd membrane reactor. In this report, first, the preparation of thin Pd membrane and the performance of the hydrogen permeability are described. The desired hydroxylation temperature is less than 500 K, although hydrogen permeation favors high temperature. Therefore, to fabricate this reactor, we deposited a Pd thin film approximately 1 μm thick on a porous $\alpha\text{-}Al_2O_3$ tube. Second, the reaction results of the hydroxylation using this Pd membrane reactor are reported. Although, in the reaction of benzene, high yield of phenol was confirmed, small amounts of byproducts were observed. To, therefore, clarify the details of the reaction, the hydroxylation of methyl benzoate was investigated. The reaction results show numerous byproducts. Finally, the reaction path and mechanism are discussed based on these reaction results of methyl benzoate.

2. Experimental

2.1. Preparation of Pd membrane

A thin Pd membrane (approximately 1 μm thick) was prepared by depositing a Pd layer on a porous $\alpha\text{-}Al_2O_3$ tube (NOK Corporation) whose outer diameter was 2.0 mm and inner diameter was 1.6 mm and average pore size was 0.15 μm. The Pd coating was deposited along a 100-mm section of the $\alpha\text{-}Al_2O_3$ tube by a metallorganic chemical vapor deposition method with $Pd(COOCH_3)_2$ as the Pd source [18]. The remainder of the surface of the tube was coated with low-melting point glass to prevent gas permeation. Three of these Pd membrane tubes were prepared: one for the reaction of methyl benzoate, one for the reaction of benzene and one for the long-term reaction of benzene.

Permeation measurements for single gas, i.e., hydrogen or nitrogen, were carried out at various reaction temperatures between 473 K and 573 K by using the permeation apparatus. The Pd membrane tube was placed in a stainless steel tube so that different gases can flow inside and outside of the membrane. These flow rates were controlled by using mass flow controllers, and the pressure was controlled by using a digital control auto pressure regulator. The permeance gas was introduced into the outside of the membrane. During a hydrogen permeate test, the hydrogen pressure was changed from 0.147 MPa to 0.392 MPa, while the permeate side (inside) of the membrane was kept below atmospheric pressure without sweeping gas. The flux of permeated hydrogen was measured by using an automatic soap-film flowmeter. In a permeance test of nitrogen, the sweeping gas of helium (50 ml/min) was introduced into the permeate side (inside) of the membrane and thus diluted the permeated nitrogen. The pressure of nitrogen and helium was fixed at atmospheric pressure. The concentration of nitrogen was determined by using a gas chromatograph (GC, Shimadzu GC-9A, molecular sieve 5A column).

The morphology of the membrane was observed by using scanning electron microscopy (Hitachi, S-800).

2.2. Reactor construction and reaction condition

The Pd membrane tube was placed inside a stainless steel tube whose outer diameter was 19.1 mm (Fig. 2). One end of the tube was sealed with epoxy resin. A quartz capillary (0.7 mm outer diameter) was then inserted inside this Pd membrane tube. The reactor tube was heated by an electric furnace and all gas lines were heated by an electric heater to prevent condensation of the reaction products.

The reaction gases were introduced into the reactor by using mass flow controllers. A ternary mixture gas of He, O_2 and aromatic compound was introduced into the inside of the Pd membrane via the quartz capillary, while H_2 diluted with He was introduced into the outside of the membrane. In the reaction of benzene, the flow rate of H_2 outside the membrane was 20 ml/min, the flow rate of O_2 inside the membrane was 5 ml/min and benzene was introduced with He gas (9 ml/min) through the gas bubbler at 282 K. In the reaction of methyl benzoate, the H_2 and He flow rates outside the membrane were 2–40 ml/min and 10 ml/min, respectively, the flow rates of O_2 and He inside the membrane were 2 ml/min and 5 ml/min, respectively, and methyl benzoate was introduced with He gas (5 ml/min) through the gas bubbler at 333 K. Also, in this reaction, the molar ratio of O_2 to methyl benzoate was kept constant at 50. The reaction temperature was set between 423 K and 493 K.

Between reaction experiments, the reactor was kept at the reaction temperature with He flow both inside and outside of the membrane to prevent damage to the membrane by any rapid change in temperature. No significant deactivation was observed during the reactions.

The reaction products were analyzed using two online gas chromatographs (Shimadzu, GC-14A); one was equipped with a thermal conductivity detector (TCD–GC) and the other with a flame ionization detector (FID–GC). The inorganic gases were analyzed using the TCD–GC with molecular sieve 13X and Gaskuropack 54 (GL Sciences) packed columns. The reaction of benzene was analyzed using the FID–GC with a HP-35 capillary column (Hewlett-Packard, 30 m). The reaction of methyl benzoate was analyzed using the FID–GC with a Supel-Q plot capillary column (SUPELCO, 30 m). The retention times of the reaction products (e.g., three isomers of methyl salicylate) were confirmed by using the authentic samples. The products were identified by using a GC–MS (Varian Saturn 2000) equipped with above-mentioned capillary columns.

The hydrogen permeation rate under the reaction conditions was calculated by subtracting the hydrogen flow rate downstream of the reactor measured by a flow meter from the hydrogen flow rate upstream. The actual H_2/O_2 ratio was calculated based on the hydrogen permeation rate.

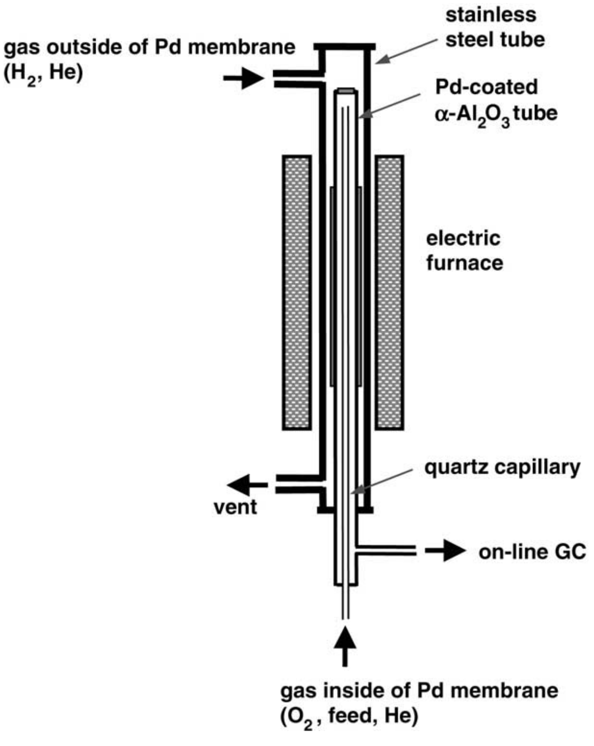

Fig. 2. Schematic of a Pd membrane reactor.

3. Results and discussion

3.1. Preparation of Pd membrane

Fig. 3 shows a SEM photograph of a cross-section of the Pd-coated membrane tube. The grains in the lower region are

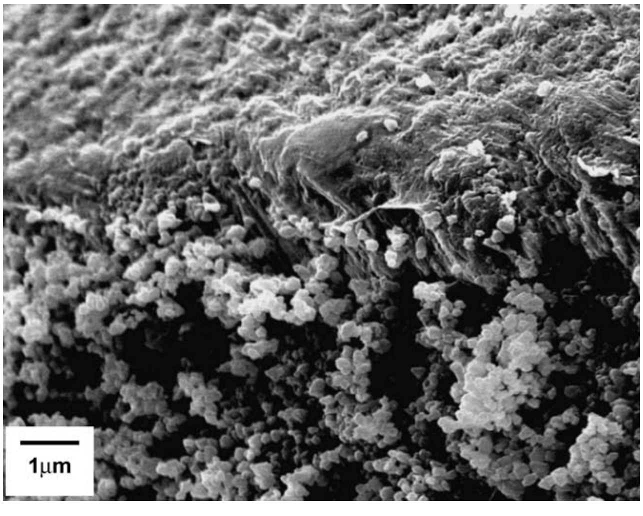

Fig. 3. SEM photograph of the cross-section of a Pd-coated α-Al_2O_3 tube.

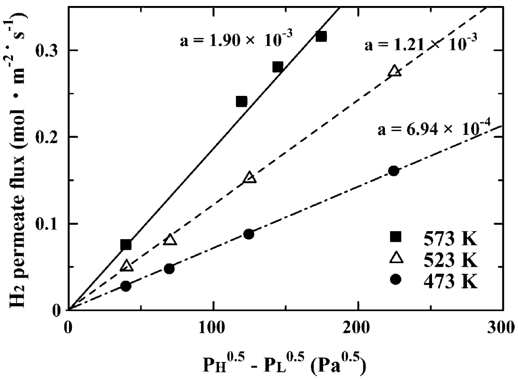

Fig. 4. Effect of temperature on hydrogen permeance of Pd membrane; *a* is the permeance (mol m^{-2} s^{-1} $Pa^{-0.5}$).

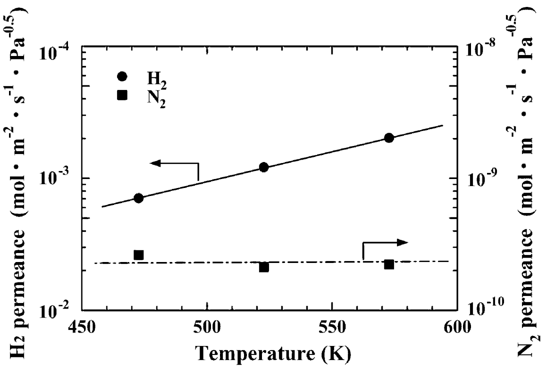

Fig. 5. Comparison hydrogen and nitrogen permeance.

Al_2O_3 particles, whereas the upper region is the cross-section and top view of the Pd layer, which is a dense layer approximately 1 μm thick. To confirm that Pd permeability occurred at less than 500 K, which is the reaction temperature for the hydroxylation of aromatic compounds, the hydrogen permeance was investigated. At 573 K, the hydrogen permeance of the prepared samples ranged from 1.0×10^{-3} mol m^{-2} s^{-1} $Pa^{-0.5}$ to 3.8×10^{-3} mol m^{-2} s^{-1} $Pa^{-0.5}$. This dispersion for the hydrogen permeance might be due to the non-uniformity in the thickness of the Pd layer. Fig. 4 shows the effect of temperature on the hydrogen permeance of the sample, which showed the average permeation performance among the prepared samples (1.9×10^{-3} mol m^{-2} s^{-1} $Pa^{-0.5}$ at 573 K). At 473–573 K, the permeance increased from 6.9×10^{-4} mol m^{-2} s^{-1} $Pa^{-0.5}$ to 1.9×10^{-3} mol m^{-2} s^{-1} $Pa^{-0.5}$. Fig. 5 shows a comparison between the hydrogen permeance and the nitrogen permeance. The nitrogen permeance was relatively independent of the reaction temperature and was very low ($<10^{-9}$ mol m^{-2} s^{-1} $Pa^{-0.5}$), whereas the hydrogen permeance increased with increasing reaction temperature. The difference in permeance between hydrogen and nitrogen was greater than 10^6. These results suggest that the Pd membrane had a very dense structure without any cracks or pinholes, and allowed sufficient hydrogen permeability even at 473 K.

3.2. Direct hydroxylation of benzene

Table 1 shows the liquid products of benzene hydroxylation at 423 K and 473 K. The gas product, i.e., a small amount of CO_2, is not shown in this table. At 423 K, the yield was over 15% and the phenol selectivity was 95%. The only confirmed byproduct under these reaction conditions was cyclohexanone formed by the hydrogenation of phenol. When the reaction temperature was increased from 423 K to 473 K, the selectivity of phenol decreased, although benzene conversion increased, probably due to the formation of numerous hydrogenated products, such as hexane, cyclohexane, cyclohexanone and 1,2-cyclohexane-di-one. Fig. 6 shows the result of the long-term reaction of benzene hydroxylation at 473 K. Even after 5 h of reaction, the phenol and cyclohexanone yields remained relatively constant. These results suggest that the prepared Pd membrane was highly stable and exhibited sufficient hydrogen permeability and catalytic activity for the hydroxylation of benzene in a low temperature range from 423 K to 473 K. In general, two different palladium hydride phases coexist below 566 K, that is, α and β phase with different unit cell sizes. The phase change, therefore, causes an embrittlement of Pd membranes. Further investigations are needed about the stability of this membrane in the low temperature range.

The surface of Pd, however, worked not only as hydroxylation catalyst but also as hydrogenation and oxidation catalyst. High temperature enhanced the hydrogenation reaction, but suppressed the selectivity of phenol. The hydroxylation activity can be improved by restricting both the hydrogenation and oxidation.

3.3. Hydroxylation of methyl benzoate

To clarify the side reactions, such as hydrogenation and oxidation, methyl benzoate was chosen as the reaction feed due to its high reactivity in comparison with benzene.

Fig. 7 shows the effect of reaction temperature on the reaction of methyl benzoate. The hydroxylation product, i.e., methyl benzoate, was confirmed at 423 K with a yield of approximately 5%, whereas the conversion of methyl benzoate was 45%. This difference was due to the production

Table 1
Direct hydroxylation of benzene

Temperature (K)	Conversion of benzene (%)	Selectivity of phenol (%)	Yield (%)				
			Hexane	Cyclohexene	Cyclohexanone	Phenol	1,2-Cyclohexane-di-one
423	15.9	95	0	0	0.8	15.1	0
473	18.0	79	1.9	0.6	0.5	14.3	0.7

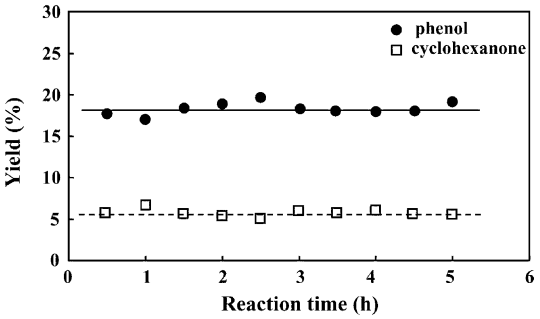

Fig. 6. Time course for hydroxylation of benzene at 473 K.

of numerous byproducts. The major byproducts were benzene, toluene, cyclohexanone, phenol, hydrogenated methyl benzoate and carbon dioxide, and the minor byproducts (shown as “other” in Fig. 7) were methanol, methyl acetate, cyclohexane and methyl cyclohexane 2-carboxylate (and its isomers). When the reaction temperature was increased, the conversion of methyl benzoate increased, while the yield of methyl salicylate decreased to near zero at 493 K. At high temperature, the formation of benzene by the decomposition of methyl benzoate was dominant, causing restriction of hydroxylation and hydrogenation. Note that no isomers of methyl salicylate, i.e., 3-hydroxy methyl benzoate and 4-hydroxy methyl benzoate, were detected.

Fig. 8 summarizes schematically the estimated reaction pathways. The Pd membrane reactor caused four different reactions: oxidation to carbon dioxide and water (A), hydroxylation to methyl salicylate (B), decomposition to benzene (C) and hydrogenation of the aromatic ring (D). In addition, consecutive hydroxylation (B), such as benzene to phenol or hydrogenation (D), i.e., phenol to cyclohexanone occurred.

The effect of the H_2/O_2 ratio was examined to investigate the effective hydroxylation conditions in which the side reactions and consecutive reactions are suppressed. Fig. 9 shows the effect of the H_2/O_2 ratio at 423 K in which the decomposition of methyl benzoate to benzene was not dominant. The H_2/O_2 ratio in parentheses is the actual H_2/O_2 ratio calculated based on the permeated hydrogen over oxygen. The product distribution was completely different at a H_2/O_2 ratio of 2.5 (actual ratio of 2) compared to that at 5 (actual ratio of 2.6). Below a H_2/O_2 ratio of 2.5 (actual ratio 2), the conversion of methyl benzoate was over 80%. However, the main product was carbon dioxide, and the hydroxylation and hydrogenation reactions were not dominant. In contrast, when the H_2/O_2 ratio exceeded 5 (actual ratio of 2.6), complete oxidation to carbon dioxide was restricted and methyl salicylate and hydrogenated methyl benzoate were detected. When the H_2/O_2 ratio was high (10, actual ratio of 4.3), the yield of hydrogenated products was the highest, and the yield of methyl salicylate was smaller than that at a H_2/O_2 ratio of 5 (actual ratio of 2.6).

In this Pd membrane reactor, both active oxygen species and water were simultaneously formed on the Pd surface by the reaction of dissociated active hydrogen from the opposite side and oxygen from the gas phase. Note that if oxygen remained, the recombination of atomic hydrogen species and desorption as hydrogen molecules did not occur. Consequently, the H_2/O_2 ratio strongly influenced the reactor atmospheric conditions in the reactor. When the actual H_2/O_2 ratio was less than 2, if all of the hydrogen was permeated, then unreacted oxygen remained in the reactor. Therefore, the entire surface was under oxidative conditions, in which complete oxidation was dominant. Under these conditions, if the active oxygen species was formed, this species was easily oxidized by oxygen. When the actual H_2/O_2 ratio was greater than 2, oxygen gas was completely consumed by the reaction with the permeated hydrogen species in the front region of the reactor. In the region of the reactor after oxygen consumption, permeated hydrogen species recombined on the Pd surface and desorbed into the inside of the reactor. Thus, this rear region in the reactor was

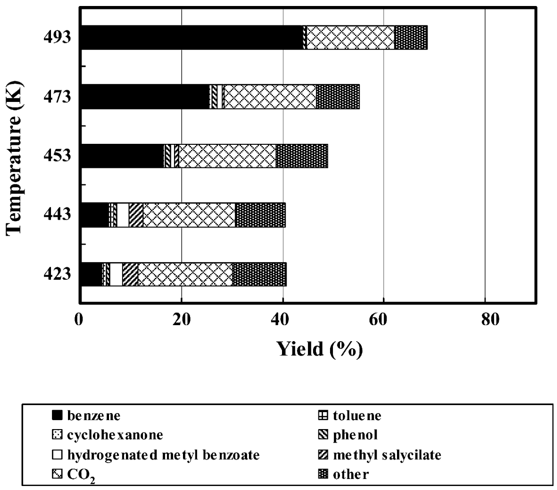

Fig. 7. Effect of reaction temperature on products distribution in the reaction of methyl benzoate (H_2/O_2 = 5).

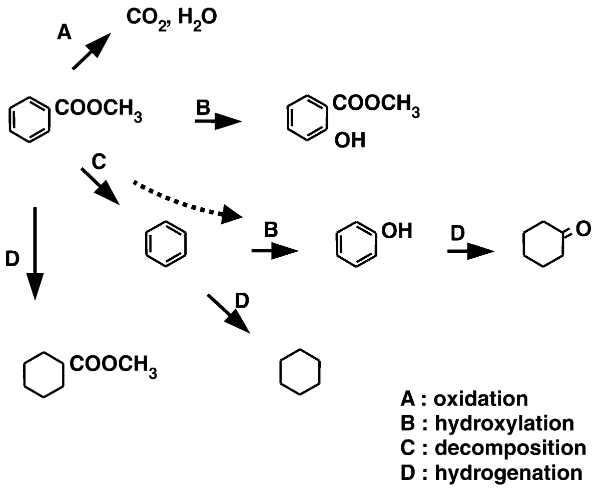

Fig. 8. Estimated reaction pathways of methyl benzoate in a Pd membrane reactor.

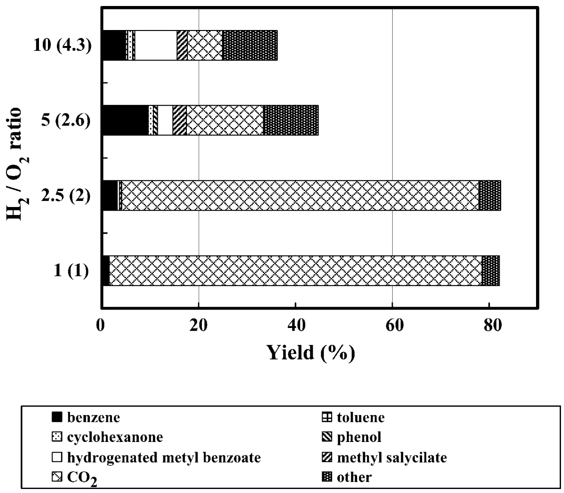

Fig. 9. Effect of H_2/O_2 ratio on products distribution in the reaction of methyl benzoate at 423 K. H_2/O_2 ratio in parentheses represents the actual H_2/O_2 calculated based on the permeated hydrogen.

under a reductive atmosphere, which is advantageous for hydrogenation. In fact, high hydrogen concentration ($H_2/O_2 > 10$) caused an increase in hydrogenation activity as suggested by the yield of hydrogenated methyl benzoate. Hydroxylation might occur in the very limited region of the Pd membrane in which the concentration of oxygen was very low. In this region, the low oxygen concentration restricted the formation of ionic active oxygen species by further oxidation.

The direct hydroxylation using the mixture of reductant and oxygen suggests that either the radical oxygen species, such as $HO^\bullet$ or $HOO^\bullet$, or the neutral oxygen species might be the active species [1,19]. In this reaction, 3-hydroxyl methyl benzoate did not form, although the methyl carboxyl group of methyl benzoate works as a meta director via the electrophilic mechanism. This result indicated that this reaction does not proceed via the electrophilic substitution mechanism. Hence, the active oxygen might be the above-mentioned species. In this reaction, the high selectivity for the formation of methyl salicylate among three isomers might be related to the form of methyl benzoate adsorbed. The steric hindrance of methyl carboxyl on Pd inhibited the direct hydroxylation of meta and para positions. In the reaction of methyl benzoate, the oxidation of the carboxyl group did not occur. In the reaction of toluene hydroxylation to cresol, the formed amounts of benzylaldehyde and benzylalchool, both of which are produced by oxidation of the methyl group, were very small [16]. These results also indicate that the active oxygen might be the above-mentioned species. Although the $HO^\bullet$ radical might produce benzylaldehyde or benzylalchool [20,21], it is difficult to specify the real active species from the present results. These active species have the advantage of preventing consecutive oxidation of the hydroxylation product, such as phenol. Conditions without oxidation or hydrogenation are favorable for hydroxylation and can be achieved by controlling the reaction conditions, such as the H_2/O_2 ratio, or by improving the reactor.

4. Conclusion

For the direct hydroxylation of aromatic compounds, a Pd membrane reactor was designed. In this reactor, the active oxygen species is formed on the surface of a thin Pd membrane by the reaction between oxygen and permeated hydrogen from opposite sides of the membrane. To fabricate the membrane, a thin layer (approximately 1 μm) of Pd was deposited on a porous α-Al_2O_3 tube. This membrane was crack-free and showed high hydrogen permeability even at 473 K.

By using this Pd membrane, hydroxylation of aromatic compounds was achieved at temperatures lower than 500 K. In the reaction of benzene at 423 K, the benzene conversion was 15% and phenol selectivity was 95%. An increase in the reaction temperature caused not only an increase in benzene conversion but also a decrease in phenol selectivity. This decrease of selectivity was responsible for hydrogenation side reactions. In the reaction of methyl benzoate, numerous side reactions occurred, both complete oxidation and hydrogenation occurred at 423 K. These side reactions were affected by the initial gas ratio of H_2/O_2. Low H_2/O_2 ratio (<2) induced an oxidative condition by the unreacted oxygen, whereas high H_2/O_2 ratio (>2) brought about the hydrogenation. The hydroxylation occurred only in a limited region in the reactor where the oxygen concentration was low. For effective hydroxylation, the reaction atmosphere on the Pd surface is therefore crucial.

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