

Successive Hydrogenation and Dechlorination Systems Using Palladized Ion Exchange Membranes

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Pd black was deposited on a cation or anion exchange membrane by electroless plating and the subsequent electroplating. Total amount of Pd black deposited on the ion exchange membranes was about one eighth of the mass of the corresponding Pd sheet used in the previous work. A hydrogenation system of styrene and a dechlorination system of 4-chlorotoluene were successfully constructed using a two-compartment cell separated by the resulting palladized ion exchange membranes. The sole hydrogenation product was ethylbenzene, and the dechlorination product was only toluene. In each case current efficiency for ethylbenzene and toluene production was markedly improved by using methanol with high polarity and was not less than that on a Pd sheet or palladized one as a reference. Considering these results, the plausible mechanism of the hydrogenation and dechlorination on the palladized ion exchange membranes was discussed.

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Heterogeneous hydrogenation with a Pd catalyst is one of the important synthetic processes.^{1,2} New hydrogenation,³⁻⁸ hydrogenolysis,⁹ and dehydrogenation^{10,11} systems using a two-compartment cell separated by a Pd sheet or palladized Pd sheet have been constructed by our group.³ This system was composed of three processes which are electrochemical production of atomic hydrogen by water electrolysis on one side of the Pd sheet, permeation of the electrogenerated atomic hydrogen through the Pd sheet, and hydrogenation of an unsaturated organic compound on the other side. The system was quite different from classical electrochemical hydrogenations in the point that the first electrochemical process and the last hydrogenation process proceed on different sides. Therefore, after the reaction we did not need to separate a supporting electrolyte from products. The thinner Pd sheet can lead to lower cost of material in addition to faster permeation of atomic hydrogen.

Ion exchange membranes such as Nafion are often used for a matrix of active noble metal catalysts for electrochemical and chemical hydrogenations, isomerization, and alcohol oxidations and so on.¹²⁻¹⁵ If Pd or Pd black with hydrogen absorbability is loaded on one side of the ion exchange membranes, we should be able to apply it to the successive hydrogenation system in place of the Pd sheet. In this work, single-sided palladized ion exchange membranes were prepared by electroless plating and the subsequent electroplating, and the resulting palladized membranes were applied to the hydrogenation system of styrene in place of a Pd sheet and the dechlorination system of 4-chlorotoluene from the environmental interest.

Experimental

A cation exchange membrane (CEM, Selemion CMV, thickness: $100 \ \mu m$) and an anion exchange membrane (AEM, Selemion AMV, thickness: $100 \ \mu m$) were provided from Asahi Glass Co. Ltd.

The palladization on a side of the CEM or AEM by electroless plating and the subsequent electroplating was carried out using reaction systems illustrated in Fig. 1a and b. In case of the CEM, a 1.13×10^{-2} M Pd(NH₃)₄Cl₂ aqueous solution, which is described as Pd(NH₃)²⁺ solution hereafter, was poured into the reaction system shown in Fig. 1a. The apparent contact area of the membrane with the Pd(NH₃)²⁺ solution was 0.64 cm². The Pd(NH₃)²⁺ ions were adsorbed on the membrane by ion exchange with original Na⁺ ions. After standing for given periods of time, the Pd(NH₃)²⁺ solution was moved from the system. The resulting Pd(NH₃)²⁺-adosorbed membrane was washed thoroughly with dis-

tilled water and then 0.92 M hypophosphorous acid (H_3PO_2) aqueous solution was poured into the cell for the electroless palladization. After 24 h, the H_3PO_2 solution was removed from the system and the palladized membrane with black color was washed thoroughly with distilled water again.

The electroplating of Pd black was performed immediately after the electroless plating. The single-sided palladized membrane was set as shown in Fig. 1b. The 2.82×10^{-2} M Pd(NH₃)₄⁺ solution was put in the cell and contacted with the palladized side of the membrane (contact area: 0.28 cm²). The Pd black was galvanostatically deposited at 10 mA cm⁻² for given periods of time.

The single-sided palladization of the AEM was based on the above, and a 1 M HCl aqueous solution containing 1.13×10^{-2} M PdCl₂, which is described as PdCl₄²⁻ solution hereafter, was used instead of the Pd(NH₃)₄²⁺ solution.

The amount of Pd(NH₃)₄²⁺ adsorbed on the CEM was evaluated from the difference in the concentration of the Pd(NH₃)₄²⁺ solution before and after contacting it with the CEM. The concentration was determined by measuring absorbance at 296 nm in absorption spectrum of each solution and applying the absorbance into the Lambert-Beer's law. Then the experimental molar extinction coefficient at 296 nm was $1.95 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$. In case of the PdCl₄²⁻ adsorbed on the AEM, absorbance at 473 nm was measured. The experimental molar extinction coefficient at 473 nm was $1.61 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$.

The palladization on a Pd sheet (thickness: $50 \ \mu$ m), for comparison, was galvanostatically carried out at 10 mA cm⁻² for given periods.

For the hydrogenation of styrene or dechlorination of 4-chlorotoluene, the palladized CEM or AEM was set in a cell illustrated in Fig. 1c. In the former reaction, substrate was pure [=8.7 mol dm⁻³ (=M)] styrene or a methanol solution containing 1 M styrene, whereas in the latter reaction the substrate was a methanol or cyclohexane solution containing 1 M 4-chlorotoluene or pure (=8.5 M) one. Each substrate was put in the Pd black-side compartment. 1 M H₂SO₄ solution for the CEM or 6 M KOH solution for the AEM was put in the other compartment. The current density for water electrolysis to produce atomic hydrogen was 36 mA cm⁻². Products were qualitatively and quantitatively determined by gas chromatography.

Results and Discussion

Palladization on the CEM and AEM by electroless plating and the subsequent electroplating.—Figure 2 shows time course of the amount of $Pd(NH_3)_4^{2+}$ and $PdCl_4^{2-}$ adsorbed on the CEM and AEM, respectively, as a function of the contact time with the corresponding solutions. In the case of the CEM, the amount of adsorbed

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Figure 1. Reaction systems for (a) electroless plating and (b) electroplating of Pd black on ion exchange membranes and (c) a hydrogenation and dechlorination system.

Pd(NH₃)²⁺ greatly increased with the contact time because the Pd(NH₃)²⁺ ions adsorbed on the CEM by an ion-exchange reaction and saturated at about 5 h, suggesting that the ion-exchange reaction came to equilibrium. When the Pd(NH₃)²⁺-adsorbed membrane came into contact with the H₃PO₂ solution, the color of the membrane changed to black, suggesting that the Pd(NH₃)²⁺ after 24 h is evaluated as 11.1 µmol from Fig. 2. Assuming that the adsorbed Pd(NH₃)²⁺ was completely reduced to Pd, then the amount of the Pd black deposit was 1.18 mg. Since the amount of a Pd sheet (50 µm) corresponding to the apparent area (0.64 cm²) covered by Pd black deposit is evaluated as 38.4 mg, the amount of Pd black deposit of the membrane by the electroless plating is less than one thirtieth of the mass of a Pd sheet with a thickness of 50 µm.

In the case of the AEM, the time course of the amount of adsorbed $PdCl_4^{2-}$ was similar to that for the CEM, as shown in Fig. 2. After 24 h, the adsorption of $PdCl_4^{2-}$ came to equilibrium. Then the amount of adsorbed $PdCl_4^{2-}$ was 9.1 µmol, which corresponds to 0.97 mg, assuming that the adsorbed $PdCl_4^{2-}$ ions are completely reduced to Pd black, and was around one fortieth of mass of the Pd sheet.

Time course of the amount of the Pd black deposit in the electroplating is shown in Fig. 3. The amount of the Pd black deposit increased linearly with electroplating time in both membranes, but over 3 h, a part of the Pd black deposit began to peel off. The total amount of the Pd black deposited in the electroplating for 3 h was 5.1 mg for the CEM and 5.0 mg for the AEM, which was nevertheless around one eighth of the mass of the Pd sheet.

Morphology of the Pd black deposited on the CEM and AEM.—Figure 4 shows SEMs of the Pd black deposited on the CEM or AEM by the electroless plating and the subsequent electroplating for 2 h. Final morphology of the Pd black deposits on the CEM and AEM after the electroplating was similar to each other as shown in Fig. 4. During the two-step palladization, the Pd black particles grew up three-dimensionally on the membranes like on a Pd aheet.⁴ In both cases, spherical deposits with various sizes covered the membrane surface. The difference in the morphology of the Pd black deposits between the CEM and AEM seems to be ascribed



Figure 2. Time course of amount of $Pd(NH_3)_4^{2+}$ and $PdCl_4^{2-}$ adsorbed on the CEM and AEM, respectively, as a function of the contact time with the corresponding solutions.

to that of the kind of Pd ions, that is $Pd(NH_3)_4^{2+}$ for the CEM and $PdCl_4^{2-}$ for the AEM. Such three-dimensional growth of the Pd black deposits should cause the increase in the surface area irrespective of the morphology, leading to the improved reactivity.^{4,5} The same effect is also expected in the present case.

Hydrogenation system of styrene on the palladized CEM or AEM .--- The hydrogenation of styrene was carried out using the twocompartment cell separated by the palladized CEM or AEM. The membranes were palladized by an electroless plating after contacted with the $Pd(NH_3)_4^{2+}$ or $PdCl_4^{2-}$ solution for 24 h and the subsequent electroplating at 10 mA cm⁻² for 3 h. The current density for water electrolysis to produce atomic hydrogen in the hydrogenation was 36 mA cm^{-2} . The results are shown in Fig. 5. In the previous paper which was reported on the hydrogenation of pure styrene on a Pd sheet,³ a sole hydrogenation product of styrene was ethylbenzene and its production rate increased linearly with time. Then current efficiency for the ethylbenzene production was about 93%. In the present case, the hydrogenation product was only ethylbenzene and other products such as oligomer or polymer of styrene were not detected. As can be seen from Fig. 5, the amount of produced ethylbenzene linearly increased with time irrespective of the kind of membrane. This indicates that the catalytic activity of the Pd black deposited on both membranes was kept during the present reaction period. The current efficiency for the ethylbenzene production



Figure 3. Time course of amount of Pd black deposited on the palladized CEM and AEM in the electroplating. Current density: 10 mA cm^{-2} .

evaluated according to the previous method³ was 79% for the palladized CEM and 82% for the palladized AEM. The remainder was ascribed to hydrogen evolution on the Pd black deposit and its hydrogen absorption. The conventional hydrogenation mechanism⁴ in which electrogenerated atomic hydrogens permeate through a palladized Pd sheet and add to styrene molecules adsorbed on the back side must be accepted for the palladized CEM and AEM although the mechanism for the production of the atomic hydrogens is different in the following way

$$H^+ + e^- \rightarrow H$$
 for CEM [1]

$$H_2O + e^- \rightarrow H + OH^-$$
 for AEM [2]

The current efficiency for the palladized membranes, however, was lower than that (*ca.* 93%) for the palladized Pd sheet. According the previous paper,³ the current efficiency depended on the current density for the production of atomic hydrogen because the current density, that is the rate of the atomic hydrogen production, could influence the diffusion rate of atomic hydrogen in the Pd and Pd black. In the present case, the production of the Pd black deposits



Figure 4. Scanning electron micrographs of Pd black deposited on a CEM and AEM after the electroless plating and the subsequent electroplating for 2 h.



Figure 5. Time course of amount of ethylbenzene produced in the hydrogenation of 1 M styrene dissolved in methanol and pure styrene on a palladized CEM and AEM. The condition for palladization and hydrogenation is shown in the text. The current efficiency for toluene production is shown in parenthesis.

led to the extension of the surface area for the electrochemical production of atomic hydrogen as well as the hydrogenation. This means that the decrease in the real current density and seems to be a part of the reason for the lower current efficiency.

The current efficiency for the ethylbenzene production was improved to 88% for the palladized CEM and 93% for the palladized AEM, respectively, with the use of methanol as a solvent in spite of the low concentration of styrene as shown in Fig. 5. This suggests that the other plausible hydrogenation mechanism can be also accepted. The CEM and AEM used in the present study were composed of segregated domains of hydrophobic polymer bones and hydrophilic pores of hydrated ion-exchange sites like Nafion. Ions, cations in the CEM, or anions in the AEM, incorporated in the membranes permeated through a network of hydrophilic pores. Pd black was likely to be deposited not only on the membrane surface but also in the membranes by the electroless plating, as shown in Fig. 6, because $Pd(NH_3)_4^{2+}$ and $PdCl_4^{2-}$ ions can easily penetrate in the hydrophilic pores of the CEM and AEM, respectively. A part of Pd black deposits in the hydrophilic pores seem to make an electric network with surface Pd black deposits in electrochemical palladization after the electroless plating. Because methanol with high polarity is miscible with water, the miscibility of methanol with water in the hydrophilic pores seems to allow the penetration of styrene into the membranes more or less in the present case, leading to the en-



Figure 6. Schematic illustration for hydrogenation mechanisms of styrene dissolved in methanol for a palladized CEM.

largement of active reaction area for the hydrogenation. The styrene molecules penetrated in the pores can directly react with atomic hydrogen produced on the Pd black surface, as shown in Fig. 6. This reaction is likely to contribute to the improvement of the current efficiency for the hydrogenation.

Dechlorination system of 4-chlorotoluene on the palladized CEM or AEM.—The dechlorination of 4-chlorotoluene was carried out using the same cell as the hydrogenation. The CEM and AEM membranes were palladized by an electroless plating after contacted with the $Pd(NH_3)_4^{2+}$ and $PdCl_4^{2-}$ solution for 24 h, respectively, and then the resulting membranes were still palladized at 10 mA cm⁻² for 2 h. The current density for water electrolysis to produce atomic hydrogen in the dechlorination was 36 mA cm⁻². The results are shown in Fig. 7. Regardless of the kind of membrane, the dechlorination system successfully operated and toluene was obtained as a dechlorination product together with hydrogen as a byproduct. The other products like biphenyl were not obtained. These suggest that a Cl group of 4-chlorotoluene was substituted with atomic hydrogen produced on the Pd black catalyst as follows.

$$\text{Cl-C}_6\text{H}_4\text{-}\text{CH}_3 + 2\text{H} \rightarrow \text{C}_6\text{H}_5\text{-}\text{CH}_3 + \text{HCl}$$
 [3]

The production of HCl was qualitatively confirmed with a silver nitrate solution in all cases.

The amount of toluene production linearly increased with time in all cases, suggesting that the activity of the Pd black catalyst is maintained for at least 5 h. Current efficiency for toluene production was evaluated based on the method reported previously³ and the results are also shown in Fig. 7. The current efficiency for pure 4-chlorotoluene was about ten times higher than that in 1 M 4-chlorotoluene dissolved in cyclohexane probably due to the increase in substrate concentration. Moreover, the current efficiency in methanol, a protic solvent with higher polarity, was about sixty times higher than that in cyclohexane, an a protic solvent with lower polarity. This result is consistent with general tendency that polar solvents such as alcohol facilitate dehalogenation.¹

The dechlorination of 4-chlorotoluene in methanol was also carried out by using a palladized Pd sheet instead of the palladized ion exchange membranes. For obtaining the maximal current efficiency for the toluene production, the palladization was performed galvano-statically at 36 mA cm⁻² for 1.5 h and the production of the atomic



Figure 7. Time course of amount of toluene produced in dechlorination of 1 M 4-chlorotoluene dissolved in methanol or cyclohexane and pure 4-chlorotoluene on a palladized CEM and AEM. The current efficiency for toluene production is shown in parenthesis.

hydrogen in the dechlorination was done at 18 mA cm⁻². In this case, the current efficiency for toluene production was *ca.* 58% which was much lower than that for the palladized ion exchange membranes. The difference in the current efficiency between the palladized Pd sheet and the palladized ion-exchange membranes suggests the enlargement of the active reaction area and the appearance of the mechanism other than the conventional one discussed in the hydrogenation of styrene as shown in Fig. 6.

The current efficiency for toluene production on a palladized CEM and AEM depended on the concentration of 4-chlorotouene.

The maximal current efficiency was achieved at the concentration of 2 M and it was 90% for the palladized CEM and 93% for the palladized AEM. Over 2 M the current efficiency gradually decreased probably due to the lowering of the miscibility of methanol with water in the hydrophilic pores of the membranes.

Conclusion

We have succeeded in reducing the amount of Pd used in the successive hydrogenation system by using ion exchange membranes palladized by electroless plating and the subsequent electroplating in place of a Pd sheet. The hydrogenation and dechlorination system using the palladized ion exchange membranes was successfully constructed, and ethylbenzene and toluene were exclusively produced from styrene and 4-chlorotoluene, respectively. The present system, however, showed low current efficiency in comparison with the previous system using a Pd sheet or palladized Pd sheet. This was markedly improved by dissolving substrates into methanol with high polarity. Considering these results, the hydrogenation and dechlorination was suggested to proceed based on not the conventional mechanism in which electrogenerated atomic hydrogens permeating through the palladized Pd sheet and add to substrate molecules but the other mechanism in which electrogenerated atomic hydrogens directly added to the substrate molecules.

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