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A NEW SUCCESSIVE HYDROGENATION SYSTEM

A highly proposed practical method for promoting the hydrogenation of organic compounds such as 4-methylstyrene and 2-octene was applied to the hydrogenation of various kinds of compounds such as amaranth, NO_3^- and N_2O . In this way, the extensive applicability of this new hydrogenation system using three-dimensionally expanded Pd sheet electrodes was verified. Furthermore, the selectivity for the hydrogenation of unsaturated organic compounds containing a benzyloxy group by using the present hydrogenation system was discussed in comparison with one using hydrogen gas and a heterogeneous catalyst such as Pd-C.

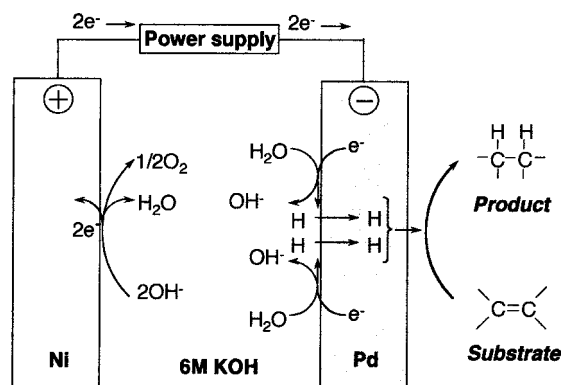
The catalytic hydrogenation of unsaturated organic compounds using catalysts such as Pd, Pt and Ni is very important in organic syntheses [1-5]. Chemisorbed atomic hydrogen is easily formed on these catalysts, especially by using an electrochemical technique[6,7], leading to the bypass of the kinetic barrier for dissociation and the mass transport of poorly soluble molecular hydrogen.

Pd, one of the catalysts for hydrogenation, has unique properties different from Pt and Ni. It can absorb and desorb hydrogen reversibly [8,9] and therefore hydrogen-absorbed Pd could operate not only as a catalyst, but also as a source of hydrogen for the hydrogenation. Based on this idea, as well as the concept of charge and discharge reactions at the negative electrode of a nickel-metal hydride battery, we have successfully constructed a new successive hydrogenation system of unsaturated organic compounds such as styrene [10,11]. In this system, atomic hydrogen is electrochemically produced at the front side of the Pd sheet electrode and supplied successively through it to be utilized for the hydrogenation at the back side of the Pd sheet electrode as shown in Scheme 1. The Pd sheet electrode plays several important roles; i. e. (1) a working electrode for the electrochemical production of atomic hydrogen, (2) a separator for the separation of both processes, (3) a selective permeation membrane for the selective permeation of atomic hydrogen and (4) a reaction field for the consumption of atomic hydrogen by hydrogenation.

Several characteristics of this system are described below:

(1) Atomic hydrogen, having a very high reactivity, can be utilized for the reaction.

(2) A compartment for the production of atomic hydrogen is separated from that for the hydrogenation.



Scheme 1. Successive hydrogenation of unsaturated organic compounds.

(3) Successive hydrogenation can be achieved by a successive supply of atomic hydrogen from the back side of the Pd sheet electrode.

(4) A supporting electrolyte is not needed for the hydrogenation and, therefore, the separation and purification between products and the supporting electrolyte are needless.

(5) Pure hydrogen can be used for the hydrogenation.

(6) Substrates in both liquid and gaseous states can be hydrogenated.

(7) The hydrogenation rate can be precisely controlled by an applied current at the 6 M KOH side.

Hydrogen absorbed in rare earth intermetallic compounds, such as LaNi_5 , PrCo_5 and SmCo_5 , exists in an active state [12,13], and therefore it possesses a high potentiality for the hydrogenation of various compounds. On the basis of this point, the hydrogenation of organic compounds using hydrogen storage alloys has already been investigated by many researchers[14-18]. In those cases, however, the reaction will terminate sooner or later because of the limited amount of hydrogen absorbed in the metal. The present system permitted hydrogenation without termination by a successive supply of atomic hydrogen.

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We have studied hydrogen storage alloys such as LaNi_5 and $\text{MmNi}_{3.6}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.7}$ in place of Pd as a working electrode and a separator [19]. Such hydrogen storage alloys are known as a negative electrode material for use in a nickel–metal hydride battery. Consequently, it was confirmed that the hydrogenation system worked well irrespective of the kind of hydrogen storage alloys. However, the hydrogenation rate was found to be dependent on the kind of substrate.

The aims of this study were mainly focused on (1) expanding the reaction zone or number of reaction site by depositing Pd black on the surface of the Pd sheet, or modifying its surface with highly active catalysts with atomic hydrogen permeating through the electrode, (2) elucidating the catalytic effect of the kind of catalyst on the hydrogenation of several kinds of substrates, and (3) comparison of the hydrogenation using this system to that with hydrogen gas using a heterogeneous catalyst such as Pd–C.

This paper describes the following five subjects; i.e. (1) the effect of Pd black deposits on the successive hydrogenation of 4-methylstyrene and 2-octene with atomic hydrogen permeating through a Pd sheet electrode, (2) the chemical deposition of foreign metals on a Pd sheet and its application to the continuous hydrogenation of 4-methylstyrene, (3) the decoloration of azo dye using atomic hydrogen permeating through a Pt-modified palladized Pd sheet electrode, (4) the catalytic reduction of nitrate ion and nitrous oxide with atomic hydrogen permeating through foreign metal-deposited palladized Pd sheet electrodes, and (5) selective alkene hydrogenation with atomic hydrogen permeating through a palladized Pd sheet electrode.

Effect of Pd black deposits on the successive hydrogenation of 4-methylstyrene and 2-octene with atomic hydrogen permeating through a Pd sheet electrode [20–22]

In our previous work, the hydrogenation system of styrene without the exhaustion of atomic hydrogen was successfully constructed using a two-compartment cell separated by a Pd sheet electrode as shown in Fig. 1(a) [10,11]. However, the rate of the hydrogenation was significantly influenced by the kind of reaction substrate. Therefore, for the purpose of enhancing the catalytic activity for the hydrogenation of substrates with lower activity, a chemical palladization method with atomic hydrogen permeating through the Pd sheet was investigated and the effectiveness of the Pd black deposits on the hydrogenation of 4-methylstyrene and 2-octene, having much lower reactivity than that of styrene, was evaluated.

The two reaction systems used for the palladization and hydrogenation of 4-methylstyrene and 2-octene are shown in Fig. 1. A 6 M KOH solution was put in a compartment having a Ni plate anode and a Pd sheet (Thickness: 50 μm) cathode for the production of atomic hydrogen. For the palladization, a 1 M HCl solution containing 2.8×10^{-2} M PdCl_2 was filled into the other compartment. The palladization was carried out chemically using atomic hydrogen, which was produced

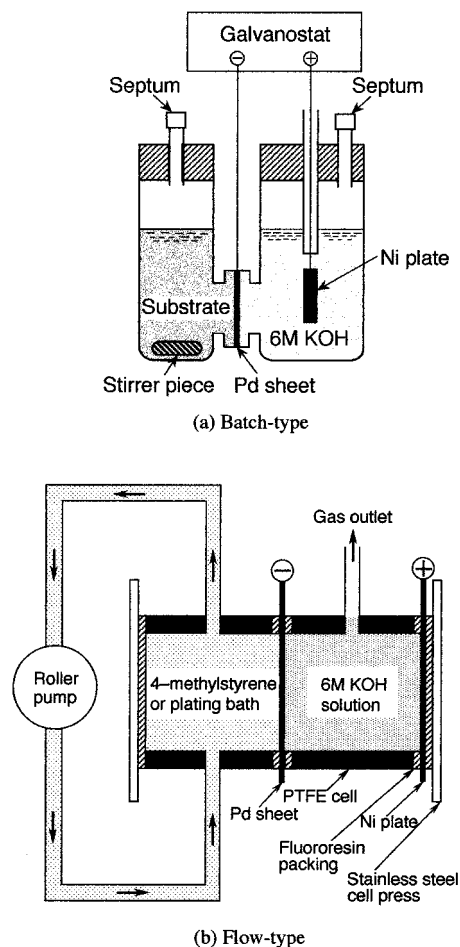
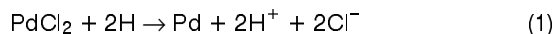


Figure 1. Schematic illustration of the cell assembly.

by galvanostatic water electrolysis, followed by permeation through the Pd sheet electrode. During the palladization, a PdCl_2 solution was circulated with a roller pump for the flow-type system or a magnetic stirrer for the batch-type one. The palladized Pd sheet electrodes were washed with degassed distilled water and then dried with Ar gas, prior to use for hydrogenation and they were potentiostatically oxidized at +0.4 V vs. Hg/HgO until the anodic current attributable to the oxidation of the stored atomic hydrogen started to flow. After that they were used for the hydrogenation.

Figure 2 shows the time course of the amount of Pd black deposited on the Pd sheet according to the following equation.



The amount of Pd black deposits increased linearly with an increase in palladization time after an induction period of a few minutes which was attributed to the diffusion of atomic hydrogen through the Pd sheet electrode. The current efficiency for the palladization, evaluated from the slope of the straight line in Fig. 2, was about 24 % and the rest is ascribed to hydrogen evolution.

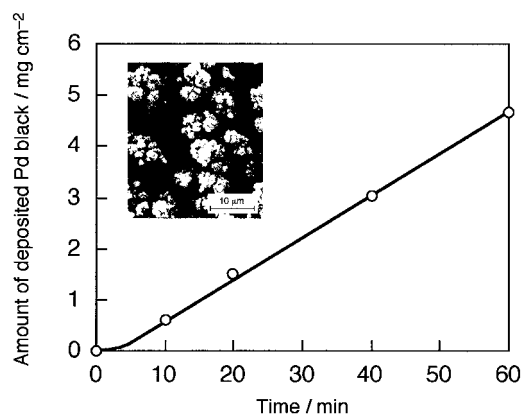


Figure 2. Time course of the amount of Pd black deposited on a Pd sheet electrode. The inset shows a SEM image for Pd black deposited for 60 min.

The inset in Fig. 2 shows SEM photograph of the Pd black deposits after palladization for 60 min. When the palladization was initiated, adhesive dendritic Pd black was first deposited on the relatively smooth Pd sheet electrode. The dendritic Pd black deposits grew to spherical ones of about 1 μm with increasing palladization time, followed by accumulating successively and three-dimensionally, and growing to a coral-like shape as shown in the inset of Fig. 2. Such growth of the Pd black deposits suggests that atomic hydrogen permeating through not only the Pd sheet electrode but also the Pd black deposits participate in the palladization. Therefore, the three-dimensional growth of Pd black deposits can cause a remarkable increase in the reaction zone or number of reaction sites for the hydrogenation.

The hydrogenation of neat 4-methylstyrene was initiated by the galvanostatic electrolysis of water at 50 mA cm^{-2} using Pd sheet electrodes with different amounts of Pd black deposits and a flow-type system. The time course of the amount of produced 4-ethyltoluene, the sole hydrogenation product, is shown in Fig. 3. In any case, the amount of produced 4-ethyltoluene increased linearly with electrolysis time for at least 5 h after the induction period of a few minutes. The rate of 4-ethyltoluene production evaluated from the slope of each straight line in Fig. 3 increased with an increase in the amount of Pd black deposits, suggesting that the hydrogenation mainly proceeded on the three-dimensionally expanded surface of the Pd black deposits as illustrated in Fig. 4. In particular, the rate of 4-ethyltoluene production for a palladization of 4.5 mg cm^{-2} was about 40 times larger than that for no palladization and the current efficiency for 4-ethyltoluene was ca. 100%, indicating that almost all of the atomic hydrogen supplied on the surface of the palladized Pd sheet electrode was effectively used for the hydrogenation of 4-methylstyrene.

The hydrogenation of 2-octene was initiated by the galvanostatic electrolysis of water at 35 mA cm^{-2} using Pd sheet electrodes palladized at 10 mA cm^{-2} for

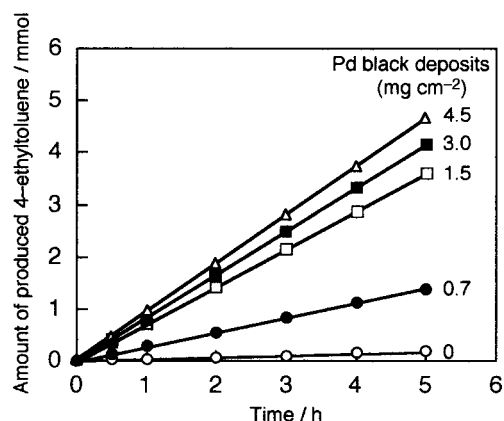


Figure 3. Time course of the amount of 4-ethyltoluene produced in the hydrogenation of 4-methylstyrene using Pd sheet electrodes with different amounts of Pd black deposits.

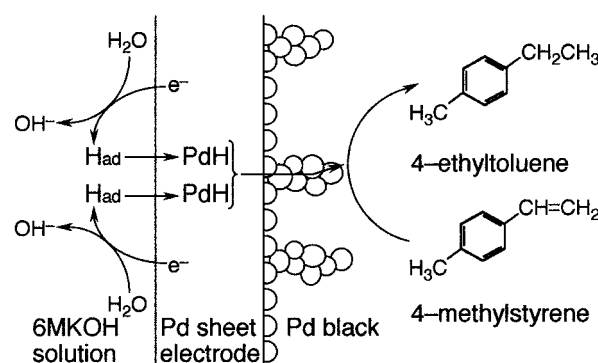


Figure 4. Schematic illustration of the hydrogenation of 4-methylstyrene on a palladized Pd sheet electrode.

different periods and a batch-type system. The time course of the amount of produced octane in each case is shown in Fig. 5. In any case, the amount of produced octane increased linearly with an increase in the reaction time. The rate of octane production also increased with an increase in palladization time, suggesting that the number of reaction sites increased remarkably due to

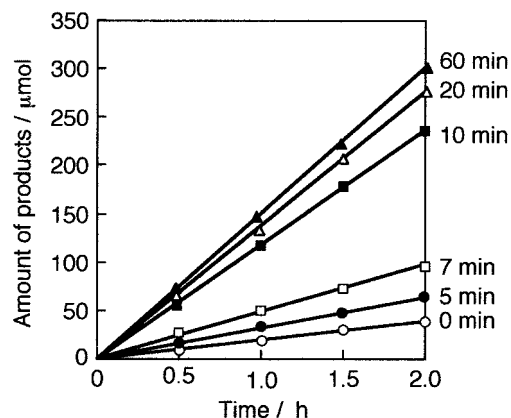


Figure 5. Time course of the amount of octane produced in the hydrogenation of 2-octene using Pd sheet electrodes palladized for different periods. Current density for palladization: 10 mA cm^{-2} .

the three-dimensional growth of Pd black deposits on the bulk. In this case, the current efficiency for octane production was 92% in the case of palladization for 60 min.

Chemical deposition of foreign metals on a Pd sheet and its application to the successive hydrogenation of 4-methylstyrene [23, 24]

In the previous part, it was elucidated that the hydrogenation rate of 4-methylstyrene can be remarkably improved by the deposition of Pd black on Pd sheet mainly due to the increase in reaction area. Since noble metals such as Pt and Au have a low overvoltage for H₂ evolution comparable to Pd, they are expected to show high catalytic activity for hydrogenation. The effect of the deposition of such novel metals on the reactivity of the hydrogenation of 4-methylstyrene was investigated in this section.

On the substrate side of the Pd sheet, Pt, Au and, for comparison, Cu and Zn having a higher overvoltage for H₂ evolution than Pt and Au were deposited chemically by using atomic hydrogen as for Pd black. The bath composition for the deposition of Pt, Au or Pd was 1.0 M HCl solution including 0.028 M H₂PtCl₆, 0.028 M HAuCl₄ or 0.028 M PdCl₂, while that for the deposition of Cu or Zn was 0.028 M CuSO₄ or 0.028 M ZnSO₄ aqueous solution. The electrolytic current density for the production of atomic hydrogen was 10 mA cm⁻².

Figure 6 shows the time course of the amount of Pt, Au, Cu and Zn deposited on the Pd sheet with atomic hydrogen. The amount of deposited Pt and Au increased linearly with an increase in the deposition time, which was comparable to that of Pd black on a Pd sheet with atomic hydrogen, whereas the deposition of Cu and Zn terminated at about 0.2 mg cm⁻². The reduction of Pt, Au, Cu and Zn with atomic hydrogen is believed to proceed according to the following equation.

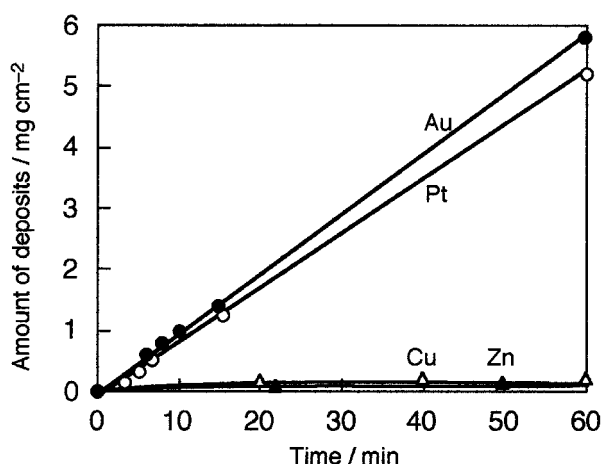


Figure 6. Time course of the amount of Pt, Au, Cu and Zn deposited on a Pd sheet.

where M^{n+} , M and H represent the metal ion, metal and atomic hydrogen, respectively. However, the behavior of the deposition depends on the kind of deposits, as can be seen from Fig. 6. Pt and Au do not permit the permeation of hydrogen, but they show a low overvoltage for H₂ evolution, suggesting that adsorbed (atomic) hydrogen is produced easily. The adsorbed (atomic) hydrogen is well-known to move on the surface of these metals, known as "spillover". In the present case, the adsorbed (atomic) hydrogen, which was moved by the spillover or produced by the redissociation of H₂ gas, seems to be used for the deposition of Pt and Au. In contrast, Cu and Zn show a high overvoltage for H₂ evolution, so that adsorbed (atomic) hydrogen must not be formed easily. This seems to be responsible for the termination of their deposition. The current efficiencies for the deposition of Pt and Au, evaluated from slope of each straight line in Fig. 6, were 26% and 27%, respectively. H₂ evolution was a side reaction of the deposition of metals.

In order to evaluate the rate of hydrogen permeation for Pt, Au and Pd black-deposited Pd sheets, the time course of the anodic current for the oxidation of permeated hydrogen in each case was measured. Hydrogen permeation experiments were conducted by using the same system as the hydrogenation, but the substrate was replaced by 6M KOH solution and, additionally, a Ni counter electrode and a Hg / HgO reference electrode were placed in it. One side of the Pd sheet electrode was galvanostatically electrolyzed at 50 mA cm⁻² for the production of atomic hydrogen, while the other side was potentiostatically electrolyzed at +0.5V vs. Hg / HgO for the reoxidation of the permeated atomic hydrogen. Then the oxidation current increased monotonously after the initiation of galvanostatic electrolysis for the production of atomic hydrogen and then saturated because the permeation of atomic hydrogen reached the steady state. The saturated oxidation currents in the case of Pd black, Pt or Au-deposited Pd sheets are shown in Fig. 7 as a function of the amount of the deposition. The saturated oxidation current refers to the steady rate of the permeation of atomic hydrogen. In the case of palladized Pd sheet, the steady permeation rate was constant regardless of the amount of Pd black deposits. On the contrary, the deposition of Pt to an extent of 1.0 mg cm⁻² leads to a marked decrease in the permeation rate. In the case of Au, a further marked decrease was observed in the hydrogen permeation rate. These results suggest that atomic hydrogen permeates through not only the Pd sheet, but also the Pd black deposits, whereas Pt and Au deposits are barriers for the permeation of atomic hydrogen.

Figure 8 shows the current efficiencies for 4-ethyltoluene production as a function of the amount of Pt and Au deposits, as well as Pd black deposits for

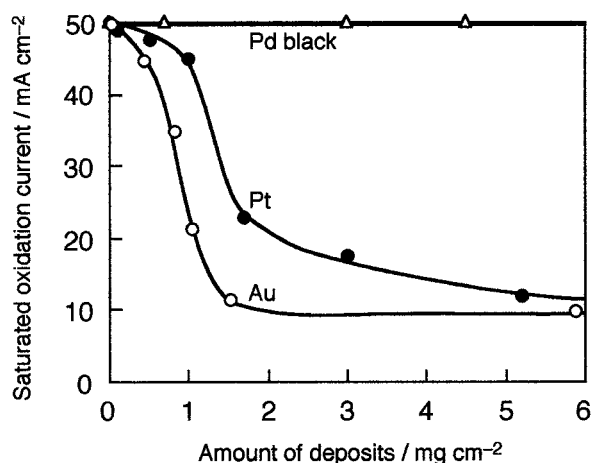


Figure 7. Anodic current for the oxidation of permeated hydrogen as a function of the amount of Pt, Au and Pd black deposits.

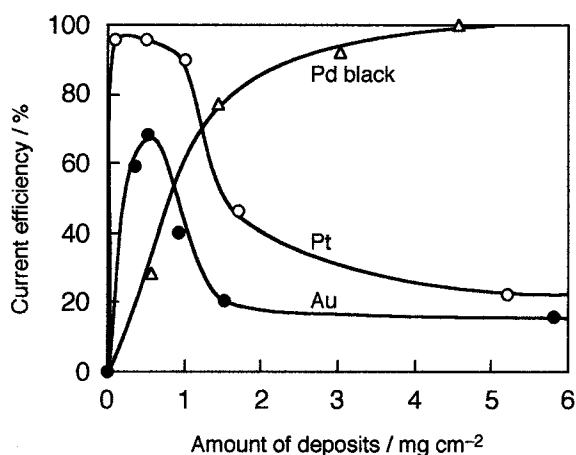


Figure 8. Current efficiency for the production of 4-ethyltoluene as a function of the amount of Pt, Au and Pd black deposits.

comparison. The hydrogenation conditions of 4-methylstyrene were the same as those in the previous section. The maximum current efficiencies for Pt and Au-deposited Pd sheets were 95% and 70%, respectively. These results clearly indicate that the modification of Pd sheet with Pt and Au deposits greatly improves the rate of hydrogenation of 4-methylstyrene in this system. However, in contrast with the case of palladized Pd sheet, a further increase in the amount of Pt and Au deposits leads to a decrease in the current efficiency for 4-ethyltoluene production. Then the saturated oxidation current of atomic hydrogen passing through the Pd sheet decreases as shown in Fig. 7. Correspondingly, the amount of H₂ evolution at 6M KOH-side increased with the amount of their deposits. Judging from these results, the suppression of hydrogen permeation seems to be responsible for the decrease in current efficiency.

Decoloration of an azo dye using atomic hydrogen permeating through a Pt-modified palladized Pd sheet electrode [25]

Dyestuff waste fluid is so conspicuous that it tends to be more hateful than any other industrial dye regardless of it causing any actual harm. Decolorizing it is one of the indispensable achievements in waste water treatment [26–30]. Several decoloration methods have been proposed so far, e.g., the adsorption method using activated carbon and chemical and electrochemical oxidation methods [31–35]. In particular, ozone and hypochlorite oxidations are efficient decoloration methods, but they are not desirable because of the high cost for plant and equipment investment, high running and raw costs, and the secondary pollution arising from the residual chlorine [36,37].

The color of the dyestuff is well-known to originate from the extension of the conjugated double bonds including the diazo group, and it varies with the length of the conjugated double bonds. Therefore, their severance must lead to decoloration. The present hydrogenation system can be applied for this purpose. This is classified as a reductive decoloration, but it is superior to the conventional electrochemical method [38–41] in terms of eliminating the need for electrolytes in the substrate, which facilitates the separation and purification of products.

Figure 9 shows a reaction system used in the decoloration experiment. The system was composed of two compartments separated by a Pd sheet (effective area : 1 cm², thickness: 50 μm). The cell was placed directly in a spectrophotometer for the ultraviolet and visible region. The amaranth solution side in the reaction system was made of quartz for the transmission of the UV light. The produced atomic hydrogen diffuses into the back side of the Pd sheet and causes the following: deposition of Pd black and Pt or the hydrogenolysis of amaranth. 6 M KOH solution and amaranth solution or

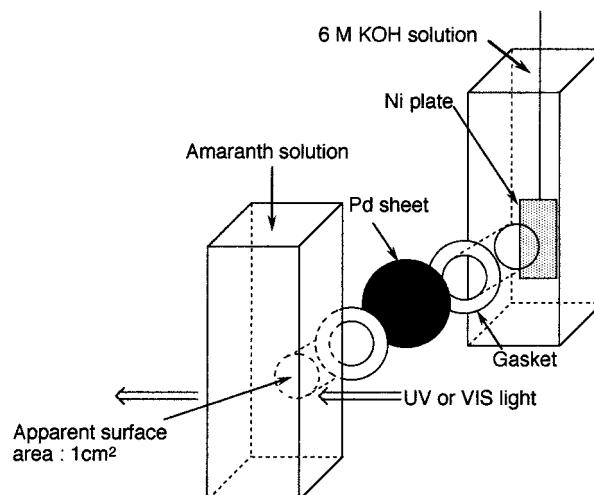


Figure 9. Schematic illustration of a reaction system for the decoloration reaction of amaranth.

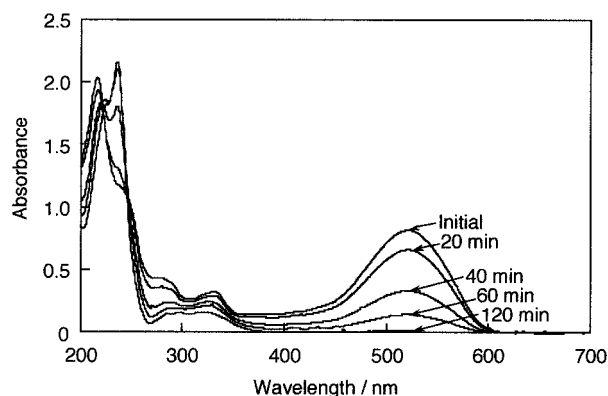


Figure 10. Time course of the absorption spectra of the amaranth solution for the Pd/Pd black/Pt sheet electrode. Initial concentration of amaranth 2.06×10^{-5} M.

different plating solutions were poured into separate compartments, respectively.

Pd black and Pt were chemically deposited on the substrate side of the Pd sheet in this order using atomic hydrogen permeating through it as previously described in previous sections. The prepared electrode was denoted as the Pd/Pd black/Pt electrode. The electrolytic current density for the production of atomic hydrogen was 10 mA cm^{-2} . The amount of the deposits, determined from the weight gain after each deposition, was 4.5 mg cm^{-2} and 19 mg cm^{-2} , respectively.

The atomic hydrogen required for the decoloration of amaranth was produced by means of galvanostatic electrolysis at 50 mA cm^{-2} . The amaranth solution was circulated with a roller pump during the experiment. The experiment was carried out at room temperature. The absorbance of the absorption peak at 521 nm was evaluated every 5 min.

The time course of the absorption spectra of 2.06×10^{-5} M amaranth solution decolorized with atomic hydrogen permeating through the Pd/Pd black/Pt sheet electrode is shown in Fig. 10. The absorbance of the peaks observed at 220 nm, 280 nm, 330 nm and 521 nm then decreased, while that of the shoulder at 250 nm

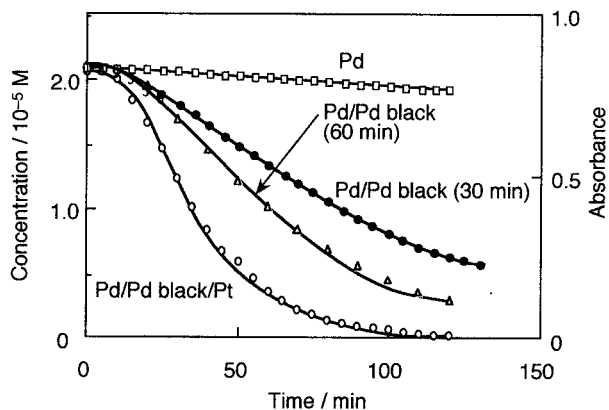


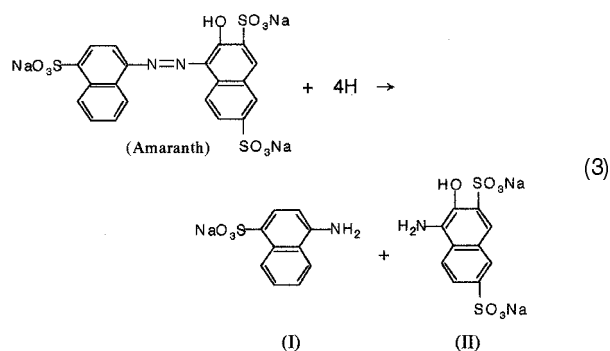
Figure 11. Time course of the concentration and absorbance of amaranth for four kinds of electrodes. Initial concentration of amaranth 2.06×10^{-5} M.

increased. The decoloration reaction is chiefly ascribed to the disappearance of the absorption peak at 520 nm. The absorption peak at 520 nm disappeared after 120 min. The time courses of the absorbance at 520 nm for three kinds of electrodes are summarized in Fig. 11. The decoloration rate of the amaranth solution changed in the following order; Pd/Pd black/Pt > Pd/Pd black > Pd. This result can be explained in terms of the difference of the roughness factor between the electrodes and the high catalytic activity of the Pt deposit as described in the last section.

For identifying the decoloration products, the decolorized solution using a Pd/Pd black/Pt sheet electrode was analyzed by HPLC or absorption spectroscopy. In the chromatogram of the decolorized solution, two peaks were observed and no peaks assigned to amaranth were detected. One of the peaks was identified as sodium 1-aminonaphthalene-4-sulfonate (denoted as compound (I)), which was one of the hydrogenolysis products of amaranth, and the hydrogenolysis of amaranth to compound (I) quantitatively proceeded.

Judging from these results, the hydrogenolysis of the azo group with atomic hydrogen probably proceeds to produce two corresponding amino compounds, compound (I) and disodium 1-amino-2-hydroxynaphthalene-3,6-disulfide (denoted as compound (II)) as shown in the following equation.

In addition, an equimolar mixed solution of the above two products was prepared by the chemical reduction of amaranth with a reducing agent such as



sodium hydrosulfite [42] and it was analyzed by HPLC. As a result, the obtained chromatogram was superimposable on that of the solution decolorized with atomic hydrogen. This clearly indicates that compounds (I) and (II) were produced by the hydrogenolysis of amaranth with atomic hydrogen permeating through the Pd/Pd black/Pt electrode.

Furthermore, the corrected absorption spectrum for the equimolar mixed solution prepared by chemical reduction was also superimposable on the solution decolorized with atomic hydrogen, thus supporting the above hypothesis.

The current efficiency for the hydrogenolysis of amaranth was evaluated assuming a 4-electron transfer reaction [26]. When the current density for producing

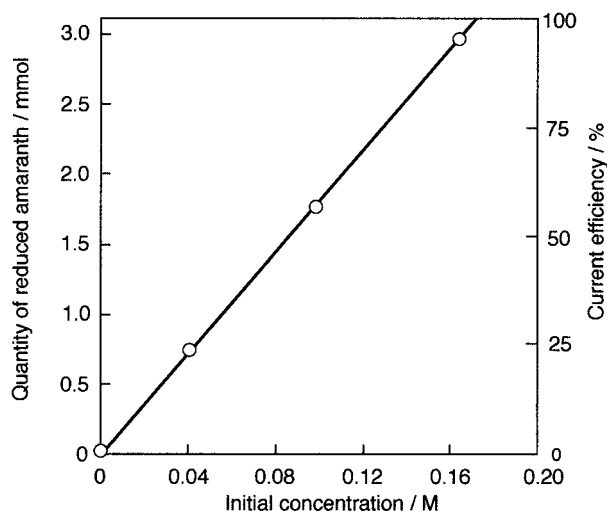


Figure 12. Quantity of reduced amaranth and its current efficiency as a function of the initial concentration of amaranth.

atomic hydrogen was 50 mA cm^{-2} , the current efficiency was 0.052 % for an initial amaranth concentration of $4.12 \cdot 10^{-5} \text{ M}$. However, the current efficiency increased linearly with the initial amaranth concentration as seen from Fig. 12. In particular, the current efficiency was 97 % when the initial concentration of amaranth was 0.17 M. These results suggest that the present system is suitable for decolorizing dyestuff waste solution of relatively high concentration.

Catalytic reduction of nitrate ion and nitrous oxide with atomic hydrogen permeating through foreign metal-deposited palladized Pd sheet electrodes [43,44]

The increase in the nitrate concentration of ground water due to the extensive use of nitrates in manufacturing processes of chemicals such as detergents and fertilizers as well as nuclear fuels for nuclear power generation is a serious problem and it is essential to reduce the nitrate uptake of people [45–48]. The conversion of nitrates to harmless products such as nitrogen or useful chemical reagents such as ammonia is very useful.

Other attention has been intensively paid to the decomposition of N_2O . N_2O gas is employed as an anesthetic carrier gas in anesthetic machines used in clinical practice, but the garbage of leftover gas is always troublesome. Moreover, it has a greenhouse effect like CO_2 gas [49–51]. Therefore, the establishment of a N_2O decomposition technique is essential also for the protection of the stratospheric ozone layer.

For the purpose of decreasing these pollutants, we applied the present hydrogenation system using Pt black, Au, Cu and Ni-modified palladized Pd sheet electrodes.

As for the reduction of NO_3^- , a 6 M KOH solution for water electrolysis was put in one compartment and a

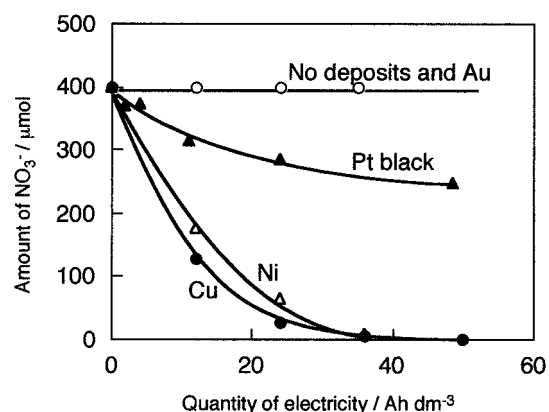
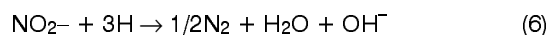
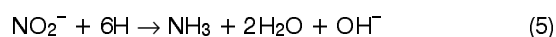
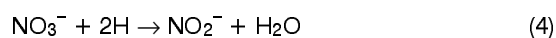


Figure 13. Time course of the amount of NO_3^- consumed on palladized Pd sheet electrodes with various deposits.

0.01 M NaNO_3 aqueous solution as substrate was filled in the other compartment. The current density for the production of atomic hydrogen in the reduction of NO_3^- was 10 mA cm^{-2} .

Figure 13 shows the time courses of NO_3^- consumed on palladized Pd sheet electrodes with various deposits at room temperature. The amount of deposits was 10 mg cm^{-2} for Pt black, 5 mg cm^{-2} for Au, 9 mg cm^{-2} for Cu and 5 mg cm^{-2} for Ni, respectively. No deposit and Au did not show catalytic activity for the reduction of the nitrate ion, while Cu and Ni showed much higher catalytic activity. Pt black showed medium catalytic activity. At the Cu and Ni-modified palladized Pd sheet electrodes, the reduction of NO_3^- was completed after 50 Ah dm^{-3} , indicating that Cu and Ni work as catalysts for the reduction of NO_3^- in this system. Atomic hydrogen permeating through palladized Pd sheet may react with the NO_3^- ion on the catalyst after spillover.

The reduction products in the case of Cu and Ni-modified palladized Pd sheet electrodes were analyzed by ion chromatography and gas chromatography. In the case of Cu-modified palladized Pd sheet electrode, NO_2^- , N_2 and NH_3 were produced with a decrease in the amount of NO_3^- . The time course of the amount of products is shown in Fig. 14. NO_2^- was obtained as an intermediate, N_2 as the main product and a small amount of NH_3 were produced with a decrease in the amount of NO_2^- . On the other hand, NO_2^- was not detected on the Ni-modified palladized Pd sheet electrode, and only NH_3 was obtained as a reduction product as shown in Fig. 15. The reduction of NO_3^- on Cu modified palladized Pd sheet electrodes can proceed by the following mechanism.



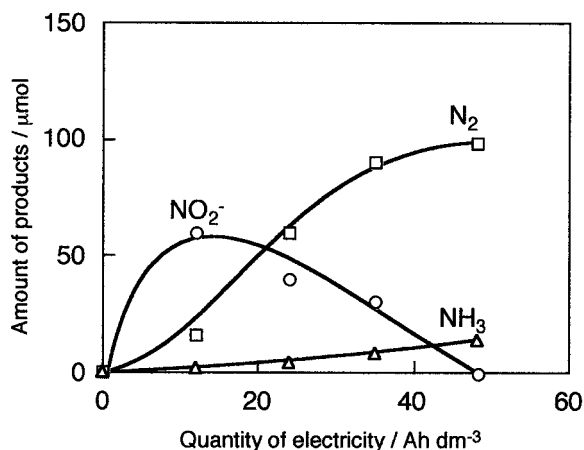


Figure 14. Time course of the amount of NO_2^- , N_2 and NH_3 produced in the reduction of NO_3^- by atomic hydrogen permeating through a Cu-modified palladized Pd sheet electrode.

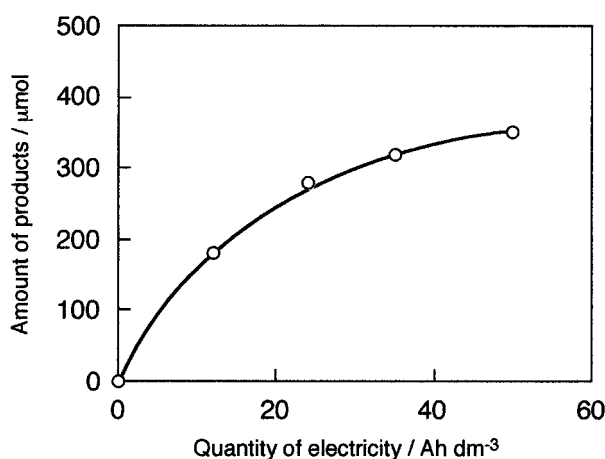
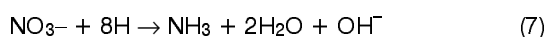


Figure 15. Time course of the amount of NH_3 produced in the reduction of NO_3^- by atomic hydrogen permeating through a Ni-modified palladized Pd sheet electrode.

On the other hand, the reduction of NO_3^- using a Ni-modified palladized Pd sheet electrode can be described as follow.



The reduction rate of NO_3^- increased with an increase in the amount of Cu deposit, while it decreased with increasing amount of Ni deposit. The current efficiency for NO_3^- reduction for a 0.6 mg cm^{-2} Ni-modified palladized Pd sheet electrode was about 54% assuming the reduction of NO_3^- proceeds in accordance with eq. (7).

As for the reduction of N_2O , pure N_2O gas at atmospheric pressure was filled in the substrate compartment. The pressure on the substrate side did not change during the experiment because N_2 was produced as a reduction product in amounts equimolar with the reduced N_2O .

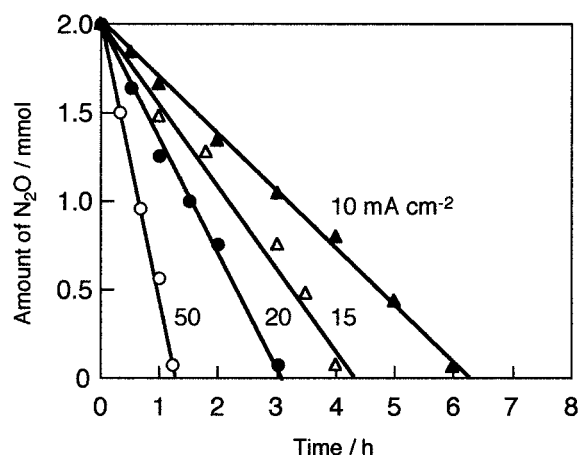


Figure 16. Time course of the amount of N_2O at various current densities using a palladized Pd sheet electrode.

The changes in the amount of N_2O with reaction time at various current densities and room temperature are shown in Fig. 16. The amount of N_2O consumed on a palladized Pd sheet electrode decreased linearly with an increase in reaction time. In this case, N_2 was the sole product and other products such as hydrazine or ammonia were not detected during the reaction. The reduction of N_2O did not proceed at all without water electrolysis on the 6 M KOH side for the generation of atomic hydrogen, suggesting that atomic hydrogen permeating through the electrode participated in the reduction of N_2O .

The reduction rate of N_2O increased almost linearly with an increase in the current density as shown in Fig. 17. The current efficiency for the reduction of N_2O was 92–94% in the range of current density from 10 to 50 mA cm^{-2} . The supply of atomic hydrogen from the back side of a Pd sheet electrode is thought to be the rate-determining step within the above range of the

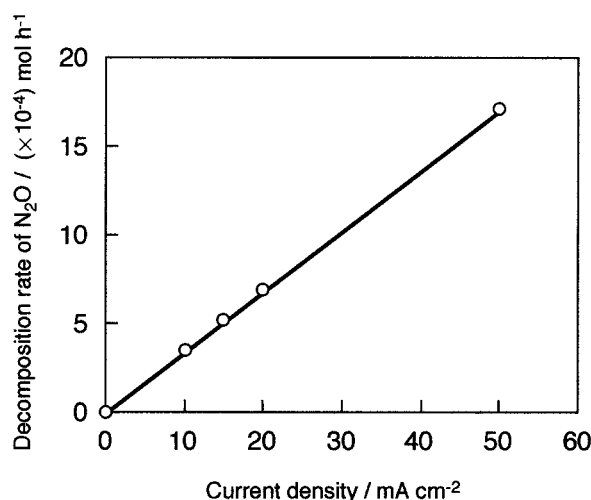


Figure 17. Decomposition rate of N_2O as a function of current density for the production of atomic hydrogen.

current density. The rest current efficiency is attributed to the hydrogen evolution reaction at the 6 M KOH side. Hydrogen evolution at the substrate side was observed after the complete amount of N_2O was consumed.

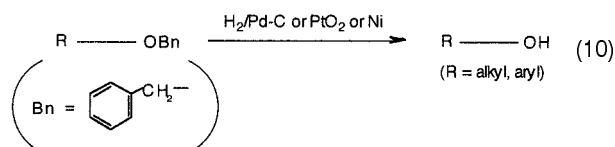
The reduction of N_2O must occur in the following reaction via adsorption on the palladized Pd sheet electrode.



The atomic hydrogen in this system is thought to serve as a proton source and a reducing agent, and the N_2O gas does not need to be dissolved in the solvents, which is also one of the greatest advantages in the application of this system to the reduction of N_2O . In addition, the decomposition of N_2O using this system can be carried out under much milder conditions than those normally required for the chemical method.

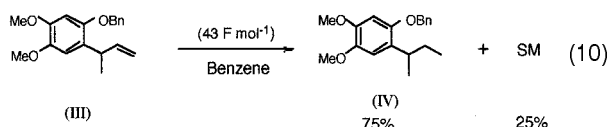
Selective alkene hydrogenation with atomic hydrogen permeating through a palladized pd sheet electrode [52]

The benzyl group (Bn) is quite important and useful for organic synthesis as protection of the hydroxyl group [53]. It is stable in both acidic and alkaline conditions, and it can be removed in neutral conditions. In general, the benzyloxy group can be removed by means of hydrogenolysis using Pd-C, PtO_2 or Ni catalyst under H_2 atmosphere in the following way.



As for alkenes containing a benzyloxy group with a heterogeneous catalyst, it is quite difficult to hydrogenate alkene without hydrogenolysis of the benzyloxy group [54,55]. Rhodium complex catalyst is known to hydrogenate C–C double bonds selectively [56] but, an unexpected side reaction occasionally occurs. In this chapter, the present continuous hydrogenation system was used for selectively hydrogenating C–C double bonds of the compounds containing benzyloxy moiety.

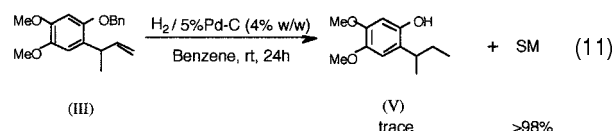
Many hydrogenations of alkene molecules containing the benzyloxy group were carried out in benzene as solvent. For example, compound (III) was hydrogenated to compound (IV) without hydrogenolysis of the benzyloxy group.



The conversion depended on the kind of molecule, but in any case the selective hydrogenation of olefins

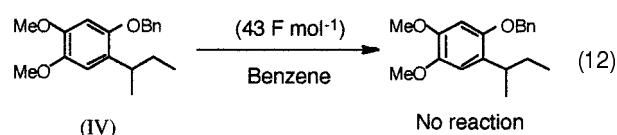
took place without hydrogenolysis of the benzyloxy group. In addition, no by-products and side reactions were not observed.

For the purpose of comparison with our hydrogenation system, conventional heterogeneous catalytic hydrogenation of compound (III) using Pd-C catalyst was carried out.



As a result, the reaction scarcely proceeded and a trace of the product was found to be compound (V). In this case, it was confirmed that both hydrogenation of the C–C bond and hydrogenolysis of the benzyloxy group took place. When another solvent, for example methanol, was used, the conversion increased up to 93%, but compound (V) was solely produced. These results indicate that the present hydrogenation system enables hydrogenation of the C–C double bond without hydrogenolysis.

Hydrolysis of the benzyloxy group in compound (IV) did not occur as long as the present hydrogenation system was used.



One possible course for the hydrogenolysis mechanism of the benzyl and allyl group can be pictured as involving an intermediate π -benzyl or π -allyl system (A) as shown in Fig. 18 [57]. Thus the present results imply that intermediate (A) is not produced on the Pd sheet surface of a new hydrogenation system employing benzene as solvent. Therefore hydrogenolysis of the benzyloxy group does not take place.

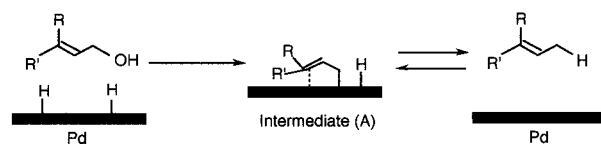
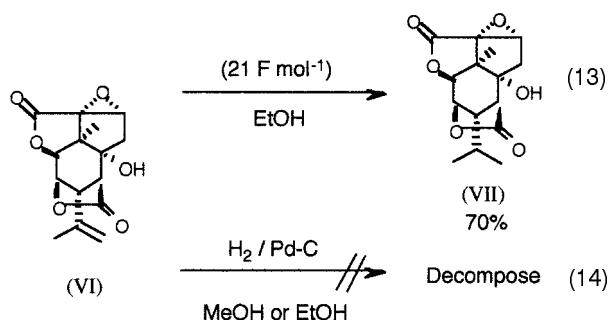


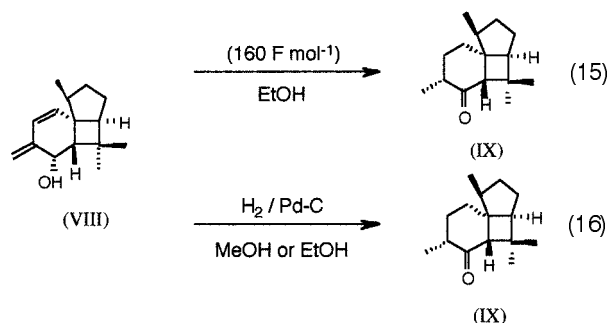
Figure 18. Hydrogenolysis mechanism of the benzyloxy or allyloxy group.

For the purpose of clarifying the effect of solvents on the hydrogenation of alkenes containing a benzyloxy group, the hydrogenation of compound (III) using two kinds of solvents such as benzene and methanol were carried out. When methanol was used, both hydrogenation of the C–C double bond and hydrogenolysis of the benzyloxy group occurred, suggesting that the selectivity of the reaction was dependent on the kind of solvent even in this system.

The application of hydrogenation for natural products and complex compounds such as compounds (VI) and (VIII) was carried out using the present hydrogenation system. For comparison, catalytic hydrogenation using Pd–C catalyst was also carried out. As for compound (VI), it was found to decompose in catalytic hydrogenation, while hydrogenation of the C–C double bond proceeded in the present hydrogenation system as shown in the following equations.



Hydrogenation of compound (VIII) was found to proceed by means of both kinds of methods to give ketone (IX) in high yields as shown in the following equations.



CONCLUSIONS

The results and conclusions obtained in this work are summarized as follows.

(1) It was elucidated that the deposition of Pd black on the surface of a Pd sheet electrode proceeds chemically with atomic hydrogen permeating through the electrode, and the amount of Pd black deposits increased linearly with an increase in palladization time. The Pd black deposits were found to grow three-dimensionally by SEM observations, causing a marked increase in the reaction zone or number of reaction sites for hydrogenation. This led to an increase in the hydrogenation rate of 4-methylstyrene and 2-octene or the current efficiency for their hydrogenation.

(2) A new successive electroless plating method, by which the surface of the Pd sheet electrode was modified with highly active catalysts such as Pt and Au, was successfully constructed using the present hydrogenation system. This method does not include stabilizers and additives required for conventional electroless plating solutions, and therefore the solution would be extremely stable. Both of the deposits showed

a considerable drop in the hydrogenation rate of 4-methylstyrene above the optimum deposits because of acting as a barrier for the permeation of atomic hydrogen. This is evidenced by the measurement of the hydrogen permeation rate for Pt or Au-deposited Pd sheet electrode.

(3) The decoloration of amaranth as an azo dyestuff solution using Pd sheet, palladized Pd sheet and platinum-modified-palladized Pd sheet electrodes was investigated with atomic hydrogen passing through the electrodes. A platinum-modified-palladized Pd sheet electrode showed excellent catalytic activity for decoloration. Sodium 1-aminonaphthalene-4-sulfonate and disodium 1-amino-2-hydroxynaphthalene-3,6-disulfonate were detected as the products, and therefore, its decoloration was supposed to be caused by the hydrogenolysis of the azo group. The current efficiency for the decoloration of amaranth increased to 97% when its initial concentration was 0.17 M.

(4) The catalytic reduction of pollutants such as NO₃⁻ and N₂O was demonstrated. Pd black and Au did not show catalytic activity for the reduction of NO₃⁻, while Cu and Ni showed much higher activity than Pt. In the case of the Cu-modified palladized Pd sheet electrode, NO₂⁻, N₂ and NH₃ were produced with a decrease in NO₃⁻. On the other hand, only NH₃ was obtained as a reduction product for the Ni-modified palladized Pd sheet electrode. In the case of the reduction of N₂O using a palladized Pd sheet electrode, N₂ was solely produced in its reduction. The current efficiency for the reduction of N₂O at current densities from 10 to 50 mA cm⁻² exceeded 90%.

(5) It was demonstrated that the present hydrogenation system enables the hydrogenation of alkenes containing a benzyloxy group selectively without hydrogenolysis of the benzyloxy group. It was found that the selectivity for the reaction was dependent on the kind of solvent. In the case of methanol solvent, both hydrogenation of the C–C double bond and hydrogenolysis of the benzyloxy group took place even in the present hydrogenation system.

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