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Journal Name

Catalysts for direct H₂O₂ synthesis taking advantage of the high H₂ activating ability of Pt: Kinetic characteristics of Pt catalysts and new additives for improving H₂O₂ selectivity

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To develop efficient catalysts for the direct H_2O_2 synthesis from H_2 and O_2 by taking advantage of the high H_2 activating ability of Pt, kinetic studies of the H_2-O_2 reaction were performed using Pt-PVP (polyvinylpyrrolidone) colloid and Pt supported on carbon (Pt/C) as catalysts, and new additives were explored. Only 10^{-9} N of protons were sufficient to maintain the H_2 reaction rate, suggesting that dissociatively adsorbed H_2 on Pt was very active. The addition of H^+ and Br^-, which is most effective for Pd catalysts, exerted much less influence on Pt, resulting in very low H_2O_2 selectivities. Inorganic and organic iodides as well as some sulfur compounds increased the H_2O_2 yield. The kinetic analysis of the reaction indicated that the H_2O_2 formation selectivity of Pt/C was maximized in combination with H^+ and *p*-iodophenol and was nearly comparable to that of Pd/C combined with H^+ and NaBr, and that its catalytic activity was higher. However, the much higher H_2O_2 destruction activity of Pt/C than that of the Pd catalyst spoiled the total catalytic performance of the Pt catalyst for H_2O_2 formation. Sulfur ($Na_2S_2O_3$) and phosphine (tris(hydroxymethyl)phosphine) unselectively depressed the H_2-O_2 reaction.

1. Introduction

The direct synthesis of H_2O_2, which is a clean oxidizing agent, from H_2 and O_2 in the liquid phase has been extensively studied due to the potential for developing the simplest H_2O_2 manufacturing process.[1-4] Various Pd catalysts combined with proton and halide ions (Cl⁻ and Br⁻) have been most often examined for this synthesis.[1,3,5,6] Br⁻ was more effective than Cl⁻ to improve the H_2O_2 selectivity, and I⁻ inhibited the reaction non-selectively.[4,6] Various catalyst supports as well as acid additives have also been studied as important factors.[3,4,7-9] There are many proposals for the reaction mechanism and the role of each component.[6,7,9-27] It is widely accepted that dissociatively adsorbed H_2 and molecularly adsorbed O_2, $2H_a$ and $(O_2)_a$, react to form H_2O_2 on the metal surfaces, and O-O bond cleavage of $(O_2)_a$, $(OOH)_a$ and $(H_2O_2)_a$ species results in the concurrent and the consecutive H_2O formation.[6,9] Here, the subscript "ₐ" means "adsorbed".

Pd is the sole metal showing high H_2O_2 selectivity without any other metals so far, except for the patent literature of Gosser et al.

that Pt produced H_2O_2 in the presence of H^+ and Br^- even though the selectivities were lower than those on Pd.[5] On the other hand, several metals such as Au, Pt, and Ru are known to exhibit synergetic effects to improve the catalytic performance of Pd. Especially, Pd-Au bimetallic catalysts have been most extensively studied as improved catalysts.[28-40] The Pd-Au catalysts exhibited high H_2O_2 productivities even without addition of any halides,[34,35] although halides have been added in other many cases. Synergy effect between Pd and Pt was also reported in a few papers to enhance the H_2O_2 formation.[41-45] For instance, addition of 5 atom% Pt to a Pd catalyst resulted in a 2.5-fold increase in the H_2O_2 formation rate and a small decrease in the H_2O_2 selectivity,[42] although addition of more Pt distinctly decreased the selectivity. Similar effects were observed in the combinations of Pd and Ru, and of Au and Ru.[46] The density functional theory (DFT) studies have been applied to investigate the reaction mechanism and the superior performance of the Au-Pd alloy catalysts.[47-53] It is desirable to calculate the reactions on various metal surfaces other than (111) and/or effects of solvents in aqueous or alcoholic solutions.[54]

Pt is located just below Pd in the periodic table and has the same outer-shell electronic structure as Pd, and therefore, Pt is expected to be potentially effective for H_2O_2 formation from H_2 and O_2 as Pd. Although Pt is also well known as an important metal component for hydrogenation catalysts, it has been rarely studied solely as a catalyst for H_2O_2 synthesis in contrast to Pd. However, Pt is important as an electrode metal for fuel cells, in which Pt adsorbs H_2 dissociatively to generate protons and electrons on the anode and adsorbs O_2 to produce $2H_2O$ via four-electron reduction on the cathode (oxygen reduction reaction; ORR). H_2O_2 formation via two-electron reduction on the cathode is unfavorable because

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H_2O_2 may cause degradation of the Pt electrode catalyst and the solid polymer electrolyte membrane due to its strong oxidizability.[55,56] The low H_2O_2 selectivity may be the reason why Pt has been rarely studied as the main metal of catalysts for H_2O_2 synthesis. The low H_2O_2 selectivity on Pt surface would result from the energy profile of the H_2+O_2 reactions, in which the energy barrier of the O-O cleavage of $(OOH)_a$ species on Pt (111) was as low as 1 kcal mol^{-1}.[51] However, it is interesting from both practical and theoretical points of view to evaluate the potential of Pt for directly catalyzing H_2O_2 synthesis from H_2 and O_2.

In our previous studies, we reported the results of our mechanistic studies of H_2O_2 synthesis over Pd catalysts and proposed the nature of the active sites of Pd catalysts along with the roles of H^+ and Br^- additives.[9,23] Structure-sensitive catalysis was determined with coordinatively more unsaturated sites (Site A) and less unsaturated ones (Site B), and H_2O_2 could be selectively produced on Site B. Direct H_2O formation and destruction of H_2O_2 could occur more easily on Site A. H^+ and Br^- may adsorb in pairs primarily on Site A to depress the side reactions. H^+ may also promote the reactions of dissociatively adsorbed H_2 to O-containing species, such as $(O_2)_a$ and $(OOH)_a$. We investigated how these factors play a role in Pt catalysts to improve their catalytic performance for directly producing H_2O_2 from H_2 and O_2.

2. Experimental and data processing

Materials. Pt- and Pd-polyvinylpyrrolidone (PVP) colloids were provided by Tanaka Kikinzoku Kogyo in the form of 4 wt% aqueous solutions and used as catalysts as received. The TEM image of Pt-PVP is shown in Fig. 1a, and the average particle diameter was approximately 2.0 nm. However, the average particle diameter of the Pd-PVP was approximately 3.6 nm.[24] The 2 wt% Pt/C was provided by the N.E. Chemcat Company and used as received as a catalyst. The TEM image is shown in Fig. 1b, and the average particle diameter was approximately 2.5 nm.

Experimental procedures. The procedures for the H_2-O_2 reaction were essentially identical to those described in a previous study.[24] The reaction was performed in a 300 ml flat-bottom separable flask made of Pyrex glass with an inner diameter of 80 mm that was equipped with a cross-shaped magnetic rotor with a length of 50 mm and a height of 15 mm. The rotation rate during the reaction was 1,200 rpm, and the gas-liquid contact was primarily due to high-rate agitation. Prescribed amounts of catalyst and water were
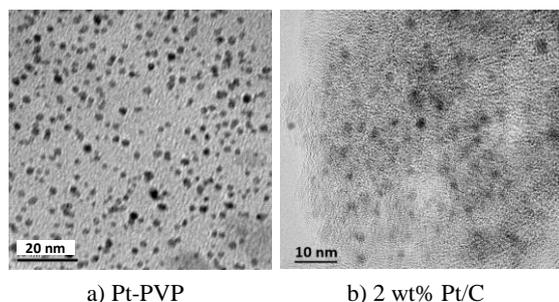

a) Pt-PVP   b) 2 wt% Pt/C

Fig. 1. TEM image of Pt-PVP and 2 wt%-Pt/C.

introduced into the flask. H_2 gas was flowed at a rate of 20 sccm at 303 K into the reactor for 40 min to activate the catalyst. Then, N_2 gas was introduced (50 sccm, 10 min) to purge the H_2 gas, and the additive(s) was added in the form of an aqueous or methanol solution. Finally, the volume of the solution was adjusted to 300 ml. After sufficient displacement with N_2 (50 sccm, 10 min), a mixture consisting of H_2, O_2 and N_2 gases was continuously passed into the reactor at atmospheric pressure, and the outlet gas composition was analyzed periodically by gas chromatography using N_2 as an internal standard to determine the consumption rates of H_2 and O_2. The reaction temperature was maintained at 303 K. It is important to note that the gas composition was often within the flammable range. The rates of H_2O_2 and H_2O accumulation were calculated using Eqs. (1) and (2), where r_{H2} and r_{O2} are the rates of H_2 and O_2 consumption (mmol L^{-1} h^{-1}), $[H_2O_2]$ and $[H_2O]$ the concentration of H_2O_2 and H_2O (mmol L^{-1}), and t time (h), respectively.

$$d[H_2O_2]/dt = 2r_{O2} - r_{H2} \tag{1}$$
$$d[H_2O]/dt = 2r_{H2} - 2r_{O2} \tag{2}$$

The H_2 consumption, $\int r_{H2}dt$, and $[H_2O_2]$ were calculated by numerical integration of r_{H2} and Eq. (1) at each sampling point ($\int r_{H2}dt = 0$ and $[H_2O_2] = 0$ when $t = 0$). The concentration of H_2O_2 at the final sampling time was also determined using a UV-Vis absorption method with a titanium sulfate solution ($[H_2O_2]_{det}$), and confirmed to be equal to the final value of $[H_2O_2]$, ($[H_2O_2]_{fin}$), within experimental error.

Data Processing. The H_2O_2 synthesis is composed of 4 elemental reactions: 1) H_2O_2 formation from H_2 and O_2, 2) direct H_2O formation from H_2 and $1/2O_2$, 3) H_2O_2 decomposition to H_2O and $1/2O_2$, 4) H_2O_2 hydrogenation to $2H_2O$. Reaction 3) may be practically negligible on Pd catalysts.[22] Selectivity of H_2O_2, S_e, is generally expressed as the ratio of the moles of H_2O_2 formed to the moles of H_2 consumed. In the case of a semi-batch type reaction, in which mixed gas containing H_2 and O_2 flows through the reactor, S_e is calculated by Eq. (3). .

$$S_e = [H_2O_2]/\int r_{H2}dt \tag{3}$$

S_e is an important index for evaluating the performance of the reaction, but it should be noted that S_e varies along with t and $[H_2O_2]$ due to the destruction of H_2O_2, and therefore is insufficient for kinetic analyses. We proposed another expression of H_2O_2 selectivity, S_f, in which the rate of reaction 1) was divided by the sum of the rates of reactions 1) and 2).[9,22] S_f is a kinetic parameter independent of t and $[H_2O_2]$ under constant conditions. Relating to the H_2O_2 destruction, another kinetic parameter, k_d, was also introduced, and the change in $[H_2O_2]$ was expressed by Eq. (4), in which [Cat] represents catalyst concentration.[9,22] S_f and k_d include the terms of H_2 and O_2 partial pressures, p_{H2} and p_{O2}. k_d is given by $k_{d1} + (1 + S_f)k_{d2}$, in which k_{d1} and k_{d2} are the rate constants for H_2O_2 destruction by decomposition and hydrogenation respectively.[22]

$$d[H_2O_2]/dt = r_{H2}S_f - k_d[H_2O_2][Cat] \tag{4}$$

When r_{H2} is constant, Eq. (4) can be mathematically integrated to Eq. (5), and S_e is connected with S_f by Eq. (6). Eq. (6) indicates that S_e decreases with the lapse of time in the semi-batch reactor.

$$[H_2O_2] = \{(r_{H2}S_f)/(k_d[Cat])\}\{1 - \exp(-k_d[Cat]t)\} \tag{5}$$
$$S_e = S_f\{1 - \exp(-k_d[Cat]t)\}/(k_d[Cat]t) \tag{6}$$

It is desirable for evaluation of catalytic performance if S_f and k_d can be used. However, Eq. (4) can be applied to determine S_f and

k_d only when the catalyst is stable during the reaction time, because otherwise S_f and k_d may vary along with r_{H2}. Thus S_f and k_d are used in this paper to evaluate catalytic performance only when they are available. H_2O_2 selectivity calculated using $[H_2O_2]_{det}$ is represented by $(S_e)_{det.}$ as shown in Eq. (7), in which $(\int r_{H2}dt)_{fin}$ denotes the overall H_2 consumption at the final sampling time. More detailed description of the experimental and the data processing is available in Supporting Information.

$$(S_e)_{det} = [H_2O_2]_{det}/(\int r_{H2}dt)_{fin} \qquad (7)$$

3. Results and discussion

3.1. Comparison of catalytic performances of Pt- and Pd-PVP for H_2O_2 synthesis in the presence of H^+ and Br^-

Fig. 2 shows a comparison of the H_2-O_2 reaction over the Pt- and Pd-PVP catalysts in the presence of H_2SO_4 and NaBr. Here, the data for the Pd catalyst were quoted from our previous paper[24] for comparison. The colloid catalysts were used as model catalysts for scientific investigation, although they would be difficult to be employed industrially. The initial value of r_{H2} for the Pt-PVP was rather higher than that for the Pd-PVP (32.0 vs. 20.3 mmol L^{-1} h^{-1}) despite of the extremely lower catalyst concentration (0.51 vs. 8.33 mg-metal L^{-1}). Although quantitative comparison of the activities is difficult due to the difference in the metal particle sizes (2.0 vs. 3.6 nm), Pt apparently showed much higher activity for the H_2-O_2 reaction than Pd in the presence of the same concentrations of H^+ and Br^-. On the other hand, the initial value of $d[H_2O_2]/dt$ for the Pt catalyst was approximately one third of that for the Pd catalyst (6.6 vs. 17.5 mmol L^{-1} h^{-1}), but the H_2O_2 productivity of Pt was likely to be again higher than that of the Pd considering the

one 16th lower catalyst concentration. S_e for the Pt catalyst, however, was lower than that of the Pd catalyst. The results supported the purpose of the present study that development of better catalysts for H_2O_2 synthesis might be realized by taking advantage of the high activity of Pt and improving the H_2O_2 selectivity.
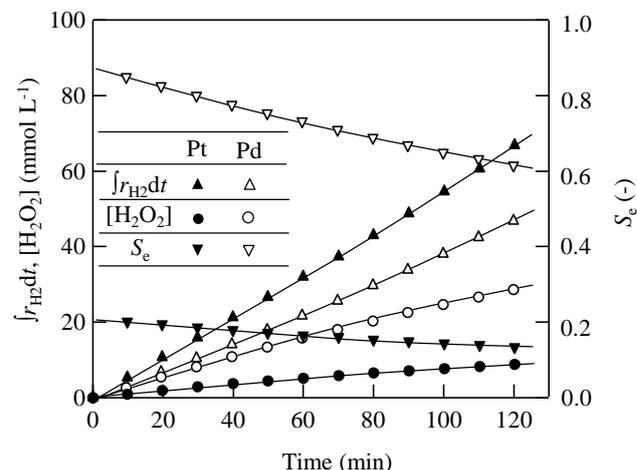

Fig. 2. Time course of H_2-O_2 reaction over Pt- and Pd-PVP catalysts in water in the presence of H_2SO_4 and NaBr. Pt 0.51 mg L^{-1}, Pd 8.33 mg L^{-1}, p_{H2} 14-13 kPa for Pt, and 17-16 kPa for Pd, p_{O2} 37 kPa for both, 303 K, 1,200 rpm. The data for the Pd catalyst were taken from our previous paper [24].
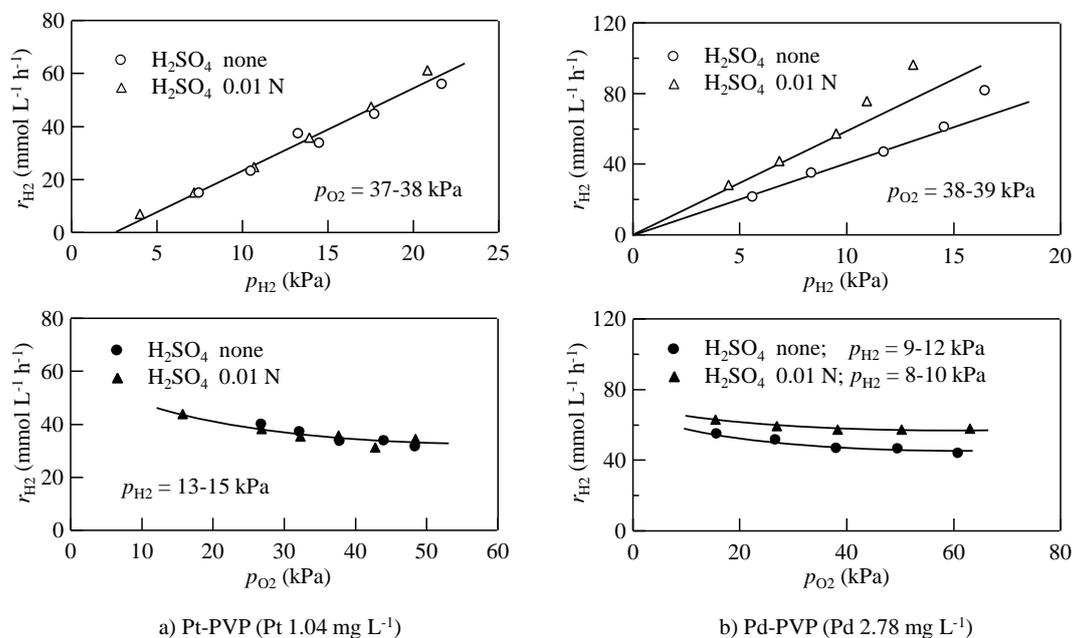

a) Pt-PVP (Pt 1.04 mg L^{-1})

b) Pd-PVP (Pd 2.78 mg L^{-1})

Fig. 3. H_2 and O_2 partial pressure dependencies of H_2-O_2 reaction rates (initial) over Pt- and Pd-PVP catalysts in water in the absence and presence of H_2SO_4 at 303 K, and 1,200 rpm. The slopes of the curves in the p_{O2} dependencies would be a little steeper if p_{H2} was constant, because the actual values of p_{H2} were increased with the increase in p_{O2} due to the constant gas feed rates. Figure 3b is an adaptation from a figure in our previous paper [24].

3.2. H_2 and O_2 partial pressure dependence in the H_2-O_2 reaction over Pt- and Pd-PVP catalysts in the absence of Br⁻
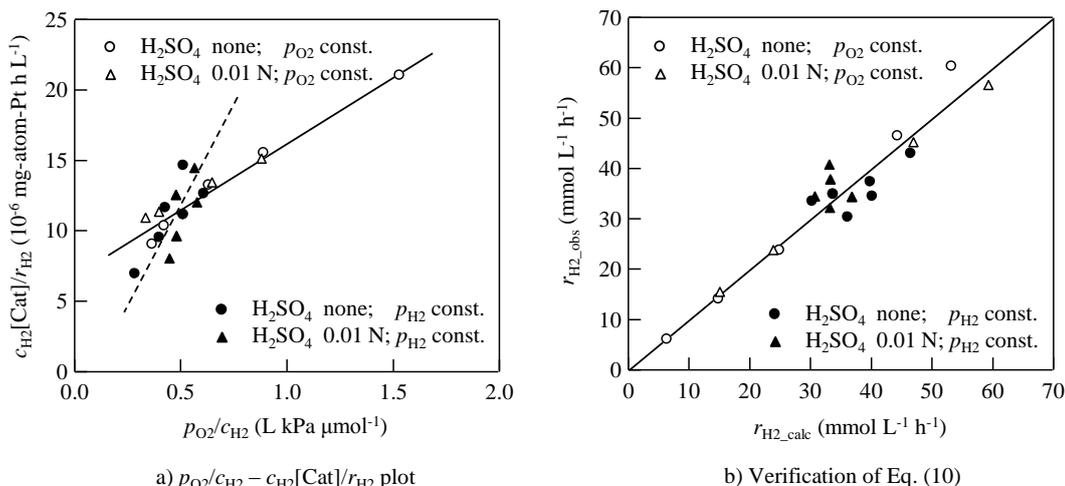
However, the plots of p_{O2}/c_{H2} as a function of $c_{H2}[Cat]/r_{H2}$ for the results in Fig. 3a result in 2 different straight lines corresponding to

a) $p_{O2}/c_{H2} - c_{H2}[Cat]/r_{H2}$ plot

b) Verification of Eq. (10)

Fig. 4. Analysis of H_2 and O_2 partial pressure dependencies of H_2-O_2 reaction rates over Pt-PVP catalyst according to Eq. (10). The data exhibited in Fig. 3a were used. $k_{s0} = 6.0\times10^5$ L mg-atom⁻¹ h⁻¹, $K_x = 5.4\times10^3$ mmol L⁻¹ kPa⁻¹, $K_y = 0.086$ kPa⁻¹.

To clarify the basic catalytic behavior of Pt with respect to the H_2-O_2 reaction, the dependence on the H_2 and O_2 partial pressures was examined using the Pt-PVP catalyst in the absence of Br⁻. H_2O was the major product in this reaction. The results are shown in Fig. 3a. In Fig. 3b, the corresponding results for the Pd-PVP catalyst are cited from our previous study.[24] Interestingly, the reaction rate (r_{H2}) over the Pt-PVP catalyst was not affected by H⁺ in contrast to that over the Pd-PVP catalyst where H⁺ enhanced the reaction rate. On the Pd surface, H⁺ promoted the reactions of the dissociatively adsorbed H species, H_a, to O-containing species, such as $(O_2)_a$ and $(OOH)_a$. Therefore, the results shown in Fig. 3a suggest that the transfer of H_a to the O-containing species is efficient on the Pt surface even in the absence of the acid. H_a may be highly active on the Pt surface, which will be discussed below.

The results in Fig. 3a indicate that r_{H2} increased linearly with the H_2 partial pressure (p_{H2}) even though the straight line did not pass through the origin. However, r_{H2} decreased with an increase in the O_2 partial pressure (p_{O2}). In our previous study,[22] a straight line, which did not pass through the origin, was observed in the H_2-O_2 reaction over the Pd/C catalyst in the presence of H⁺ and Br⁻. The hypothesis that the active sites of the catalyst existed on the reduced surfaces of Pd and redox equilibrium for H_2/O_2 was maintained on the surfaces was proposed to explain this observation.[9] Therefore, Eq. (8) was derived, where c_{H2} represents the H_2 concentration in the liquid phase, and k_{s0} and K_x are constants. k_s denotes the overall rate constant. c_{H2} was calculated using Eq. (9), where H_{H2} and k_La represent the Henry's law constant and the mass transfer coefficient of H_2 in water, respectively.[9] The value of k_La was determined in the previous study.[24] Eq. (8) was applied for the partial pressure dependencies of Pd/C catalysis due to the linear relationship between p_{O2}/c_{H2} and $c_{H2}[Cat]/r_{H2}$.

$$r_{H2} = k_{s0}c_{H2}[Cat]/\{1 + K_x(p_{O2}/c_{H2})\} = k_s c_{H2}[Cat] \quad (8)$$
$$c_{H2} = p_{H2}/H_{H2} - r_0/k_La \quad (9)$$

the experimental series, as shown in Fig. 4a. Assuming that the reason was due to contribution from a Langmuir-Hinshelwood type of depression effect by O_2, a correction term ($K_y p_{O2}$) was added to Eq. (8) to obtain Eq. (10), which was transformed to Eq. (11). Here, K_y is a constant. By applying the linear least-squares method to Eq. (11), k_{s0}, K_x and K_y were determined for the Pt-PVP catalyst as shown in the caption of Fig. 4. Fig. 4b shows the relationship between the calculated values of r_{H2}, r_{H2_calc}, according to Eq. (10) using the determined constants and the observed ones, r_{H2_obs}, and the results indicate that Eq. (10) can be applied with some data scattering.

$$r_{H2} = k_{s0}c_{H2}[Cat]/\{1 + K_x(p_{O2}/c_{H2}) + K_y p_{O2}\} = k_s c_{H2}[Cat] \quad (10)$$
$$c_{H2}[Cat]/r_{H2} = (1/k_{s0})\{1 + K_x(p_{O2}/c_{H2}) + K_y p_{O2}\} \quad (11)$$

When r^0_{H2} is defined as the value of r_{H2} at $p_{O2} = 0$, r_{H2}/r^0_{H2} corresponds to the proportion of oxygen-free sites to the total Pt sites. The values of r_{H2}/r^0_{H2} calculated using the data in Fig. 3a varied in the range of 8% ($p_{H2} = 4.0$, $p_{O2} = 37.6$ kPa) to 24% ($p_{H2} = 12.5$, $p_{O2} = 15.7$ kPa), indicating that a considerable part of the Pt surface was covered by molecular and atomic oxygen under the experimental conditions. Eqs. (10) and (8) also assume that the rate-determining step of the reaction is H_2 activation, which agrees with the observation that H⁺ did not accelerate the H_2-O_2 reaction over the Pd/C catalyst in the presence of H⁺ and Br⁻ or the Pt-PVP catalyst in the absence of Br⁻. It should be noted that some other equations might also explain the observed phenomena, but that at present we could derive the above equations based on plausible reaction mechanisms. These equations are practically useful to simulate the influence of the H_2 and O_2 partial pressures and to evaluate the catalytic activities.

For Pd-PVP in the absence of Br⁻ (Fig. 3b), the straight lines for the relationship between r_{H2} and p_{H2} passed through the origin even though r_{H2} deviated higher than the line in the higher range of p_{H2} both in the absence and presence of H_2SO_4. Eq. (11) was applied to the partial pressure dependencies assuming that $K_x = 0$ due to the proportional relationship between r_{H2} and p_{H2} as well as the
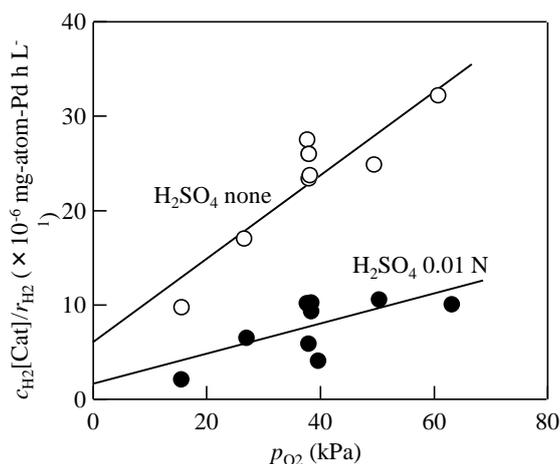
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Fig. 5. Analysis of H_2 and O_2 partial pressure dependencies of H_2-O_2 reaction rates over Pd-PVP catalyst according to Eq. (10) assuming that $K_x = 0$. The data exhibited in Fig. 1b were used. $k_{s0} = 1.7 \times 10^5$ and 5.8×10^5 L mg-atom^{-1} h^{-1}, $K_y = 0.081$ and 0.095 kPa^{-1} in the absence and presence of H_2SO_4, respectively.

depression effect of O_2. The results are shown in Fig. 5. Although the plots were considerably scattered, linear relationships were recognized, and the values of k_{s0} and K_y were determined, as shown in the caption. k_{s0} tripled due to the addition of H_2SO_4. The value of k_{s0} in the presence of H_2SO_4 (5.8×10^5 L mg-atom^{-1} h^{-1}) was comparable to that for Pt-PVP (6.0×10^5 L mg-atom^{-1} h^{-1}), and the values of K_y were also comparable to that for Pt-PVP. Since the particle sizes and the atomic radii of Pt- and Pd-PVP were 2.0 nm and 1.39 Å, and 3.6 and 1.37, respectively, the catalytic activity per surface atom of the former was approximately 60% of that of the latter, indicating that the activities of Pt and Pd for the H_2-O_2 reaction would be roughly in the same range, although the accuracy was low due to the scattering of the data in Figs. 4 and 5..

Although the reaction rate over the Pd-PVP catalyst followed Eq. (10), the rate-determining step would not include H_2 activation

because the rate varied in the absence and presence of H_2SO_4. Therefore, the reversible adsorption of H_2 would be involved, and the succeeding reactions would determine the rate. Although it is difficult to specify the mechanism from the limited experimental results, various surface sites would participate, and their role sharing would most likely involve some sites taking part in the activation of H_2 and other sites being involved in the reaction of O_2.

3.3. Effects of the H^+ and Br^- concentrations on the H_2-O_2 reaction over the Pt-PVP catalyst

H^+ and Br^- are the most effective combination of additives for H_2O_2 synthesis over Pd catalysts. To investigate the basic catalytic nature of the Pt catalysts, the effects of the H^+ and Br^- concentrations on the H_2-O_2 reaction over the Pt-PVP catalyst were studied. The results are summarized in Fig. 6a, and $(S_e)_{det}$ is used as the H_2O_2 selectivity because $[H_2O_2]$ was too low to determine S_f and k_d reliably based on Eq. (4). The results demonstrate that r_{H2} was nearly independent of the H^+ and Br^- concentrations, suggesting that the active sites of the Pt particles were barely inactivated due to HBr adsorption. Therefore, the adsorption of HBr on Pt was weak in contrast to that on Pd. In addition, $(S_e)_{det}$ was very low even though increased with an increase in the product $[H^+][Br^-]$, suggesting that the non-selective sites were partially blocked by HBr adsorption similar to the Pd catalysts.[23,24]

The effect of H^+ was further investigated by adding NaOH to the reaction system rather than H_2SO_4. The results are shown in Fig. 6b. r_{H2} remained at the same level as in the presence of H_2SO_4 up to $[OH^-] = 10^{-5}$ N (i.e., $[H^+] = 10^{-9}$ N) and then steeply decreased. However, slight activity of the H_2-O_2 reaction remained even at $[OH^-] = 10^{-2}$ N, where no H_2O_2 was detected. The results suggest that H^+ plays an important role on Pt to accelerate the transfer of H_a to the adsorbed O-containing species, which is consistent with that observed for the Pd catalysts. In addition, these results indicate that the H^+ concentration was lower than that necessary for Pd but sufficient for the acceleration of the H_2-O_2 reaction over Pt, suggesting that the
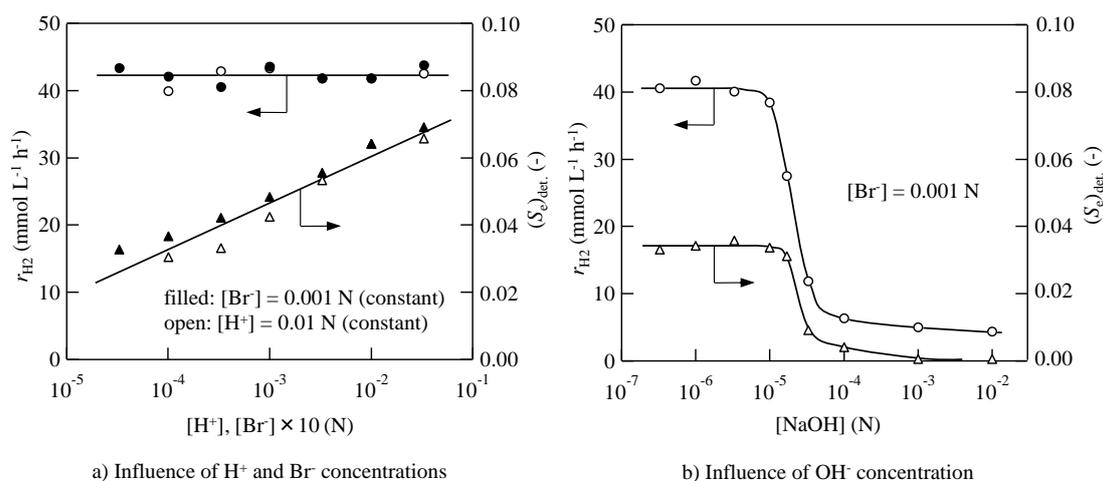

a) Influence of H^+ and Br^- concentrations

b) Influence of OH^- concentration

Fig. 6. Influence of H^+/OH^- and Br^- concentrations on H_2-O_2 reaction rate and effective H_2O_2 selectivity over Pt-PVP catalyst. Pt 1.04 mg L^{-1} (5.3×10^{-3} mg-atom L^{-1}), gas feed rate 50 sccm ($H_2 : O_2 : N_2 = 1 : 2 : 2$), p_{H2} a) 12-13 kPa, b) 13-19 kPa, p_{O2} 37-39 kPa, 303 K, and 1200 rpm for 2 h.

activity of the dissociatively adsorbed hydrogen is very high on the Pt surfaces. This result agrees with the conclusion that the activation of H_2 was rate determining over Pt-PVP.
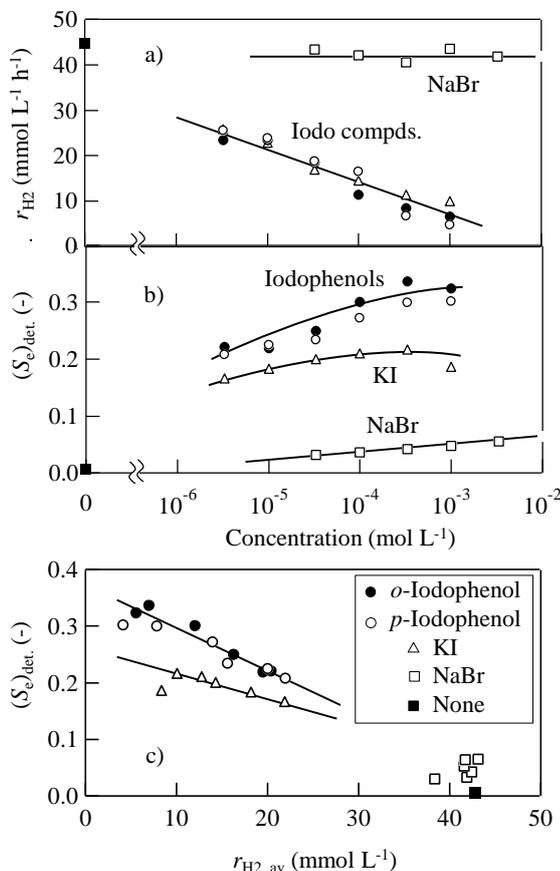
3.4. Screening of additive effects on the H_2O_2 synthesis

Fig. 7. Effect of iodo-compounds on H_2-O_2 reaction over Pt-PVP catalyst. Pt 1.04 mg L^{-1} (5.3×10^{-3} mg-atom L^{-1}), H_2SO_4 0.01 N, gas feed rate 50 sccm ($H_2 : O_2 : N_2$ = 1 : 2 : 2), p_{H2} 15-19 kPa, p_{O2} 36-37 kPa, 303 K, and 1200 rpm for 2 h. r_{H2} in Fig. 7a shows the initial reaction rates, and the reaction rates decreased to about 70% of the initial ones after the reaction for 2h in the cases of KI, and iodophenols. r_{H2_av} in Fig. 7c shows the average value of r_{H2} during the reaction time.

As is previously mentioned, the addition of H^+ and Br^- slightly increased the H_2O_2 selectivity of the H_2-O_2 reaction over Pt-PVP, and the reaction rate was nearly independent of their concentrations. The main cause of these phenomena was the insufficient ability of a pair of H^+ and Br^- to adsorb on Pt. Therefore, additives with adequate adsorbability are required. Several kinds of additives were examined from a point of view to achieve scientific interests, without considering their practical usability.

3.4.1. Iodide compounds

The effects of the iodide ion as well as non-ionic organic iodide compounds were examined using Pt-PVP as the catalyst. I^- has higher adsorbability than Br^- and non-selectively inhibits the H_2-O_2 reaction over Pd catalysts.[6,54] The results are summarized in Fig. 7. $(S_e)_{det.}$ was adopted to show the selectivities because Eq. (2) could not be applied to determine S_f and k_d due to the catalyst deterioration. In contrast to Br^-, the iodide additives depressed the catalytic activity of Pt and improved the H_2O_2 selectivity $(S_e)_{det}$ as the concentration increased, suggesting that the iodide compounds adsorbed on the Pt surfaces more strongly than Br^-. In addition, the sites that promoted direct H_2O formation and H_2O_2 destruction were more advantageously blocked.

Because r_{H2} and $(S_e)_{det}$ varied simultaneously, the relationship between r_{H2_av}, the average value of r_{H2}, and $(S_e)_{det}$ is shown in Fig. 7c. $(S_e)_{det}$ explicitly increased with decrease in r_{H2}, and iodophenols yielded higher $(S_e)_{det}$ than iodide ion at the same values of r_{H2}, indicating that the extents of deactivation of the surface sites favorable for H_2O_2 production and for H_2O_2 destruction were dependent on the additives. The additives apparently worked not as promotors but as selective deactivators. Although the values of $(S_e)_{det}$ were still low compared to those obtained on Pd catalysts combined with H^+ and Br^-, it should be noted that iodide ion was a non-selective deactivator for Pd catalysts[6,54] but a rather modifier for Pt-PVP to improve the H_2O_2 selectivity to some extent.

3.4.2. Organic sulfur and phosphorus compounds

In this study, some organic sulfur and phosphorus compounds improved the H_2O_2 selectivity of the Pt-PVP catalyst. The effects of dimethyl sulfoxide (DMSO), sulfolane and diethylphosphine oxide (DEPO) are summarized in Fig. 8 together with the relationship between r_{H2_av} and $(S_e)_{det}$. r_{H2} was depressed and simultaneously $(S_e)_{det}$ increased as the concentrations of these compounds increased. The results were different for each compound, and DMSO exhibited the most distinct effect with the least amount. The phosphoxide was less effective than the sulfoxide. These additives showed almost the same relationship between r_{H2_av} and $(S_e)_{det}$, suggesting their site-deactivation behaviors were almost the same despite of the significant difference in the working concentrations. Although $(S_e)_{det}$ of DMSO (approximately 0.45) was slightly higher than that of p-iodophenol, the catalyst exhibited significant deterioration with this additive, and r_{H2} decreased to approximately 20 % of the initial value during the reaction time (2 h) with the addition of 0.0003 M DMSO. The sulfoxide might be reduced in the redox environment to the corresponding sulfide, which most likely poisoned the Pt catalyst.

The addition of DMSO to the Pd-PVP catalyst system was examined. The results are shown in Fig. 9 and compared to the results with Br^-. The results indicate that r_{H2} was less depressed with DMSO than with the same concentration of Br^-, and the H_2O_2 formation rate was lower, indicating much lower H_2O_2 selectivity. Therefore, the order of adsorbability of the additives varied between Pd and Pt as follows: $I^- > Br^- >$ DMSO to Pd, and $I^- \approx$ DMSO $> Br^-$ to Pt, respectively. The correlation among the metal, the surface site, and the additive should be revealed in the near future.
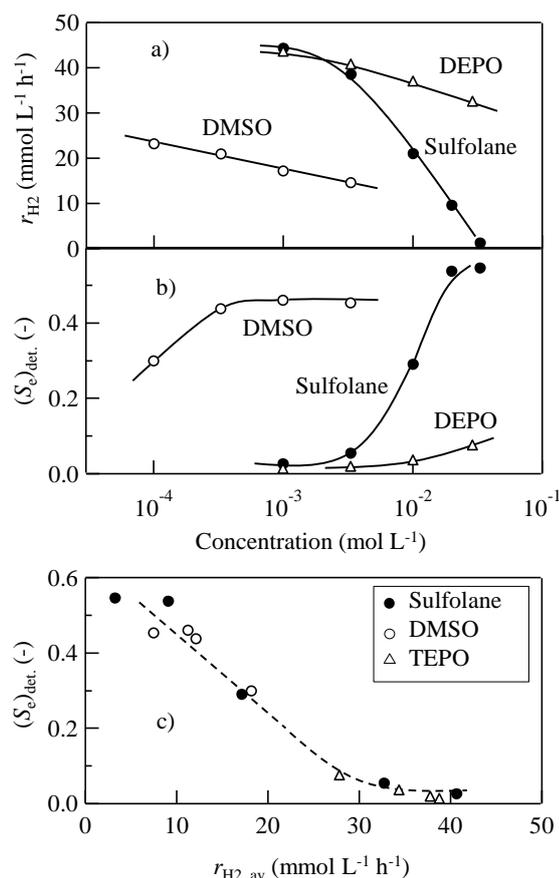
Fig. 8. Effect of organic sulfur and phosphorus oxides on H_2-O_2 reaction over Pt-PVP catalyst. Pt 1.04 mg L^{-1} (5.3×10^{-3} mg-atom L^{-1}), H_2SO_4 0.01 N, gas feed rate 50 sccm (H_2 : O_2 : N_2 = 1 : 2 : 2), p_{H2} 12-20 kPa, p_{O2} 35-36 kPa, 303 K, and 1200 rpm for 2 h. r_{H2} in Fig. 8a shows the initial reaction rates. r_{H2_av} in Fig. 8c shows the average value of r_{H2} during the reaction time.
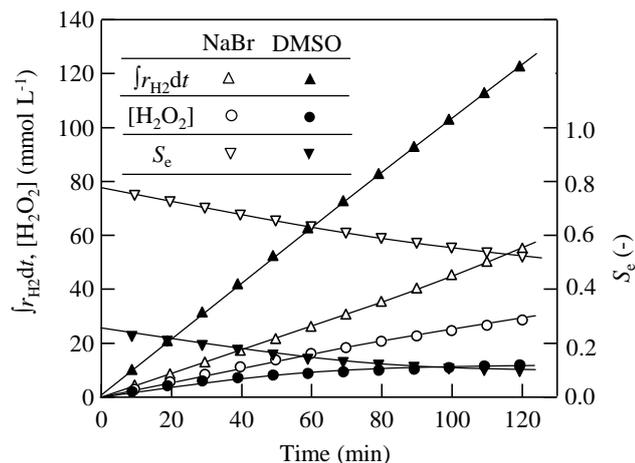

Fig. 9. Effect of dimethylsufoxide (DMSO) on H_2-O_2 reaction over Pd-PVP catalyst. Pd 8.33 mg L^{-1} (78×10^{-3} mg-atom L^{-1}), H_2SO_4 0.01 N, NaBr or DMSO 0.001 M, gas feed rate 50 sccm (H_2 : O_2 : N_2 = 1 : 2 : 2), p_{H2} 8-9 kPa (NaBr), 15-17 kPa (DMSO), p_{O2} 36-37 kPa, 303 K, 1200 rpm, and 2 h.
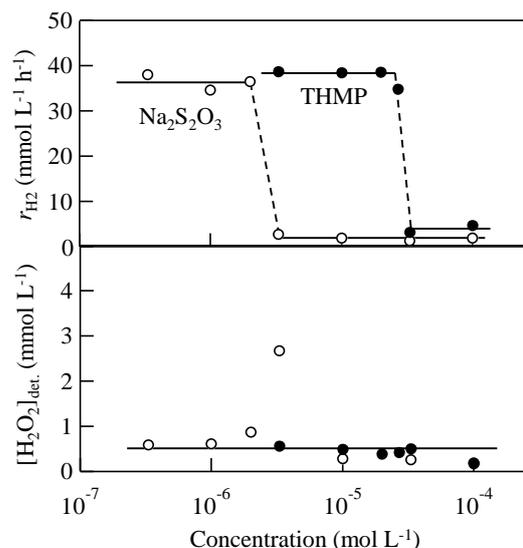
3.4.3. Effect of sulfur and phosphine

Fig. 10. Effect of $Na_2S_2O_3$ and tris(hydroxymethyl) phosphine (THMP) on H_2-O_2 reaction over Pt-PVP catalyst. Pt 1.04 mg L^{-1} (5.3×10^{-3} mg-atom L^{-1}), H_2SO_4 0.01 N, gas feed rate 50 sccm (H_2 : O_2 : N_2 = 1 : 2 : 2), p_{H2} 13-20 kPa, p_{O2} 37-38 kPa, 303 K, and 1200 rpm for 2 h. r_{H2} shows the initial reaction rates.

It is interesting to investigate how sulfides, which typically poison Pt catalysts, and phosphines, which are typically ligands in Pt compounds, function in the H_2-O_2 reaction over Pt catalysts. In our previous study,[23] one atom of sulfur, which was added in the form of $Na_2S_2O_3$, inactivated 5-8 surface Pd atoms on Pd/C, which was used for the H_2-O_2 reaction in the presence of H^+ and Br^-. Fig. 10 summarizes the addition effects of $Na_2S_2O_3$ and tris(hydroxymethyl)phosphine (THMP) on the H_2-O_2 reaction over the Pt-PVP catalyst. Both compounds substantially deactivated the catalyst when more than certain critical amounts were added even though the critical amounts were different from each other. For $Na_2S_2O_3$, the critical amount was an atomic ratio with Pt of approximately 0.6. Because the dispersion calculated based on the average particle size of Pt (i.e., 2.0 nm) was ca. 50 %, the critical number of S atoms was nearly equal to the number of the surface Pt atoms. The poisoning of Pt with sulfur appears to be primarily substantially non-selective. However, a slight increase in H_2O_2 formation was observed related to the amount of sulfur added, which resulted in vanishing of the catalyst activity. This result indicated that the non-selective sites suffered more poisoning than the selective ones. When the critical amount of sulfur was added, the initial activity of the catalyst was depressed almost completely but the activity recovered with time, and r_{H2} increased from 2.7 to 9.3 mmol L^{-1} h^{-1} for 2 h. The S atom bonded to Pt was most likely oxidized to SO_2 or another compound in the redox environment to be detoxified. Because such a reaction would proceed faster with a higher ratio of active surface sites, the poisoning effect would be quickly disappear when the amount of S was small, which resulted in a discontinuous poisoning effect.

The critical amount of THMP to cause the discontinuous deactivation was one order larger most likely due the phosphine adsorbed on the Pt surface being in equilibrium in contrast to sulfur, which was irreversibly adsorbed. The recovery of the activity with time was also observed for THMP. The phosphine was most likely oxidized to the phosphoxide to reverse the poisoning effect.

3.5. Effect of additives on the Pt/C catalyst

The addition effects of *p*-iodophenol, DMSO and sulfolane selected from the effective additives described above were examined using the Pt/C catalyst instead of Pt-PVP. The results are summarized in Fig. 11 together with the relationship between r_{H2_av} and $(S_e)_{det}$, and the effect of NaBr is also shown. Pt/C afforded higher $(S_e)_{det}$ than Pt-PVP (See Figs. 7 and 8) and the additives exhibited similar effects to those on Pt-PVP. In all of the cases, r_{H2} decreased and $(S_e)_{det}$ increased as the concentration of the additives increased. The order of $(S_e)_{det}$ at the same values of r_{H2} was *p*-iodophenol > DMSO > Sulfolane. It is important to note that the effective range of the concentration was significantly different depending on the

additives, and *p*-iodophenol was effective in the lowest concentration range. It would be reasonable to assume that these additives affected the catalytic performance by disabling the active sites on the Pt surfaces for the H_2O formation depending on the individual adsorption characteristics, as with our previous results that Br^- adsorbed on the Pd/C catalyst caused increase in S_f and decrease in r_{H2} and k_d.[23] The deactivation ability of NaBr was very weak compared to that of *p*-iodophenol, but NaBr showed certain levels of $(S_e)_{det}$ at the levels of r_{H2} at which *p*-iodophenol showed no accumulation of H_2O_2. NaBr might deactivate preferentially sites active for H_2O_2 destruction.

Fig. 12 shows the time courses of the reaction using NaBr, *p*-iodophenol and DMSO. The H_2 consumption was in the order NaBr > DMSO > *p*-iodophenol, and the deviation of H_2O_2 accumulation from H_2 consumption was in the same order. Because r_{H2} was nearly constant within this experiment, Eq. (4) could be applied to determine the kinetic parameters, S_f and $k_d[Cat]$. One can easily break down the products H_2O_2 and H_2O using the parameters; that is, the amounts of directly formed H_2O_2 during the reaction time, of directly formed H_2O, and of H_2O_2 destruction are $r_{H2}S_f t_{fin}$, $r_{H2}(1 - S_f)t_{fin}$, and $\int k_d[Cat][H_2O_2]dt$ (= $r_{H2}S_f t_{fin} - [H_2O_2]_{fin}$, as derived from Eq. (4)), respectively. Table 1 summarizes the kinetic parameters and the final product breakdown thus obtained.

The order of S_f was *p*-iodophenol > DMSO > NaBr, and the order of $k_d[Cat]$ was *p*-iodophenol < DMSO < NaBr, which is the reverse

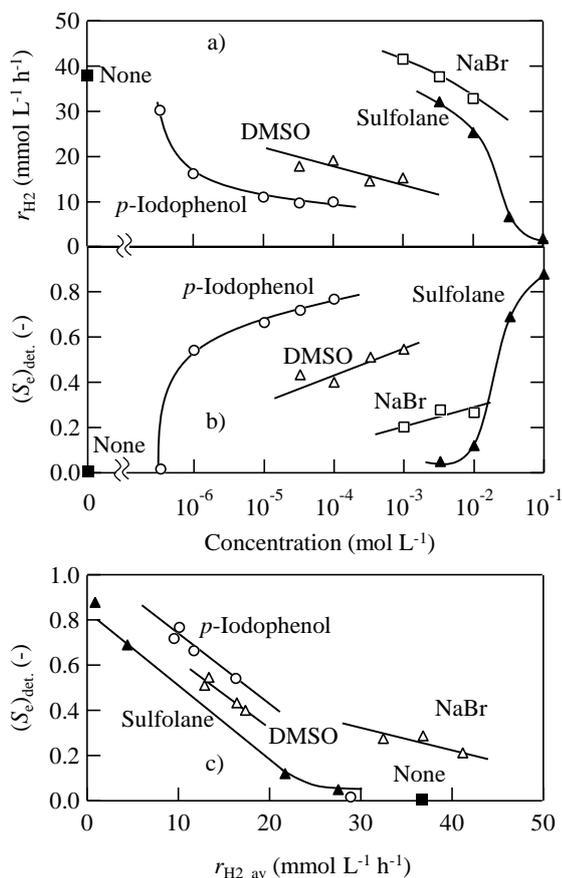**Fig. 11.** Effect of additives on H_2-O_2 reaction over Pt/C catalyst. Pt 1.04 mg L^{-1} (5.3×10^{-3} mg-atom L^{-1}), H_2SO_4 0.01 N, gas feed rate 50 sccm ($H_2 : O_2 : N_2 = 1 : 2 : 2$), p_{H2} 13-20 kPa, p_{O2} 37-38 kPa, 303 K, 1200 rpm, and 2 h. r_{H2} in Fig. 11c shows the initial reaction rates. r_{H2_av} in Fig. 11c shows the average value of r_{H2} during the reaction time.

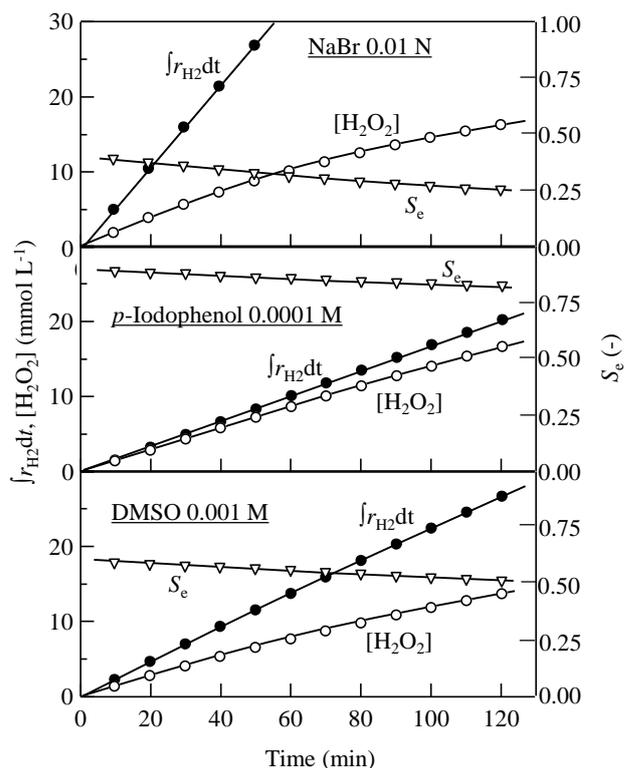**Fig. 12.** Time course of H_2-O_2 reaction over Pt/C catalyst combined with NaBr, *p*-iodophenol, or dimethylsulphoxide (DMSO) in the presence of H_2SO_4. Pt 1.04 mg L^{-1} (5.3×10^{-3} mg-atom L^{-1}), H_2SO_4 0.01 N, gas feed rate 50 sccm ($H_2 : O_2 : N_2 = 1 : 2 : 2$), p_{H2} 15-19 kPa, p_{O2} 37-38 kPa, 303 K, 1200 rpm, and 2 h.

Table 1. Kinetic parameters and final product breakdown of H_2-O_2 reactions over Pt/C combined with NaBr, *p*-iodophenol or DMSO in the presence of H_2SO_4. The original data and the reaction conditions are shown in Fig. 12.

Additive	Kinetic parameter			Product breakdown (mmol L^{-1})			
	r_{H2} (mmol L^{-1} h^{-1})	S_f (-)	k_d[Cat] (h^{-1})	directly generated H_2O_2	H_2O	H_2O_2 accumulated	H_2O_2 destructed
NaBr	32.8-32.4	0.40	0.73	26.3	38.6	16.3	9.9
p-Iodophenol	10.0	0.89	0.084	18.1	2.2	16.7	1.4
DMSO	14.8-12.2	0.60	0.16	16.1	10.6	13.7	2.4

Table 2. Comparison of kinetic parameters of H_2-O_2 reactions over Pt/C and Pd/C catalysts.[a]

Catalyst (mg-metal L^{-1})	d_{av}[c] (nm)	Additive (mN or mmol L^{-1})	p_{H2} (kPa)	p_{O2} (kPa)	r_{H2} (mmol L^{-1} h^{-1})	k_s[d]	S_f (-)	k_d[d]
Pt/C (1.05)	2.5	*p*-iodophenol (0.1)	18.5	38.0	10.0	14.2×10^3	0.89	16
Pd/C[b] (8.33)	3.2	NaBr (1.0)	13.9	35.2	38.0	6.8×10^3	0.86	1.7

[a] H_2SO_4 0.01 N, gas feed rate 50 sccm (H_2 : O_2 : N_2 = 1 : 2 : 2), 303 K, 1200 rpm, and 2 h. The values of p_{H2}, p_{O2}, and r_{H2} are initial ones. [b] The data are taken from our previous paper [9]. [c] Average diameter of the metal particles of the catalyst. [d] The unit is L mg-atom^{-1} h^{-1}.

order of S_f. This result suggests that the surface sites involved in direct H_2O formation also probably caused H_2O_2 destruction, which is consistent with hypothesis proposed in the studies of Pd catalysts.[23] The amount of directly generated H_2O_2 with NaBr was largest, but the amounts of directly generated H_2O and H_2O_2 destruction were also largest, resulting in the H_2O_2 accumulation much smaller than the generated amount. In contrast, the amounts of directly generated H_2O and of H_2O_2 destruction with *p*-iodophenol were by far smaller than those with NaBr, and the accumulation of H_2O_2 was comparable to that with NaBr despite of the smaller amount of directly generated H_2O_2.

The results of the kinetic analysis of the H_2-O_2 reaction using the Pt/C catalyst combined with H^+ and *p*-iodophenol, which was the most effective additive, are compared in Table 2 to that using Pd/C combined with H^+ and Br^-. The metal particle size of Pt/C was approximately the same as that of Pd/C, and therefore the similar surface structure of Pt to that of Pd was assumed in the discussion. It is important to note that the Pt catalyst exhibited a S_f value as high as 0.9, which is comparable to that of Pd, because only low values of S_f over Pt catalysts were deduced from the low energy barrier (1 kcal mol^{-1}) toward O-O cleavage of $(OOH)_a$ species on Pt (1 1 1).[51] The highly active H_a species on the Pt surface might react with $(OOH)_a$ to produce H_2O_2 prior to the O-O cleavage in the aqueous medium. Because the value of k_s (See Eq. (10)) was 2 times higher than that of Pd, the initial H_2O_2 productivity ($k_s S_f$) was higher than that of the Pd catalyst. However, the catalytic performance of the Pt catalyst was unfortunately inferior to the Pd catalyst because the H_2O_2 destruction activity of the former was one order higher than that of the latter, spoiling the overall catalytic performance.

The depression of the H_2O_2 destruction activity is crucial for developing better Pt catalysts. For one thing, S_f could be improved and k_d could be decreased by controlling the size and shape of the Pt particles. When the particle size of Pd on C increased, S_f was improved and k_d was decreased due to the decreasing ratio of Site A,

coordinatively unsaturated sites,[9] suggesting the similar behaviors of Pt. In addition, since Pd-PVP was indicated to contain more amount of unsaturated sites than Pd/C,[24] the content of Site A on Pt/C might be less than that on Pt-PVP. This would be the reason why Pt/C exhibited better performances than Pt-PVP.

4. Conclusions

The H_2-O_2 reaction over Pt catalysts was kinetically studied to find new catalytic systems for the direct synthesis of H_2O_2. The catalytic properties of Pt for the H_2-O_2 reaction in water were first investigated using the Pt-PVP colloid as a catalyst, and the results were compared to those obtained using Pd. The activities of Pt and Pd were roughly in the same range. However, the addition of H^+ accelerated the H_2-O_2 reaction on Pd, but no acceleration effect was observed on Pt. The rate-determining step of the H_2-O_2 reaction over Pt-PVP involved H_2 activation under neutral conditions, and only 10^{-9} N of H^+ was sufficient to maintain the reaction rate at this level, suggesting that the dissociatively adsorbed H_2 on Pt was very active.

To take the advantage of the high H_2 activating ability of Pt, new additives were explored. The combination of H^+ and Br^-, which was the most effective for Pd catalysts, exerted much less influence on Pt and resulted in very low H_2O_2 selectivities. Inorganic and organic iodides as well as some sulfur compounds increased the H_2O_2 yield. Sulfur (i.e., $Na_2S_2O_3$) and phosphine (i.e., tris(hydroxymethyl)-phosphine) unselectively depressed the H_2-O_2 reaction.

The catalytic performances of Pt/C combined with H^+ and *p*-iodophenol and Pd/C combined with H^+ and Br^- were kinetically compared. S_f over the Pt/C was improved to reach 0.9, as high as that over the Pd/C combined with H^+ and Br^-, while k_d was still higher than that over the Pd/C. This finding that the best additives for Pt are different from those for Pd would encourage exploration for more effective modification of the Pt catalysts. Exploration of second additives including surface-modifying hetero metal

components would be a possible trial for depressing H_2O_2 destruction more effectively. The combination of modifiers for improving the S_f and for decreasing k_d might give a best Pt catalyst, although such trials to modify Pt catalysts have scarcely studied so far.

Acknowledgement

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