



Reaction mechanism of direct H₂O₂ synthesis from H₂ and O₂ over Pd/C catalyst in water with H⁺ and Br⁻ ions

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ABSTRACT

Kinetic analyses including mass transfer processes were applied for the title reaction and the H₂O₂ decomposition. Adsorption of Br⁻ ion on the catalyst was also measured. A hydride-hydroperoxy species H-M-OOH (M, the metal surface) was proposed as the key intermediate in the H₂O₂ formation, the direct H₂O formation, and the H₂O₂ decomposition. The H⁺ added would accelerate Br⁻ adsorption, reductive elimination and β-elimination of the H-M-OOH species, and desorption of surface H₂O₂ species. Two types of metal surface sites were suggested, one of which had a high degree of coordinative unsaturation and catalyzed the direct H₂O formation and the H₂O₂ decomposition. Both reactions would be inhibited by adsorption of the Br⁻ and H⁺ pairs. Another had a low degree of unsaturation and was active for the H₂O₂ formation. Sulfur poisoning study revealed that several surface Pd atoms were inactivated at once by adsorption of a sulfur atom for H₂-O₂ reaction.

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1. Introduction

Many efforts have been devoted to catalytic synthesis of H₂O₂ in water from H₂ and O₂ since it is a clean oxidizing agent and will lead a simple manufacturing process. Most of studies were carried out on Pd catalysts, and Au was also investigated in the form of alloy with Pd as reviewed in literatures [1–3]. Recently, Pd or Au–Pd nano-particle catalysts were intensively studied by several research groups [4–10]. The Pd catalyst was usually combined with proton and halide ions such as Cl⁻ or Br⁻.

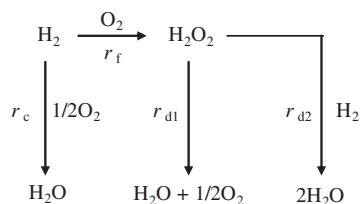
The synthesis reaction is widely recognized to consist of H₂O₂ formation, direct H₂O formation, and subsequent decomposition and hydrogenation of H₂O₂ produced as shown in Scheme 1, in which r_f , r_c , r_{d1} , and r_{d2} represent the respective reaction rates. However, the detailed reaction mechanisms including the intermediates and the role of each component were still under debate [1–3,11–25]. It is widely accepted that proton and halide ions accelerate the H₂O₂ formation and depress the unfavorable side reactions. Liu and Lunsford claimed that H⁺ possessed two roles that it reacted with an active form of oxygen to produce H₂O₂ and changed the electronic state of Pd surface to facilitate H₂O₂ formation [11]. The similar interaction between H⁺ and adsorbed

O₂ was suggested by the others [12]. The adsorption of Cl⁻ or Br⁻ on Pd was confirmed by EDAX and XPS after the H₂-O₂ reaction and was suggested to inhibit homolytic cleavage of O–O bond of O₂ and H₂O₂ through blocking catalytic sites [13–15]. The H⁺ was reported to enhance the adsorption of halide ions by lowering the pH below the isoelectric point of support and to inhibit the H₂O₂ adsorption on the catalyst [13]. On the other hand, the dissociative adsorption of O₂ and H₂O₂ was suggested to proceed on more energetic Pd sites (defects, edges, corners, etc.), and they would be blocked by Br⁻ to result in improved selectivity [16]. Br⁻ was also proposed to act as an electron scavenger and inhibit radical-type decomposition [16].

Many kinds of reaction mechanisms and the roles of additives were suggested as described above. To reach more clear understanding of them, sufficient kinetic studies should be carried out. One of the reasons for difficulties of the kinetic analyses of H₂O₂ synthesis was the transportation limitation of the reaction gases in water [1]. Liu and Lunsford therefore carried out the kinetic studies in ethanol which shows higher solubility of the gases [11]. Voloshin et al. studied them by using a micro-reactor since the reaction in the reactor was generally unrestricted from mass transfer limitation [17,18]. In spite of these previous studies, it would be desirable to establish a method of kinetic analysis that was applicable to batch-wise reactions with less assumption. Another reason for the difficulties of kinetic studies was the

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Scheme 1. Suggested reaction routes in the direct H_2O_2 synthesis.

complicated reaction routes as shown in Scheme 1. It was not easy to determine the individual reaction rates on the basis of kinetics measurements [3].

We reported a systematic rate analysis method that included the mass transfer processes of gasses and distinguished the respective rates of concurrent and consecutive reactions [26]. This method could be successfully applied to the H_2O_2 synthesis from H_2 and O_2 in water on Pd/C catalyst with H^+ and Br^- ions. Reaction rate of H_2 (r_0) and H_2O_2 accumulation rate were expressed by Eqs. (1) and (2). Assuming that r_{d1} and r_{d2} were expressed by Eqs. (3) and (4), in which k_{d1} and k_{d2} were the rate constants, and that H_2O_2 formation selectivity (S_f , defined by Eq. (5)) and overall H_2O_2 destruction rate constant (k_d , defined by Eq. (6)) were constant, Eq. (7) was derived. Here, $[\text{H}_2\text{O}_2]$ and $[\text{Cat}]$ were the concentrations of H_2O_2 and catalyst, and k_{d1} and k_{d2} included the terms of partial pressures of H_2 (p_{H_2}) and O_2 (p_{O_2}). S_f and k_d could be determined from the time course of $[\text{H}_2\text{O}_2]$ based on Eq. (7). The detailed calculation method was described in the previous paper [26].

$$r_0 = r_f + r_c + r_{d2} \quad (1)$$

$$d[\text{H}_2\text{O}_2]/dt = r_f - r_{d1} - r_{d2} \quad (2)$$

$$r_{d1} = k_{d1}[\text{H}_2\text{O}_2][\text{Cat}] \quad (3)$$

$$r_{d2} = k_{d2}[\text{H}_2\text{O}_2][\text{Cat}] \quad (4)$$

$$S_f = r_f / (r_f + r_c) \quad (5)$$

$$k_d = k_{d1} + (1 + S_f)k_{d2} \quad (6)$$

$$d[\text{H}_2\text{O}_2]/dt = r_0 S_f - k_d[\text{H}_2\text{O}_2][\text{Cat}] \quad (7)$$

On the other hand, defining an apparent rate constant (k_{0a}) as Eq. (8), the relation of k_{0a} with the overall mass transfer coefficient ($k_1 a$) was expressed by Eq. (9), in which k_0 and H were the intrinsic rate constant independent of mass transfer rate of H_2 and the Henry's law constant of H_2 , respectively [26]. Mass transfer rate of O_2 was regarded as sufficiently large because of much higher p_{O_2} than p_{H_2} . When the value of $k_1 a$ of the reaction system is known, one can calculate k_0 from k_{0a} by Eq. (9). In the previous study, k_0 depended on p_{H_2} and was not a constant in a strict sense, but it is useful as the index in the comparison of the catalytic activities [26].

$$r_0 = k_{0a} p_{\text{H}_2} [\text{Cat}] \quad (8)$$

$$1/k_{0a} = 1/k_0 + [\text{Cat}] / (k_1 a / H) \quad (9)$$

In the previous paper [26], the H_2 and O_2 partial pressure dependencies were analyzed by the above method, and also the progress in reaction was simulated based on them. In this study, we investigated the influence of H^+ and Br^- ions, the kinetics of H_2O_2 decomposition, and the adsorption behaviors of Br^- on Pd to discuss the whole catalytic reaction mechanism.

2. Experimental

2.1. H_2O_2 synthesis

The H_2 – O_2 reaction was carried out in a 300-ml glass flask equipped with a magnetic stirrer, a gas baffle, a gas feeding nozzle, a liquid sampling nozzle, and a thermometer. A football-shaped stirring rotor of 20 mm in diameter and 45 mm in length was used to agitate the aqueous suspension and increase gas dispersion. To avoid ignition by static electricity, all apparatus except for the reactor was made of stainless steel tube of 1 mm inner diameter. The dead volume in the reactor was minimized, and the glass plug was put in the reactor as a safety valve. Pd/C catalyst with 5 wt.% Pd (AER type suitable to hydrogenation of nitro compounds, the average particle size of ca. 20 μm) was provided by NE Chemcat Company, Japan and used for the experiments as received. All gases were of industrial grades, and respective flow rates were controlled by mass flow controllers. All experiments were carried out at an atmospheric pressure.

A selected amount of the Pd/C catalyst was introduced in a calculated amount of water in the flask and activated by supplying H_2 (20 $\text{Ncm}^3 \text{min}^{-1}$) in an aqueous suspension at 30 °C for 1 h. Subsequently, N_2 gas was introduced to displace the H_2 gas, and the additive(s) was supplied in the form of an aqueous solution. Unless otherwise stated, H_2SO_4 was employed as the H^+ source and NaBr as the Br^- source. When the effects of H^+ and Br^- ions were studied, Na_2SO_4 was added to regulate the concentration of $[\text{SO}_4^{2-}]$ species to 0.01 N. Finally, the volume of solution was adjusted at 300 ml. After the sufficient displacement with N_2 , the mixture of H_2 , O_2 , and N_2 gases was flowed at a constant rate into the reactor through the nozzle. The composition of supplied gases was determined by gas chromatography in advance. The gas flow rate and the gas composition at the reactor outlet were measured every 30 min to determine the H_2 consumption rate and the partial pressure of each gas. A small part of the suspension was picked out at the same time through the nozzle, and the H_2O_2 concentration was analyzed by a UV–Vis absorption method using a titanium sulfate solution. It was confirmed in separated experiments that no further reaction proceeded in the collected solution after mixed with the titanium sulfate solution.

The reaction temperature was usually 30 °C, and the agitation rate was 1355 rpm in the standard experiments. The $k_1 a$ value in the experiments was measured by the method described in the previous paper [26] and was 560 h^{-1} .

2.2. H_2O_2 decomposition

The reaction was carried out in a 100-ml glass flask. The suspension containing catalyst was undergone the same pretreatment as the above, and finally, the volume of solution was adjusted at 98 ml. Then, 2 ml of a 17 wt.% H_2O_2 solution was added, and the H_2O_2 concentration was periodically followed.

2.3. Br^- adsorption

The catalyst was activated in the same manner as the above. N_2 was then introduced to displace H_2 , mixture of O_2 and N_2 (1:9) gases was flowed for 10 min in order to eliminate possibly adsorbed hydrogen atoms, and finally, N_2 was again introduced. The H_2SO_4 , NaBr, and Na_2SO_4 solutions of desired concentrations were added. The mixture was agitated at 30 °C for 1 h. After the settlement of catalysts, the Br^- concentration in the solution was measured by ion chromatography.

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