Journal of Catalysis 280 (2011) 239–246

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Reaction mechanism of direct H_2O_2 synthesis from H_2 and O_2 over Pd/C catalyst in water with H^+ and Br^- ions

Takashi Deguchi, Masakazu Iwamoto *

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259-R1-5 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:
Received 10 February 2011
Revised 22 March 2011
Accepted 23 March 2011
Available online 6 May 2011

Keywords:
Hydrogen peroxide
Direct synthesis
Decomposition
Palladium catalyst
Reaction mechanism
Kinetics
Bromide adsorption
Reaction intermediate
Coordinative unsaturation
Sulfur poisoning

ABSTRACT

Kinetic analyses including mass transfer processes were applied for the title reaction and the H_2O_2 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 H_2O_2 formation, the direct H_2O formation, and the H_2O_2 decomposition. The H^+ added would accelerate Br^- adsorption, reductive elimination and β-elimination of the H-M-OOH species, and desorption of surface H_2O_2 species. Two types of metal surface sites were suggested, one of which had a high degree of coordinative unsaturation and catalyzed the direct H_2O formation and the H_2O_2 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 H_2O_2 formation. Sulfur poisoning study revealed that several surface Pd atoms were inactivated at once by adsorption of a sulfur atom for H_2–O_2 reaction.

1. Introduction

Many efforts have been devoted to catalytic synthesis of H_2O_2 in water from H_2 and O_2 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^-.

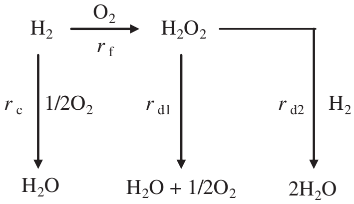
The synthesis reaction is widely recognized to consist of H_2O_2 formation, direct H_2O formation, and subsequent decomposition and hydrogenation of H_2O_2 produced as shown in Scheme 1, in which r_f, r_c, r_{d1}, and r_{d2} represent the respective reaction rates. However, the detailed reaction mechanisms 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 H_2O_2 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 H_2O_2 and changed the electronic state of Pd surface to facilitate H_2O_2 formation [11]. The similar interaction between H^+ and adsorbed O_2 was suggested by the others [12]. The adsorption of Cl^- or Br^- on Pd was confirmed by EDAX and XPS after the H_2–O_2 reaction and was suggested to inhibit homolytic cleavage of O—O bond of O_2 and H_2O_2 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 H_2O_2 adsorption on the catalyst [13]. On the other hand, the dissociative adsorption of O_2 and H_2O_2 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 H_2O_2 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 gasses [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

---

* Corresponding author. Fax: +81 45 924 5228.
E-mail address: Iwamoto@res.titech.ac.jp (M. Iwamoto).

0021-9517/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2011.03.019



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, $[H_2O_2]$ and [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_{H2}) and O_2 (p_{O2}). S_f and k_d could be determined from the time course of $[H_2O_2]$ based on Eq. (7). The detailed calculation method was described in the previous paper [26].

$$r_0 = r_f + r_c + r_{d2} \tag{1}$$

$$\mathrm{d}[H_2O_2]/\mathrm{d}t = r_f - r_{d1} - r_{d2} \tag{2}$$

$$r_{d1} = k_{d1}[H_2O_2][\mathrm{Cat}] \tag{3}$$

$$r_{d2} = k_{d2}[H_2O_2][\mathrm{Cat}] \tag{4}$$

$$S_f = r_f/(r_f + r_c) \tag{5}$$

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

$$\mathrm{d}[H_2O_2]/\mathrm{d}t = r_0 S_f - k_d[H_2O_2][\mathrm{Cat}] \tag{7}$$

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_La) 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_{O2} than p_{H2}. When the value of k_La 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_{H2} and was not a constant in a strict sense, but it is useful as the index in the comparison of the catalytic activities [26].

$$r_0 = k_{0a} p_{H2}[\mathrm{Cat}] \tag{8}$$

$$1/k_{0a} = 1/k_0 + [\mathrm{Cat}]/(k_La/H) \tag{9}$$

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 $\mathrm{Ncm^3\,min^{-1}}$) 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 $[SO_4^{2-}]$ 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_La 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.

3. Results and discussion

3.1. Adsorption behavior of Br^- ion

It was widely reported that Br^- adsorbed on the Pd surface and influenced the catalyst performance in H_2O_2 synthesis while acid assisted the Br^- adsorption by raising the acidity at the catalyst surface [13]. The present study would suggest Eq. (10) in which H^+ and Br^- were adsorbed in pairs on the active sites (M, reduced metal surface), and the adsorption was in equilibrium.

$$M + H^+ + Br^- \rightleftarrows H - M - Br \tag{10}$$

The Br^- adsorption on the catalyst was quantitatively studied as a function of the concentrations of H^+ and Br^-. The results are shown in Fig. 1, where the numbers on the abscissa indicated the square roots of $[H^+][Br^-]$ for convenience because they could represent the magnitudes of $[H^+][Br^-]$ in an appropriate abscissa range. $[H^+]$ and $[Br^-]$ were varied in the ranges 2.0×10^{-7} to 9.8×10^{-4} and 2.7×10^{-6} to 9.2×10^{-5} N, respectively. The Br^- adsorption was little observed after the catalyst was deactivated by addition of $Na_2S_2O_3$ (S/Pd ratio was 1.32), which confirmed that Br^- was adsorbed only on the activated Pd surface and not on the active carbon support. Fig. 1 shows that the amount of adsorbed Br^- depended on the product of $[H^+]$ and $[Br^-]$ unequivocally, supporting Eq. (10) that H^+ and Br^- were adsorbed in pairs.

Fig. 1 also shows the amounts of Br^- adsorbed in the presence of H_2. The great decrement in the Br^- adsorption suggested competitive adsorption of HBr and H_2 on the catalyst. The experimental data revealed that most of HBr on the active sites was replaced by H even at very low H_2 partial pressure, but small part maintained the affinity for HBr on such conditions. The particle size of Pd in the present catalyst, measured by TEM, was ca. 3–5 nm in diameter. The ratio of the surface atoms to the whole atoms of fcc crystals was calculated to be 0.25–0.4 and that of the edge and corner atoms was 0.05–0.14. The latter might be the HBr-preferential sites because of their coordinatively unsaturated nature, and the most unsaturated corner atoms might adsorb HBr even in the presence of H_2.

3.2. Kinetics of H_2O_2 decomposition in the absence of H_2 and effects of H^+ and Br^-

Since H_2O_2 decomposition was closely related to the H_2O_2 synthesis, it was studied by a few research groups. The dissociation of H_2O_2 into 2 OH species [12,13,16] and a redox mechanism expressed by Eqs. (11) and (12) [27,28] were suggested.

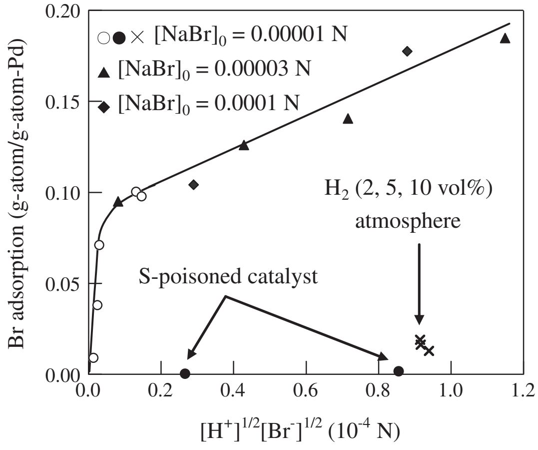


Fig. 1. Adsorption of Br^- ion on Pd/C catalyst. [Cat] 160 mg L^{-1}, $[SO_4^{2-}]$ 0.01 N, $[H^+]$ 2.0×10^{-7}–9.8×10^{-4} N, $[Br^-]$ 2.7×10^{-6}–9.2×10^{-5} N, 30 °C.

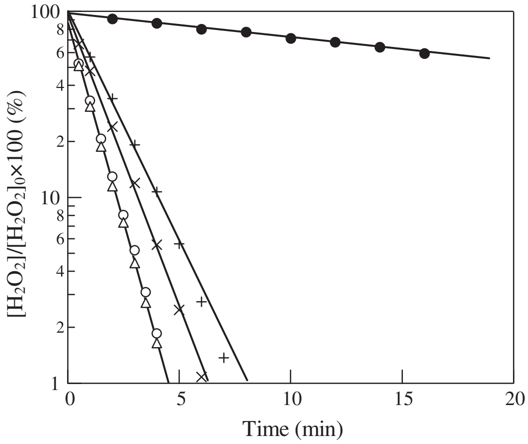


Fig. 2. Effects of H_2 activation of the catalyst and O_2 treatment on the H_2O_2 decomposition activity. [Cat] 151 mg L^{-1}, $[H_2O_2]_0$ 106 mmol L^{-1}, 30 °C. ● No H_2 activation, ○ H_2 activation (100%, 1 h), Δ H_2 activation (5%, 1 h), × O_2 treatment (100%, 1 h) after H_2 activation (100%, 1 h), + O_2 treatment (100%, 5 h) after H_2 activation (100%, 1 h).

$$M + H_2O_2 \rightarrow MO + H_2O \tag{11}$$

$$MO + H_2O_2 \rightarrow M + H_2O + O_2 \tag{12}$$

The time courses of H_2O_2 decomposition were precisely followed in a batch reactor, and the results without additives are summarized in Fig. 2. The reaction proceeded in proportion to $[H_2O_2]$ and was drastically accelerated by H_2 pre-reduction of the catalyst. The effect of the pretreatment with 5% H_2 for 1 h was the same as that with 100% H_2, suggesting very easy reduction of the catalyst surface. The catalyst that was activated by H_2 and then treated by O_2 showed somewhat lower activities than that of H_2 pre-reduced one, but much higher activities than that of the unreduced one. The oxidation of Pd surface, Eq. (13), was reported to generate direct H_2O formation sites in the H_2O_2 synthesis [12,13,16]. Fig. 2 indicates that the phenomenon was really observed, but the contribution was not significant. The latter was consistent with the previous reports [26] that the H_2O_2 selectivity was independent of O_2 partial pressure, and O_2 was not directly involved in the step to determine the selectivity.

$$M + O_2 \rightarrow 2MO \tag{13}$$

On the basis of Fig. 2, one can conclude that the active sites of Pd existed on the reduced surface. Similar conclusion was recently suggested on Pd/SiO_2 catalyst in direct formation of H_2O_2 from H_2 and O_2 [29]. It should be added that the reduced site was responsible for both formation and decomposition of H_2O_2.

Fig. 3 shows the time courses of H_2O_2 decomposition in the Pd/C-H_2SO_4 system. Two findings could be pointed out. Firstly, the respective reaction profiles in the presence of the acid could be divided into two parts; the initial stage in which the reaction rate gradually lowered (named as stage A) and the period with approximately steady reaction after stage A (stage B). Secondly, the periods of stages A and the reaction rates at stages B decreased with increasing acid concentration. The results suggest that the deactivation was caused by the surface oxidation through Eq. (11) which would be accelerated by acid. The surface oxidation was indeed reconfirmed by the experiment that the activity was recovered by H_2 treatment of the resulting catalyst. We suppose that the surface oxidation by Eq. (11) and the reduction by Eq. (12) were equilibrated at stage B. It follows that the redox mechanism indeed

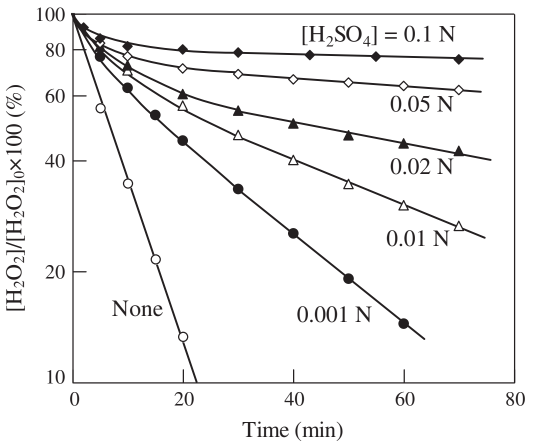


Fig. 3. Influence of H_2SO_4 concentration on H_2O_2 decomposition. [Cat] 20 mg L^{-1}, $[H_2O_2]_0$ 59 mmol L^{-1}, 30 °C.

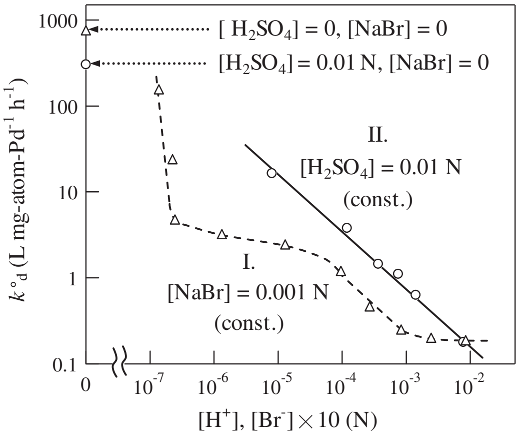


Fig. 4. Addition effect of H^+ and Br^- ions on H_2O_2 decomposition. k^o_d was determined based on Eq. (17) at [Cat] 160 mg L^{-1}, $[SO_4^{2-}]$ 0.01 N, initial $[H_2O_2]$ 106 mmol L^{-1}, 30 °C.

occurred in the presence of H_2SO_4, but the contribution to the whole reactions would be small because the reaction rate at stage B decreased with the increase of H^+ concentration, whereas the rate of the surface oxidation increased.

On the basis of the above results and discussion, the following reaction mechanism, Eqs. (14) and (15), could be proposed here. H_2O_2 would be adsorbed preferentially on the edge and the corner Pd atoms similarly to HBr, and the resulting hydrido-hydroperoxy species would release O_2 to form the hydride species. The hydride would readily react with H_2O_2 regenerating the reduced surface. It should be noted that the reverse reaction of Eq. (14) could be formally H_2O_2 formation from H_2 and O_2. The hydrido-hydroperoxy species would release H_2O by β-elimination resulting in oxidized species as shown in Eq. (16), which would be included in Eq. (11).

$$M + H_2O_2 \rightleftarrows H - M - OOH \rightleftarrows MH_2 + O_2 \quad (14)$$

$$MH_2 + H_2O_2 \rightarrow M + 2H_2O \quad (15)$$

$$H - M - OOH \rightarrow MO + H_2O \quad (16)$$

The correlations in Fig. 2 and the straight-line portions in Fig. 3 can be analyzed by Eq. (17) where k^o_d is the rate constant of H_2O_2 decomposition.

$$-d[H_2O_2]/dt = k^o_d[\mathrm{Cat}][H_2O_2] \quad (17)$$

The influence of the concentrations of H^+ or Br^- on the k^o_d value was systematically measured on constant and high $[Br^-]$ condition (series I) or on constant and high $[H^+]$ condition (series II). The results are summarized in Fig. 4, where $[H^+]$ was calculated from the pH value of the solution after the reaction and $[Br^-]$ was obtained by using the ion chromatography similarly to that in the adsorption measurements. In the series I, at pH = 7, the relatively high $[Br^-]$ exhibited little inhibition effect, and at pH = 6.5–7, the k^o_d value decreased drastically with lowering pH. This is consistent with Eq. (10) that H^+ and Br^- adsorbed in pairs on the active sites to inhibit the activity. At pH = 6.5–2, it was decreased stepwise, indicating the presence of at least three kinds of active sites.

The activity in series II also decreased with increasing $[Br^-]$. If the H^+ and Br^- ions inhibited the decomposition alone according to Eq. (10), the plots of series I and II should fall into a single line, but it was not the case; actually the correlation line of series II was somewhat higher than that of series I. The redox reaction by H^+, Eqs. (11) and (12), would be actualized around this region where the reaction via the hydride species of Eqs. (14) and (15) was depressed.

3.3. Kinetics of H_2O_2 destruction in the presence of H_2

It is widely recognized that H_2O_2 synthesized from H_2 and O_2 is mainly destructed by hydrogenation [12,14,19,20]. We showed in the previous paper that the destruction rate was proportional to H_2O_2 concentration, roughly proportional to H_2 partial pressure and inversely proportional to O_2 partial pressure on the Pd/C catalyst in the presence of H^+ and Br^- [26]. Fig. 5 shows the time courses of hydrogenation of H_2O_2 at various H_2 pressures in the absence of O_2 on the same catalyst. Clearly, the reaction rate r_0 was independent of $[H_2O_2]$ and dependent on p_{H2}. The former was quite different from the previous results but very similar to the dependency reported by Choudhary et al. on Pd/C catalyst [21]. This means that the kinetic orders with respect to H_2O_2 and p_{H2} were zero and one in the absence of O_2, the rate determining step of the decomposition was the H_2 activation, and the reaction between adsorbed H and H_2O_2 was sufficiently rapid. The different dependencies on $[H_2O_2]$ with and without O_2 would be due to that O_2 and H_2O_2 compete for adsorbed H in the presence of O_2. Note that r_0 for H_2–O_2 reaction on the same catalyst was linear to H_2 concentration in the aqueous phase and slightly depressed by O_2 due to its adsorption on the catalyst surface [26].

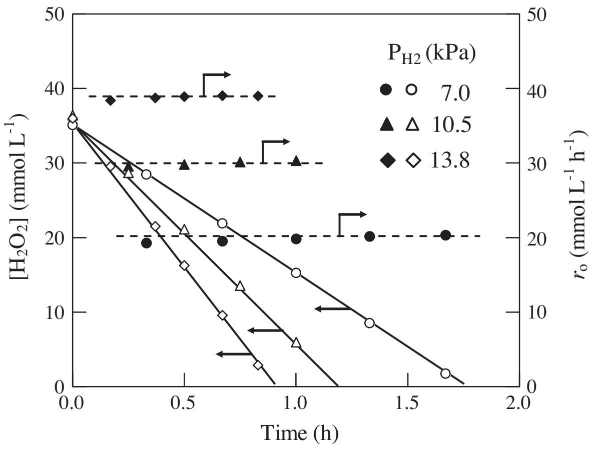


Fig. 5. Time course of H_2O_2 hydrogenation. [Cat] 166 mg L^{-1}, HBr 0.001 N, H_2 feed rate 6.0, 9.0, and 12.0 Ncm^3 min^{-1}, N_2 40.0, 30 °C, 1355 rpm.

3.4. Effect of H^+ and Br^- on the H_2O_2 synthesis

The influences of H^+ and Br^- concentrations on the H_2O_2 synthesis were studied in the same manner as that in the H_2O_2 decomposition. The results are shown in Fig. 6. Fig. 6a indicates that k_0 was linearly reduced in proportion to the product $[H^+][Br^-]$. It follows that the number of the active sites for the synthesis decreased with the amount of HBr adsorbed.

The S_f values in series II with higher $[H^+]$ were larger than those in series I as shown in Fig. 6b. This indicated that H^+ induced the increment of HBr adsorption and also improvement of the selectivity, the latter of which will be discussed later.

Fig. 6c shows the k_d values in comparison with those of k_d^o in H_2O_2 decomposition (Fig. 4). The dependencies of k_d were entirely different from those of k_d^o, which could be explained by the followings. Firstly, the decomposition via hydride species (Eqs. (14) and (15)) was depressed in H_2–O_2 reaction because O_2 lowered the rate of the forward reaction of Eq. (14) to result in decreasing k_d value, which was pronounced especially in the low HBr adsorption range. Secondly, the reduced surface could be rapidly regenerated in the redox system of Eqs. (11) and (12) through Eq. (18) in H_2–O_2 reaction, which might result in increasing k_d values in the range of high acidity.

$$MO + H_2 \rightarrow M + H_2O \qquad (18)$$

Thirdly, the destruction of H_2O_2 by hydrogenation, Eq. (15), had a significant role to raise the k_d value in the whole range.

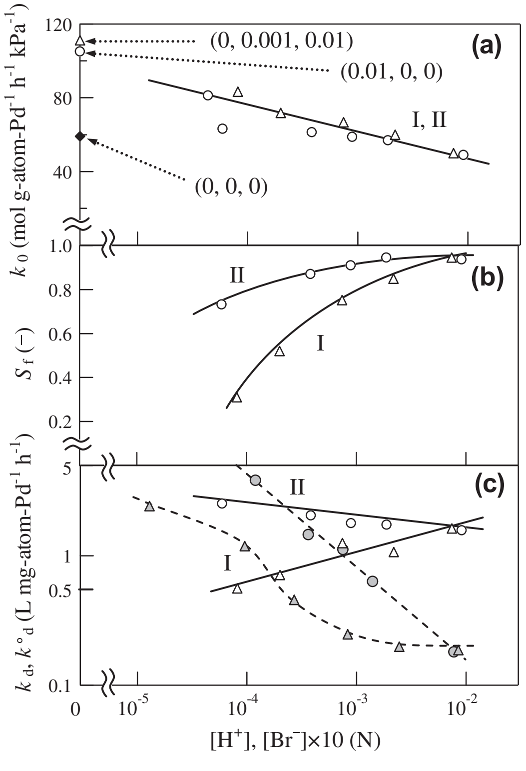


Fig. 6. Effect of H^+ and Br^- ions on H_2–O_2 reaction. [Cat] 166 mg L^{-1}, $[SO_4^{2-}]$ 0.01 N, H_2 feed rate 7.0 Ncm^3 min^{-1}, O_2 34.6, N_2 13.4, p_{H2} 8.5–9.6 kPa, p_{O2} 58–60 kPa, 30 °C, 1,355 rpm. Series I, [NaBr] 0.001 N (triangle); Series II, $[H_2SO_4]$ 0.01 N (circle). The numerical values in parentheses in part (a) were the amounts of added H_2SO_4, NaBr and Na_2SO_4 (N). The solid lines in part (c) were k_d of H_2-O_2 reaction determined by Eq. (7), while the broken lines k^o_d of H_2O_2 decomposition in the absence of H_2 which were identical with the plots in Fig. 4.

3.5. Influence of sulfur poisoning of the catalyst on H_2O_2 synthesis

In order to reveal catalytically active sites, influence of sulfur poisoning on the kinetics was investigated. The effect of $Na_2S_2O_3$ addition before H_2 activation of the catalyst is summarized in Fig. 7. The k_0/k_{00} ratio, in which k_{00} was the k_0 value at no addition of *S*, decreased exponentially with the S/Pd ratio, whereas S_f was almost constant and k_d linearly increased.

The experimental results were interpreted using several models of the active sites for H_2–O_2 reaction. At first, it was supposed in common that S atoms added could be adsorbed on surface Pd atoms at random, since poisoning of active sites through selective adsorption of S did not result in the exponential dependence observed in Fig. 7. When a specified Pd atom worked as an active site and was deactivated by adsorption of a S atom, the decrement in the number of active sites caused by addition of small amount of S could be expressed by Eq. (19). Here, N_0, x, N_A, N_{A0}, and N_S were number of total Pd atoms, Pd dispersion, number of the active Pd atoms free from S, initial value of N_A, and number of S added. Eq. (20), an integrated form of Eq. (19), showed a linear relationship between N_A/N_{A0} and N_S. This was not the case of Fig. 7 because N_A/N_{A0} could be replaced with k_0/k_{00}.

$$-dN_A = (N_{A0}/xN_0)dN_s \qquad (19)$$

$$N_A/N_{A0} = 1 - N_s/xN_0 \qquad (20)$$

Next, it was considered that adsorption of one S atom induced deactivation of plural Pd atoms at once. The decrement in the active Pd atoms should change with S addition according to Eq. (19′), in which n represents the number of Pd atoms deactivated by a single S atom. Integration of Eq. (19′) gave Eq. (20′), which agreed with the correlation in Fig. 7.

$$-\mathrm{d}N_A = \mathrm{n}(N_A/\mathrm{x}N_0)\mathrm{d}N_s \qquad (19')$$

$$\ln(N_A/N_{A0}) = -(\mathrm{n}/\mathrm{x})(N_s/N_0) \qquad (20')$$

The relationship between k_0/k_{00} and S/Pd values (=N_S/N_0) in Fig. 7 gave the *n*/*x* value of 20. Because the dispersion of an fcc Pd particle with 3–5 nm diameter was 0.40–0.25, the value of n should be 8–5 including the number of the atoms disabled by HBr adsorption. There would be two possibilities for deactivation of several Pd atoms by a single S adsorption. One is that an adsorbed S poisoned

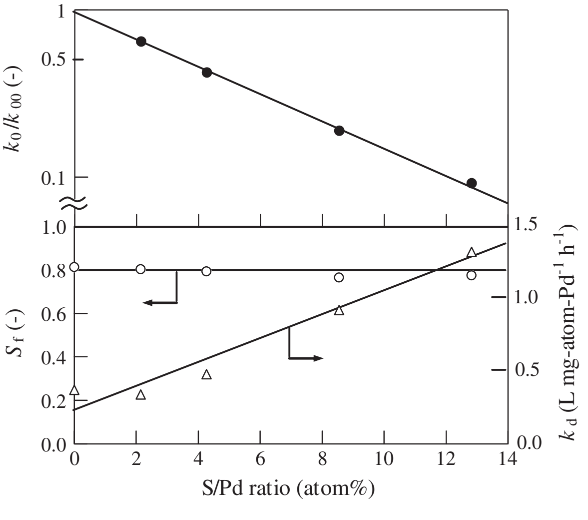


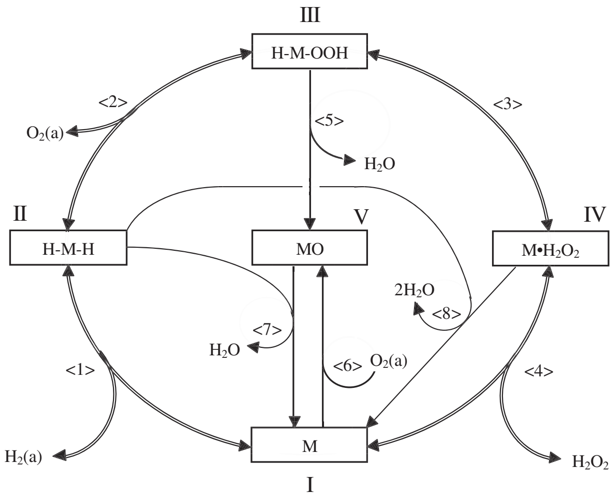
Fig. 7. Influence of sulfur poisoning of the catalyst on kinetic parameters of H_2O_2 synthesis. [Cat] = 166 mg L^{-1}, HBr 0.001 N, H_2 feed rate 5.7 Ncm^3 min^{-1}, O_2 48.4, N_2 0, p_{H2} 7.3–10.0 kPa, p_{O2} 87–90 kPa, 30 °C, 1355 rpm. k_{00} = 55.6 mol g-atom-Pd^{-1} h^{-1} kPa^{-1}.

surrounding several Pd atoms through some electronic effects. Another is that molecular rearrangement of H_2 and O_2 to form H_2O_2 or H_2O required a surface domain consisting of plural Pd atoms and was inhibited by adsorption of a single S atom.

The relationship between k_d and S/Pd indicated the acceleration of H_2O_2 destruction by the addition of S. This indicated that Pd atoms in the domain would still be effective for H_2O_2 hydrogenation, or that the destruction proceeded on a smaller domain. Thus, the competition for activated hydrogen would become advantageous to H_2O_2 hydrogenation. The electronic effect of S adsorption, the presence of domain for the H_2O_2 synthesis, and the acceleration of H_2O_2 hydrogenation should be confirmed by theoretical calculation in the near future.

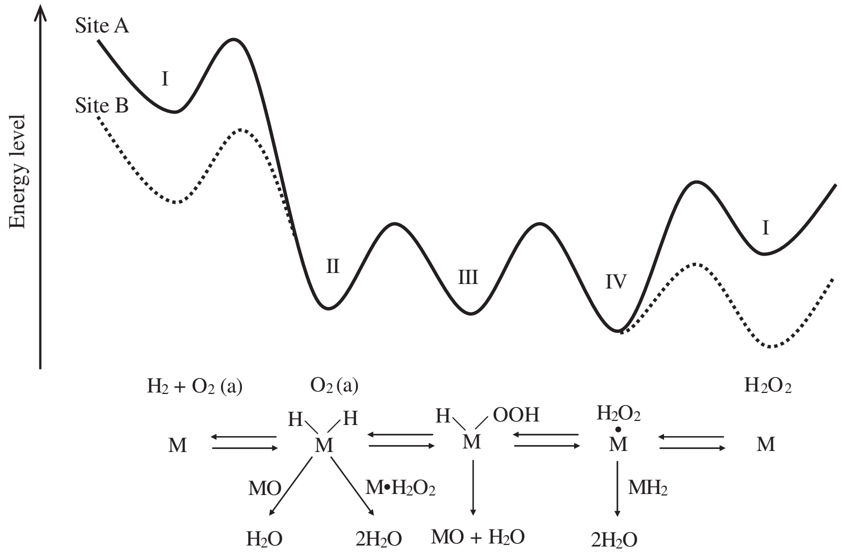
3.6. Whole reaction mechanism and the roles of H^+ and Br^-

Scheme 2 is the whole reaction mechanism suggested on the basis of the present results. The hydrido-hydroperoxy species H-M-OOH (III) was treated as the key intermediate in the H_2–O_2 reaction on Pd. The hydroperoxy species assumed in Eq. (14) was indeed detected in H_2–O_2 reaction on Au [30]. In this scheme, a H_2 molecule adsorbs dissociatively on the reduced metal surface (I) (Route ⟨1⟩) to form the hydride species (II) as is widely suggested. Insertion of O_2 to the M—H bond (Route ⟨2⟩) leads the formation of (III). The species (III) changes into the adsorbed H_2O_2 species (IV) via reductive elimination and subsequently into H_2O_2 with regeneration of the reduced surface (Routes ⟨3⟩, ⟨4⟩). On the other hand, β-elimination of III results in the H_2O formation and the oxide species MO (V) (Route ⟨5⟩, Eq. (16)). MO is also directly formed by reaction of the reduced surface with O_2 (Route ⟨6⟩, Eq. (13)). MO is reduced by the hydride species to form H_2O, and the reduced surface can be regenerated (Route ⟨7⟩, Eq. (18)). In the H_2O_2 decomposition, H_2O_2 adsorbs on the reduced surface and forms the intermediate III (Routes ⟨4⟩, ⟨3⟩, Eq. (14)). The intermediate releases O_2 or H_2O (Route ⟨2⟩, Eq. (14) or ⟨5⟩, Eq. (16)). The adsorbed H_2O_2 also reacts with the hydride species to form H_2O (Route ⟨8⟩, Fig. 5). In conclusions, H_2O_2 would be produced through the route ⟨1⟩–⟨2⟩–⟨3⟩–⟨4⟩, and H_2O is directly formed through the routes ⟨1⟩–⟨2⟩–⟨5⟩–⟨7⟩, ⟨1⟩–⟨6⟩–⟨7⟩, and ⟨1⟩–⟨2⟩–⟨3⟩–⟨8⟩. H_2O_2 is eliminated through the routes ⟨4⟩–⟨3⟩–⟨2⟩–⟨8⟩, ⟨4⟩–⟨3⟩–⟨5⟩–⟨1⟩–⟨7⟩, and ⟨4⟩–⟨1⟩–⟨8⟩.

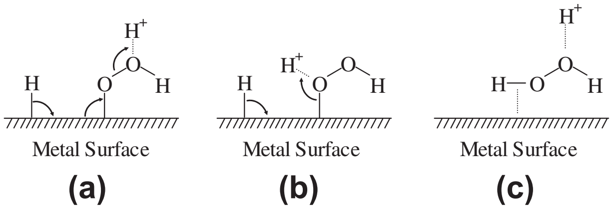


Scheme 2. Suggested whole reaction mechanism of H_2–O_2 reaction on Pd catalyst. M represents reduced metal surface. Reaction rate of each route depended on the Pd surface sites such as corner, edge, and plane (see Scheme 3).

It was clarified in the previous paper [26] that activation of H_2 (Route ⟨1⟩) was certainly the rate determining step in the presence of sufficient H_2 on the present catalyst system, although the rate determining step would move to the reductive elimination of the hydrido-hydroperoxy species at lower p_{H2} region. It was also shown that another hydride species MH_2 would be involved in the reductive elimination. The reaction rates of the respective routes shown in the scheme should be dependent on the situations of Pd active sites. Here, two kinds of sites, Sites A and B, were suggested and depicted qualitatively in Scheme 3. Unsaturation degrees of Pd atoms on Site A were higher than those on Site B. The former site would be a Pd atom at a corner, an edge or a defect Pd, while the latter at a flat surface. Because the unsaturation degree or activity of Site A would be higher than that of Site B, H_2O_2 would more easily adsorb on Site A and its desorption would be less easy. The hydrido-hydroperoxy intermediates III at Site A thus showed preferential formation of H_2O by the β-elimination or of the hydride species by O_2 elimination. It could be suggested that Site A was highly active not only for H_2O_2 decomposition but also for non-selective H_2O_2 formation in H_2–O_2 reaction. In



Scheme 3. Schematic energy diagrams along the reaction.



Scheme 4. Action of proton for the key intermediate.

contrast, Site B would produce H_2O_2 from H_2 and O_2 more smoothly and decompose H_2O_2 less easily. It would be reasonable that HBr was more easily added onto Site A to make the site inactive. Accordingly, addition of H^+ and Br^- caused the decrease in the total activity, the increase in H_2O_2 selectivity as well as the depression of H_2O_2 decomposition.

The results in Fig. 1 indicated that Site A could be divided into two kinds of sites; one could adsorb HBr even in the presence of H_2 and another only in the absence of H_2. Although the former site would be more responsible for the side reactions, contribution of the latter could not be neglected. Since the H_2 activation was a rate determining step in the H_2–O_2 reaction and concentration of adsorbed H should be kinetically controlled, HBr might partly adsorb on the latter site even in the presence of H_2 showing a Langmuir–Hinshelwood type depression effect. Moreover, it should be noted that the $[H^+][Br^-]$ range in Fig. 6 (10^{-8}–10^{-5} N^2) was much larger than that in Fig. 1 (0–10^{-8} N^2), and therefore, HBr could adsorb on the latter site in competition with H_2 in the H_2–O_2 reaction. The decrease in k_0 with increasing value of $[H^+][Br^-]$ in Fig. 6a might be due to the above mechanism. The difference of the edge/corner site and the flat sites should be investigated in near future.

Action of H^+ was rather complicated. H^+ was so far confirmed to promote the adsorption of Br^- (Eq. (10)) and the oxidation of the reduced metal surface (Eq. (16)). The latter action would be acceleration of β-elimination of the key intermediate (III) as illustrated in Scheme 4a. Because this route was included in direct H_2O formation and H_2O_2 decomposition by redox mechanism, H^+ would accelerate both. In a similar manner, H^+ might promote reductive elimination of the intermediate III as shown in Scheme 4b. This would compete with the direct H_2O formation through Scheme 4a. Furthermore, H^+ would assist desorption of H_2O_2 from the intermediate IV by protonation (Scheme 4c). Thus, H^+ would increase the H_2O_2 selectivity, since otherwise, the adsorbed H_2O_2 species IV was possibly hydrogenated before desorption. This might be the reason that the series II in Fig. 6b with higher H_2SO_4 concentration afforded higher H_2O_2 selectivity.

The comparison among the experimental results in Fig. 6a with H_2SO_4, NaBr, and Na_2SO_4 of (0.01 N, 0 N, 0 N), (0, 0.001, 0.01), and (0, 0, 0) was very significant. Although the concentration of H_2O_2 detected in each reaction was very low, it was analyzed to obtain further information. Table 1 shows the detail, in which k_d^o values were obtained by separate experiments. When NaBr was not added, the k_d^o value was very large and $[H_2O_2]$ was almost constant during the reaction, indicating formation and destruction of H_2O_2 were balanced. Thus, S_f was estimated by $S_f = k_d^o[H_2O_2][Cat]/r_0$ which was derived from Eq. (7) by substituting k_d^o for k_d. Note that the S_f values contained large errors because of the substitution and the small values of $[H_2O_2]$. On the other hand, when NaBr and Na_2SO_4 were added without H_2SO_4, k_d^o was small and $[H_2O_2]$ increased linearly with reaction time due to the small H_2O_2 destruction rate. The H_2O_2 formation rate was thus directly estimated and S_f was calculated by $S_f = d[H_2O_2]/dt/r_0$.

As shown in Table 1, the estimated S_f value with no additives was fairly high, and the value of k_0 was only about half of that in the other two cases (Fig. 6a) indicating that Site A was little active for H_2–O_2 reaction in the absence of the acid and the salts. It follows that H_2O_2 was produced on Site B and destructed on Site A. Besides H^+, the salt ions would also accelerate the β-elimination of H-M-OOH species probably because β-elimination was accompanied with charge transfer.

It is also noteworthy that k_0 was fairly large in the presence of NaBr, Na_2SO_4, and no H_2SO_4, whereas the k_d^o value was considerably decreased. This suggests that adsorption of H_2O_2 was hindered by HBr adsorbed in equilibrium on Site A, whereas H_2 could be still activated by eliminating HBr presumably due to the unsaturated nature of the site. The small S_f values in the presence of the acid or the salt ions suggested that most of H_2 activated on Site B was consumed on Site A probably for reduction of MO species to produce H_2O. Site A would be blocked more effectively with the increasing value of $[H^+][Br^-]$.

It should be noted that H_2O_2 destruction by hydrogenation, r_{d2} in Scheme 1, included not only the simple hydrogenation (Eq. (15)) but also the redox mechanism (Eqs. (11) and (18)) as Abate et al. pointed out [12]. Since H^+ accelerated the latter, clearly H^+ had both the negative effect to consume H_2O_2 and the positive effects to assist HBr adsorption and raise H_2O_2 selectivity.

4. Conclusions

Kinetic analyses including mass transfer processes of direct H_2O_2 synthesis and H_2O_2 decomposition were carried out over Pd/C catalyst in water containing H^+ and Br^- ions. The Br^- ion adsorption equilibrium was also measured. The following whole reaction mechanism, the roles of H^+ and Br^-, and the situation of active sites were revealed or suggested.

(1) The hydrido-hydroperoxy species H-M-OOH was the key intermediate of H_2O_2 formation, direct H_2O formation, and H_2O_2 destruction. H_2O_2 was produced by reductive elimination of H-M-OOH. On the sites with higher degree of coordinative unsaturation, the β-elimination of H-M-OOH tended to form MO. MO further reacted with the hydride species to regenerate the reduced metal surface. H_2O was possibly

Table 1
Estimated S_f values without H_2SO_4 or NaBr. Reaction conditions were the same as those in Fig. 6.

Added amount (N)			r_0 (mmol L^{-1} h^{-1})	$[H_2O_2]$ (mmol L^{-1})	S_f (–)	$k°_d$ (L mg-atom-Pd^{-1} h^{-1})
H_2SO_4	NaBr	Na_2SO_4				
0.01	0	0	23.8	0.06	0.1**	600
0	0.001	0.01	24.3	–*	0.02***	3.1
0	0	0	20.4	0.12	0.9**	2100

* Linearly increased with time.
** Estimated by $S_f = k°_d[H_2O_2][Cat]/r_0$.
*** Estimated by $S_f = d[H_2O_2]/dt/r_0$.

formed through oxidation of the reduced metal surface by O_2, but the contribution was small in this catalyst system. H_2–O_2 reaction proceeded in proportion to H_2 concentration as activation of H_2 was rate determining but the rate determining step moved to the reductive elimination step in the range of low H_2 partial pressure. O_2 depressed the whole reaction through Langmuir-type adsorption inhibition and also hydrogenation of H_2O_2 through competition for the hydride species.

(2) Br^- and H^+ adsorbed in pair on the sites with higher degree of coordinative unsaturation and blocked the sites to depress the side reactions. H^+ facilitated the adsorption of HBr and the β-elimination and reductive elimination on H-M-OOH. In addition, H^+ accelerated desorption of H_2O_2, which was formed by reductive elimination of H-M-OOH to reduce the hydrogenation before desorption. H_2O_2 decomposition over the catalyst without Br^- mainly proceeded through the reaction that H-M-OOH released O_2 and the resultant MH_2 reacted with H_2O_2. The difference between the edge/corner and plane sites was also discussed.

(3) Several surface Pd atoms were inactivated at once by adsorption of a sulfur atom for H_2–O_2 reaction, whereas H_2O_2 destruction was rather accelerated. Electronic effects of the adsorbed S and requirement of a domain consisting of plural Pd atoms for H_2–O_2 reaction were considered as possible reasons.

Acknowledgments

The authors thank Sumitomo Chemical Company for financial and technical supports and useful information as well as NE Chemcat Company for an offer of the Pd/C catalyst.

References

[1] J.H. Lunsford, J. Catal. 216 (2003) 455.
[2] J.K. Edwards, G.J. Hutchings, Angew Chem. Int. Edit. 47 (2008) 9192.
[3] C. Samanta, Appl. Catal. A: Gen. 350 (2008) 133.
[4] A.A. Herzing, A.F. Carley, J.K. Edwards, G.J. Hutchings, C.J. Kiely, Chem. Mater. 20 (2008) 1492.
[5] J.K. Edwards, A. Thomas, A.F. Carley, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Green Chem. 10 (2008) 388.
[6] J.K. Edwards, B. Solsona, N.E. Ntainjua, A.F. Carley, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Science 323 (2009) 1037.
[7] Q. Liu, J.C. Bauer, R.E. Schaak, J.H. Lunsford, Angew. Chem. Int. Edit. 47 (2008) 6221.
[8] Y. Nomura, T. Ishihara, Y. Hata, K. Kitawaki, K. Kaneko, H. Matsumoto, ChemSusChem 1 (2008) 619.
[9] K. Mori, T. Araki, S. Shironita, J. Sonoda, H. Yamashita, Catal. Lett. 131 (2009) 337.
[10] S. Abate, R. Arrigo, M.E. Schuster, S. Perathoner, G. Centi, A. Villa, D. Su, R. Schloegl, Catal. Today 157 (2010) 280.
[11] Q. Liu, J.H. Lunsford, Appl. Catal. A: Gen. 314 (2006) 94.
[12] S. Abate, G. Centi, S. Perathoner, S. Melada, F. Pinna, G. Strukul, Topics Catal. 38 (2006) 181.
[13] V.R. Choudhary, C. Samanta, J. Catal. 238 (2006) 28.
[14] V.R. Choudhary, C. Samanta, P. Jana, Appl. Catal. A: Gen. 317 (2007) 234.
[15] C. Samanta, V.R. Choudhary, Appl. Catal. A: Gen. 330 (2007) 23.
[16] S. Abate, G. Centi, S. Melada, S. Perathoner, F. Pinna, G. Strukul, Catal. Today 104 (2005) 323.
[17] Y. Voloshin, R. Halder, A. Lawal, Catal. Today 125 (2007) 40.
[18] Y. Voloshin, A. Lawal, Chem. Eng. Sci. 65 (2010) 1028.
[19] Y.-F. Han, J.H. Lunsford, J. Catal. 230 (2005) 313.
[20] C. Samanta, V.R. Choudhary, Appl. Catal. A: Gen. 326 (2007) 28.
[21] V.R. Choudhary, C. Samanta, J. Prabhas, Ind. Eng. Chem. Res. 46 (2007) 3237.
[22] R. Burch, P.R. Ellis, Appl. Catal. B: Environ. 42 (2003) 203.
[23] D.P. Dissanayake, J.H. Lunsford, J. Catal. 214 (2003) 113.
[24] S. Chinta, J.H. Lunsford, J. Catal. 225 (2004) 249.
[25] Q. Liu, J.H. Lunsford, J. Catal. 239 (2006) 237.
[26] T. Deguchi, M. Iwamoto, Ind. Eng. Chem. Res., in press, doi:10.1021/ie102074z.
[27] G. Bianchi, F. Mazza, T. Mussini, Electrochim. Acta 7 (1962) 457.
[28] Y. Voloshin, J. Manganaro, A. Lawal, Ind. Eng. Chem. Res. 47 (2008) 8119.
[29] Q. Liu, K.K. Gath, J.C. Bauer, R.E. Schaak, J.H. Lunsford, Catal. Lett. 132 (2009) 342.
[30] C. Sivadinarayana, T.V. Choudhary, L.L. Daemen, J. Eckert, D.W. Goodman, J. Am. Chem. Soc. 126 (2004) 38.