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Selective synthesis of α,β-unsaturated aldehydes from allylic alcohols using oxidatively supplied hydrogen peroxide from electrochemical two-electron water oxidation†

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Selective oxidation of allylic alcohols to α,β-unsaturated aldehydes using electrochemically formed hydrogen peroxide (H_2O_2) is performed in the presence of Pt black catalyst. In this reaction, H_2O_2 is oxidatively supplied from the electrochemical two-electron water oxidation (2e-WOR) of an aqueous $KHCO_3/K_2CO_3$ mixed solution at a fluoride-doped tin oxide (FTO) anode. Geraniol was oxidized to the corresponding geranial in 86% yield with 99% selectivity when the appropriate amounts of Pt black catalyst with one equivalent of H_2O_2 by 2e-WOR toward geraniol was employed in toluene solution at 60 °C. The H_2O_2 by 2e-WOR can oxidize various kinds of allylic alcohols to give the corresponding aldehydes in 64–89% isolated yields. The detailed tuning of the amounts of Pt black and the rate of introduction of H_2O_2 to the vessel allows the selective oxidation to proceed despite the low concentration of H_2O_2 derived by 2e-WOR.

Introduction

Oxidation is known as a straightforward means of transforming alcohols to aldehydes, then be used to make various useful chemicals.[1] Oxidants such as hydrogen peroxide aqueous solution (H_2O_2 aq.), O_2, and air can be used to achieve an environmentally benign synthesis because they form only water as a co-product.[2,3] Liquid oxidants such as H_2O_2 are especially used for liquid phase oxidation of value-added fine chemicals.[3] And the use of a solid catalyst is crucial for the sustainable oxidation process due to its easy separation from the targeted aldehydes.[1c,2,4,5] Heterogeneous Pt-catalysed oxidation of allylic alcohols to α,β-unsaturated aldehydes, which are frequently used as building blocks for pharmaceutical syntheses,[1c,6] has been reported by using purchased H_2O_2 from industrial processes.[7]

For the industrial production of H_2O_2, an anthraquinone process was developed by BASF and has been widely used in chemical processes.[8a] However, this process requires plant technology capable of handling large sizes as well as strict transportation and storage controls.[9] Among the many methods of producing H_2O_2 or related compounds from water, air, and/or H_2,[8,9] the oxidative H_2O_2 production from H_2O at an anode by electrochemical synthesis is among the most appealing, since it promises constant and on-demand production of H_2O_2, with H_2 production on a cathode using renewable energy power.[10] This route is economical because it produces both H_2 and H_2O_2, two valuable chemicals. H_2O_2 generation using a fluoride-doped tin oxide (FTO) anode with aqueous carbonate salts solution is known as an effective process which generates H_2O_2 by two electron oxidation of water (2e-WOR).[11a–c] Moreover, the mixing of K_2CO_3 and $KHCO_3$ enhances the yield of H_2O_2 from carbonate solution through 2e-WOR at an FTO anode coated with $LaAlO_3$.[11b,d] Although there are some examples of H_2O_2 formation by electrochemical 2e-WOR,[11] it is still rare to utilize the H_2O_2 by 2e-WOR for the production of fine chemicals *via* organic synthesis.[12] For example, Neumann's group performed Baeyer–Villiger oxidation of cyclic ketones and oxidation of sulfides by using *in situ*-produced H_2O_2 at an FTO anode by 2e-WOR.[13] To our knowledge, however, the combination of H_2O_2 by 2e-WOR and a solid catalyst for the dehydrative oxidation of alcohols has not been reported.

Our research concept is to develop a two-step process that can produce H_2O_2 by 2e-WOR stably and can accommodate scale-up and a broad substrate scope for allylic alcohol oxidation by the H_2O_2 by 2e-WOR (Fig. 1). Fine-tuning of the contact between the solid catalyst, diluted H_2O_2 and substrates is required to realize a high-yielding oxidation *via* 2e-WOR-generated H_2O_2 that can overcome the use of a disadvantageously low concentration H_2O_2 aq. containing large amounts

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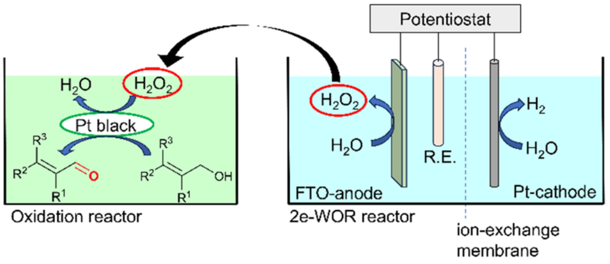


Fig. 1 The electrochemical setup for oxidative H_2O_2 production from water with H_2 evolution and the oxidation of allylic alcohol to α,β-unsaturated aldehyde using the H_2O_2 derived from 2e-WOR. R.E. is reference electrode.

of carbonate. Carbonate salt, which is essential for the formation of H_2O_2 by 2e-WOR, is also expected to inhibit the over-oxidation of the formed aldehydes through the salting-out effect.[14]

We herein report the application of H_2O_2 by 2e-WOR to the oxidation of allylic alcohols, and the precise tuning of Pt and H_2O_2 contact frequency toward the Pt-catalysed oxidation of H_2O_2 derived by 2e-WOR. We then show that our selective oxidation method can successfully produce various α,β-unsaturated aldehydes in 64–89% yield. The use of H_2O_2 produced by 2e-WOR for the oxidation realizes the on-demand production of fine chemicals without the need for considering the handling and storage of explosive H_2O_2.

Results and discussion

Electrochemical generation of H_2O_2 using an FTO anode

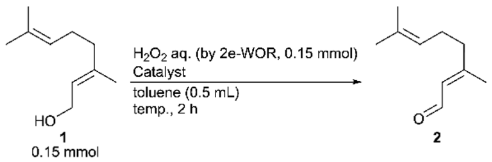
Production of H_2O_2 from an aqueous carbonate solution through 2e-WOR is carried out by using an FTO anode (with Pt as cathode).[11c] The cooperative effect of K_2CO_3 and $KHCO_3$ is also known to increase the yields of H_2O_2 by tuning the pH to basic.[11d] In our present approach, partially refined conditions are employed; that is, H_2O_2 is produced at 3–5 °C without introducing additional CO_2 gas. Two electron oxidations of H_2O proceeded to generate H_2O_2 using an FTO anode from an electrolyte solution containing K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}). The electrochemically formed H_2O_2 was obtained at around 70 mmol per L H_2O_2 aq. at 50 mA cm^{-2} current density. We diluted the H_2O_2 aq. to 68 mmol L^{-1} and used it for the selective oxidation of allylic alcohols.

Screening of the reaction conditions using noble metal catalysts for the H_2O_2 oxidation of geraniol (1)

The electrochemically formed H_2O_2 aq. by 2e-WOR was collected in a sample vial, and then added dropwise to a toluene solution of **1** and catalyst over 15 min, followed by stirring at 1000 rpm to attempt the formation of geranial (**2**). The data in Table 1 were analysed by extracting the sample after the reaction with toluene, adding an internal standard (biphenyl), and introducing them directly into the gas chromatography (GC). As a catalyst for the oxidation, we screened Pd black, Ru black, and Pt black and the yields of **2** were compared to that under the non-catalyst conditions (Table 1, entries 1–4). Pd black and Ru black did not show any reactivity toward **1** at 60 °C over 2 h. However, Pt black gave **2** in 36% yield at 60 °C, and after optimization of the amounts of Pt black, it gave **2** in 86% yield with 99% selectivity over 2 h (Table 1, entry 5).

In general, if carboxylic acid is formed in an oxidation reaction, it can be transferred to sodium carboxylate in NaOH aq., followed by the conversion to carboxylic acid by HCl aq. to purify the product, and the peak of the formed carboxylic acid can be detected by GC. In this case, the peak belongs to geranic

Table 1 The oxidation of **1** using H_2O_2 produced by 2e-WOR



Entry	Catalyst (mg)	Temperature (°C)	Conv.[a] of **1** (%)	Yield[a] of **2** (%)	Selectivity[b] (%)
1	None	60	0	0	—
2	Pd black (5)	60	0	0	—
3	Ru black (5)	60	0	0	—
4	Pt black (5)	60	36	36	>99
5	Pt black (15)	60	87	86	99
6	Pt black (15)	40	64	61	95
7	Pt black (15)	80	77	74	96
8	3wt% Pt/C (167)	60	76	45	59
9	PtO_2 (15)	60	0	0	—

[a] Reaction conditions: **1** (0.15 mmol), catalyst, 0.5 mL toluene, electrochemically formed 68 mmol per L H_2O_2 aq. (2.2 mL, 0.15 mmol, containing 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$), 1000 rpm, total reaction time was 2 h. Conversions and yields were calculated by gas chromatography (GC) analysis based on **1** using biphenyl as a standard. [b] Selectivity = yield/conversion × 100 (%).

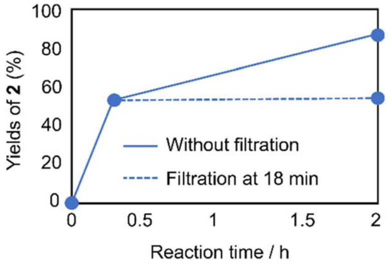
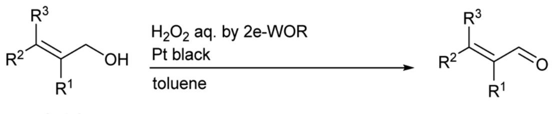
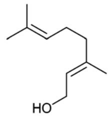
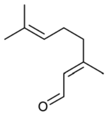
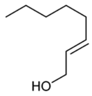
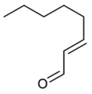
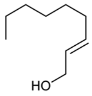
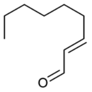
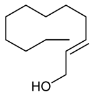
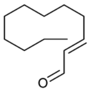
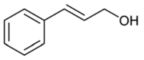
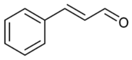
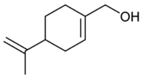
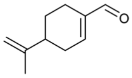
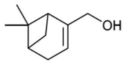
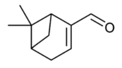


Fig. 2 Hot-filtration test in the H_2O_2 oxidation of **1**.

Table 2 Oxidation of various allylic alcohols using H_2O_2 by 2e-WOR



1, **4-9** → **2**, **10-15**

Entry	Allylic alcohol	α,β-unsaturated aldehyde	Isolated yield[a] (%)
1	 **1**	 **2**	89
2	 **4**	 **10**	64[b]
3	 **5**	 **11**	80[c]
4	 **6**	 **12**	77[b]
5	 **7**	 **13**	70[c]
6	 **8**	 **14**	78[b]
7	 **9**	 **15**	82[c]

[a] Reaction conditions: allylic alcohol (0.75 mmol), Pt black (75 mg), 2.5 mL toluene, 68 mmol per L H_2O_2 aq. (11 mL, 0.75 mmol, drop time 1.25 h) supplied by 2e-WOR (containing 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$), 1000 rpm, 60 °C, and a total reaction time of 3 h unless otherwise stated. Isolated yields were calculated using the weight of the obtained aldehydes as follows: [moles of product (mmol)]/[moles of initial substrate (mmol)] × 100 (%), structure of the produced aldehydes was checked by ^{1}H NMR analyses. [b] Allylic alcohol (0.45 mmol), Pt black (45 mg), 1.5 mL toluene, 68 mmol per L H_2O_2 aq. (6.6 mL, 0.45 mmol, drop time 45 min) supplied by 2e-WOR (containing 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$), 80 °C, and a total reaction time of 2.5 h. [c] The reaction was conducted at 80 °C.

acid (**3**) was not detected at all in GC from the solution prepared by NaOH aq. and HCl aq. after the H_2O_2 oxidation of **1** (Table 1, entry 5). The result with the excellent selectivity (99%) in Table 1, entry 5, clearly showed that the developed oxidation did not give any byproducts such as **3**.

The reaction depends on the reaction temperature, with a temperature of 60 °C showing the best performance to give **2** in 86% yield with 87% conversion of **1** (Table 1, entry 5). The lower temperature of 40 °C was in-sufficient to advance the oxidation, giving **2** in only 64% conversion and 61% yield, and additional heating from 60 °C to 80 °C appeared to upset the balance of the catalytic reaction, dropping the conversion of **1** and the yield of **2** to 77% and 74%, respectively (Table 1, entries 6 and 7).

When diluted H_2O_2 aq. by 2e-WOR was used, the decomposition of H_2O_2 by Pt black at 80 °C was decisive, unlike when a high concentration of industrially produced H_2O_2 was used. In addition, the balance of the H_2O_2: substrate ratio was largely preserved when we used 1.0 equivalent of H_2O_2 by 2e-WOR. The use of 3wt% Pt/C catalyst with the weight per Pt of 5 mg gave **2** in 45% yield, and the yield of **2** was almost the same as when using 5 mg Pt black (Table 1, entries 4 and 8). However, the Pt/C showed low selectivity of 59% because of the chemisorption of organic compounds on the carbon support. The use of Pt black would be better in consideration of the selectivity of **2**. The oxidized PtO_2 did not show any catalytic reactivity, giving **2** in 0% yield (Table 1, entry 9). Zero valent Pt is required for the H_2O_2 oxidation.[7]

A hot filtration experiment was performed using Pt black catalyst. When the catalyst was removed at 18 min and the oxidation of **1** was continued by the addition of filtrate, the yield of **2** remained almost constant at 55% from the 18 min reaction time (the yield at 18 min was 53%). In contrast, the reaction with Pt black for 2 h gave a yield of 86% (Fig. 2). The ICP-AES analyses of the filtrate from the reaction in Table 1, entry 5, did not detect the presence of Pt. These two results showed that the oxidation of **1** proceeded on the surface of the solid Pt black.

Oxidation of various allylic alcohols

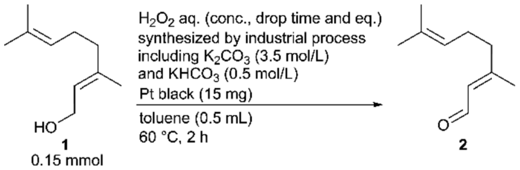
The oxidation of various allylic alcohols (**1** and **4–9**) using H_2O_2 aq. by 2e-WOR proceeded to provide various kinds of α,β-unsaturated aldehydes, such as **2** and **10–15** (Table 2). The choice of 60 °C or 80 °C reaction temperature was made to achieve a target yield of 80% depending on the substrate. The isolation of the targeted aldehydes was carried out through column chromatography after the separation of the organic phase from the reaction solution. The acyclic allylic alcohols such as (*E*)-2-octen-1-ol (**4**), (*E*)-2-nonen-1-ol (**5**), (*E*)-2-dodecen-1-ol (**6**), and **1** were selectively oxidized to give the corresponding (*E*)-2-octen-1-al (**10**), (*E*)-2-nonen-1-al (**11**), (*E*)-2-dodecen-1-al

(**12**), and **2** in 64%, 80%, 77%, and 89% isolated yields, respectively (Table 2, entries 1–4). Although it is difficult to separate the volatile α,β-unsaturated aldehydes such as **10** from the solvent,[15] heavier α,β-unsaturated aldehydes **2**, **11** and **12** were successfully isolated with good purity. (*E*)-Cinnamyl alcohol (**7**) was oxidized with slight low reactivity to (*E*)-cinnamaldehyde (**13**) in 70% yield at 80 °C (Table 2, entry 5). Selective oxidation of cyclic allylic alcohols such as perillyl alcohol (**8**) and myrtenol (**9**) proceeded with H_2O_2 aq. by 2e-WOR to give the corresponding aldehydes **14** and **15** in 78% and 82% yields at 80 °C, respectively (Table 2, entries 6 and 7).

Effect of carbonate salts and a low concentration of aqueous H_2O_2 solution by 2e-WOR on the oxidation

The detailed reaction conditions were screened focusing on the efficiency of the contact between H_2O_2 and Pt under various concentrations and amounts of H_2O_2 (Table 3). These investigations were conducted using a pseudo aqueous H_2O_2 solution instead of H_2O_2 by 2e-WOR. The solution was made by adding K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}) to industrially purchased H_2O_2 in advance, and was diluted to 20, 36, 68 and 91 mmol L^{-1}.

Table 3 Detailed screening of reaction conditions using as-synthesized H_2O_2



Entry	H_2O_2 equivalent toward **1**	Concentration (mmol L^{-1}) Volume (ml)	Drop time (min)	Conv[a]. of **1** (%)	Yield[a] of **2** (%)
1	0.90	68 2.0	15	81	75
2	1.4	68 3.0	15	92	84
3	1.0	68 2.2	15	90	89
4	1.0	20 7.5	15	86	86
5	1.0	36 4.1	15	84	82
6	1.0	91 1.7	15	96	96
7[b]	1.0	68 2.2	15	88	85
8	1.0	68 2.2	0	80	77
9	1.0	68 2.2	10	87	84
10	1.0	68 2.2	20	87	85
11	1.0	68 2.2	30	78	75
12[c]	0	0 2.2	15	22	19
13[d]	0	0 2.2	15	18	16
14[e]	1.0	9.7×10^3 0.015	60	100	99
15[f]	2.0	1.6×10^3 0.18	—	99	97

[a] Reaction conditions: **1** (0.15 mmol), Pt black (15 mg), 0.5 mL toluene, H_2O_2 aq. (containing 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$), 1000 rpm, 60 °C, total reaction time was 2 h. Conversions and yields were calculated by gas chromatography (GC) analysis based on **1** using biphenyl as a standard. [b] Without 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$. [c] Using K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}) mixed aqueous solution instead of H_2O_2 aq. with K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}). [d] Using water instead of H_2O_2 without K_2CO_3 nor $KHCO_3$. [e] Ref. 7*a*, using 5%Pt, 1% Bi/C catalyst, concentration and the volume of H_2O_2 was formally calculated to fit the 0.15 mmol scale, 60 °C, 1 h. [f] Ref. 7*b*, 90 °C, 3 h, no data about drop time, concentration and the volume of H_2O_2 was formally calculated to fit the 0.15 mmol scale.

The ratio of $H_2O_2:\mathbf{1}$ directly affected the yields of **2**, with 1.0 equivalent of H_2O_2 toward **1** expected to be a better reaction condition for the viewpoint of both the yields and the conversions (Table 3, entries 1–3). The concentration of H_2O_2 was also critical to the oxidation. The H_2O_2 aq. diluted to 20 and 36 mmol L^{-1} gave **2** in 86% and 82% yields, respectively (Table 3, entries 4 and 5). The 68 mmol per L H_2O_2 aq. gave an 89% yield of **2** and the yield increased to 96% by using 91 mmol per L H_2O_2 aq. (Table 3, entries 3 and 6). The concentration of H_2O_2 by 2e-WOR could be set as high as 70 mmol L^{-1} in our system, and the yields of **2** when using 68 mmol per L H_2O_2 by 2e-WOR and 68 mmol per L H_2O_2 prepared as described above were similar, at 86% and 89% (Tables 1 and 3, entries 5 and 3). The yield of **2** slightly decreased to 85% when we used the 68 mmol per L H_2O_2 aq. without K_2CO_3 and $KHCO_3$ salts because the extraction capability of **2** from the water phase to organic phase was weakened (Table 3, entry 7).[14] Changing the drop time of H_2O_2 aq. to the reaction vessel tuned the yield of **2**. When H_2O_2 was added with **1** simultaneously, the oxidation of **1** gave **2** in 77% yield and the 10, 15, 20 and 30 min drop time of H_2O_2 aq. gave **2** in 84%, 89%, 85% and 75% yields, respectively (Table 3, entries 3, 8–11). The adsorption rate of H_2O_2 on the Pt black surface should be balanced with the oxidation reaction on the Pt surface to produce **2**. If the drop time was set earlier than 15 min, the decomposition of H_2O_2 by Pt was accelerated compared to that by a drop time of 15 min. The resulting decrease in the amount of H_2O_2 reduced the yield of **2**. Thus, the reason that the desired oxidation on the Pt surface did not proceed with appropriate speed when the drop time was set to later than 15 min might have been that the supply of H_2O_2 to the Pt surface was delayed.

When the oxidation of **1** was carried out using a mixed aqueous solution of K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}) without H_2O_2, the conversion of **1** dropped to 22% and the yield of **2** was 19% (Table 3, entry 12). Although Pt black can catalyse the oxidation of aliphatic and benzyl alcohols to give the corresponding aldehyde using O_2 as an oxidant,[4,5] the yield of **2** from **1** was low without H_2O_2 because of the lower reactivity of allylic alcohols. The use of H_2O_2 would facilitate the oxidation of allylic alcohols such as **1** through the formation of Pt=O and Pt–OH active species on the surface of Pt black.[7] In the oxidation with water under conditions where not only H_2O_2 but also K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}) were not added to the sample vial, the conversion of **1** was 18% and the yield of **2** was 16% (Table 3, entry 13). The use of K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}) mixed aqueous solution improved the yield of **2** even in the absence of H_2O_2 because the formed **2** might be extracted into the organic phase.[14]

The previously reported H_2O_2 oxidations of **1** using Pt catalyst are known to show the high conversion with good yields, for example, 1.0 eq. of 30% H_2O_2 toward **1** with the 5% Pt, 1% Bi/C catalyst showed 99% yield of **2** with 100% conversion of **1** (Table 3, entry 14).[7a] This reaction condition shows the highest yield due to the high concentration of H_2O_2. However, it is necessary to increase the drop time of H_2O_2 to avoid explosion, which is a significant deviation from the reaction conditions developed in this study. In the case of using lower concentrations of H_2O_2, the use of 5% H_2O_2 (2.0 eq.) using Pt black gave **2** in 97% yield and 99% conversion (Table 3, entry 15).[7b] Generally, the use of concentrated H_2O_2 is critical to proceed the oxidation of allylic alcohol. Our optimised reaction conditions about equivalent and drop time enabled to reach the yield of **2** from **1** in 89% having the advantages of low concentration of H_2O_2, which was produced cleanly by electrochemical 2e-WOR without explosion hazard.

The relationship between the reaction time and product yield was studied using the 68 mmol per L H_2O_2 including K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}) prepared from the industrially formed H_2O_2 (Table S1 and Fig. S1†). The yields were calculated as the average of three experiments conducted at each reaction time. The reaction proceeded as time progressed, with yields of 60%, 79% and 89% at 20 min, 1 and 2 h, respectively (Table S1,† entries 1–9). The reaction was almost complete in 2 h, and a yield of 87% was maintained even at 3 h due to the lack of H_2O_2 (Table S1,† entries 10–12).

To check the degree of decomposition of H_2O_2 under our developed reaction conditions, the reaction was carried out under the same conditions as in Table 1, entry 5 except for Pt black, and the concentration of H_2O_2 before and after the reaction was analysed using the colour change reaction analysis of $FeSO_4$ (0.1 mol L^{-1}) and HCl (1 mol L^{-1}) with UV-vis spectrometer. As a result, little decomposition of H_2O_2 occurred during the reaction.

Discussion about reaction mechanism

X-ray diffraction (XRD) patterns obtained before and after the oxidation showed no change in the signals belonging to Pt black (Fig. 3(a)). Peaks of $2\theta = 39.8$, 46.2, and 67.6 of Pt black before the oxidation of **1** in the XRD measurement were attributed to (111), (200), and (220) planes of Pt black, respectively, based on the comparison with the data in previous reports.[16] The detailed XRD was analysed about the (111) peaks of Pt black before and after the reaction (Fig. S2†), and the measured Full Width at Half Maximum (FWHM) were used to estimate Pt crystallite diameter to be 10.0 nm and 10.2 nm (before and after the oxidation of **1**, respectively, Table 1, entry 5) from Scherrer's equation. Those values were usual as the Pt crystallite diameter of Pt black.[16] Calculations were performed according to the following equation; L (crystallite diameter) $= K\lambda/(\beta\cos\theta)$, where $K = 1$, $\lambda = 0.154$ nm, $\beta = 0.01634$ rad, and $\theta = 19.943°$ for the Pt

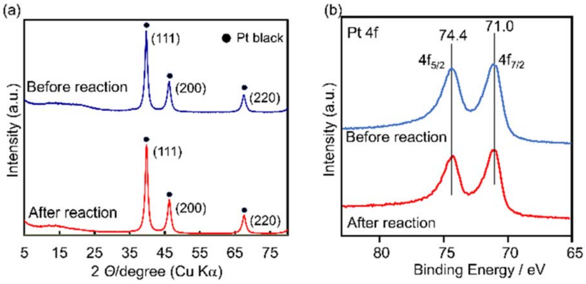


Fig. 3 (a) XRD patterns of Pt black before and after the oxidation of **1**, (b) XPS signals of Pt black before and after the oxidation of **1**.

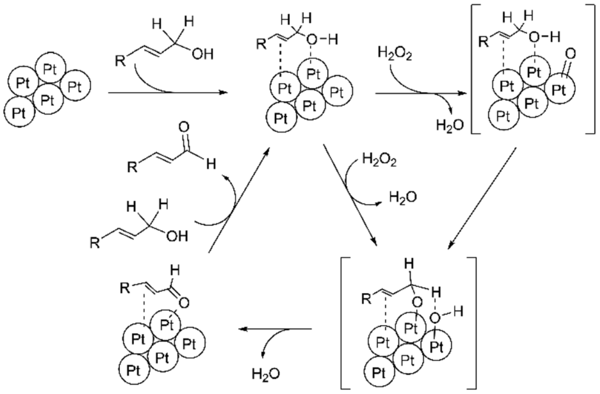


Fig. 4 Plausible reaction mechanism.

black before the reaction, and $K = 1$, $\lambda = 0.154$ nm, $\beta = 0.01597$ rad, and $\theta = 19.987°$ for the Pt black after the reaction, respectively.

The reaction would proceed on the surface of Pt based on the results of the hot-filtration experiment (Fig. 2). In the hot filtration experiment, the reaction did not proceed in the filtrate after the removal of Pt black through a filtration with a pore size of 0.20 μm, suggesting that the Pt particles having crystallite diameter of *ca.* 10 nm from (111) peak would mostly agglomerate into Pt black particles of over 200 nm. It was difficult to conduct electrochemical tests on this oxidation because the H_2O_2 oxidation proceeded on the Pt surface and H_2O_2 was quickly decomposed by Pt. Although highly dispersed Pt is effective for the aerobic oxidation,[4,5] H_2O_2 oxidation can advance the oxidation of allylic alcohols by the employment of micrometer-order Pt particles such as Pt black.[7b] The dispersed Pt of 3wt% Pt/C also showed the reactivity, but the support chemisorbed the organic compounds and decreased the selectivity of **2** (Table 1, entries 4 and 8).

X-ray photoelectron spectroscopy (XPS) was checked about the oxidation state of the employed Pt black (Fig. 3(b)). The signals belonging to Pt black was observed at 71.0 eV and 74.4 eV which were attributed to $4f_{7/2}$ and $4f_{5/2}$ of Pt(0). And the signals of Pt(0) did not change before and after the reaction.[17] The Pt(0) would be the active species that initiated the reaction, which was consistent with previous reports.[4,5,7,18,19] The presence of a certain particle size of Pt may be useful for maintaining Pt(0) by introducing H_2O_2 into the flask at the appropriate concentration and rate.

Compared to the previous Pt black-catalysed oxidation, the electrochemically formed H_2O_2 showed good reactivity despite its low concentration. And the inclusion of K_2CO_3 (3.5 mol L^{-1}) and $KHCO_3$ (0.5 mol L^{-1}), which were required to advance the 2e-WOR, showed a positive effect on the oxidation through salt-induced precipitation of α,β-unsaturated aldehydes from the water phase to inhibit the hydrolysis.[14]

The mechanism of the oxidation of alcohol on the surface of Pt group metals is quite complex, with various routes to the formation of byproducts.[4,5,18] We here adopted the mechanism by which allylic alcohols poison the Pt black surface and then oxidize the alcohols,[4,5,7,18,19] leading to the efficient used of H_2O_2 as an oxidant for the alcohol oxidation (Fig. 4).

It is assumed that when the allylic alcohol is present on the Pt black surface, the active species such as Pt=O is generated from the reaction of H_2O_2 and Pt, which immediately promotes the generation of alkoxide on Pt surface and the formation of Pt–OH, accompanied by dehydration. The formation of aldehyde from the corresponding alkoxide on the Pt surface is carried out with dehydration by the formed Pt–OH species. The produced α,β-unsaturated aldehyde is desorbed from the Pt surface by exchange with the new allylic alcohols to continue the catalytic process.[4,5,7]

Conclusions

The electrochemically formed H_2O_2 by 2e-WOR was applied to the oxidation of various allylic alcohols to synthesize the α,β-unsaturated aldehydes in good yields. Our results suggested that the detailed tuning of the amounts of H_2O_2 with the H_2O_2 concentration and drop time was able to control the selective H_2O_2 oxidation of allylic alcohols because the efficiency of contact between H_2O_2 and the Pt surface was balanced with the oxidation reaction proceeding on the Pt surface. This resulted in a process that can be implemented from the production of H_2O_2 to the synthesis of functional chemicals in a clean and on-demand manner.

Experimental

Electrochemical H_2O_2 generation using an FTO anode

The electrochemical properties of the electrocatalyst FTO anode were evaluated in a mixed aqueous solution of K_2CO_3 (3.5 mol L^{-1})/$KHCO_3$ (0.5 mol L^{-1}) (pH 10.8) with an ice bath (3–5 °C) by using an electrochemical analyser (BAS, ALS1140C). An experiment on the accumulation of H_2O_2 was conducted *via* a three-electrode method using a two-compartment cell. The volume of the electrolyte solutions of the anode and cathode chambers was 35 mL, and the solution was stirred magnetically. The reference electrode used was Ag/AgCl (3 mol per L NaCl), and the counter electrode was a Pt wire. Between the anode and cathode chambers, Nafion 212 (Sigma-Aldrich) was used as an ion-exchange resin membrane. The FTO (F-doped SnO_2, Nippon Sheet Glass Company, Ltd) electrodes were used as the working electrodes, and a stainless-steel alligator clip was used to connect the FTO glass electrode. The alligator clip was not immersed in the electrolyte. The geometric area of the FTO electrode was 0.5–1 cm^2. Before electrochemical measurements, UV ozone treatment was carried out to clean the FTO surface. All potentials in this paper are given relative to the reversible hydrogen electrode (RHE), according to the Nernst equation. $E(vs.\ \text{RHE}) = E(vs.\ \text{Ag/AgCl}) + 0.0591\_\text{pH} + 0.197$, where pH values of the electrolytes were determined by a HM-30P pH meter (TOA DKK). For the generation of H_2O_2, the electrochemical reaction was conducted with the current constant with 50 mA and the voltage fluctuations were checked (Fig. S3†). The reaction proceeded until *ca.* 1260 coulomb was achieved. After electrolysis, the generated H_2O_2 was detected by using the colour change reaction analysis in a mixed aqueous solution of $FeSO_4$ (0.1 mol L^{-1}) and HCl (1 mol L^{-1}) with UV-vis spectrometer (JASCO Co. V-770).

Oxidation of geraniol (1) to geranial (2) by using H_2O_2 derived from electrochemical 2e-WOR

The reaction mixture of Pt black (75 mg), toluene (2.5 mL), and **1** (115 mg, 0.75 mmol) was stirred in a glass test tube at 60 °C, and an electrochemically formed 68 mmol per L of H_2O_2 (11 mL, 0.75 mmol containing 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$ by 2e-WOR) was then added dropwise to the mixture over 1.25 h, with additional stirring at 60 °C for 1.75 h. After the reaction, the organic phase was extracted by toluene (8 mL × 2) and treating the remaining peroxides in the toluene solution with aqueous $Na_2S_2O_3$ (0.05%, 8 mL). Extraction of the toluene phase by using the additional toluene (8 mL), followed by the evaporation of toluene to form a colourless oil. Purification of **2** was carried out using an SiO_2 column chromatograph (*n*-hexane : ethyl acetate = 9 : 1) to give 99 mg of **2** in 89% isolated yield. The reaction conditions were screened by following the procedures reported in the captions of Table 2.

Hot filtration experiments

Hot filtration tests were executed using a reaction mixture of Pt (15 mg), toluene (0.5 mL), and **1** (23.1 mg, 0.15 mmol). The mixture was stirred in a glass test tube at 60 °C and a solution of electrochemically formed H_2O_2 (68 mmol L^{-1}, 2.20 mL, 0.15 mmol containing 3.5 mol per L K_2CO_3 and 0.5 mol per L $KHCO_3$ by 2e-WOR) was then added to the mixture with the drop time of 15 min, and afterward, the mixture was subjected to quick filtration using a membrane filter (0.20 μm pore size) at 18 min to separate Pt black particles from the reaction solution. The filtrate was additionally stirred at 60 °C for 2 h without the addition of any new additives. The yield of **2** was determined by GC in 58% using biphenyl as a standard. The oxidation of **1** at 60 °C over 2 h without hot filtration resulted in an 86% yield of **2**.

Materials and methods

Materials

Pt black was obtained from N.E. CHEMCAT Co. (*E*)-2-octen-1-ol, (*E*)-2-nonen-1-ol, (*E*)-2-dodecen-1-ol, (*E*)-cinnamyl alcohol, geraniol, (*S*)-(−)-perillyl alcohol, (1*R*)-(−)-myrtenol, K_2CO_3 and $KHCO_3$ were obtained from Tokyo Chemical Industry Co. Ethyl acetate, 3wt%Pt/C, toluene, biphenyl, *n*-hexane, NaOH aq., HCl aq., $Na_2S_2O_3$ and $CDCl_3$ (containing 0.05 wt% of tetramethylsilane (TMS)) were obtained from FUJIFILM Wako Pure Chemical Corporation. The Nafion membrane, Pd black, and Ru black were purchased from Sigma-Aldrich.

Sample analysis

GC analyses were performed on a Shimadzu GC-2014 using an InertCAP 1 column (0.25 mm × 30 m; GL Sciences Inc.). ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVANCE 400 spectrometer at 25 °C. The chemical shifts (δ) were in parts per million (ppm) relative to TMS at 0 ppm for ^1H, and to $CDCl_3$ at 77.0 ppm for ^{13}C. The chemical compositions of the Pt were checked using the ICP-AES (Shimadzu ICPE-9000 spectrometer). XRD patterns were collected using a Rigaku MiniFlex 600 diffractometer equipped with Cu-Kα radiation. All the powder samples were scanned over a 2θ range from 5° to 80° at a rate of 5° min^{-1}. XRD analyses of (111) planes of Pt black before and after the reaction was performed on a Bruker D8 Discover diffractometer, with a Cu microfocus X-ray source ($\lambda = 0.15418$ nm) and a two-dimensional Vantec 500 detector. The measurements were performed in a 2θ range from 30° to 50° with an exposure time of 960 s. The data analysis was performed using the program Diffrac.Eva (Bruker). XPS spectra were recorded on a QuanteraII spectrometer (PHI Co.) equipped with an Al Kα X-ray source (1486.6 eV). Binding energies were referenced to the C 1s peak at 284.3 eV.

Data availability

The data supporting this article have been included as part of the electronic ESI.†

Author contributions

Conceptualization, investigation, and writing, Yo. K.; investigation and formal analysis, Yu. K. and K. M.; supervision, investigation, and writing, K. S.

Conflicts of interest

There are no conflicts to declare.

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