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Pt-Catalyzed selective oxidation of alcohols to aldehydes with hydrogen peroxide using continuous flow reactors†

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The oxidation of alcohols to aldehydes is a powerful reaction pathway for obtaining valuable fine chemicals used in pharmaceuticals and biologically active compounds. Although many oxidants can oxidize alcohols, only a few hydrogen peroxide oxidations can be employed to continuously synthesize aldehydes in high yields using a liquid–liquid two-phase flow reactor, despite the possibility of the application toward a safe and rapid multi-step synthesis. We herein report the continuous flow synthesis of (*E*)-cinnamaldehyde from (*E*)-cinnamyl alcohol in 95%–98% yields with 99% selectivity for over 5 days by the selective oxidation of hydrogen peroxide using a catalyst column in which Pt is dispersed in SiO₂. The active species for the developed selective oxidation is found to be zero-valent Pt(0) from the X-ray photoelectron spectroscopy measurements of the Pt surface before and after the oxidation. Using Pt black diluted with SiO₂ as a catalyst to retain the Pt(0) species with the optimal substrate and H₂O₂ introduction rate not only enhances the catalytic activity but also maintains the activity during the flow reaction. Optimizing the contact time of the substrate with Pt and H₂O₂ using a flow reactor is important to proceed with the selective oxidation to prevent the catalytic H₂O₂ decomposition.

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Introduction

The selective oxidation of alcohols to obtain their corresponding aldehydes is a central issue in the synthesis of various fine chemicals used in pharmaceuticals and biologically active compounds.¹ Many reports exist on the selective oxidation of alcohols using heavy metals containing oxidants and hypervalent iodide oxidants.^{1a,2} These oxidants allow the syntheses of aldehydes in high yields, but their by-products include heavy metals and iodide compounds, which are harmful to the environment.³ Although H₂O₂ is a clean oxidant that forms only water after oxidation, it is less reactive and thus needs an appropriate catalyst to accelerate the oxidation.⁴ Recently, flow reactors have been frequently applied to produce valuable compounds that are useful as pharmaceuticals.⁵ The use of flow reactors for selective H₂O₂ oxidation reactions offers the advantages of not

only application to tandem reactions, but also improvement in the selectivity of aldehyde formation by adjusting the contact time of the substrate with H₂O₂ and catalyst. Many environmentally benign oxidation reactions use flow reactors in the presence of catalysts, with water being the co-product.^{6,7} For example, RuO₂/Mn₃O₄, Au–Pd/TiO₂, Au-doped Fe_nO_m particles, Au–Pd nanoparticles, Ru(OH)_x/Al₂O₃, and biocatalysts in the presence of O₂ and Br[−] with H₂SO₄ and a phase transfer catalyst with polyoxometalates in the presence of H₂O₂ have been reported.⁶ In particular, some of them can also oxidize allylic alcohols to obtain α,β-unsaturated aldehydes.⁷ However, no examples exist on long-term oxidation using a flow reactor for several days in the presence of environmentally friendly oxidants such as O₂ and H₂O₂.^{6,7} Although H₂O₂ offers the advantage of being easier to activate than O₂, its disadvantage is that it is an explosive oxidant.^{6b} Various solid catalysts for selective H₂O₂ oxidation in batch processes have been reported.⁸ We selected Pt black as an excellent candidate for the selective synthesis of α,β-unsaturated aldehydes because the oxidation proceeded significantly fast.⁹ However, mixing Pt and H₂O₂ in a flask results in immediate H₂O₂ decomposition^{9,10} thereby making it difficult to control the contact between Pt and H₂O₂ to achieve selective H₂O₂ oxidation.⁹ Flow synthesis is one of the best choices for controlling the contact time of Pt and H₂O₂

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with substrates by adjusting the flow rate, H_2O_2 concentration, substrate concentration, and reaction temperature.

Herein, we report the continuous selective oxidation of useful alcohols, including aliphatic, benzyl, and allylic alcohols, by a continuous flow method. The optimized reaction conditions using a catalyst in which Pt black was dispersed in SiO_2 (*i.e.*, Pt + SiO_2), in the presence of H_2O_2 , enabled the oxidation of (*E*)-cinnamyl alcohol (**1**) to (*E*)-cinnamaldehyde (**2**) in more than 95% yield with excellent selectivity while retaining high reactivity for over 5 days. The surprisingly well-preserved catalytic activity of Pt during the reaction was studied through substrate screening and oxidation state measurements by X-ray photoelectron spectroscopy (XPS). The appropriate flow rate of the reactants and H_2O_2 to optimize the contact time with the Pt + SiO_2 catalyst maintains zero-valent Pt (Pt(0)) at the Pt black surface, which is crucial for selective H_2O_2 oxidation.

Results and discussion

Screening of catalysts in the Pt-catalyzed H_2O_2 oxidation of (*E*)-cinnamyl alcohol (**1**)

(*E*)-Cinnamyl alcohol (**1**) was selected as a test sample for the selective oxidation of alcohols because it is a less-reactive alcohol having a C=C double bond in its skeleton. Pt black was selected as an oxidation catalyst because it was known to show good catalytic activity among various solid catalysts in the batch processes.^{9a} Because the contact time in the catalytic column is around 2 minutes (min), there is an actual demand for selection of a highly active catalyst to proceed with quick oxidation. On the other hand, Pt has enough redox potential to decompose H_2O_2 . Therefore, the optimization of reaction conditions such as the selection of catalysts, the concentration of reactants and H_2O_2 , and the tuning of the flow rate to tune the contact time and contact order for Pt black, H_2O_2 , and **1** is required.

We screened the mixture of Pt black and metal oxides as catalysts by using a flow reactor equipped with a glass column reactor (length (*L*): 100 mm, inner diameter (ID): 5 mm) packed with a catalyst, two pumps (one for delivering **1** and the other for delivering aq. H_2O_2 to the column reactor), a connecting attachment, and flasks for solution storage, as shown in Fig. 1. Eluent **1** was set to *tert*-amyl alcohol (*t*-amylOH) because the reaction required a tertiary alcohol that would not oxidize and have a high boiling point over 90 °C.

The Pt black catalyst has good chemoselectivity for the oxidation of **1** in a batch process.⁹ However, the simple appli-

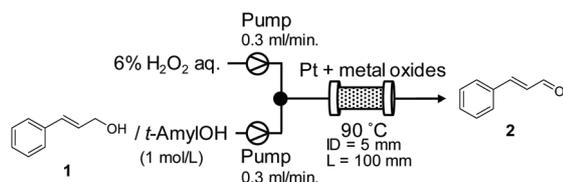


Fig. 1 H_2O_2 oxidation of **1** using a flow reactor.

Table 1 Screening of catalysts regarding the oxidation of **1**

Entry	Catalysts	Time (min.)	Conv. of 1 ^a (%)	Yield of 2 ^a (%)
1	Pt + Al_2O_3	15	13	13
2	Pt + Al_2O_3	30	12	12
3	Pt + Al_2O_3	60	12	12
4	Pt + MgO	15	7	7
5	Pt + MgO	30	6	6
6	Pt + MgO	60	5	5
7	Pt + SiO_2	15	22	22
8	Pt + SiO_2	30	19	19
9	Pt + SiO_2	60	18	18

Reaction conditions: 10 mg of Pt black, 990 mg of metal oxide, 1 mol L^{-1} of **1** in *t*-amylOH solution, 6 wt% aq. H_2O_2 , 90 °C reaction temperature, and 0.3 ml min^{-1} flow rate. Conversions and yields were examined by sampling at 15, 30, and 60 min. ^a Determined by gas chromatography (GC) analysis based on **1**.

cation of the Pt black catalyst itself to a flow reactor column seems to be dangerous because it causes the explosive decomposition of H_2O_2 .^{6b,9} An optimal catalyst was thus required to avoid the explosive decomposition of H_2O_2 and the aggregation of Pt black. Upon using TiO_2 and CeO_2 to dilute Pt black individually, the flow stopped owing to the small particles of TiO_2 and CeO_2 . Al_2O_3 and MgO also did not show good reactivity (Table 1). Al_2O_3 was known to coordinate with Pt because of its low binding energy (BE) toward the O atom in the support, which would affect the oxidation state of Pt.¹¹ MgO worked as a solid base catalyst and facilitated H_2O_2 decomposition. In the case of using a mixture of Pt black and SiO_2 (1 : 99 w/w, *ca.* 1.0 g), a clear improvement in the catalytic activity was observed to obtain (*E*)-cinnamaldehyde (**2**) in up to 22% yield. The TOF value (h^{-1}) of the Pt catalyst was calculated to be 77.¹² We used a mixture of Pt black and SiO_2 for the following flow oxidation reactions.

Optimization of the reaction conditions for the continuous flow oxidation

Optimizing the contact time of the substrate with Pt and H_2O_2 is important to proceed with selective oxidation. The catalyst column packed with 40 mg of Pt and 960 mg of SiO_2 was prepared, and the reaction conditions were optimized by adjusting the reaction temperature, flow rate, and concentrations of **1** and H_2O_2 (Fig. 2 and Tables S1–S4†). The yield of **1** increased upon raising the reaction temperature from 60 °C to 90 °C (Fig. 2a). A reaction temperature over 90 °C is not appropriate for the oxidation, as H_2O_2 decomposition tends to occur at temperatures over 95 °C, and the boiling point of water is 100 °C, at which the generated steam would inhibit the flow of **1** and H_2O_2 . We selected 0.4 mol L^{-1} as the optimal concentration of **1** in *t*-amylOH solution to obtain **2** in 97% yield (Fig. 2b). In the case of using 0.6 mol L^{-1} **1**/*t*-amylOH solution, the conversion of **1** stopped at approximately 80% (Fig. 2b), as the activity of the Pt catalyst was not sufficient to oxidize all the amount of the supplied **1**. However, the overreaction of **1** to form (*E*)-cinnamic acid (**3**) was observed at a 0.2 mol L^{-1} concentration of **1**. The second stage oxidation of **2** to give **3** by

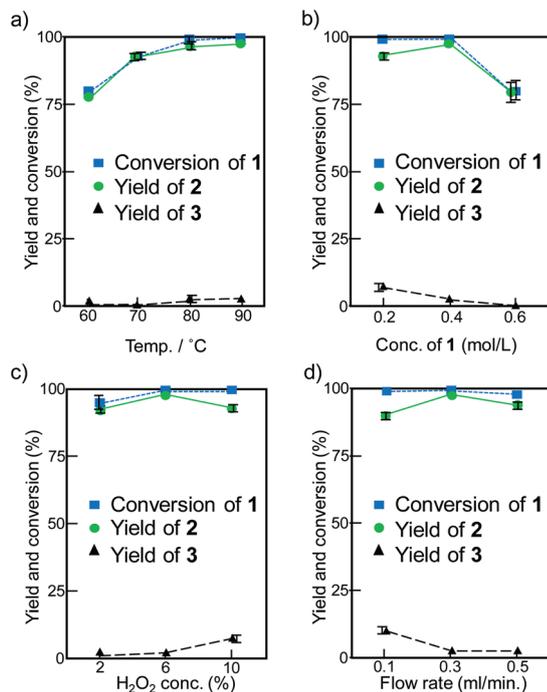


Fig. 2 (a) Reaction temperature optimization. (b) Screening of the concentration of **1**. (c) Screening of the concentrations of aq. H_2O_2 . (d) Flow rate optimization. The base reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO_2 , 0.4 mol L^{-1} **1** in *t*-amylOH solution, 6 wt% aq. H_2O_2 , 90°C reaction temperature, and 0.3 ml min^{-1} flow rate. The conversion and yield were the average of the results at 15, 30, and 60 min reaction times, respectively.

the Pt catalyst began before the ejection of **2** from the column reactor, although the second stage oxidation was difficult to proceed for compounds with the $\text{C}=\text{C}$ double bond, such as **2** (Fig. 2b). Delivering only water in the absence of H_2O_2 did not give **2** at all. The oxidation reaction required H_2O_2 as a terminal oxidant. A higher concentration of H_2O_2 caused the formation of **3** in 8% yield when we used 10% aq. H_2O_2 (Fig. 2c). The concentration of 6% aq. H_2O_2 is sufficient for the oxidation to proceed (Fig. 2c). A flow rate of 0.3 ml L^{-1} was the best when we set the concentration of **1** to 0.4 mol L^{-1} and 6% aq. H_2O_2 at 90°C as reaction conditions, to give **2** in 97% yield (Fig. 2d). The only side product was the corresponding acid **3** with a yield of 2% (Fig. 2d). These results showed the possibility of tuning the reaction that could stop at the first stage oxidation reaction from **1** to **2**, resulting in the achievement of the selective oxidation of **1** using a flow reactor under the optimized conditions.

Next, we checked the correlation between the catalyst amounts and the yields of **2** in the flow oxidation (Fig. 3, Tables S5 and S6[†]). When the reaction conditions were set as 0.4 mol L^{-1} **1** in *t*-amylOH solution, 6 wt% aq. H_2O_2 , 90°C , and a flow rate of 0.3 ml min^{-1} for **1** and H_2O_2 , then 20 mg of Pt black in the catalyst column was not sufficient to complete the oxidation to give **2** in ca. 70% yield (Fig. 3a). However, 60 mg of Pt resulted in overoxidation to give **3** in 6% yield

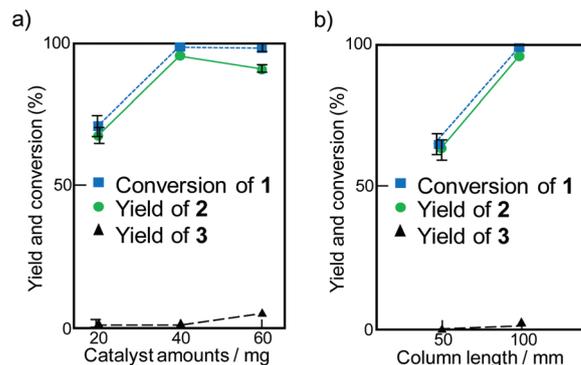


Fig. 3 Pt catalytic activity test. (a) Screening of the catalyst amounts at the $L = 100 \text{ mm}$ column; (b) comparison of the column lengths (50 and 100 mm) using the same Pt + SiO_2 catalyst. The base reaction conditions are as follows: 0.4 mol L^{-1} **1** in *t*-amylOH solution, 6 wt% aq. H_2O_2 , 90°C reaction temperature, and 0.3 ml min^{-1} flow rate. The conversion and yield were the average of the results at 15, 30, and 60 min reaction times, respectively.

(Fig. 3a). Notably, using 40 mg Pt black, the highest yield of **2** under the same reaction conditions was achieved (Fig. 3a). A comparison of conversions of **1** and yields of **2** between the reactions using a 10 cm column (using 40 mg of Pt and 960 mg of SiO_2) and a 50 mm column (using 20 mg of Pt and 480 mg of SiO_2) showed the remaining capacity of the Pt catalytic activity (Fig. 3b). In the case of the 100 mm column, the oxidation completed giving **2** in 97% yield, whereas the 50 mm Pt column achieved approximately 60% conversion (Fig. 3b). The amount of Pt black in the column reactor was related to the yields of **2** because Pt did not give other by-products except for **3**. The reaction conditions might be freely designed to obtain a reaction with a high-yield of over 90% by optimizing the reaction temperature, concentrations of **1** and H_2O_2 , flow rate, and catalyst amounts.

The continuous flow oxidation was performed for over 50 h under the optimized conditions (Fig. 4 and Table S7[†]). A slight

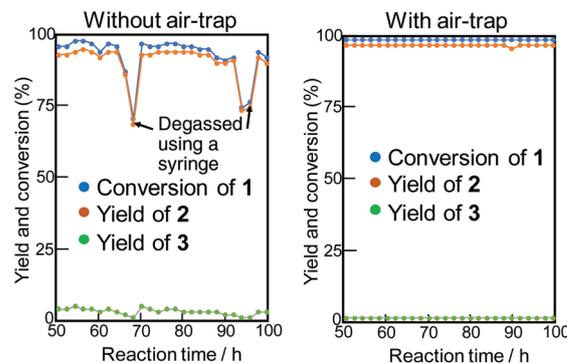


Fig. 4 Effect of the air trap on long-term H_2O_2 oxidation. The reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO_2 , 0.4 mol L^{-1} **1** in *t*-amylOH solution, 6 wt% aq. H_2O_2 , 90°C reaction temperature, and 0.3 ml min^{-1} flow rate. Yields and conversions were determined by GC analysis based on **1**.

decomposition of H₂O₂ in a storage flask occurred over 40 h, and the O₂ generated inhibited the pump delivery. Therefore, a connection of an air-trap system immediately before the pump in the H₂O₂ feeding route was useful for a long-term flow oxidation. Without setting an air trap, the conversion dropped every 24 h owing to the inhibition of H₂O₂ delivery by the O₂ bubbles generated (Fig. 4, left). The reactivity was recovered when we degassed the O₂ bubbles from the route using a syringe (Fig. 4, left). The inhibition of H₂O₂ delivery was countered using an air trap (Fig. 4, right).

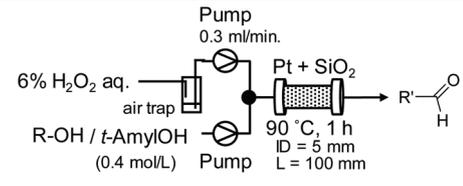
After the connection of the air trap, the oxidation of **1** proceeded well to produce **2** in 95%–98% yields with excellent selectivity for over 120 h (Fig. 5 and Table S8†). The optimized reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO₂, 0.4 mol L⁻¹ **1** in *t*-amylOH solution, 6 wt% aq. H₂O₂, 90 °C reaction temperature, and 0.3 ml min⁻¹ flow rate. The only by-product was **3** in 1% yield.

Application to various alcohols in the Pt-catalyzed selective oxidation using H₂O₂ as an oxidant

The developed flow reaction was applicable to various alcohols, including aliphatic, benzyl, and allylic alcohols (Table 2).

In addition to **2**, other allylic alcohols were also successfully oxidized to give their corresponding aldehydes, *i.e.*, **4–8**, in 83%–95% yields. 2-Methyl- and 3-methyl-substituted allylic alcohols were also oxidized to give their corresponding aldehydes (**4** and **8**) in 92% and 95% yields, respectively. The results suggested that steric hindrance due to the methyl group did not affect the reactivity and that the substrates approached the Pt surface from the direction in which the C=C double bond was parallel to the Pt surface plane. Substituted cinnamyl alcohol and linear allylic alcohols were successfully oxidized to give their corresponding aldehydes (**5**, **6** and **7**) in 91%, 83% and 92% yields, respectively. Benzyl alcohol is easily converted to benzaldehyde (**9**) by the oxidation

Table 2 H₂O₂ oxidation of various alcohols using a flow reactor^a



Entry	Substrates	Products	Yield (%)	Selectivity (%)
1			96 ^b	99 ^c
2			92 ^b	98 ^c
3			91 ^{b,d}	99 ^c
4			83 ^b	95 ^c
5			92 ^b	93 ^c
6			95 ^b	95 ^c
7			91 ^e	93 ^c
			7 ^e	
8			94 ^e	99 ^c
9			55 ^e	99 ^c
10			52 ^e	62 ^c
			31 ^e	

^a Reaction conditions: 40 mg of Pt black, 960 mg of SiO₂, 0.4 mol L⁻¹ alcohol in *t*-amylOH solution, 6 wt% aq. H₂O₂, 90 °C reaction temperature, 1 h, and 0.3 ml min⁻¹ flow rate. ^b Isolated yield. ^c Selectivity = yield/(100 – remaining alcohol yield) × 100 (%). ^d 0.1 mol L⁻¹ alcohol in *t*-amylOH solution. ^e Determined by GC analysis based on alcohol.

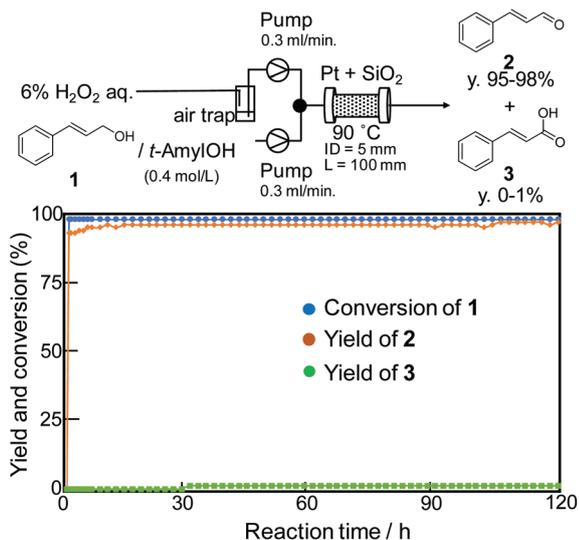


Fig. 5 Oxidation of **1** to **2** for over 120 h.

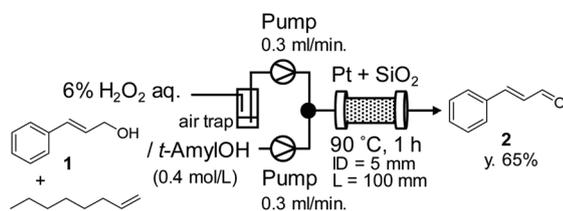
of H₂O₂ because of the easy contact between the Pt black and substrate facilitated by the aromatic ring and its high electrophilicity at the benzyl position. An electrophilic character of *para*-substituted benzyl alcohols in the presence of a Pt black catalyst was reported from the Hammett plot.^{9b} The overoxidation of **9** also occurred to form its corresponding carboxylic acid (**10**) in 7% yield. Substituted benzyl alcohols also reacted with H₂O₂ to give their corresponding aldehydes (**11** and **12**) in 94% and 55% yields, respectively. Aliphatic alcohols, including simple chain-shaped primary alcohols, were also easily oxidized to give their corresponding aldehydes and carboxylic acids. For example, 1-octanol oxidized to give its corres-

ponding aldehyde (**13**) and carboxylic acid (**14**) in 52% and 31% yields, respectively. Nevertheless, under the reaction conditions developed, it was still difficult to inhibit the overoxidation of **13**.¹³ However, no products other than **13** and **14** were produced.

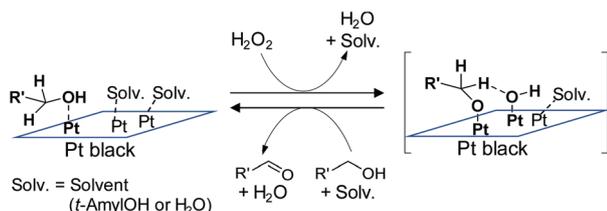
Reaction mechanism of H₂O₂ flow oxidation

From the ICP-AES analysis, Pt black was not detected at all from the solution after the oxidation of **1**. Additionally, the pore size of the filter connected to the column reactor was 2 μm, suggesting that the reaction proceeded on the surface of Pt black, as the size of Pt particles exceeded 2 μm. The reaction mechanism was estimated considering the reactivities of various alcohols and XPS data, in addition to following the previous work on Pt black-catalyzed oxidation in a batch process.⁹ The oxidation of **1** in the presence of 1-octene decreased the yield of **2** from 95% to 65%, thereby confirming the importance of the coordination of **1** toward a Pt active site because the coordination of 1-octene to Pt inhibited the progress of the reaction (Scheme 1 and Table S9†).

We developed the reaction by setting the concentration of aq. H₂O₂ to as low as 6% (Fig. 2c), which could result in the oxidation of **1** before the decomposition of H₂O₂ under the optimized reaction conditions because the reaction did not proceed in the absence of H₂O₂. Considering the results in Fig. 2, Table 2, and Scheme 1 and previous reports, the reaction mechanism was estimated as shown in Scheme 2. Pt black would be covered almost completely by a solvent and substrates, thereby preventing the extra H₂O₂ decomposition due to the contact between Pt black and H₂O₂. Afterward, H₂O₂ addition resulted in the formation of an aldehyde, followed by the coordination of the new alcohol to the Pt surface, which facilitated the desorption of the aldehyde from the Pt surface.



Scheme 1 H₂O₂ flow oxidation of **1** in the presence of 1-octene. The reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO₂, a mixture of each 0.4 mol L⁻¹ **1** and 0.4 mol L⁻¹ 1-octene in *t*-AmylOH solution, 6 wt% aq. H₂O₂, 90 °C reaction temperature, and 0.3 ml min⁻¹ flow rate. Yields and conversions were determined by GC analysis based on **1**.



Scheme 2 Estimated reaction mechanism of H₂O₂ flow oxidation.

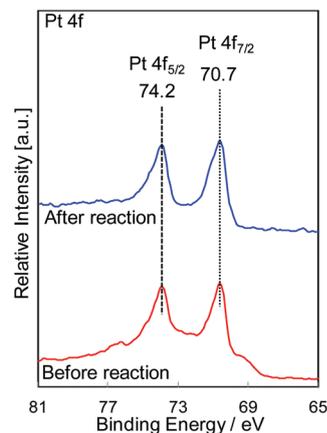


Fig. 6 XPS spectra of Pt black before and after the reaction.

The preservation of Pt(0) during the reaction is the key to the developed flow oxidation. Pt(0) enables the coordination of C=C double bonds, and this coordination prevents the contact of H₂O₂ with the Pt surface to cause the catalytic H₂O₂ decomposition. The surface oxidation state of Pt black in the Pt + SiO₂ column reactor was examined by XPS before and after the reaction (Fig. 6). By referencing to C 1s (284.3 eV), the peaks at 70.7 and 74.2 eV BEs were ascribed to Pt 4f_{7/2} and Pt 4f_{5/2}, respectively. These values of the Pt 4f peaks were close to 70.9 and 74.2 eV, which were assigned to the BEs of the bulk Pt metal, and the observed peaks corresponded to Pt(0).¹⁴ After the reaction, there was no change in the peaks assigned at Pt 4f_{7/2} and Pt 4f_{5/2}, demonstrating the preservation of Pt(0) during the reaction. Additionally, PtO₂, which is a good precursor of platinum black,¹⁵ did not exhibit the reactivity for the oxidation.⁹ The preservation of Pt(0) was thus critical to achieving the high-yield syntheses of aldehydes.

Concerning the quantification of the strength of the Pt-oxide-support interaction, Nagai *et al.* suggested that SiO₂ showed the lowest interaction with Pt in Pt-supported SiO₂, among various metal oxides, including Al₂O₃, ZrO₂, TiO₂, and CeO₂, which are frequently used as support oxides.¹¹ Moreover, Pt-supported Al₂O₃ showed a similar Pt-support interaction strength to that of Pt-supported SiO₂ and thus had the second-lowest BE of the O (1s) electron after Pt-supported SiO₂.¹¹ The slightly less reactivity of Pt + Al₂O₃ than that of Pt + SiO₂ is in good accordance with the order of the Pt-support interaction strength (Table 1). SiO₂ seems to retain Pt(0) during the reaction. The low interaction between Pt and SiO₂ facilitates the access of the C=C double bonds in allylic alcohols toward the Pt(0) surface in the Pt + SiO₂ catalyst, as Pt can freely coordinate with substrates without binding with SiO₂.

Conclusions

A fixed-bed flow reactor equipped with the Pt + SiO₂ catalyst for the selective synthesis of α,β-unsaturated aldehydes was developed. During the oxidation reaction, the contact time of

the substrate with H₂O₂ and Pt was controlled, inhibiting the decomposition of H₂O₂ to utilize selective oxidation. A mixture of Pt black and SiO₂ enabled the preservation of Pt(0) during the catalytic reaction because of the weak interaction between Pt and SiO₂. The oxidation of **1** proceeded selectively to obtain **2** in over 95% yield for 120 h continuously because of the preservation of the Pt(0) species on the Pt black surface in the Pt + SiO₂ catalyst column under the optimized reaction conditions.

The developed continuous flow reaction can be used to oxidize various alcohols, including allylic, benzylic, and aliphatic alcohols, to their corresponding aldehydes. It may be directly utilized for the next reactions, such as amide synthesis and esterification, as tandem reactions because the co-product derived from H₂O₂ is only water.

Experimental

As examples, we herein report some optimized methods. The reaction conditions have been screened by following the procedures reported in the table captions.

H₂O₂ oxidation of (*E*)-cinnamyl alcohol (**1**) by using a continuous flow reactor for over 120 h reaction time (as standard reaction conditions)

SiO₂ (960 mg) and Pt black (40 mg) were mixed and packed in a column reactor (*L* = 100 mm and ID = 5 mm) equipped with double plunger pumps. The first plunger pump was used for passing **1** in *t*-amylOH solution (0.40 M) and the other for passing 6% H₂O₂ aqueous solution. The two lines were combined just before the column reactor by using a connector. Before the reaction began, *t*-amylOH was passed at 25 °C for 10 min to prepare the flow reactor conditions. The reaction was initiated at a 0.3 mL min⁻¹ flow rate for each plunger pump under almost atmospheric pressure (0.4 MPa). The residence time was estimated to be 2.25 min at the column reactor. The column was heated at 90 °C, and the 6 ml reaction solution was corrected every hour to check the product yields by using GC. The sample used for GC was prepared as follows: extraction of the organic phase from the collected sample, followed by dilution using acetonitrile. An air trap was utilized to maintain steady delivery of aq. H₂O₂ to the column reactor.

Synthesis of (*E*)-cinnamaldehyde (**2**) using a continuous flow reactor (isolation experiment under standard reaction conditions)

The flow oxidation reaction was performed under the same conditions as those stated in the previous section. The column reactor was finally rinsed by passing *t*-amylOH (20 mL), and all the solutions that were passed through the catalyst column were collected. After separating the organic phase from the water phase, the product was purified by column chromatography by eluting with *n*-hexane : ethyl acetate (10 : 1 (v/v)). The product (*E*)-cinnamaldehyde (**2**) was obtained after the removal of the eluents as a colorless oil (0.92 g, 96% yield). As confirmed by GC analysis, (*E*)-cinnamic acid (**3**) was also

obtained in 2% yield. The ¹H NMR spectroscopic data of the product were in accordance with the reported NMR data.¹⁶

Other aldehydes **4–9** and **11–13** were also synthesized, and carboxylic acids **10** and **14** were produced by the same methodology.¹⁶

Materials and methods

Pt black was obtained from N.E. CHEMCAT Co. Aluminum oxide (Al₂O₃) was obtained from Nikki Universal Co., Ltd (JCS-ALO-6, a reference catalyst in the Catalysis Society of Japan (CSJ)). Cerium oxide (CeO₂) was obtained from Daiichi Kigenso Kagaku Kogyo Co., Ltd. Titanium oxide (TiO₂) was obtained from Merck Co., Ltd. (*E*)-Cinnamyl alcohol, 2-methyl-3-phenyl-2-propen-1-ol, geraniol, (*E*)-2-octen-1-ol, *n*-dodecane, *tert*-amyl alcohol, 1-octanol, 1-octene, (*E*)-4-nitrocinnamyl alcohol, (*E*)-2-nonen-1-ol, 4-methoxybenzyl alcohol, 4-bromobenzyl alcohol and benzyl alcohol were obtained from the Tokyo Chemical Industry Co., Ltd. Silica (SiO₂, Wakogel C-200), magnesium oxide (MgO), acetonitrile, ethyl acetate, *n*-hexane, and CDCl₃ (containing 0.05 wt% of tetramethylsilane (TMS)) were obtained from FUJIFILM Wako Pure Chemical Industries, Ltd. 35 wt% hydrogen peroxide was obtained from Kanto Chemical Co., Inc.

Sample analysis

GC analyses were performed using a Shimadzu GC-2014 gas chromatograph system equipped with an Inert Cap 1 column (0.25 mm × 30 m, GL Sciences Inc.). The ¹H NMR (400 MHz) spectra were recorded using a JEOL ECX-400P spectrometer at 25 °C. Chemical shifts (δ) were measured in parts per million relative to TMS at 0.00 ppm for ¹H, unless otherwise noted. XPS spectra were recorded using a VG ESCALab 250 spectrometer fitted with an Al Kα X-ray source (1486.6 eV). The elemental analysis of Pt after the reaction was performed using a Shimadzu ICPE-9000 inductively coupled plasma-atomic emission spectrometer (ICP-AES). The BE was based on C 1s (284.3 eV).

Flow reactors

As the apparatus of the flow synthesis system, an LC plunger pump (FLOM, Inc., Intelligent pump UI22-110S for substrates and UI22-110P for aq. H₂O₂), a column reactor oven (TOKYO RIKAKIKAI CO., LTD, Column Flow Reactor MCR-1000 and XCR-1000), and a fraction collector (Advantec Toyo Kaisha, Ltd, fraction collector CHF122SC) were used. An air trap (Nihon Seimitsu Kagaku Co. Ltd, AD-2) was used for delivering degassed aq. H₂O₂. An empty column (SUS316, *L* = 100 mm, ID = 5 mm, and filter pore size = 2 μm) was purchased from TOMOE WORKS CO., LTD.

Conflicts of interest

There are no conflicts to declare.

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