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PAPER

Ethylene oxidation activity of silica-supported platinum catalysts for the preservation of perishables

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The ethylene oxidation activities of silica-supported platinum-based catalysts (Pt/A380 and PtRu/A380) were studied under a semi-practical condition (liter-sized batch system, containing moisture and perishables). Storage tests of premature bananas, cucumbers and apples have proved that the catalyst can remove ethylene generated from the perishables. Ripening of these perishables is significantly delayed by the catalytic removal of ethylene, which confirms that these catalysts are effective for extension of the shelf-lives of the perishables. Two crucial parameters, the rate of ethylene production from the perishables and the rate of ethylene decomposition by the catalysts, were successfully quantified through storage tests of the perishables. The minimum amount of catalyst necessary for practical application in a storage room can be estimated by simple numerical analysis using the determined parameters.

Introduction

Ethylene (C_2H_4) is a gaseous phytohormone that controls various aspects of plant growth, such as germination, ripening of fruit and vegetables (perishables) and abscission of leaves.[1–4] Ethylene is synthesized from amino acids in plants through a pathway with multiple enzymatic reactions and is released to the surrounding environment.[5] Postharvest spoilage of perishables is often ascribed to ethylene in storage containers or rooms. Even a trace amount of ethylene accelerates the aging and ripening of perishables.[6] Continuous removal of ethylene is thus a key technology to extend shelf-life and minimize the postharvest loss of perishables.

Various types of ethylene scavengers, including oxidants,[7–10] adsorbents [11–20] and solid catalysts,[21–29] have been reported and are commercially available. For example, potassium permanganate ($KMnO_4$) is one ethylene scavenger due to its nature as a powerful oxidant. This scavenger oxidizes gaseous ethylene into carbon dioxide in a stoichiometric reaction,[21] and it requires replacement when it is consumed and thus loses its oxidation activity.

Ethylene can also be removed through the use of adsorbents such as zeolites[11–16] and activated carbons.[17–20] These materials possess high volumes of micropores where ethylene molecules can be stored through physical adsorption. These adsorbents are also inexpensive and readily available. However, the adsorbents are not able to continuously remove ethylene because their adsorption capacity is limited to a certain level (saturation capacity). Once the uptake of ethylene reaches the saturation capacity, the adsorbents must be replaced or regenerated by heating or vacuum treatment.

The use of solid catalysts is an effective approach to remove ethylene. Such catalysts oxidize ethylene to carbon dioxide through the reaction shown in Equation 1.[21] This reaction can continuously proceed over these catalysts without loss of performance, unlike adsorbents and oxidants. This is an advantage of using solid catalysts because replacement and regeneration are not necessary. Several solid catalysts, such as Au/Co_3O_4,[22,23] $Pt/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{0.19}/\gamma\text{-}Al_2O_3$,[24] copper manganese oxide,[25] Pt/MnO_2 nanosheets,[26] Ag/zeolite,[27] Pt/cerium-doped TiO_2[28] and WO_3[29] are active for the aerobic oxidation reaction of ethylene. However, none of the catalysts previously reported satisfy the following two requirements for the preservation of perishables. One is the oxidation of ethylene at low temperatures around the freezing point. Perishables are generally stored at such low temperatures to delay the growth of microorganisms.[30] Another requirement is high conversion of ethylene to completely remove trace amounts of ethylene.

$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O \qquad (1)$$

The mesoporous silica-supported platinum catalyst is promising for the preservation of perishables. This catalyst can oxidize and remove trace amounts of ethylene (50 ppm) with extremely high conversion (ca. 100%) at low temperature (0 °C).[31] It has been experimentally and theoretically shown that the metal-support interaction between platinum and mesoporous silica is a key to the high performance for ethylene oxidation.[32,33] The catalyst partially loses its activity during the

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reaction due to the physisorption of water formed as a byproduct. This loss of activity can be minimized by employing hydrophobic SBA-15 (mesoporous silica) as a support,[34] which has led to an improved conversion of ethylene and yield of carbon dioxide. A more cost-effective amorphous silica, Aerosil 380 (abbreviated as A380), is also found to be a good catalytic support for the aerobic oxidation of ethylene,[35] and the Pt/A380 catalyst has shown performance comparable to Pt/SBA-15. Such results have paved the way for the mass production of such catalysts, which has resulted in the commercialization of refrigerator units loaded with the catalysts by Hitachi Global Life Solutions, Inc.[36] Considering the production cost of these catalysts, we have decided to use A380 as the silica support in this work.

The catalyst has the potential to be used in food storage rooms due to its excellent catalytic performance. One of our major issues is optimization of the catalyst amount. However, the optimum amount of catalyst is not readily predictable from previous data measured by using a laboratory-scaled flow reactor. This is because the reaction conditions (reactor type, size and presence/absence of moisture and perishables) of laboratory and storage room are greatly different. In this work, we studied catalytic performance under conditions close to those for the storage room. Estimation of the optimal amount of catalyst requires two parameters. One is the rate of ethylene production from each perishable (r). Another is the rate of ethylene decomposition by the catalyst (R). The parameter r is classified in the literature into five categories (very low, low, moderate, high and very high).[30] Recently the parameter r of various types of perishables has also been reported and available.[37] On the other hand, the parameter R is not available and should be measured in batch reaction system. Because the parameter R is not available, it has been difficult to precisely estimate the minimum amount of catalyst to keep the ethylene concentration lower than the threshold (0.1 ppm), where perishables begin to ripen.[21] In this work, storage tests of perishables were conducted with and without the catalyst to determine these two parameters. The amount of catalyst required in the food storage room was then estimated by a simple numerical analysis using the two parameters.

Experimental

Materials

Silica-supported catalysts (1 wt% Pt/A380 (Pt/A380) and 0.5 wt% Pt 1.0 wt% Ru/A380 (PtRu/A380)) were purchased from Nikki-Universal Co., Ltd. The catalysts were dried at 150 °C in an oven for 3 h prior to use. Apples, cucumbers and bananas were purchased at a local supermarket in Sapporo. Premature bananas were provided by Secoma Co., Ltd.

Measurement of ethylene production and ethylene decomposition rates

An apple (0.21 kg), a cucumber (0.10 kg), a premature banana (0.20 kg) and a banana (0.15 kg) were used for this measurement. The perishable item was placed in a vacuum desiccator with a volume of 10.5 L (Sibata Scientific Technology Ltd.) or in an acrylic box with a volume of 33.0 L (AS ONE Co., Ltd.) together with granular Pt/A380 (7.0 g) or PtRu/A380 (10 g). The acrylic box was used only for storage test of banana (Figures S1 and S2). Except for this storage test, the desiccator with a volume of 10.5 L was used. For the storage test with the cucumber at 25 °C, silica gel (Tokai gel A-type 5UP, Tokai Chemical Industry Co., Ltd., 200 g) was also introduced in the desiccator to adjust the humidity. For the storage test with the cucumbers at 10 °C, three pieces of cucumbers were stored in the desiccator. The desiccator was placed in a testing chamber kept at a constant temperature and stored for 2-27 days. The storage temperature of premature banana was set to be 13 °C, because chilling injury to damage banana occurs at lower temperature around the freezing point.[38] This also occurs in the case of cucumbers.[37] The concentrations of ethylene and carbon dioxide were measured with a gas analyzer (F-950, Felix Instruments). Storage tests without catalyst were also conducted to investigate the effect of the catalyst. Storage test of premature banana at 13 °C (Figures 1 and 2) was conducted in dark condition. This is because the premature banana generally stored in dark condition in large storage rooms.

Using the data obtained from the storage tests, the rate of ethylene production from each perishable (r) and the rate of ethylene decomposition by the catalyst (R) was quantified. The parameter r [$\mu L_{C2H4}\ h^{-1}\ kg_{per}^{-1}$], which is the rate of ethylene production of the perishable stored without the catalyst, is determined as follows: $r = G_p/m_p$, where G_p [$\mu L_{C2H4}\ h^{-1}$] is the rate of ethylene production per unit time and m_p [kg_{per}] is the mass of the perishable. G_p is the slope of time course for ethylene concentration during the storage tests without catalyst. Similarly, from the tests with catalysts, G_p' [$\mu L_{C2H4}\ h^{-1}$] was obtained and r' [$\mu L_{C2H4}\ h^{-1}\ kg_{per}^{-1}$] was calculated from $r' = G_p'/m_p$. The parameter R [$\mu L_{C2H4}\ h^{-1}\ kg_{cat}^{-1}$], was determined using Equation 2 where m_c [kg_{cat}] denotes the mass of the catalyst.

$$R = \frac{m_p\,(r - r')}{m_c} \qquad (2)$$

Evaluation of degree of ripening for a premature banana

The sugar content and mechanical strength of the premature banana were evaluated to quantify the degree of ripening. The banana was cut into ca. 2 cm long cylindrical samples. The samples were crushed in a mortar and the paste obtained was mounted on a handheld refractometer (PAL-1, Atago Co., Ltd.) to measure the sugar content. The mechanical strength was measured using a digital force gauge (FGP-5, Nidec-Shimpo Corporation) equipped with a cylindrical aluminum probe (2.0 cm diameter). Compressive force was exerted onto the top surface of the sample, as shown in Figure S3. The fracture strength is defined as the compressive force when the displacement of the probe reaches 1.5 cm. The mechanical strength was calculated by dividing the fracture strength by the surface area of the probe (3.14 cm^2).

Test reaction using ethylene gas to measure ethylene oxidation activity of the catalysts

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A reaction using standard ethylene gas was performed in a batch reactor under ambient pressure (Figures S4 and S5). Here we call this experiment as "test reaction." Granular Pt/A380 (7.0 g) was placed on a petri dish that was placed on a mesh-plate in the vacuum desiccator (10.5 L). A magnetic stirring bar was placed at the bottom of the desiccator. Pure ethylene gas (5.25 mL, equivalent to 50 ppm) was charged to a gas tight syringe (1001RN, GL Sciences Inc.) from an ethylene gas cylinder (4.5 L, GL Sciences Inc.), and the gas was then injected into the desiccator. The gaseous contents in the desiccator were mixed by the magnetic stirring bar at a rotational speed of 1,000 rpm. The concentration of ethylene in the desiccator was measured by the gas analyzer. We conducted a blank control experiment without catalysts and perishables (Figure S5, open triangles). The concentration of ethylene only slightly decreased by the adsorption on the desiccator, and thus this adsorption has almost no effect.

Results and discussion

Storage tests of perishables

Storage tests of premature bananas were conducted at 13 °C. A premature banana stored without the catalyst (Pt/A380) produced a negligible amount of ethylene at the initial stage of the storage test (from day 0 to day 10) as shown in Figure 1. Ethylene then emerged and its concentration increased almost linearly with time. When a premature banana was stored with Pt/A380, the concentration of ethylene was less than the detection limit of the sensor (<0.15 ppm) throughout the test. Figure 2 shows photographs of the premature bananas during the storage test. Without the catalyst, the green-colored banana turned yellow within day 14-21. Ethylene generated from banana induces chlorophyll loss in plants, which results in the color change.[5,6]

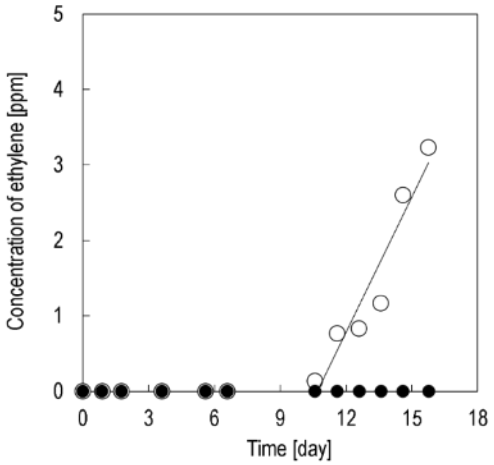


Figure 1. Time course for the ethylene concentration during storage tests of premature banana stored with Pt/A380 (closed circles) and without any catalysts (open circles) at 13 °C. The solid line shows a linear fitting in a range of day 10-15 used to calculate the parameter *r*. Reaction conditions: catalyst Pt/A380 7.0 g, premature banana 0.20 kg, initial relative humidity 50%, desiccator 10.5 L.

On the other hand, the premature banana stored with Pt/A380 remained green, even after 27 days. This result clearly shows that the catalytic removal of ethylene is effective to delay the ripening of bananas.

Using the data in Figure 1, the rate of ethylene production from premature banana (*r*) and the rate of ethylene decomposition by the catalyst (*R*) were calculated. As summarized in Table 1, *r* was 0.76 $\mu L_{C2H4}\ h^{-1}\ kg_{per}^{-1}$, which is slightly lower than values previously reported (1.0-10.0 $\mu L_{C2H4}\ h^{-1}\ kg_{per}^{-1}$).[30] *R* was also calculated to be 51 $\mu L_{C2H4}\ h^{-1}\ kg_{cat}^{-1}$.

In the test reaction using ethylene gas (Figure S5), 14 ppm of ethylene (50-36 ppm) is removed by 7.0 g of Pt/A380 through adsorption in initial one day. Based on this data, adsorption capacity *q* is estimated to be 21 $mL_{C2H4}\ kg_{cat}^{-1}$ at ethylene concentration *C* of 36 ppm. Hypothesizing that *q* is proportional to *C* (Henry's isotherm), the Henry adsorption constant *k* is 0.58 $mL_{C2H4}\ kg_{cat}^{-1}\ ppm^{-1}$ ($q = kC$, Figure S5 footnote). In Figure 1, ethylene concentration of "with catalyst" case was less than the detection limit of the sensor (0.15 ppm) throughout the test.

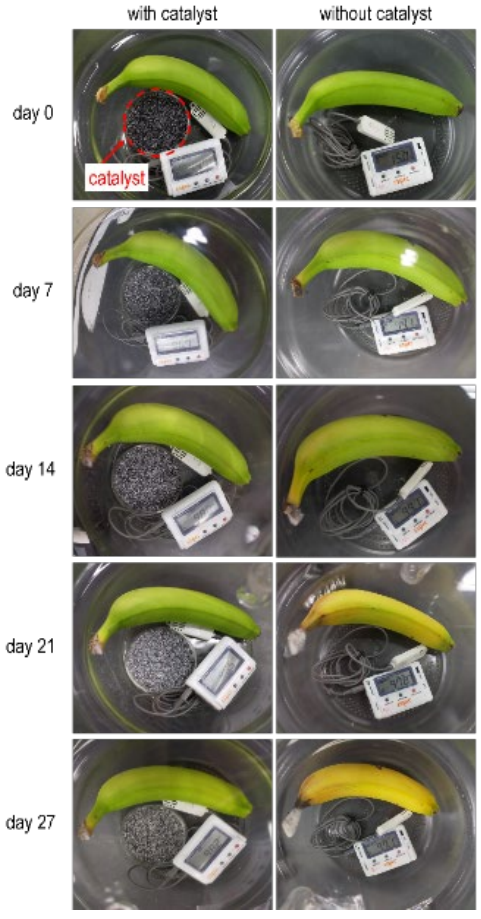


Figure 2. Photographs of premature bananas stored with Pt/A380 (left column) and without any catalysts (right column) at 13 °C. Reaction conditions: catalyst Pt/A380 7.0 g, premature banana 0.20 kg, initial relative humidity 50%, desiccator 10.5 L.

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Table 1. Rates of ethylene production from perishables *r* and *r'*, and rate of ethylene decomposition by Pt/A380 catalyst *R*.

Type of perishables	Storage temperature [°C]	Mass of the perishable m_p [kg_{per}]	r^a [μL_{C2H4} h^{-1} kg_{per}^{-1}]	r'^b [μL_{C2H4} h^{-1} kg_{per}^{-1}]	R^c [μL_{C2H4} h^{-1} kg_{cat}^{-1}]
Premature banana	13	0.20	0.76	0	51
Premature banana	22	0.20	3.3	0	94
Cucumber	25	0.10	0.70	0.15	7.9
Apple	25	0.21	290	150	3,900

a) $r = G_p$ [μL_{C2H4} h^{-1}]/m_p [kg_{per}] without catalyst. See Experimental.
b) $r' = G_p'$ [μL_{C2H4} h^{-1}]/m_p [kg_{per}] with catalyst.
c) $R = m_p(r - r')/m_c$, where m_c [kg_{cat}] is the mass of Pt/A380 catalyst.

It is possible that small amount of ethylene (<0.15 ppm) is produced from the premature banana before day 10 in Figure 1 (induction period). This value is close to the threshold concentration whether the ripening of the perishable proceeds or not (0.1 ppm). Thus, the ripening effects by ethylene concentration in the induction period is limited or negligible. Ethylene production rate is accelerated by the internal content of ethylene, which is synthesized and resides in the perishable body. In the storage test of the premature banana, this factor seems to trigger the abrupt increase in ethylene production rate after day 10.

In the test reaction (Figure S5), 30 ppm of ethylene was removed by Pt/A380 in 12 days. The apparent ethylene decomposition rate was 2.5 ppm/day. On the other hand, in the storage test (Figure 1), 3.5 ppm of ethylene was removed by Pt/A380 in six days (from day 10 to day 16). The apparent ethylene decomposition rate was 0.58 ppm/day, which is approximately one-fourth of that of the test reaction (Figure S5). This decrease is ascribed to higher relative humidity in the storage test. Relative humidity was 100%RH in this storage test, while that was 30-50%RH in the test reaction. This causes significant decrease in the apparent removal rate.

The sugar content and mechanical strength also represent the degree of ripening of fruits. As ripening proceeds, sugars are synthesized in the fruit and the sugar content increases.[39] Post-harvested premature bananas soften and their mechanical strength decreases.[40] Table 2 summarizes the results of sugar content and mechanical strength measurements for premature bananas. The sugar content of the premature banana increased from 5.2 Brix% to 20.1 Brix% without the catalyst, but with the catalyst it increased to only 12.5 Brix%. The mechanical strength of the premature banana decreased from >2.5 kgf cm^{-2} to 0.73 kgf cm^{-2} without the catalyst, but with the catalyst it decreased to 2.0 kgf cm^{-2}. These results show that removal of ethylene by the catalyst positively affects the quality of premature bananas.

The respiration rate of the bananas was estimated from the time course for carbon dioxide concentration during the storage tests (Figure S6). Without the catalyst, the respiration rate was 12 mg_{CO2} kg_{per}^{-1} h^{-1} during the first 10 days and then increased to 33 mg_{CO2} kg_{per}^{-1} h^{-1}, which is higher than the value reported in the literature (23.6 mg_{CO2} kg_{per}^{-1} h^{-1} at 15 °C).[39] When the premature banana was stored with the catalyst, the respiration rate was 12 mg_{CO2} kg_{per}^{-1} h^{-1} throughout the test, which is almost equivalent to that of a banana stored at 5 °C (10.0 mg_{CO2} kg_{per}^{-1} h^{-1}).[39] Catalytic removal of ethylene can reduce the respiration rate to a significantly low level without a decrease in the storage temperature. The parameters *r* and *R* for the storage test at higher temperature (22 °C) can also be obtained. As summarized in Table 1, *r* and *R* were calculated to be 3.3 μL_{C2H4} h^{-1} kg_{per}^{-1} and 94 μL_{C2H4} h^{-1} kg_{cat}^{-1}, respectively. Time course for ethylene concentration and photograph of premature banana during the test are shown in Figures S7 and S8.

A storage test of three cucumbers was conducted at 10 °C. In this case, no detectable ethylene was emerged (Figure S9). To observe the effect of the catalyst, we raised the temperature to 25 °C to induce ethylene production by the cucumbers. Figure 3 shows the time course for the ethylene concentration from cucumbers at 25 °C. Ethylene was generated at a rate of 0.66 μL_{C2H4} h^{-1} kg_{per}^{-1}. The concentration of ethylene reached 2 ppm in 12 days. The catalyst could remove ethylene down to 0.3 ppm with a decomposition rate of 7.9 μL_{C2H4} h^{-1} kg_{cat}^{-1}. This ethylene removal affected the appearance of the cucumbers. Figure 4

Table 2. Sugar content and mechanical strength of premature bananas.

Time stored [day]	Sugar content[a] [Brix%]	Mechanical strength[b] [kgf cm^{-2}]
0	5.2	>2.5
27 (stored without any catalysts)	20.1	0.73
27 (stored with Pt/A380)	12.5	2.0

a) Sugar content of paste of bananas measured by a handheld refractometer
b) Mechanical strength is calculated by dividing the fracture strength by the surface area of the probe (3.14 cm^2). The fracture strength is defined as the compressive force when displacement of the probe reaches 1.5 cm.

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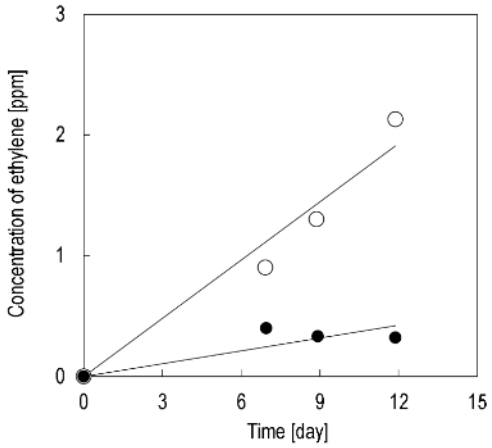


Figure 3. Time course for the ethylene concentration during the storage tests of cucumbers stored with Pt/A380 (closed circles) and without any catalysts (open circles) at 25 °C. The solid lines show the fittings in the range of day 0-12 to calculate r and r'. Reaction conditions: catalyst Pt/A380 7.0 g, cucumber 0.10 kg, desiccator 10.5 L.

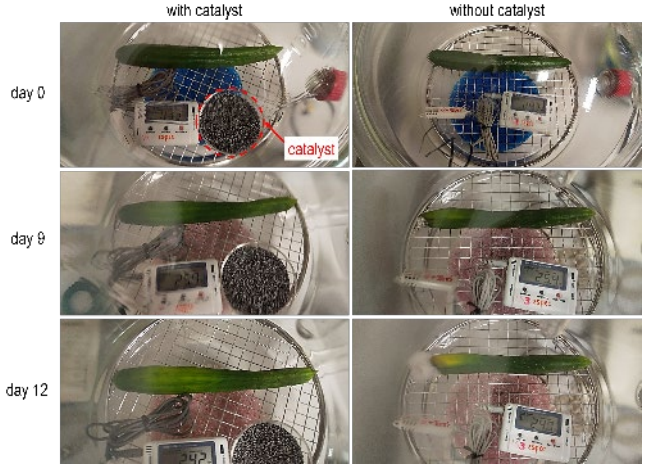


Figure 4. Photographs of cucumbers stored with Pt/A380 (left column) and without any catalysts (right column) at 25 °C. Reaction conditions: catalyst Pt/A380 7.0 g, cucumber 0.10 kg, desiccator 10.5 L.

shows photographs of the cucumber. Without the catalyst, the cucumber turned yellow within day 9-12. This is the typical symptom when cucumbers are affected by ethylene. The growth of mold was also observed on the surface of the cucumber. In contrast, a cucumber stored with the catalyst remained green and no mold was observed on its surface. The ripening of cucumbers could also be delayed by the catalyst.

Similarly, storage tests of apples were conducted at 25 °C. Without the catalyst, the ethylene concentration reached up to 200 ppm, which is almost the upper limit of detection of the sensor. This value could be decreased to 100 ppm with the catalyst (Figure S10). The rates r and R for this storage test are shown in Table 1.

Estimation of ethylene concentration from cucumbers in a large storage room

In practical application, optimization of the catalyst amount is a crucial factor in the introduction of a catalytic system. Here we conducted an analysis of the minimum amount of catalyst that was necessary to keep the quality of cucumbers in a storage room. The minimum amount of catalyst to keep the ethylene concentration in a large storage room lower than 0.1 ppm was calculated using a simple numerical analysis. The mass balance equation for ethylene in the storage room (Equation 3) was derived from the following four terms: the rate of ethylene accumulation in the storage room, the volumetric flow rate of ethylene released from the room by ventilation (denoted as F), the rate of ethylene production from the cucumbers (containing r), and the rate of ethylene decomposition by the catalyst (containing R). The ethylene concentration and total volume of the storage room are denoted as $C(t)$ and V, respectively. The derivation of Equation 3 is shown in the Supporting Information. Several ethylene concentration profiles were calculated for various amounts of the catalysts. This calculation was conducted using a discretized equation (Equation S2) with a time span Δt of 24 h. The duration of the storage test was set to 30 days.

$$V\frac{dC(t)}{dt} = rm_{\mathrm{p}} - FC(t) - Rm_{c} \qquad (3)$$

The concentration of ethylene was calculated using Equation 3, provided that the volume of the storage room was 1,800 m^3 and that 5,000 kg of cucumbers with a unit ethylene production rate of 0.70 $\mu L_{\ C2H4}\ h^{-1}\ kg_{per}^{-1}$ were stored. The observed rate is independent of ethylene concentration. In the storage test of banana at 22 °C, ethylene concentration profiles of both “with catalyst” case and “without catalyst” case are shown in Figure S1. From Figure S1, the amount of ethylene decomposed by catalyst was linearly increased with time (Figure S2). This means the decomposition rate is constant and independent of ethylene concentration. This is because water (moisture) and intermediates generated from perishables are adsorbed on the active sites of the catalyst and the total number of active sites is decreasing during the storage test. Because of this effect, the apparent reaction rate seems like zeroth order. In the storage test of cucumber, the apparent reaction rate also seems like zeroth order and the parameter R is assumed to be constant. This is because both of the plots of “with catalyst” case and “without catalyst” case can be fitted with a linear equation (Figure 3). In this section, the goal was to determine the amount of catalyst required to achieve an ethylene concentration less than 0.1 ppm, which is the threshold whether the ripening of the perishables proceeds or not.[21] The concentration of ethylene increased up to approximately 1.0 ppm in 30 days without the catalyst (Figure 5). The introduction of 0.1 kg of catalyst could slightly reduce the concentration to 0.9 ppm. An increase in the amount of catalyst up to 0.5 kg was effective to further reduce ethylene. However, the concentration was still higher than the threshold.

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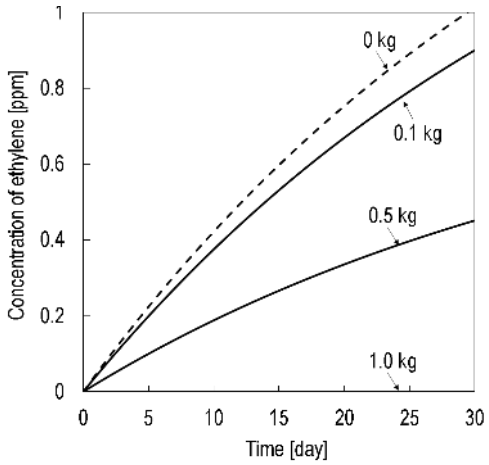


Figure 5. Estimation of time course for the ethylene concentration in a storage room using Equation 3. Conditions: catalyst Pt/A380 0-1.0 kg, cucumber 5,000 kg (unit ethylene production rate of 0.70 μL $_{C2H4}$ h^{-1} kg_{per}^{-1}), storage room 1,800 m^3.

The concentration remained less than the threshold throughout the 30 day-storage test by the introduction of 1.0 kg of catalyst. This demonstrates that the optimum amount of catalyst can be determined using a simple numerical analysis and several parameters.

Conclusions

Silica-supported platinum catalysts have been used for the preservation of perishables. Storage tests of three different perishables (premature banana, cucumber and apple) were conducted to quantify the ethylene production rates and the ethylene decomposition rate by the catalyst. The catalyst could successfully remove ethylene produced from the perishables. In addition, the catalytic removal of ethylene positively affected the respiratory behavior, appearance and quality of the perishables. The minimum amount of the catalyst necessary for practical application in a storage room was estimated by a simple numerical analysis and the determined parameters.

An ethylene removal system that uses this catalyst can be readily introduced into a large-scale storage room by simply placing a filter-like module filled with the catalyst onto built-in air-conditioning fans. This advantage will be useful as a cost-effective food preservation technique. This work focused on optimization of the amount of catalyst to guarantee the ethylene removal effect. Beside the amount of catalyst, there are several other factors that may affect the performance of the catalytic system, such as the location of the catalytic modules and air-flow patterns in the storage rooms.

Author contributions

T. M.: conceptualisation, investigation, formal analysis, data curation, visualisation, methodology, and writing – original draft. T. S.: investigation and methodology. T. N.: investigation and methodology. Y. O.: investigation, formal analysis, and data curation. K. N.: investigation, formal analysis, data curation, methodology, and writing – review and editing. A. F.: conceptualisation, funding acquisition, methodology, supervision, validation, resources, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 R. Gane, *Nature*, 1934, **134**, 1008.
2 L. Alexander and D. Grierson, *J. Exp. Bot.*, 2002, **53**, 2039–2055.
3 N. Iqbal, N. A. Khan, A. Ferrante, A. Trivellini, A. Francini and M. I. R. Khan, *Front. Plant Sci.*, 2017, **8**, 1–19.
4 I. I. Vaseva, E. Qudeimat, T. Potuschak, Y. Du, P. Genschik, F. Vandenbussche and D. Van Der Straeten, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, E4130–E4139.
5 S. F. Yang and N. E. Hoffman, *Annu. Rev. Plant Physiol.*, 1984, **35**, 155–189.
6 M. E. Saltveit, *Postharvest Biol. Technol.*, 1999, **15**, 279–292.
7 F. R. Forsyth, C. A. Eaves and C. L. Lockhart, *Can. J. Plant Sci.*, 1967, **47**, 717–718.
8 P. M. Harrison, M. Henry and J. Wendland, *J. Phys. IV Fr. 125*, 2005, **125**, 869.
9 K. Syamsu, E. Warsiki, S. Yuliani and S. M. Widayanti, *Int. J. Sci. Basic Appl. Res.*, 2016, **30**, 93–103.
10 A. G. Sanches, M. B. da Silva, E. G. S. Moreira, E. X. dos Santos, K. R. P. Menezes and C. A. M. Cordeiro, *Emirates J. Food Agric.*, 2019, **31**, 605–612.
11 N. Y. Chen, *J. Phys. Chem.*, 1976, **80**, 60–64.
12 N. A. Al-Baghli and K. F. Loughlin, *J. Chem. Eng. Data*, 2005, **50**, 843–848.
13 S. I. Kim, T. Aida and H. Niiyama, *Sep. Purif. Technol.*, 2005, **45**, 174–182.
14 G. Peiser, T. V Suslow and V. Crops, *Perishables Handl. Q.*, 2008, **95**, 17–19.
15 L. Cisneros, F. Gao and A. Corma, *Microporous Mesoporous Mater.*, 2019, **283**, 25–30.
16 N. J. Abreu, H. Valdés, C. A. Zaror, F. Azzolina-Jury and M. F. Meléndrez, *Microporous Mesoporous Mater.*, 2019, **274**, 138–148.

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17 K. Abe and A. E. Watada, *J. Food Sci.*, 1991, **56**, 1589–1592.
18 Z.-X. Liu, J.-N. Park, S. H. R. Abdi, S.-K. Park, Y.-K. Park and C. W. Lee, *Top. Catal.*, 2006, **39**, 221–226.
19 G. Bailen, F. Guillen, S. Castillo, P. J. Zapata, M. Serrano, D. Valero and D. Martínez-Romero, *Spanish J. Agric. Res.*, 2007, **5**, 579–586.
20 X. Ma and F. Ouyang, *Appl. Surf. Sci.*, 2013, **268**, 566–570.
21 N. Keller, M. N. Ducamp, D. Robert and V. Keller, *Chem. Rev.*, 2013, **113**, 5029–5070.
22 J. Li, C. Ma, X. Xu, J. Yu, Z. Hao and S. Qiao, *Environ. Sci. Technol.*, 2008, **42**, 8947–8951.
23 W. J. Xue, Y. F. Wang, P. Li, Z. T. Liu, Z. P. Hao and C. Y. Ma, *Catal. Commun.*, 2011, **12**, 1265–1268.
24 N. Imanaka, T. Masui, A. Terada and H. Imadzu, *Chem. Lett.*, 2008, **37**, 42–43.
25 E. C. Njagi, H. C. Genuino, C. K. King'Ondu, S. Dharmarathna and S. L. Suib, *Appl. Catal. A Gen.*, 2012, **421**–**422**, 154–160.
26 M. Wang, L. Zhang, W. Huang, Y. Zhou, H. Zhao, J. Lv, J. Tian, X. Kan and J. Shi, *RSC Adv.*, 2017, **7**, 14809–14815.
27 H. Yang, C. Ma, X. Zhang, Y. Li, J. Cheng and Z. Hao, *ACS Catal.*, 2018, **8**, 1248–1258.
28 H. Guo, P. Warnicke, M. Griffa, U. Müller, Z. Chen, R. Schaeublin, Z. Zhang and M. Luković, *ACS Nano*, 2019, **13**, 14337.
29 Y. Wicaksana, S. Liu, J. Scott and R. Amal, *Molecules*, 2014, **19**, 17747–17762.
30 V. K. Mishra and T. V. Gamage, *Handbook of Food Preservation*, CRC Press, New York, 2nd edn., 2007.
31 C. Jiang, K. Hara and A. Fukuoka, *Angew. Chemie - Int. Ed.*, 2013, **52**, 6265–6268.
32 S. S. Satter, J. Hirayama, H. Kobayashi, K. Nakajima and A. Fukuoka, *ACS Catal.*, 2020, **10**, 13257–13268.
33 R. Miyazaki, N. Nakatani, S. V. Levchenko, T. Yokoya, K. Nakajima, K. Hara, A. Fukuoka and J. Y. Hasegawa, *J. Phys. Chem. C*, 2019, **123**, 12706–12715.
34 S. S. Satter, J. Hirayama, K. Nakajima and A. Fukuoka, *Chem. Lett.*, 2018, **47**, 1000–1002.
35 S. S. Satter, T. Yokoya, J. Hirayama, K. Nakajima and A. Fukuoka, *ACS Sustain. Chem. Eng.*, 2018, **6**, 11480–11486.
36 https://www.hitachi.com.au/products/product-categories/home-appliances/refrigerator/made-in-japan/RZX740KA.html, (accessed 12 February 2021).
37 https://postharvest.ucdavis.edu/Commodity_Resources/Fact_Sheets/, (accessed 12 February 2021).
38 H. Gemma, Y. Matsuyama and H.-G. Wang, *Japanese J. Trop. Agric.*, 1994, **38**, 216.
39 R. Gane, *NEW Phytol.*, 1936, **XXXV**, 383–402.
40 M. Soltani, R. Alimardani and M. Omid, *J. Am. Sci.*, 2011, **7**, 1545–1003.

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