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"Release and catch" catalysis by tungstate species for the oxidative cleavage of olefins†

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Abstract

The oxidative cleavage of olefins produces valuable carbonyl compounds, and thus, the development of green catalytic methods using H_2O_2 in the role of oxidant is highly desired. In this work, we have successfully developed an efficient catalytic system for the oxidative cleavage of olefins and related compounds using H_2O_2. In the presence of tungstate species supported on zinc-modified tin dioxide (W/Zn–SnO_2), the oxidative cleavage of 1-methyl-1-cyclohexene proceeds efficiently through multistep reaction pathways involving oxygenation, hydrolysis, perhydrolysis, and isomerization reactions. In this reaction system, active peroxotungstate species, generated by the reaction of the supported tungstate species with H_2O_2, are released into solution during the course of the reaction. At the end of the reaction (after the complete consumption of H_2O_2), the released tungstate species are re-captured by the support. The W/Zn–SnO_2 catalyst can be reused at least nine times for the oxidative cleavage of 1-methyl-1-cyclohexene without loss in catalytic performance and can be applied to the oxidation of various other substrate molecules.

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† Electronic Supplementary Information (ESI) available: Data of products, Figs. S1–S10 and Tables S1–S7. See DOI: 10.1039/x0xx00000x

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Introduction

The oxidation reactions of simple organic compounds into functionalized products, such as alcohols, phenols, epoxides, and carbonyl compounds, are of significant importance because these oxy-functionalized products are very useful in the production of commodity and specialty chemicals.[1] The oxidative cleavage of olefins generates valuable carbonyl compounds, such as ketones, aldehydes, and carboxylic acids.[2] One typical method for olefin cleavage is ozonolysis, which is a conventional industrial process that uses ozone in the role of oxidant.[3] Other typical methods include processes that use transition metal-based stoichiometric oxidants (e.g., potassium permanganate and chromyl chloride) or transition metal catalysts (e.g., osmium tetroxide and ruthenium chloride) with suitable co-oxidants (e.g., sodium periodate and oxone).[4] However, these dated methods have several drawbacks, including the use of hazardous and expensive reagents and the formation of by-products derived from these oxidants. Therefore, the development of new and efficient catalytic methods using greener oxidants is highly desired.

In recent years, various liquid-phase oxidations using H_2O_2 as the terminal oxidant have attracted significant attention because H_2O_2 is considered to be a green oxidant since it is much safer and less expensive than peroxides and peracids, it has a high content of active oxygen species (47 wt%), and it theoretically generates water as the sole by-product.[5] To date, catalytic systems for the H_2O_2-based oxidative cleavage of olefins using various transition-metal catalysts, including W, Mo, V, Ti, Ru, Re, Cr, and Fe, have been reported.[6–8] Among them, tungsten-based catalytic systems have been widely developed.[6,7] For example, Noyori and co-workers demonstrated the oxidative cleavage of various cyclic olefins in the presence of a catalytic amount of $Na_2WO_4{\cdot}2H_2O$ and a quaternary ammonium salt.[6a] Furthermore, H_2WO_4,[6b,c] polyoxotungstate species,[6d–g] and peroxotungstate species[6h–k] have also been reported as efficient homogeneous catalysts for the oxidative cleavage of olefins. The use of heterogeneous catalysts for liquid-phase reactions is more desirable owing to their facile separation and reusability.[9] Although several tungsten-based "heterogeneous" catalytic systems for oxidative olefin cleavage have been reported,[7] most of these systems experience leaching of the active tungstate species and/or their severe deactivation in repeat catalyst reuse experiments. In addition, in most cases, no reliable experimental evidence is presented as to whether the observed catalysis was truly heterogeneous and based on the supported tungstate species or originated from leached tungstate species.

Herein, we report an efficient catalytic system for the oxidative cleavage of olefins and related compounds using H_2O_2 as the oxidant and tungstate species supported on zinc-modified tin dioxide (W/Zn–SnO_2) as the catalyst. On the basis of the evidences from several control experiments, we discovered that the active peroxotungstate species formed by the reaction of the supported tungstate species with H_2O_2 were released into solution during the course of the reaction and were re-captured onto the support at the end of the reaction (after the complete consumption of H_2O_2). The W/Zn–SnO_2 catalyst could be reused at least nine times without any appreciable loss in performance and could be used to oxidize various substrate molecules. This "release and catch" catalytic system combines the advantages of both homogeneous and heterogeneous catalyses.

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Results and discussion

Detailed investigation into the WO_3-catalyzed oxidative olefin cleavage

Initially, we investigated the WO_3-catalyzed oxidative cleavage of olefins using H_2O_2 as the oxidant since WO_3 is easily available and frequently utilized as the heterogeneous catalyst for various oxidation reactions.[7b–d,10] The results for the WO_3-catalyzed oxidative cleavage of 1-methyl-1-cyclohexene (**1a**) with 30% aqueous H_2O_2 (5 equivalents with respect to **1a**) are summarized in Table 1. The reaction using WO_3 under the present conditions effectively produced the desired cleavage product 6-oxoheptanoic acid (**2a**) in 92% yield after 24 h (Table 1, entry 2), and the H_2O_2 oxidant was completely consumed in the course of the reaction. The reaction did not proceed at all in the absence of either WO_3 or H_2O_2 (Table 1, entries 4 and 5). For the WO_3-catalyzed reaction, the insoluble species were removed by hot filtration after 4 h (33% yield of **2a**; Table 1, entry 1), and the reaction was conducted with the filtrate under the same conditions. In this case, the reaction did not stop, and **2a** was produced in 90% yield after a total time of 24 h (Table 1, entry 3). In addition, it was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis that 24% of the tungsten species had leached into the reaction solution after 4 h. Therefore, it is possible that the soluble tungstate species that are generated during the reaction act as the truly active "homogeneous" catalytic species in the oxidative olefin cleavage under the present conditions.

In order to clarify the nature of the active species, the following control experiments were conducted. WO_3 was reacted with H_2O_2 (without **1a**) under the conditions described in Table 1 (Fig. 1a). After 1 h, the unreacted insoluble WO_3 was removed by hot filtration, yielding a colorless transparent filtrate (Fig. 1b). Cold-spray ionization (CSI) mass analysis (negative-ion mode) of the filtrate indicated signals assignable to various peroxotungstate species, such as $[HWO_2(O_2)_2]^-$ (m/z = 280.9), $[H_3WO_4(O_2)]^-$ (m/z = 282.9), $[HWO(O_2)_3]^-$ (m/z = 296.9), $[H_3WO_3(O_2)_2]^-$ (m/z = 298.9), $[H_5WO_5(O_2)]^-$ (m/z = 300.9), $[HW_2O_3(O_2)_4]^-$ (m/z = 544.9), $[W_2O_2(O_2)_4O^tBu]^-$ (m/z = 600.9), $[HW_3O_4(O_2)_6]^-$ (m/z = 808.8), and $[HW_4O_5(O_2)_8]^-$ (m/z = 1072.7) (Figs. 2 and S1, ESI†). The addition of **1a** to the peroxotungstate-containing filtrate, followed by stirring of the resultant solution at 80 °C for 24 h, produced **2a** in 86% yield. At this point, the solution was transparent and still contained some H_2O_2. After 72 h, the H_2O_2 was completely consumed, and a white precipitate appeared as shown in Fig. 1c. The precipitate was collected by filtration and analyzed by ICP-AES and Raman spectroscopy. The tungsten content in the precipitate was approximately 72 wt%. The Raman spectrum of the precipitate exhibited characteristic bands at 962 cm^{-1} and 815 cm^{-1} assignable to the ν(W=O) and ν(W–O–W) vibrations, respectively (Fig. S2, ESI†).[11] These results suggest that the precipitate contained polytungstate species.

On the basis of the above-mentioned experimental results, it is most likely that dissolved peroxotungstate species are the catalytically active species in this reaction. During the catalytic reaction, a significant amount of tungstate species leached into the solution, specifically 24% of the tungsten species had leached into the reaction solution after 4 h. (Table 1, entry 1). Once the H_2O_2 had been consumed, the amount of the leached tungsten species decreased significantly; however, a non-negligible amount of tungstate species (7%) remained in the solution (Table 1, entry 2). The CSI-mass spectrum of the filtrate of the solution after the reaction for entry 2 presented a signal assignable to hexatungstate, $[HW_6O_{19}]^-$ (m/z = 1408.6) (Fig. S3, ESI†); thus the remained species are relatively small anionic polytungstate species.

We propose that the WO_3-catalyzed oxidative cleavage of **1a** proceeds through the following mechanism

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(Fig. 3). Initially, various peroxotungstate species are formed by the reaction of WO_3 with H_2O_2 and leached into solution (Step 1: Release). The reaction of **1a** with the leached peroxotungstate species yields the corresponding cleavage product and tungstate species (Step 2: Reaction). The tungstate species are reacted with H_2O_2 to regenerate the active peroxotungstate species (Step 3: Regeneration). After the H_2O_2 is consumed, majority of the dissolved tungstate species become insoluble polytungstate species (Step 4: Catch). Such a system is known as a "release and catch" (or "boomerang") catalytic system.[12] In "release and catch" systems, the high reusability of a catalyst can be achieved through the re-immobilization of most of the released active species onto suitable supports at the end of the reaction. In the case of WO_3-catalyzed oxidative cleavage of **1a** with H_2O_2, a non-negligible amount of soluble tungsten species still remained in the reaction solution even after the complete consumption of H_2O_2. In addition, a significant decrease in the product yield was observed when WO_3 was reused.[13]

Use of supported tungstate catalysts

We prepared two kinds of supported tungstate catalysts using SnO_2 and SiO_2 and the impregnation method (referred to as W/support, see the Experimental section).[14] The XRD pattern of W/SnO_2 had the same signals as that of the parent SnO_2 (Figs. S4a and b, ESI†). The XRD pattern of W/SiO_2 exhibited weak and broad signals assignable to monoclinic WO_3 in addition to the SiO_2 signals (Figs. S4c and d, ESI†). Raman spectra of the catalysts indicated bands assignable to the tungstate species in addition to those of the supports; the broad bands at 960–980 cm^{-1} are assignable to the ν(W=O) vibrations of polytungstate species, and the bands around 807 cm^{-1}, 710 cm^{-1}, and 272 cm^{-1} are characteristic of WO_3 vibrations (Fig. S5, ESI†).[11] These results indicate that non-crystalline polytungstate species and small crystals of WO_3 are probably supported on the surface of these catalysts.

Next, these two catalysts were utilized in the oxidative cleavage of **1a** with H_2O_2 (Table 2). We confirmed that the desired **2a** was not produced in the presence of just SnO_2 or SiO_2 under the current conditions (Table 2, entries 3 and 4). After 24 h, W/SnO_2 and W/SiO_2 produced **2a** in 64% and 63% yields, respectively (Table 2, entries 1 and 2). In the case of W/SiO_2, most of the leached tungsten species remained dissolved in the reaction solution even at the end of the reaction (Table 2, entry 2). On the other hand, when W/SnO_2 was used, the amount of leached tungsten species significantly decreased, and most of the dissolved tungsten species were re-immobilized onto the surface of the support at the end of the reaction (Table 2, entry 1). This discrepancy likely arises from the difference in the point of zero charge (pzc) values of SnO_2 and SiO_2, which are reported to be 6–7 and approximately 2, respectively.[15] Thus, the surface of SiO_2 is more negatively charged than the SnO_2 surface. The negatively charged dissolved tungstate species are less repelled by the SnO_2 surface compared with the SiO_2 surface, thereby facilitating re-immobilization onto the SnO_2 surface.

Oxidative olefin cleavage using W/Zn–SnO_2

To further improve the catalytic performance of the supported tungstate catalyst, we focused on our previous report that indicated that the catalytic performance of a supported polyoxotungstate catalyst for various kinds of H_2O_2-based oxidation reactions, such as epoxidation, sulfoxidation, and *N*-oxidation, was improved by modification of the SnO_2 support with zinc species.[16] Therefore, we prepared a tungstate catalyst supported on zinc-modified tin dioxide (W/Zn–SnO_2, see the Experimental section).[16] The XRD pattern of the W/Zn–SnO_2

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catalyst showed the same signals as SnO_2 (Fig. S6, ESI†). A Raman spectrum of the W/Zn–SnO_2 catalyst presented bands assignable to tungstate species and to SnO_2; the broad bands at 960–980 cm^{-1} are assignable to the ν(W=O) vibrations of polytungstate species, and the bands at 807 cm^{-1}, 710 cm^{-1}, and 272 cm^{-1} are characteristic of WO_3 vibrations (Fig. S7, ESI†).[11] These results indicate that non-crystalline polytungstate species and small crystals of WO_3 are supported on the surface.

Fig. 4a shows the reaction profile for the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** under the same reaction conditions described in Table 2.[17] The yield of **2a** after 24 h was 92%, which was higher than that obtained when W/SnO_2 was used (64%, Table 2, entry 1). The amount of released tungsten species increased soon after the reaction began, reaching a maximum value (14% of total tungsten species) after 2 h, and then decreased as the reaction progressed, becoming negligible (<1%) at the reaction time of 24 h (after the complete consumption of H_2O_2). The leaching of other metal species (Zn and Sn) was negligible throughout the course of the reaction. In order to confirm the reaction mechanism, W/Zn–SnO_2 was stirred under the reaction conditions described in Fig. 4 (without **1a**) for 1 h and removed by hot filtration, in a manner identical to the experiment performed with WO_3. The CSI-mass analysis of the filtrate indicated the presence in the reaction solution of virtually the same peroxotungstate species as those formed by the reaction of WO_3 with H_2O_2 (Fig. S1, ESI†). The addition of **1a** to the filtrate, followed by stirring of the resultant solution at 80 °C for 24 h, produced **2a** in 89% yield. These results clearly indicate that the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** using H_2O_2 also proceeds through a “release and catch” catalytic mechanism and that most of the leached tungstate species are re-immobilized on the surface of the catalyst at the end of the reaction.

Next, we examined the reusability and the durability of W/Zn–SnO_2 for the oxidative cleavage of **1a**. After the reaction, the W/Zn–SnO_2 catalyst was recovered by hot filtration, washed with acetone, dried in open air, and reused in a subsequent reaction. In this manner, W/Zn–SnO_2 could be reused at least nine times without a significant decrease in catalytic performance (Fig. 5a, 89–93% yields of **2a**).[13] The XRD and the Raman spectra of the nine-times reused W/Zn–SnO_2 were in good agreement with the spectra of the freshly prepared W/Zn–SnO_2 catalyst (Figs. 5b and c). These results indicated no significant structural changes in W/Zn–SnO_2 even after the nine reuses.

It has been reported that the oxidative cleavage of olefins using H_2O_2 proceeds through several multistep reaction pathways, which include various types of oxidation and hydrolysis reactions.[6a,7a] In order to determine the reaction pathways active in the present W/Zn–SnO_2 catalytic system, the time course of the intermediates was traced as well as **1a** and **2a**. Fig. 4b presents the yields of the observed intermediates by GC analysis, 1-methyl-1,2-epoxycyclohexane (**3a**), 1-methyl-1,2-cyclohexanediol (**4a**), 6-oxoheptanal (**5a**), and 2-methylcyclohexanone (**6a**), which were produced in the oxidative cleavage of **1a**; the major intermediates were **4a** and **5a**. When the oxidation of **3a** was carried out, almost the same reaction profile as described in Fig. 4 was observed (Fig. S8, ESI†), indicating that **3a** is the initial intermediate in this reaction system and converted into subsequent intermediates immediately. The most widely accepted reaction pathway for the H_2O_2-based oxidative cleavage of olefins proposed by Noyori and co-workers[6a] includes epoxidation, epoxide hydrolysis to 1,2-diols, and oxidation of 1,2-diols, followed by Baeyer–Villiger oxidation (Path A in Fig 6). In the present W/Zn–SnO_2 catalytic system, the corresponding 1,2-diol **4a** was one of the major intermediates. When the reaction of **4a** was conducted,

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2a was selectively produced in 91% yield after 24 h (Fig. S9, ESI†). Therefore, we consider that the present oxidative cleavage possibly proceeds through Path A in Fig. 6 although the intermediates produced through this reaction pathway were hardly detected. In addition, **5a** was not detected in the oxidation of **4a** (Fig. S9, ESI†). Venturello and co-workers proposed another reaction pathway, namely perhydrolytic pathway (Path B in Fig 6).[6i] In Path B, the perhydrolysis of epoxides produces β-hydroperoxy alcohols, which are converted into the desired cleavage products through decomposition to carbonyl compounds (like **5a**) and/or oxidation to α-oxo hydroperoxides.[6i] In the present W/Zn–SnO_2-catalyzed oxidative cleavage of **1a**, **5a** was also the major intermediate. Thus, Path B should also be considered. In addition to the intermediates in Path A (**4a**) and Path B (**5a**), a small amount of **6a** was also observed in the oxidation reactions of **1a** and **3a** (Figs. 4b and S8, ESI†). On the basis of the Lewis acid or Brønsted acid-catalyzed isomerization of epoxides into ketones,[18] we attribute the formation of **6a** to the isomerization of **3a**. The oxidation of **6a** proceeded to produce **2a** in 35% yield after 24 h, and 7-methyl-2-oxepanone (**7a**) was also detected at the initial stage of the reaction (Fig. S10, ESI†). Thus. the oxidation of **6a** into **2a** most likely proceeded through Path C as described in Fig. 6, which comprises Baeyer–Villiger oxidation, hydrolysis, and alcohol oxidation, as has been reported elsewhere.[19] On the basis of the aforementioned experimental results, we propose that the present W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** using H_2O_2 as the oxidant proceeds through three parallel pathways described in Fig. 6; the initial intermediate is the epoxide **3a**, which is subsequently converted into the 1,2-diol **4a** through hydrolysis, the β-hydroperoxy alcohols through perhydrolysis, and the ketone **6a** through isomerization. Many steps in Fig. 6 are facilitated by the acidic reaction conditions, and the acidic natures of the dissolved peroxotungstate species, which were detected by CSI-mass spectroscopy (Fig. S1, ESI†), and the Zn–SnO_2 support are likely critical to the reaction.[20]

Finally, we turn our attention to the examination of the substrate scope for the current W/Zn–SnO_2-catalyzed oxidative cleavage reaction. The oxidative cleavage of different substrate molecules was conducted under the optimized reaction conditions in the presence of W/Zn–SnO_2, and the results are summarized in Fig. 7. A variety of cyclic and linear olefins (**1a**–**1f**) were cleaved to give their corresponding carbonyl compounds (**2a**–**2f**) in moderate to high yields (Fig. 7, entries 1–6). In addition to olefins, the reaction of phenylacetylene (**1g**) produced benzoic acid (**2c**) in a moderate yield (Fig. 7, entry 7). Acenes, such as naphthalene (**1h**) and anthracene (**1i**), were converted into phthalic acid (**2h**) and 2,3-naphthalenedicarboxylic acid (**2i**), respectively, and quinones were also produced in these cases (Fig. 7, entries 8 and 9). In most cases, however, the total yields of the observed products were somewhat lower than the substrate conversions likely owing to several intermediates and/or by-products that could not be detected by GC and/or HPLC analyses.

Conclusion

We began the current work with a detailed investigation of the WO_3-catalyzed oxidative cleavage of **1a** using H_2O_2 as the oxidant. The detailed CSI-mass analysis revealed that various kinds of peroxotungstate species formed by the reaction of WO_3 with H_2O_2 leached into solution during reaction and became insoluble at the end of the reaction. Thus, it was determined that the present catalytic system can be categorized as “release and catch.” On the basis of our results, we developed a supported tungstate catalyst, W/Zn–SnO_2, that efficiently catalyzed the oxidative

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cleavage of olefins using H_2O_2 through a "release and catch" catalytic mechanism. This W/Zn–SnO_2 catalyst could be reused at least nine times without an appreciable decline in catalytic performance and was successfully applied to the oxidation of various substrate molecules. Thus, we developed W/Zn–SnO_2 and applied it as a highly promising (pseudo)heterogeneous catalyst for the oxidative cleavage of olefins and related compounds using H_2O_2.

Experimental Section

Materials

Solvents and substrates were obtained from Kanto Chemical or TCI and purified prior to use if necessary.[21] H_2O_2 (30% aqueous solution, Kanto Chemical), WO_3 (Junsei Chemical), $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$ (Wako), $Zn(NO_3)_2\cdot 6H_2O$ (Wako), $CDCl_3$ (Acros Organics), and $Ce(NH_4)_4(SO_4)_4\cdot 2H_2O$ (Wako) were used as received. SnO_2 (Guaranteed Reagent, >98%, Kanto Chemical, BET surface area: 45 $m^2\ g^{-1}$), SiO_2 (CARiACT Q-10, Fuji Silysia Chemical, BET surface area: 274 $m^2\ g^{-1}$), γ-Al_2O_3 (KHS-24, Sumitomo Chemical, BET surface area: 160 $m^2\ g^{-1}$), TiO_2 (ST-01, Ishihara Sangyo, BET surface area: 308 $m^2\ g^{-1}$), ZrO_2 (RC-100, Daiichi Kigenso Kagaku Kogyo, BET surface area: 89 $m^2\ g^{-1}$), ZnO (Wako, BET surface are: 37 $m^2\ g^{-1}$), and MgO (NO-0012-HP, Ionic Liquids Technologies, BET surface area: 36 $m^2\ g^{-1}$) were commercially available. These oxides were pretreated by calcination in air at 400 °C for 3 h.

Instruments

GC measurements were performed on a Shimadzu GC-2014 gas chromatograph equipped with a flame ionization detector (FID) and an InertCap FFAP capillary column (internal diameter = 0.25 mm and length = 30 m) or an InertCap 5 capillary column (internal diameter = 0.25 mm and length = 30 m). GC-MS spectra were recorded on a Shimadzu GCMS-QP2010 equipped with an InertCap 5 capillary column at an ionization voltage of 70 eV. HPLC analyses were performed on a Shimadzu Prominence system using a UV detector (Shimadzu SPD-20A, 254 nm) equipped with an Inertsil ODS-3 column (internal diameter = 4.6 mm and length = 250 mm) using a mixed solvent of MeOH/H_2O (9/1 v/v) as an eluent. ICP-AES analyses were performed on a Shimadzu ICPS-8100 spectrometer. Raman spectra were measured on a JASCO NRS-5100 spectrometer using a 532 nm laser. XRD patterns were recorded using a Rigaku SmartLab instrument under Cu Kα radiation (λ = 1.5418 Å, 45 kV, 200 mA). CSI mass spectra (in CH_3CN) were recorded on a JEOL JMS-T100CS spectrometer. Typical measurement conditions were as follows: orifice voltage of −10 V for negative ions, sample flow of 0.1 mL min^{-1}, spray temperature of −10 °C, and ion source at room temperature. Liquid-state ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA 500. ^1H and ^{13}C NMR spectra were measured at 500 MHz and 125 MHz, respectively, using tetramethylsilane as an internal standard (δ = 0 ppm). BET surface areas were measured by N_2 adsorption at −196 °C using a Micromeritics ASAP 2010 instrument.

Preparation of tungstate supported catalysts

W/Zn–SnO_2 catalyst was prepared according to the following procedure.[16] An aqueous solution (50 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (120.8 mg) containing SnO_2 (2.5 g) was stirred vigorously for 1 h at room temperature. The solution was evaporated to dryness, and the resulting solid was calcined in air for 2 h at 300 °C, yielding Zn–SnO_2 (Zn: 1.0 wt%). Next, an aqueous solution (30 mL) of $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$ (143.0 mg) containing Zn–SnO_2 (1.0 g) was stirred vigorously for 1 h at room temperature. The solution was evaporated to dryness, and the resulting solid was calcined for 3 h at 400 °C to give W/Zn–SnO_2. The tungsten and zinc contents were 9.1 wt% and 0.9 wt%, respectively. The other supported tungstate catalysts on SnO_2 (W/SnO_2) and SiO_2 (W/SiO_2) were prepared in the same manner. The tungsten content was 9.1 wt% in both W/SnO_2 and W/SiO_2.

Catalytic reaction

A typical procedure for the oxidative cleavage of olefins proceeded as follows: **1** (0.5 mmol), W/Zn–SnO_2 (100 mg, W: 10 mol% with respect to **1**), and ^{t}BuOH or CH_3CN (1.5 mL) were charged to a glass reactor with a Teflon-coated magnetic stir bar. The reaction was initiated by the addition of 30% aqueous H_2O_2 (2.5 mmol), followed by stirring at 80 °C for 24 h. The conversions and product yields were determined by GC or HPLC analysis using *o*-dichlorobenzene, naphthalene, or biphenyl as an internal standard. The products were identified by the comparison of their GC or HPLC retention times and/or GC-MS spectra with those of pure samples (ESI†). The complete consumption of H_2O_2 was confirmed using a test paper for H_2O_2 detection (QUANTOFIX Peroxide 100, Macherey-Nagel). After the reaction, the used catalyst was retrieved by hot filtration, washed with acetone, and dried under open air at room temperature. The recovered catalyst was reused, and the quantity of leached metal species in the filtrate was determined by ICP-AES analysis. As for the isolation of **2a**, the filtrate was concentrated by evaporation, and the crude product was subjected to column chromatography on silica gel using acetone/chloroform as an eluent to give pure **2a** in 82% isolated yield. The purity of **2a** was confirmed by ^{1}H and ^{13}C NMR analysis (ESI†).

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13 Under the conditions described in Table 1, the WO_3-catalyzed oxidative cleavage of **1a** produced **2a** in 92% yield after 24 h (Table 1, entry 2). When WO_3 was reused under the same reaction conditions, the yield of **2a** decreased to 63%. In the previously reported WO_3-catalyzed oxidative cleavage of cyclohexene, a deactivation of WO_3 is also observed.[7b]

14 To use supported catalysts along with H_2O_2, the non-productive decomposition of H_2O_2 induced by supports should be avoided. The decomposition of H_2O_2 in the presence of various supports, such as SnO_2, SiO_2, Al_2O_3, ZrO_2, TiO_2, ZnO, and MgO, was examined (Table S1, ESI†). While the decomposition was significantly promoted by Al_2O_3, ZrO_2, TiO_2, ZnO, and MgO under the current conditions, the reaction barely proceeded when SnO_2 and SiO_2 were used, indicating that these two supports are suitable for the oxidation with H_2O_2.

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17 The reaction conditions and the loading amounts of tungsten and zinc species were optimized from the

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perspective of the yield of **2a** and the amount of tungsten leaching (Tables S2–S6, ESI†).

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20 The amounts of **6a** formation during the W/SnO_2-catalyzed reaction of **1a** were larger than those during the W/Zn–SnO_2-catalyzed reaction (Table S7, ESI†). The formation of **6a** is undesirable because the conversion of **6a** into **2a** (Path C) is somewhat slower than Path A and Path B (Fig. S10, ESI†). One possible role of zinc-modification is to reduce the formation of **6a**. During the W/SnO_2-catalyzed reaction of **1a**, significant amounts of *tert*-butyl hydroperoxide (TBHP) were formed by the reaction of *tert*-butyl alcohol (solvent) and H_2O_2. We confirmed that the oxidation of **1a**, **3a**, and **4a** into **2a** did not proceed at all when using TBHP instead of H_2O_2. Thus, the TBHP formation is a non-productive reaction in the present system, which lowers the efficiency of H_2O_2 utilization. Notably, the TBHP formation was much suppressed by utilizing the zinc-modified SuO_2 support (Table S7, ESI†). This is also an important role of the zinc-modification.

21 *Purification of Laboratory Chemicals 5th ed.*, ed. W. L. F. Armarego and C. L. L. Chai, Butterworth-Heinemann, Oxford, 2003.

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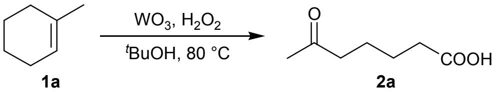
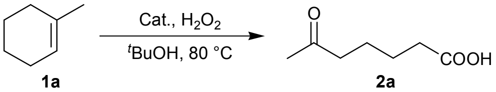
Table 1 Oxidative cleavage of **1a** into **2a** using WO_3 and H_2O_2[a]



Entry	Time (h)	Yield (%)	Tungsten leaching (%)
1	4	33	24
2	24	92	7
3[b]	4 + 20	90	–
4[c]	24	nd	nd
5[d]	24	nd	–

[a] Reaction conditions: **1a** (0.5 mmol), WO_3 (10 mol% with respect to **1a**), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis. [b] The insoluble species were removed from the reaction mixture by hot filtration after 4 h, and the reaction was carried out with the filtrate for further 20 h (a total time of 24 h). [c] Without H_2O_2. [d] Without WO_3. nd = not detected.

Table 2 Oxidative cleavage of **1a** into **2a** using supported tungstate catalysts[a]



Entry	Cat.	Yield (%)	Tungsten leaching (%)
1	W/SnO_2	64	<1
2	W/SiO_2	63	53
3	SnO_2	<1	–
4	SiO_2	<1	–

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (100 mg), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C, 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

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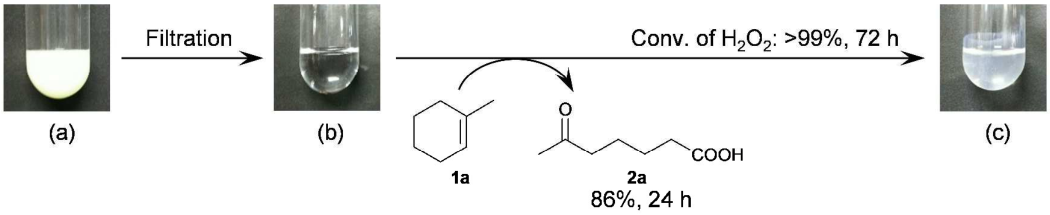

Fig. 1 Pictures of (a) the suspension containing ^{t}BuOH (1.5 mL), WO_3 (50 µmol), and 30% aqueous H_2O_2 (2.5 mmol), (b) the filtrate after the removal of insoluble species by hot filtration, and (c) the suspension obtained after the reaction of **1a** at 80 °C for 72 h.

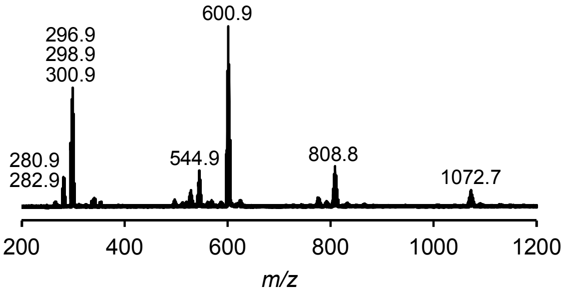

Fig. 2 CSI-mass spectrum (negative-ion mode) of the filtrate shown in Fig. 1b. The signals at *m/z* 280.9, 282.9, 296.9, 298.9, 300.9, 544.9, 600.9, 808.8, and 1072.7 were assignable to $[HWO_2(O_2)_2]^-$, $[H_3WO_4(O_2)]^-$, $[HWO(O_2)_3]^-$, $[H_3WO_3(O_2)_2]^-$, $[H_5WO_5(O_2)]^-$, $[HW_2O_3(O_2)_4]^-$, $[W_2O_2(O_2)_4O^tBu]^-$, $[HW_3O_4(O_2)_6]^-$, and $[HW_4O_5(O_2)_8]^-$, respectively. The magnified views are shown in Fig. S1, ESI†.

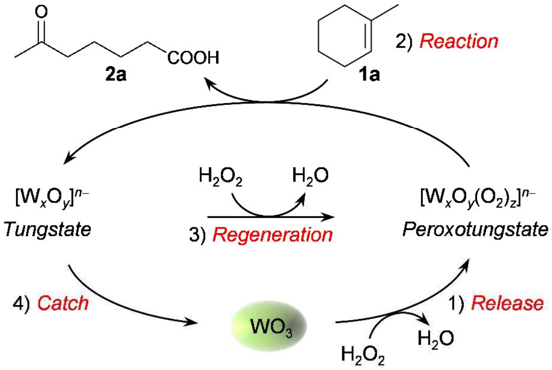

Fig. 3 Possible reaction mechanism for the WO_3-catalyzed oxidative cleavage of **1a**.

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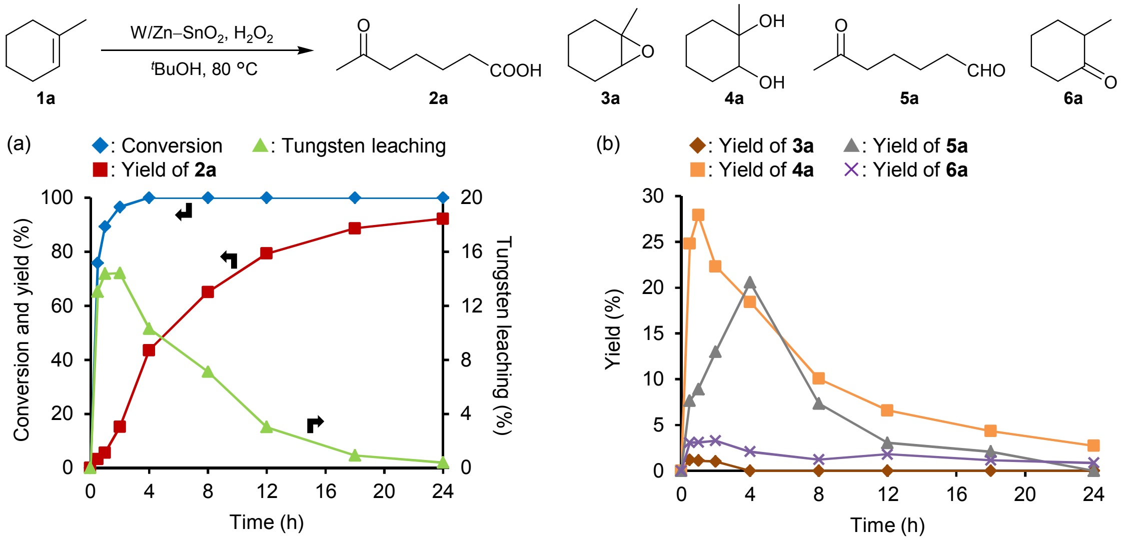

Fig. 4 Reaction profile for the W/Zn–SnO$_2$-catalyzed oxidative cleavage of **1a** into **2a** using H$_2$O$_2$ as the oxidant. (a) Conversion, yield of **2a**, and tungsten leaching. (b) Yields of **3a**, **4a**, **5a**, and **6a**. Reaction conditions: **1a** (0.5 mmol), W/Zn–SnO$_2$ (100 mg, W: 10 mol% with respect to **1a**), 30% aqueous H$_2$O$_2$ (2.5 mmol), ^{t}BuOH (1.5 mL), and 80 °C. Conversions and yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

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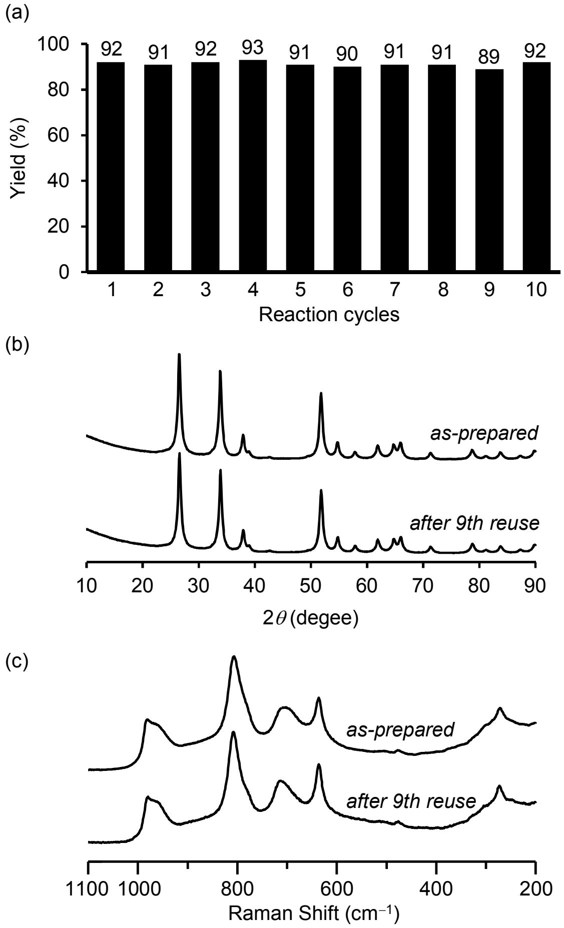

Fig. 5 Reuse of W/Zn–SnO_2 for the oxidative cleavage of **1a** using H_2O_2 as the oxidant. (a) Yield of **2a** in the reuse test. (b) XRD patterns and (c) Raman spectra of as-prepared W/Zn–SnO_2 and W/Zn–SnO_2 recovered after ten cycles of oxidative cleavage of **1a**.

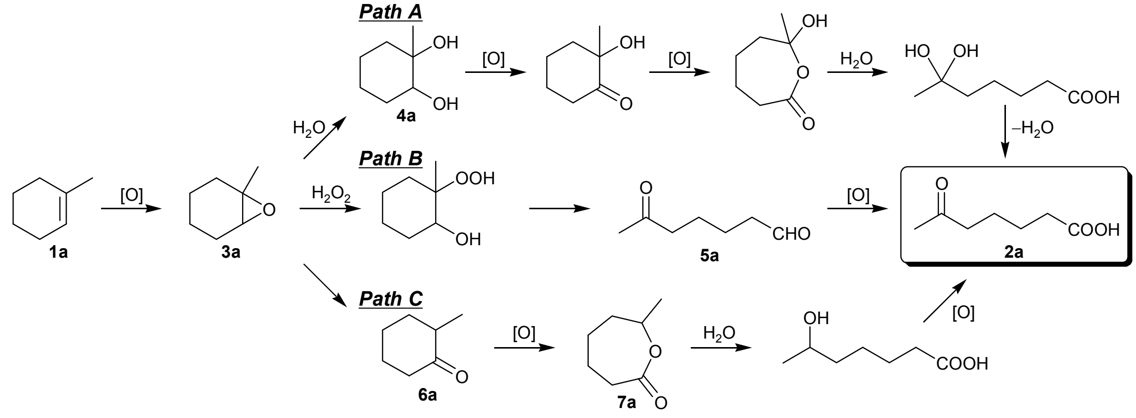

Fig. 6 Possible reaction pathways for the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** into **2a** using H_2O_2 as the oxidant.

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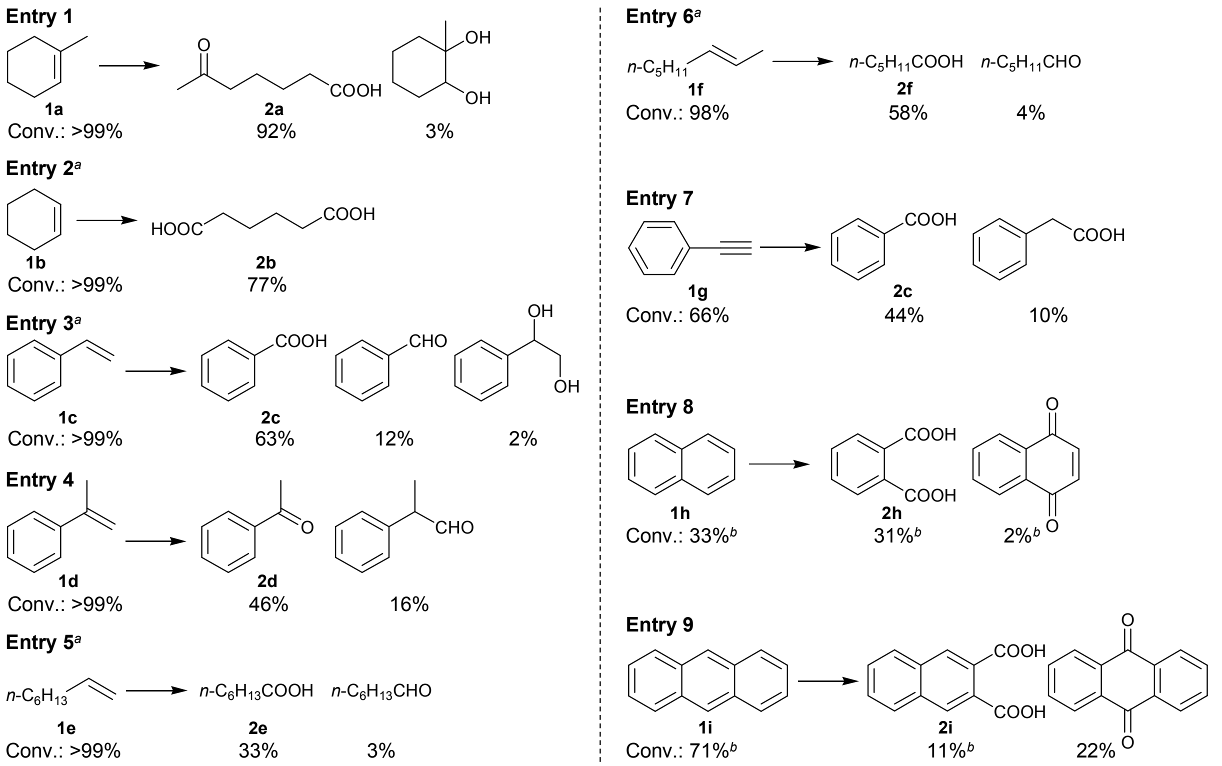

Fig. 7 W/Zn–SnO_2-catalyzed oxidative cleavage of different substrate molecules using H_2O_2 as the oxidant. Reaction conditions: **1** (0.5 mmol), W/Zn–SnO_2 (100 mg, W: 10 mol% with respect to substrates), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C, and 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. [a] CH_3CN (1.5 mL) was used instead of ^{t}BuOH. [b] Conversions and yields were determined by HPLC analysis using biphenyl and naphthalene as internal standards for entry 8 and 9, respectively.

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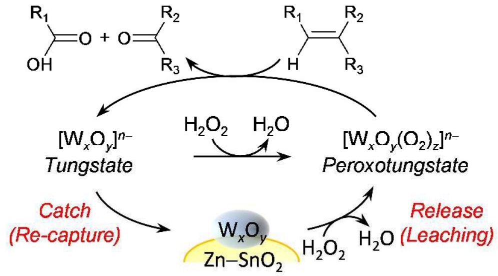

In the presence of tungstate species supported on zinc-modified tin dioxide (W/Zn–SnO_2), oxidative cleavage of olefins and related compounds using H_2O_2 efficiently proceeds through a “release and catch” catalytic mechanism.