Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Submitted to ***Catal. Sci. Technol.*** as a paper.

Composites of [γ-$H_2PV_2W_{10}O_{40}$]$^{3-}$ and [α-$SiW_{12}O_{40}$]$^{4-}$ supported on Fe_2O_3 as heterogeneous catalysts for selective oxidation with aqueous hydrogen peroxide

Ye Wang,[a,b] Keigo Kamata,[a,c] Ryo Ishimoto,[a] Yoshiyuki Ogasawara,[a] Kosuke Suzuki,[a]
Kazuya Yamaguchi[a] and Noritaka Mizuno*[a]

[a] Department of Applied Chemistry, School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[b] Present Address: Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA

[c] Present Address: Materials and Structures Laboratory, Tokyo Institute of Technology
Nagatsuta-cho 4259, Midori-ku, Yokohama-city, Kanagawa 226-8503, Japan

Fax: +81-3-5841-7220, E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

Abstract

Composites of [γ-$H_2PV_2W_{10}O_{40}$]$^{3-}$ and [α-$SiW_{12}O_{40}$]$^{4-}$ supported on Fe_2O_3 (PV2-SiW12/Fe_2O_3, in particular, the molar ratio of PV2/SiW12 = 1/1) could act as effective and reusable heterogeneous catalysts for selective oxidation with aqueous hydrogen peroxide. In the presence of PV2-SiW12/Fe_2O_3, various kinds of organic substrates such as alkenes, sulfides, arenes, and alkanes could selectively be converted into the corresponding oxygenated products in moderate to high yields. The observed catalyses for the present oxidations were intrinsically heterogeneous, and PV2-SiW12/Fe_2O_3 could be reused at least three times for each oxidation (epoxidation, sulfoxidation, and arene hydroxylation) without appreciable losses of the high catalytic performances.

Introduction

Selective oxidation of petroleum-based feedstocks to value-added oxygenated products such as epoxides, diols, alcohols, carbonyl compounds, and carboxylic acids is an important key technology because these products have frequently been utilized as intermediates not only for large-scale commodities but also for pharmaceuticals and agrochemicals.[1] In recent years, developments of environmentally-benign oxidation systems with hydrogen peroxide (H_2O_2) have attracted much attention because of its high content of active oxygen species (47 % by weight) and co-production of only water.[1] To date, efficient systems based on metal catalysts such as titanium,[2] vanadium,[3] molybdenum,[4] tungsten,[5] rhenium,[6] manganese,[7] iron,[8] ruthenium,[9] tin,[10] copper,[11] and zinc[12] have been reported for selective H_2O_2-based oxidation of various substrates such as alkanes, alkenes, alcohols, sulfides, and arenes. However, these systems have several drawbacks; (i) most of them are homogeneous, and the catalyst/product separation and reuse of catalysts are very difficult in some cases, (ii) there are only a few catalytic systems applicable to both C–H activation (for example, oxygenation of alkanes and arenes) and electrophilic oxidation (for example, epoxidation and sulfoxidation), and/or (iii) there is still plenty of room for improvement in their catalytic activities, chemo-, regio- and diastereoselectivities, and efficiencies of H_2O_2 utilization. Therefore, developments of efficient heterogeneous catalysts for H_2O_2-based green oxidation systems applicable to a wide range of substrates are still in great demand.

Polyoxometalates (POMs) are a large family of anionic metal–oxygen clusters of early transition metals with discrete and versatile structures.[13] Because their physical and chemical properties, for example, solubilities, redox potentials, and acidities, can finely be tuned by choosing the constituent elements and counter cations, POMs have extensively been investigated in various research areas such as catalysis, photocatalysis, biological chemistry, molecular magnetism, and material science.[14] Especially, the oxidation catalysis by POMs has received much attention because (i) well-defined mono- and polynuclear catalytically active sites can readily be designed and created and (ii) POMs are relatively stable under the thermal and oxidative conditions in comparison with organometallic compounds and organocatalysts. Thus, many efficient homogeneous molecular POM catalysts for selective oxidation with H_2O_2 have been developed to date.[14] In addition, several efficient "molecular heterogeneous catalysts" have been prepared by solidification[15] or immobilization[16] of catalytically active POM molecules.

Recently, we have reported that a divanadium-substituted phosphotungstate $[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$ (PV2, Fig. 1) can act as an efficient homogeneous catalyst for several oxidative functional group transformations with H_2O_2 such as hydroxylation of alkanes and arenes, oxidative bromination of unsaturated compounds, epoxidation of alkenes, and oxygenation of sulfides. In addition, PV2 shows unique activities and chemo-, regio-, and diastereoselectivities based on non-free radical and electrophilic active oxygen species with the high steric hindrance generated on PV2, probably hydroperoxide and/or $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo species.[17] However, heterogeneous and recyclable catalysts based on PV2 have never been reported until now.

In this study, we have successfully prepared the "PV2-based molecular heterogeneous catalysts" by immobilization of PV2 together with a fully-occupied α-Keggin silicododecatungstate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (SiW12) onto a commercially available Fe_2O_3 support (PV2-SiW12/Fe_2O_3). The PV2-SiW12/Fe_2O_3 catalysts (in particular, the molar ratio of PV2/SiW12 = 1/1) showed high catalytic performance for oxidation of various kinds of structurally diverse alkenes, sulfides, arenes, and alkanes to the corresponding epoxides, sulfoxides, phenols, and alcohols, respectively, with almost the same chemo-, regio-, and diastereoselectivities as those observed for our previously reported homogeneously PV2-catalyzed oxidation.[17] Moreover, the catalyses of PV2-SiW12/Fe_2O_3 for these oxidations were intrinsically heterogeneous, and PV2-SiW12/Fe_2O_3 could be reused for several times (at least three times) for each oxidation (epoxidation, sulfoxidation, and arene hydroxylation) without appreciable losses of the high catalytic performances.

Results and discussion

Effect of catalysts

Initially, the epoxidation of 1-octene (**1a**) with 60 % aqueous H_2O_2 (one equivalent with respect to **1a**) was carried out with various kinds of catalysts. We utilized TBA (TBA = tetra-*n*-butylammonium) salts of POMs and a mixed solvent of ethyl acetate and *tert*-butyl alcohol (EtOAc/*t*-BuOH 1/1, v/v) for the epoxidation because of the following reasons; (i) TBA salts of POMs $[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$ (PV2) and $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (SiW12) are intrinsically insoluble in these solvents and (ii) *t*-BuOH is required to attain the high yields of oxygenated products for our previously reported homogeneously PV2-catalyzed epoxidation of alkenes with aqueous H_2O_2 as the oxidant.[17]

The epoxidation hardly proceeded with PV2 or SiW12 alone (Table 1, entries 9 and 10). We prepared a composite of PV2 and SiW12 (PV2-SiW12, the molar ratio of SiW12/PV2 = 1/1) according to the procedure described in the Experimental section. Notably, the PV2-SiW12 composite showed much higher catalytic activity than those of PV2 and SiW12; when the epoxidation of **1a** was carried out with PV2-SiW12, 1,2-epoxyoctane (**2a**) was obtained in 54 % yield with >99 % epoxide selectivity under the present reaction conditions (Table 1, entry 6). On the other hand, a simple physical mixture of PV2 and SiW12 gave only 2 % yield of **2a** (Table 1, entry 11). Therefore, the mixing of PV2 and SiW12 at molecular level is very crucial to achieve the high catalytic performance. Previously, we have found that solid POMs, for example, $TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (in EtOAc), can sorb organic substrates (for example, alkenes, sulfides, and organosilanes) and H_2O_2 together with EtOAc.[15a,15b] EtOAc molecules (probably substrates and H_2O_2 as well) are highly mobile in the bulk of $TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$, and thereby the

POM can act as an efficient heterogeneous catalyst for selective oxidation of these substrates with aqueous H_2O_2 in EtOAc.[15a,15b] In the present case also, it is likely that the PV2-SiW12 composite can sorb **1a** and H_2O_2 together with the solvent(s), resulting in realizing the efficient heterogeneously PV2-SiW12-catalyzed epoxidation. Only EtOAc or *t*-BuOH was not effective for the PV2-SiW12-catalyzed epoxidation of **1a** in comparison with the mixed solvent of EtOAc and *t*-BuOH (Table 1, entries 7 and 8). As above-mentioned, *t*-BuOH is an indespensable solvent to attain the high yields of oxygenated products for the PV2-catalyzed oxidation with H_2O_2.[17] The role of EtOAc is possibly to take substrates and H_2O_2 inside the bulk of the PV2-SiW12 composite.[15a,15b]

Fig. 2 shows the EtOAc vapor sorption-desorption isotherms of TBA salts of PV2-SiW12, PV2, and SiW12 measured at 298 K. Compounds PV2-SiW12 and PV2 started to sorb significant amounts of EtOAc from the lower relative pressures (P/P_0) in comparison with SiW12. At higher P/P_0, the behaviors of the isotherms of PV2-SiW12 and PV2 were quite different from each other. At higher P/P_0, the amount of the sorption by PV2-SiW12 was larger than that by PV2. The amount of sorption by PV2-SiW12 was 3.9 mol mol^{-1} at $P/P_0 = 0.915$ and more than 130 times as large as that of the surface adsorption.[18] In addition, the characteristic hysteresis loop was observed for the isotherm of PV2-SiW12. Compounds that give rise to the hysteresis can sorb relatively large amounts of molecules into the bulk, and such hysteretic sorption behaviors have frequently been observed for flexible soft porous materials (crystals).[19] Therefore, we possibly explain that the reason for the higher catalytic performance of PV2-SiW12 in comparison with PV2 is caused by this unique favorable sorption property of PV2-SiW12.[15a,15b]

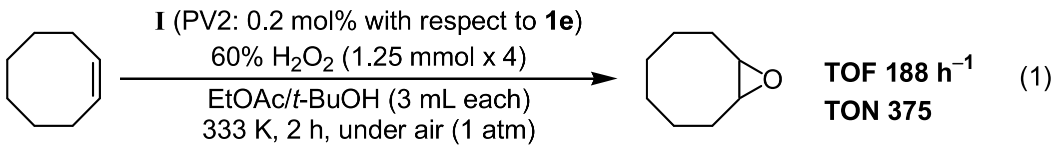
In order to further improve the performance of the PV2-SiW12 composite, the composite was immobilized onto various metal oxide supports (POMs (total: 10 μmol, SiW12/PV2 = 1/1) were immobilized onto 75 mg of metal oxide supports according to the procedure described in the Experimental section), and their catalytic performances were examined. Among the metal oxide supports examined, commercially available Fe_2O_3 was the most effective support for PV2-SiW12. When using the supported catalyst PV2-SiW12/Fe_2O_3, 68 % yield of **2a** was achieved with keeping the exclusive selectivity to **2a** (Table 1, entry 1 vs entry 6, 54 % yield). All the POM species supported on Fe_2O_3 could easily be dissolved by the treatment of PV2-SiW12/Fe_2O_3 with CD_3CN (see the Experimental section). After removal of the Fe_2O_3 support by filtraion, the ^{51}V NMR spectrurm of the resulting filtrate containing POMs was measured. The ^{51}V NMR spectrum showed a single signal at –579.8 ppm (Fig. 3c), and the chemical shift as well as the full width at the half maximum were almost the same as those of the parent PV2 (Fig. 3b), indicating that the molecular structure of PV2 in the supported catalyst is preserved during the immobilization process of PV2-SiW12 onto Fe_2O_3. The X-ray diffraction (XRD) pattern of PV2-SiW12/Fe_2O_3 showed intence signals of Fe_2O_3 together with broad signals of POMs at around $2\theta = 6–8°$ (Fig. 4a). The peak broadening in comparison with the XRD pattern of the parent PV2-SiW12 composite (Fig. 4b) suggests that the composite is highly dispersed onto Fe_2O_3,[20] thus resulting in the higher catalytic performance of PV2-SiW12/Fe_2O_3 in comparison with the parent unsupported PV2-SiW12 composite (Table 1, entry 1 vs entry 6).

Other metal oxide supports such as Fe_3O_4, FeO, SiO_2, Al_2O_3, CeO_2, and WO_3 were less effective than Fe_2O_3 (Table 1, entries 16–21). SnO_2 modified with zinc (Zn-SnO_2) was not so effective (Table 1, entry 22), while Zn-SnO_2 can act as a good anion-exchange support for the catalytically active polytungstates with dioxo groups.[16a] In the absence of catalysts or in the presence of PV2/Fe_2O_3, SiW12/Fe_2O_3, Fe_2O_3, or $HClO_4$, the epoxidation hardly proceeded (Table 1, entries 12–15 and 23). The yield of and the selectivity to **2a** for the epoxidation of **1a** with PV2-SiW12/Fe_2O_3 under argon atmosphere were almost the same as those of the epoxidation under air atmosphere, showing that the possibility of participation of molecular oxygen in air can be excluded (Table 1, entry 1 vs entry 2). In addition, the yield of **2a** reached up to 85 % when prolonging the reaction time to 1 h under the present reaction conditions (Table 1, entry 3).

Furthermore, we prepared the PV2-SiW12/Fe_2O_3 catalysts by immobilization of the composites with different molar ratios of SiW12/PV2 (0/1–4/1, total POMs: 10 μmol) onto different amounts of Fe_2O_3 (30–200 mg with respect to 10 μmol of POMs) (see the Experimental section). Their catalytic activities for the epoxidation of **1a** were strongly dependent on the molar ratios of SiW12/PV2; the yield of **2a** increased with an increase in the molar ratio of SiW12/PV2 up to SiW12/PV2 = 1/1, reached the maximum at SiW12/PV2 = 1/1, and then gradually decreased in the presence of excess SiW12 with respect to PV2 (SiW12/PV2 ≥1/1) (Fig. 5a). The amounts of Fe_2O_3 utilized did not strongly affect the catalytic performance, and yields of **2a** did not much change using ≥30 mg of Fe_2O_3 (Fig. 5b). On the basis of these results, the PV2-SiW12/Fe_2O_3 catalyst prepared using the composite with the molar ratio of SiW12/PV2 = 1/1 and Fe_2O_3 (75 mg) (hereafter denoted by catalyst **I**) was found to be the most effective catalyst for the present epoxidation. Thus, we hereafter utilized the catalyst **I** for further investigations of the substrate scope and the catalyst reuse.

Substrate scope

Next, the scope of the **I**-catalyzed system was investigated for oxidation of various kinds of structurally diverse organic substrates including alkenes, sulfides, arenes, and alkanes with 30–60 % aqueous H_2O_2 as the sole oxidant (Table 2). In the presence of **I**, various terminal, internal, and cyclic alkenes were epoxidized with >98 % selectivities using an equimolar amount of H_2O_2 with respect to the substrates. Non-activated terminal alkenes such as **1a** and even propene (**1b**) could be converted into the corresponding epoxides **2a** and 1,2-epoxypropane (**2b**) in 85 % and 56 % yields, respectively (Table 2, entries 1 and 2). For the epoxidation of *cis*- (**1c**) and *trans*-2-octenes (**1d**), the configurations around the C=C moieties were completely retained in the corresponding epoxides *cis*- (**2c**) and *trans*-2,3-epoxyoctane (**2d**) (Table 2, entries 3 and 4), indicating no involvement of free-radical intermediates in the present **I**-catalyzed epoxidation. In addition, the yield (reaction rate) of **2c** was much higher than that of **2d** under the same conditions, even though the π(C=C) HOMO energy of **1c** (–0.342 eV) calculated at the HF/6-311G(d,p) level was almost the same as that of **1d** (–0.343 eV). This is likely due to the steric effect of the active oxygen species generated on PV2, and such a *cis*-preferential epoxidation is also observed for our previously reported homogeneously PV2-catalyzed epoxidation.[17c] Therefore, it is likely that the structure of PV2 in the catalyst **I** is mostly preserved during the catalytic epoxidation and that the degradated vanadate and/or tungstate species are not the active species. Cyclooctene (**1e**) was smoothly epoxidized to 1,2-epoxycyclooctane (**2e**) (Table 1, entry 5). The **I**-catalyzed system could be applied to the larger-scale (5 mmol-scale) epoxidation of **1e**, and **2e** was obtained in 75 % GC yield (63 % isolated yield) with >99 % epoxide selectivity even with the low catalyst loading (0.2 mol% of PV2) using an equimolar amount of H_2O_2 with respect to **1e** [eqn (1)]. In this case, the turnover frequency (TOF) was 188 h^{-1}, and the turnover number (TON) reached up to 375.



1e (5 mmol) **2e** (75% GC yield, 63% isolated yield)

Not only simple alkenes but also relatively inactive electron-deficient alkenes were selectively epoxidized; for example, the epoxidation of allyl acetate (**1f**) proceeded to give glycidyl acetate (**2f**) in 68 % yield (Table 2, entry 6). The sulfoxidation of thioanisole (**1g**) and methyl *n*-octyl sulfide (**1h**) efficiently proceeded at 298 K, giving the corresponding sulfoxides methyl phenyl sulfoxide (**2g**) and methyl *n*-octyl sulfoxide (**2h**) with high sulfoxide selectivities (Table 2, entries 7 and 8).

In addition, the present **I**-catalyzed system could be applied to chemo- and regioselective hydroxylation of arenes to the corresponding phenols. The hydroxylation of anisole (**1i**) preferentially proceeded at the *para*-position to give the isomers of methoxyphenols (**2i**), and the *ortho*-/*meta*-/*para*-**2i** ratio was 3/<1/97 (Table 2, entry 9). The present exclusive regioselectivity to *para*-**2i** (97 %) was much higher than those of the previously reported catalysts[21] and almost the same as that of the homogeneous PV2 catalyst (96 %).[17e] Toluene (**1j**) was chemo- and regioselectively converted into cresols (**2j**) without formation of side-chain oxygenated products (Table 2, entry 10), and the hydroxylation also preferentially proceeded at the *para*-position with 72 % regioselectivitiy to *para*-**2j** in a similar way to that of the homogeneous PV2 catalyst.[17e]

Furthermore, hydroxylation of inert alkanes could also be accomplished by using the present system. Cyclohexane (**1k**) was efficiently oxidized to cyclohexanol (**2k**) and cyclohexanone (**2k'**), and the total yield (**2k** + **2k'**) based on H_2O_2 and the selectivity to **2k** were 90 % and 94 %, respectively (Table 1, entry 11). The hydroxylation of linear *n*-hexane (**1l**) also proceeded to give a mixture of 2- (**2l**) and 3-hexanols (**2l'**) (15% total yield, **2l**/**2l'** = 77/23) (Table 1, entry 12).

Once again, we emphasize that the above-mentioned high chemoselectivites, stereospecificity, regioselectivities, and efficiencies of H_2O_2 utilization of **I** have also been observed for our previously reported homogeneous PV2 catalyst and explained by the formation of non-free radical and electrophilic active oxygen species with steric constraints of the active site on PV2.[17] Therefore, **I** showed high performance for the heterogeneously catalyzed selective oxidation of various substrates with H_2O_2 possessing the intrinsic catalytic nature of the parent homogeneous PV2.

Heterogeneous catalysis and catalyst reuse

In order to verify whether the observed catalyses were derived from solid **I** or leached vanadate and/or tungstate species, the epoxidation of **1a** and the sulfoxidation of **1g** were carried out under the conditions described in Fig. 6. The catalyst was removed from the reaction mixtures by hot filtration at approximately 50–60 % conversions of the substrates. Although the resulting filtrates were then heated again, no further productions of the corresponding oxygenated products **2a** and **2g** were observed in both cases (Fig. 6). These facts can rule out any contribution to the observed catalyses from metal species that leached into the reaction solutions, and the observed catalyses for these oxidations are intrinsically heterogeneous.[22]

Finally, the reuse experiments of **I** were carried out for three kinds of oxidations, that is, the epoxidation of **1a**, the sulfoxidation of **1g**, and the hydroxylation of **1i**. After each reaction was completed, the catalyst was retrieved from the reaction mixtures by simple filtration. The leaching of vanadium species after the catalytic reactions was confirmed by ICP-AES, and only small amounts of vanadium species with respect to the vanadium content in the fresh catalyst **I** were leached into the reaction solutions; for example, 3.4 % for the epoxidation of **1a** and 2.9 % for the sulfoxidation of **1g** under the conditions described in Fig. 7. The ^{51}V NMR spectrum of the vanadium species in the retrieved **I** after the epoxidation of **1a** showed two signals at –579.6 and –581.6 ppm assignable to PV2 and $[\gamma\text{-HPV}_2\text{W}_{10}\text{O}_{40}]^{4-}$, respectively, indicating the partial deprotonation of PV2 to the inactive monoprotonated species $[\gamma\text{-HPV}_2\text{W}_{10}\text{O}_{40}]^{4-}$ during the epoxidation (Fig. 3d).[17a] Fortunately, the catalyst could readily be regenerated by simple treatment (protonation) with perchloric acid (0.5–1.0 equivalents with respect to PV2 in **I**, see the Experimental section). Indeed, the regenerated catalyst could be reused at least three times for the epoxidation of **1a**, the sulfoxidation of **1g**, and the hydroxylation of **1i** without appreciable losses of the high catalytic activities and chemo- and regioselectivities (Fig. 7).

Conclusion

In this work, we have obtained several significant findings for design of POM-based molecular heterogeneous catalysts. Firstly, the composite PV2-SiW12 (PV2/SiW12 = 1/1) was found to be an efficient heterogeneous catalyst for epoxidation. In the presence of PV2, SiW12, or a physical mixture of PV2 and SiW12, epoxidation hardly proceeded, thus suggesting that PV2 can effectively be utilized by mixing of PV2 and SiW12 at molecular level. The much higher catalytic performance of PV2-SiW12 in comparison with PV2 is possibly caused by the unique sorption property of PV2-SiW12. Secondly, the PV2-SiW12 composite could readily be supported onto various kinds of metal oxides with preserving the structure of PV2, and the catalytic performance of PV2-SiW12 could be improved by supporting it onto Fe_2O_3. Thirdly, in particular, the PV2-SiW12 composite supported onto Fe_2O_3 (PV2-SiW12/Fe_2O_3, PV2/SiW12 = 1/1, **I**) could act as an effective and reusable heterogeneous catalyst for H_2O_2-based selective oxidation. In the presence of **I**, various kinds of organic substrates such as alkenes, sulfides, arenes, and alkanes could be converted into the corresponding epoxides, sulfoxides, phenols, and alkanols, respectively, with the maintenance of the unique stereospecificity and chemo- and regioselectivities of the corresponding homogeneous analogue PV2. Although small amounts of vanadium leaching were observed, the catalyses of **I** for the above-mentioned oxidations were heterogeneous in nature. In addition, **I** could be reused at least three times for each oxidation without appreciable losses of the high catalytic performance.

Experimental section

Materials

Acetonitrile (Kanto Chemical) and toluene (Kanto Chemical) were purified by The Ultimate Solvent System (GlassContour Company) prior to use.[23] The other solvents and substrates were obtained from TCI or Aldrich (reagent grade) and purified according to the reported procedures.[24] Deuterated solvents (CD_3CN, $CDCl_3$, and D_2O) were purchased from ACROS and used as received. Metal oxides such as Fe_2O_3 (12593, Alfa Aesar), Fe_3O_4 (310069, Aldrich), FeO (091-06411, Wako Chemical), SiO_2 (CARiACT G-3CN, Fuji Silysia Chemical), γ-Al_2O_3 (KHS-24, Sumitomo Chemical), CeO_2 (544841, Aldrich), and WO_3 (3K1020, Junsei Chemical) were commercially available. Zinc-modified SnO_2 was prepared by using SnO_2 (Guaranteed Reagent (>98%), Kanto Chemical) according to the literature procedures.[16a] POMs $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$[17a] and SiW12[25] were synthesized and characterized according to the literature procedures.

Instruments

IR spectra were measured on a Jasco FT/IR-4100 spectrometer Plus using KCl disks. NMR spectra were recorded on a JEOL ECA-500 spectrometer (^{1}H, 500.0 MHz; ^{13}C, 125.0 MHz; ^{51}V, 131.3 MHz) by using 5 mm tubes. Chemical shifts (δ) were reported in ppm downfield from $SiMe_4$ (solvent, $CDCl_3$) for ^{1}H and ^{13}C NMR spectra and $VOCl_3$ for ^{51}V NMR spectra, respectively. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed with a Shimadzu ICPS-8100 spectrometer. XRD patterns were recorded on a Rigaku Smartlab diffractometer (CuKα, λ=1.5405 Å, 45 kV–200 mA). The diffraction data were collected in the range of $2\theta = 4–90°$ at 0.01° point and 5 s/step. The EtOAc sorption isotherms of PV2-SiW12, PV2, and SiW12 were measured at 303 K using an automatic volumetric vapor sorption apparatus Belsorp. Before the measurement, the sample (ca. 100 mg) was evacuated at 303 K for 3 h. The sorption equilibrium was judged by the following criteria; ±0.3 % of pressure change in 5 min. The vapor saturation pressure (P_0) of EtOAc at 298 K was 12.9 kPa. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with a DB-WAX etr capillary column (internal diameter = 0.25 mm, length = 30 m), an InertCap-5 capillary column (internal diameter = 0.25 mm, length = 30 m), or a TC-1 capillary column (internal diameter = 0.25 mm, length = 30 m). Biphenyl or naphthalene was used as an internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column at an ionization voltage of 70 eV. The π(C=C) HOMO energies of *cis*- and *trans*-2-octenes were calculated at the HF/6-311G(d,p) level with the Gaussian 09 program package.[26]

Synthesis of TBA salt of PV_2

An acetonitrile solution (10 mL) containing $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (17.9 mg, 5.0 μmol) and

70 % aqueous $HClO_4$ (5.0 μmol) was stirred at 298 K for 5 min. The solution was evaporated to dryness at 308 K for 1 h. The resulting yellow solid of PV2 (TBA salt) was collected and directly used. ^{51}V NMR (131.3 MHz, CD_3CN, 298 K, $VOCl_3$): −579.7 ppm.

Preparation of the PV2-SiW12 composite

An acetonitrile solution (10 mL) containing $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (17.9 mg, 5.0 μmol), $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$ (19.2 mg, 5.0 μmol), and 70 % aqueous $HClO_4$ (5.0 μmol) was stirred at 298 K for 5 min. The solution was evaporated to dryness at 308 K for 1 h. The resulting yellow solid of the composite was collected and directly used. ^{51}V NMR (131.3 MHz, CD_3CN, 298 K, $VOCl_3$): −579.6 ppm.

Preparation of the PV2-SiW12 composite supported on Fe_2O_3 (PV2-SiW12/Fe_2O_3 (I))

An acetonitrile solution (10 mL) containing $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (17.9 mg, 5.0 μmol), $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$ (19.2 mg, 5.0 μmol), and 70 % aqueous $HClO_4$ (5.0 μmol) was stirred at 298 K for 5 min followed by addition of Fe_2O_3 (75 mg). The solution was vigorously stirred at 298 K for 30 min, and then evaporated to dryness at 308 K for 1 h. The resulting solid of **I** (110 mg, V: 0.46 wt% determined by ICP-AES) was collected and directly used. Catalyst **I** was added in CD_3CN (0.5 mL), and the mixture was sonicated for 5 min. Then, Fe_2O_3 was removed by filtration, and the ^{51}V NMR spectrum of the resulting filtrate was measured. ^{51}V NMR (131.3 MHz, CD_3CN, 298 K, $VOCl_3$): −579.8 ppm (Fig. 3c). In addition, we prepared the PV2-SiW12/Fe_2O_3 catalysts by immobilization of the composites with different molar ratios of SiW12/PV2 (0/1–4/1, total POMs: 10 μmol) onto different amounts of Fe_2O_3 (30–200 mg with respect to 10 μmol of POMs) or onto different metal oxide supports (75 mg with respect to 10 μmol of POMs) in a similar way to that of **I**.

Procedure for catalytic oxidation

The catalytic oxidation of various organic substrates was carried out in a 30-mL glass vessel containing a magnetic stir bar. The epoxidation of **1b** was carried out with an autoclave having a

Teflon vessel. A typical procedure for the catalytic oxidation was as follows: Into the glass vessel were successively placed **I** (44 mg, PV2: 1.0 mol% with respect to **1a** and H_2O_2), **1a** (0.2 mmol), and EtOAc/*t*-BuOH (1 mL each) with a magnetic stir bar, and the mixture was stirred at 313 K for 15 min. Then, the reaction was initiated by addition of 60 % aqueous H_2O_2 (0.2 mmol), and the reaction solution was periodically analyzed by GC. Remaining H_2O_2 after the reaction was analyzed by the $Ce^{3+/4+}$ titration and determined to be less than 5 % after each reaction.[27] The products are known and identified by comparison of their GC-MS and/or ^1H and ^{13}C NMR signals with the literature data.

Larger-scale (5 mmol scale) epoxidation of 1e

Into the glass vessel were successively placed **I** (220 mg, PV2: 0.2 mol% with respect to **1e** and H_2O_2), **1e** (5 mmol), and EtOAc/*t*-BuOH (3 mL each) with a magnetic stir bar, and the reaction mixture was stirred at 333 K for 15 min. Then, 60 % aqueous H_2O_2 (5 mmol) was added in four portions (i.e., 1.25 mmol × 4) every 20 min. After the addition was completed, the mixture was stirred at 333 K for further 1 h (i.e., total reaction time was 2 h). The GC yield and the selectivity to **2e** were 75 % and >99 %, respectively. As for isolation of **2e**, an internal standard was not used. After the reaction, the catalyst was removed by filtration, and the filtrate was dried over $MgSO_4$. Then, $MgSO_4$ was filtered off followed by removal of the solvent and remaining **1e** by evaporation, affording **2e** in 63 % isolated yield.

Procedure for recycling I

Into the glass vessel were successively placed **I** (44 mg, PV2: 2.0 mol% with respect to H_2O_2), **1a** (2 mmol), and EtOAc/*t*-BuOH (1 mL each) with a magnetic stir bar, and the mixture was stirred at 313 K for 15 min. Then, the reaction was initiated by addition of 60 % aqueous H_2O_2 (0.1 mmol). After the reaction was carried out for 30 min, the catalyst was filtrated, washed with EtOAc (10 mL × 5), evacuated at room temperature for 2 h, and then directly used for the next cycle with addition of $HClO_4$ (1 μmol).

Acknowledgements

We thank Dr. Y. Nakagawa for his help with preliminary experiments. This work was supported in part by the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)" and Grants-in-Aid for JSPS Fellows and Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology of Japan.

References and notes

1 (*a*) C. Jia, T. Kitamura and Y. Fujiwara, *Acc. Chem. Res.*, 2001, **34**, 633; (*b*) J. A. Labinger and J. E. Bercaw, *Nature*, 2002, **417**, 507; (*c*) D. Schröder and H. Schwarz, *Proc. Natl. Acad. Sci. USA*, 2008, **105**, 18114; (*d*) T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329; (*e*) F. Cavani and J. H. Teles, *ChemSusChem*, 2009, **2**, 508; (*f*) *Modern Heterogeneous Oxidation Catalysis*, ed. N. Mizuno, Wiley-VCH, Weinheim, 2009; (*g*) *Modern Oxidation Methods*, ed. J.-E. Bäckvall, Wiley-VCH, Weinheim, 2004; (*h*) B. S. Lane and K. Burgess, *Chem. Rev.*, 2003, **103**, 2457; (*i*) *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*, ed. S. T. Oyama, Elsevier, Amsterdam, 2008; (*j*) D. E. De Vos, B. F. Sels and P. A. Jacobs, *Adv. Catal.*, 2001, **46**, 1; (*k*) R. A. Sheldon, I. W. C. E. Arends and U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, 2007.

2 (*a*) B. Notari, *Adv. Catal.*, 1996, **41**, 253; (b) Y. Sawada, K. Matsumoto, S. Kondo, H. Watanabe, T. Ozawa, K. Suzuki, B. Saito and T. Katsuki, *Angew. Chem. Int. Ed.*, 2006, **45**, 3478; (*c*) A. Berkessel, T. Günther, Q. Wang and J.-M. Neudörfl, *Angew. Chem. Int. Ed.*, 2013, **52**, 8467; (*d*) O. Lifchits, M. Mahlau, C. M. Reisinger, A. Lee, C. Farès, I. Polyak, G. Gopakumar, W. Thiel and B. List, *J. Am. Chem. Soc.*, 2013, **135**, 6677; (*e*) Y. Kuwahara, K.

Nishizawa, T. Nakajima, T. Kamegawa, K. Mori and H. Yamashita, *J. Am. Chem. Soc.*, 2011, **133**, 12462; (*f*) H. Zhou, L. Xiao, X. Liu, S. Li, H. Kobayashi, X. Zheng and J. Fan, *Chem. Commun.*, 2012, **48**, 6954; (*g*) L. Wang, J. Sun, X. Meng, W. Zhang, J. Zhang, S. Pan, Z. Shen and F.-S. Xiao, *Chem. Commun.*, 2014, **50**, 2012.

3 (*a*) T. Hirao, *Chem. Rev.*, 1997, **97**, 2707; (*b*) V. Conte, F. Di Furia and G. Licini, *Appl. Catal. A*, 1997, **157**, 335; (*c*) G. J. Hutchings, *J. Mater. Chem.*, 2004, **14**, 3385; (*d*) F. Cavani, N. Ballarini and A. Cericola, *Catal. Today*, 2007, **127**, 113; (*e*) S. Takizawa, T. Katayama and H. Sasai, *Chem. Commun.*, 2008, 4113; (*f*) A. G. J. Ligtenbarg, R. Hage and B. L. Feringa, *Coord. Chem. Rev.*, 2003, **237**, 89; (*g*) C. Bolm, *Coord. Chem. Rev.*, 2003, **237**, 245.

4 (*a*) J. J. Boruah, S. P. Das, S. R. Ankireddy, S. R. Gogoi and N. S. Islam, *Green Chem.*, 2013, **15**, 2944; (*b*) S. K. Maiti, K. M. A. Malik, S. Gupta, S. Chakraborty, A. K. Ganguli, A. K. Mukherjee and R. Bhattacharyya, *Inorg. Chem.*, 2006, **45**, 9843; (*c*) J.-Y. Piquemal, S. Halut and J.-M. Brégeault, *Angew. Chem. Int. Ed.*, 1998, **37**, 1146; (*d*) C. Dinoi, M. Ciclosi, E. Manoury, L. Maron, L. Perrin and R. Poli, *Chem. Eur. J.*, 2010, **16**, 9572.

5 (*a*) Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida and M. Ogawa, *J. Org. Chem.*, 1988, **53**, 3587; (*b*) C. Venturello, R. D'Aloisio, J. C. J. Bart and M. Ricci, *J. Mol. Catal.*, 1985, **32**, 107; (*c*) D. C. Duncan, R. C. Chambers, E. Hecht and C. L. Hill, *J. Am. Chem. Soc.*, 1995, **117**, 681; (*d*) K. Sato, M. Aoki and R. Noyori, *Science*, 1998, **281**, 1646; (*e*) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi and N. Mizuno, *Science*, 2003, **300**, 964; (*f*) K. Kamata, T. Hirano, S. Kuzuya and N. Mizuno, *J. Am. Chem. Soc.*, 2009, **131**, 6997; (*g*) R. Ishimoto, K. Kamata and N. Mizuno, *Angew. Chem. Int. Ed.*, 2012, **51**, 4662.

6 (*a*) J. Rudolph, K. L. Reddy, J. P. Chiang and K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189; (*b*) W. A. Herrmann, R. M. Kratzer, H. Ding, W. R. Thiel and H. Glas, *J.*

Organomet. Chem., 1998, **555**, 293; (*c*) H. Adolfsson, C. Copéret, J. P. Chiang and A. K. Yudin, *J. Org. Chem.*, 2000, **65**, 8651; (*d*) S. Yamazaki, *Org. Biomol. Chem.*, 2010, **8**, 2377; (*e*) P. Altmann, M. Cokoja and F. E. Kühn, *Eur. J. Inorg. Chem.*, 2012, 3235.

7 (*a*) D. E. De Vos, B. F. Sels, M. Reynaers, Y. V. S. Rao and P. A. Jacobs, *Tetrahedron Lett.*, 1998, **39**, 3221; (*b*) B. S. Lane, M. Vogt, V. J. DeRose and K. Burgess, *J. Am. Chem. Soc.*, 2002, **124**, 11946; (*c*) P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort and D. Mansuy, *J. Am. Chem. Soc.*, 1988, **110**, 8462; (*d*) P. Saisaha, J. W. de Boer and W. R. Browne, *Chem. Soc. Rev.*, 2013, **42**, 2059; (*e*) H.-K. Kwong, P.-K. Lo, K.-C. Lau and T.-C. Lau, *Chem. Commun.*, 2011, **47**, 4273.

8 (*a*) M. C. White, A. G. Doyle and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 7194; (*b*) M. M. Forde, R. D. Armstrong, C. Hammond, Q. He, R. L. Jenkins, S. A. Kondrat, N. Dimitratos, J. A. Lopez-Sanchez, S. H. Taylor, D. Willock, C. J. Kiely and G. J. Hutchings, *J. Am. Chem. Soc.*, 2013, **135**, 11087; (*c*) K. Hasan, N. Brown and C. M. Kozak, *Green Chem.*, 2011, **13**, 1230; (*d*) I. Prat, J. S. Mathieson, M. Güell, X. Ribas, J. M. Luis, L. Cronin and M. Costas, *Nat. Chem.*, 2011, **3**, 788; (*e*) M. S. Chen and M. C. White, *Science*, 2010, **327**, 566.

9 (*a*) A. Behr, N. Tenhumberg and A. Wintzer, *RSC Adv.*, 2013, **3**, 172; (*b*) S.-I. Murahashi, N. Komiya and H. Terai, *Angew. Chem. Int. Ed.*, 2005, **44**, 6931; (*c*) V. Kogan, M. M. Quintal and R. Neumann, *Org. Lett.*, 2005, **7**, 5039; (*d*) M. K. Tse, C. Döbler, S. Bhor, M. Klawonn, W. Mägerlein, H. Hugl and M. Beller, *Angew. Chem. Int. Ed.*, 2004, **43**, 5255.

10 (*a*) A. Corma, L. T. Nemeth, M. Renz and S. Valencia, *Nature*, 2001, **412**, 423; (*b*) H. Y. Luo, L. Bui, W. R. Gunther, E. Min and Y. Román-Leshkov, *ACS Catal.*, 2012, **2**, 2695; (*c*) A. Corma, M. T. Navarro, L. Nemeth and M. Renz, *Chem. Commun.*, 2001, 2190.

11 (*a*) A. Conde, L. Vilella, D. Balcells, M. M. Díaz-Requejo, A. Lledós and P. J. Pérez, *J. Am. Chem. Soc.*, 2013, **135**, 3887; (*b*) O. Perraud, A. B. Sorokin, J.-P. Dutasta and A. Martinez,

Chem. Commun., 2013, **49**, 1288; (*c*) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, E. Y. Karabach, M. Haukka, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Adv. Synth. Catal.*, 2006, **348**, 159.

12 J.-B. Feng, J.-L. Gong and X.-F. Wu, *RSC Adv.*, 2014, **4**, 29273.

13 (*a*) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983; (*b*) M. T. Pope, in *Comprehensive Coordination Chemistry II, Vol. 4*, eds., J. A. McCleverty, T. J. Meyer, Elsevier Pergamon, Amsterdam, 2004, pp. 635–678; (*c*) P. Mialane, A. Dolbecq and F. Sécheresse, *Chem. Commun.*, 2006, 3477; (*d*) D.-L. Long and L. Cronin, *Chem. Eur. J.*, 2006, **12**, 3698; (*e*) A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2008, 1837; (*f*) H. N. Miras, E. F. Wilson and L. Cronin, *Chem. Commun.*, 2009, 1297; (*g*) U. Kortz, A. Müller, J. van Slageren, J. Schnack, N. S. Dalal and M. Dressel, *Coord. Chem. Rev.*, 2009, **253**, 2315; (*h*) T. Zhang, J. Brown, R. J. Oakley and C. F. J. Faul, *Curr. Opin. Colloid Interface Sci.*, 2009, **14**, 62; (*i*) D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed.*, 2010, **49**, 1736; (*j*) P. Kögerler, B. Tsukerblat and A. Müller, *Dalton Trans.*, 2010, **39**, 21.

14 (*a*) C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407; (*b*) T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, 1996, **41**, 113; (*c*) R. Neumann, *Prog. Inorg. Chem.*, 1998, **47**, 317; (*d*) Thematic issue on “Polyoxometalates”, ed., C. L. Hill, *Chem. Rev.*, 1998, **98**, 1−390; (*e*) I. V. Kozhevnikov, *Catalysts for Fine Chemical Synthesis, Volume 2, Catalysis by Polyoxometalates*, John Wiley & Sons, Chichester, 2002; (*f*) C. L. Hill in *Comprehensive Coordination Chemistry II, Vol. 4*, eds., J. A. McCleverty, T. J. Meyer, Elsevier Pergamon, Amsterdam, 2004, pp. 679–759; (*g*) N. Mizuno, K. Kamata and K. Yamaguchi, in *Surface and Nanomolecular Catalysis*, ed., R. Richards, Taylor and Francis Group, New York, 2006, pp. 463–492; (*h*) N. Mizuno, K. Kamata, S. Uchida and K. Yamaguchi in *Modern Heterogeneous Oxidation Catalysis*, ed.,

N. Mizuno, Wiley-VCH, Weinheim, 2009, pp.185−216.

15 (*a*) N. Mizuno, S. Uchida, K. Kamata, R. Ishimoto, S. Nojima, K. Yonehara and Y. Sumida, *Angew. Chem. Int. Ed.*, 2010, **49**, 9972; (*b*) S. Uchida, K. Kamata, Y. Ogasawara, M. Fujita and N. Mizuno, *Dalton Trans.*, 2012, **41**, 9979; (*c*) Q. Han, C. He, M. Zhao, B. Qi, J. Niu and C. Duan, *J. Am. Chem. Soc.*, 2013, **135**, 10186; (*d*) P. Zhao, Y. Leng, M. Zhang, J. Wang, Y. Wu and J. Huang, *Chem. Commun.*, 2012, **48**, 5721; (*e*) M. V. Vasylyev and R. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 884; (*f*) J. T. Rhule, W. A. Neiwert, K. I. Hardcastle, B. T. Do and C. L. Hill, *J. Am. Chem. Soc.*, 2001, **123**, 12101; (*g*) C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 87; (*h*) L.-X. Shi, W.-F. Zhao, X. Xu, J. Tang and C.-D. Wu, *Inorg. Chem.*, 2011, **50**, 12387.

16 (*a*) K. Kamata, K. Yonehara, Y. Sumida, K. Hirata, S. Nojima and N. Mizuno, *Angew. Chem. Int. Ed.*, 2011, **50**, 12062; (*b*) J. Kasai, Y. Nakagawa, S. Uchida, K. Yamaguchi and N. Mizuno, *Chem. Eur. J.*, 2006, **12**, 4176; (*c*) N. M. Okun, T. M. Anderson and C. L. Hill, *J. Am. Chem. Soc.*, 2003, **125**, 3194; (*d*) K. Yamaguchi, C. Yoshida, S. Uchida and N. Mizuno, *J. Am. Chem. Soc.*, 2005, **127**, 530; (*e*) S. Pathan and A. Patel, *Dalton Trans.*, 2011, **40**, 348; (*f*) C. M. Granadeiro, A. D. S. Barbosa, S. Ribeiro, I. C. M. S. Santos, B. de Castro, L. Cunha-Silva and S. S. Balula, *Catal. Sci. Technol.*, 2014, **4**, 1416.

17 (*a*) K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara and N. Mizuno, *Nat. Chem.*, 2010, **2**, 478; (*b*) K. Yonehara, K. Kamata, K. Yamaguchi and N. Mizuno, *Chem. Commun.*, 2011, **47**, 1692; (*c*) K. Kamata, K. Sugahara, K. Yonehara, R. Ishimoto and N. Mizuno, *Chem. Eur. J.*, 2011, **17**, 7549; (*d*) T. Yamaura, K. Kamata, K. Yamaguchi and N. Mizuno, *Catal. Today*, 2013, **203**, 76; (*e*) K. Kamata, T. Yamaura and N. Mizuno, *Angew. Chem. Int. Ed.*, 2012, **51**, 7275.

18 The amount of surface adsorption of EtOAc by PV2-SiW12 was estimated from the BET surface area and the cross-section area of a EtOAc molecule (0.326 nm^2). The N_2

adsorption isotherm (at 77 K) showed that the PV2-SiW12 composite was non-porous, and the BET surface area of PV2-SiW12 was 1.5 m^2 g^{-1}.

19 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695.

20 (*a*) S. Farhadi and M. Zaidi, *Appl. Catal. A*, 2009, **354**, 119; (*b*) Z. Kang, Y. Wang, E. Wang, S. Lian, L. Gao, W. You, C. Hu and L. Xu, *Solid State Commun.*, 2004, **129**, 559; (*c*) S. Sachdeva, N. Sharma, M. M. Emery, S. J. Hamrock and A. M. Herring, *ECS Trans.*, 2009, **19**(30), 63.

21 (*a*) D. Bianchi, R. D'Aloisio, R. Bortolo and M. Ricci, *Appl. Catal. A*, 2007, **327**, 295; (*b*) J.-F. Bartoli, V. Mouries-Mansuy, K. L. Barch-Ozette, M. Palacio, P. Battioni and D. Mansuy, *Chem. Commun.*, 2000, 827; (*c*) A. Marsella, S. Agapakis, F. Pinna and G. Strukul, *Organometallics*, 1992, **11**, 3578; (*d*) F. Gao and R. Hua, *Appl. Catal. A*, 2004, **270**, 223; (*e*) J. D. McClure and P. H. Williams, *J. Org. Chem.*, 1962, **27**, 627; (*f*) S. Tamagaki, K. Suzuki and W. Tagaki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 148; (*g*) J.-F. Bartoli, K. L. Barch, M. Palacio, P. Battioni and D. Mansuy, *Chem. Commun*., 2001, 1718; (*h*) J.-F. Bartoli, F. Lambert, I. Morgenstern-Badarau, P. Battioni and D. Mansuy, *C. R. Chim.*, 2002, **5**, 263.

22 (*a*) J. Hagen, *Industrial Catalysis: A Practical Approach*, Wiley-VCH, Weinheim, 1999; (*b*) R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, *Acc. Chem. Res.*, 1998, **31**, 485.

23 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

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

25 A. Tézé and G. Hervé, *Inorg. Synth.*, 1990, **27**, 85.

26 Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M.

A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

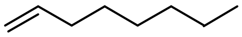
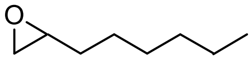
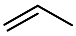
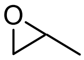
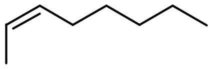
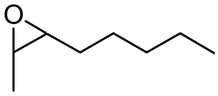
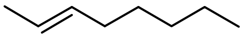
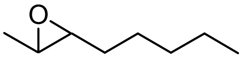
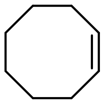
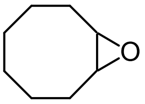
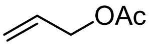
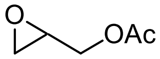
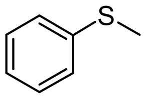
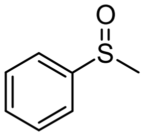
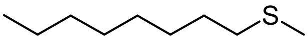
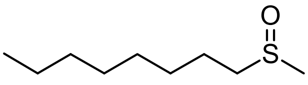
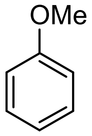
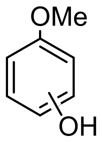
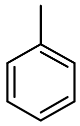
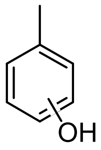
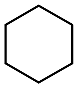
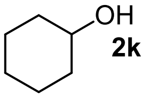
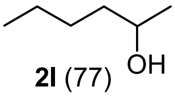
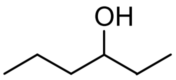
27 A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, Longman, New York, 1978.

Table 1 Effects of catalysts and solvents on the epoxidation of 1-octene (**1a**) with aqueous H_2O_2[a]

Entry	Catalyst	Solvent	Yield of **2a** (%)
1	PV2-SiW12/Fe_2O_3 (**I**)	EtOAc/*t*-BuOH	68
2[b]	**I**	EtOAc/*t*-BuOH	67
3[c]	**I**	EtOAc/*t*-BuOH	85
4[d]	**I**	EtOAc	39
5[d]	**I**	*t*-BuOH	20
6[e,f]	PV2-SiW12	EtOAc/*t*-BuOH	54
7[d]	PV2-SiW12	EtOAc	20
8[d]	PV2-SiW12	*t*-BuOH	7
9[e]	PV2	EtOAc/*t*-BuOH	3
10[f]	SiW12	EtOAc/*t*-BuOH	<1
11[e,f]	PV2 + SiW12	EtOAc/*t*-BuOH	2
12[e,g]	PV2/Fe_2O_3	EtOAc/*t*-BuOH	6
13[f,g]	SiW12/Fe_2O_3	EtOAc/*t*-BuOH	<1
14[g]	Fe_2O_3	EtOAc/*t*-BuOH	<1
15[h]	$HClO_4$	EtOAc/*t*-BuOH	<1
16	PV2-SiW12/Fe_3O_4	EtOAc/*t*-BuOH	37
17	PV2-SiW12/FeO	EtOAc/*t*-BuOH	52
18	PV2-SiW12/SiO_2	EtOAc/*t*-BuOH	57
19	PV2-SiW12/Al_2O_3	EtOAc/*t*-BuOH	8
20	PV2-SiW12/CeO_2	EtOAc/*t*-BuOH	7
21	PV2-SiW12/WO_3	EtOAc/*t*-BuOH	42
22	PV2-SiW12/Zn-SnO_2	EtOAc/*t*-BuOH	33
23	without	EtOAc/*t*-BuOH	<1

[a] Reaction conditions: PV2-SiW12/support (44 mg, PV2: 2 μmol, SiW12: 2 μmol), **1a** (0.2 mmol), 60 % aqueous H_2O_2 (0.2 mmol), EtOAc/*t*-BuOH (1 mL each), 313 K, 0.5 h, under air (1 atm). Yield of **2a** was determined by GC analysis using an internal standard (biphenyl). Yield (%) = **2a** (mol)/initial **1a** (mol) × 100. [b] Under Ar (1 atm). [c] 1 h. [d] Solvent (2 mL). [e] PV2 (2 μmol). [f] SiW12 (2 μmol). [g] Catalyst (75 mg). [h] $HClO_4$ (2 μmol).

Table 2 Selective oxidation of various substrates with aqueous H_2O_2 catalyzed by **I**[a]

Entry	Substrate	Time (h)	Yield (%)	Product (Selectivity (%))
1	 **1a**	1	85	 **2a** (>99)
2[b]	 **1b**	4	56	 **2b** (98)
3	 **1c**	2	70	 **2c** (99)
4	 **1d**	4	28	 **2d** (>99)
5	 **1e**	1	89	 **2e** (>99)
6	 **1f**	4	68	 **2f** (99)
7	 **1g**	2	99 (78)[c]	 **2g** (87)
8	 **1h**	2	99	 **2h** (87)
9[d,e]	 **1i**	4	90	 **2i** (>99) *o*/*m*/*p* = 3/<1/97
10[d,e]	 **1j**	4	25	 **2j** (99) *o*/*m*/*p* = 9/19/72
11[d,e]	 **1k**	2	90	 **2k** (94)
12[d,f]	 **1l**	5	15	 **2l** (77)  **2l'** (23)

[a] Reaction conditions: **I** (PV2: 2 μmol), substrate (0.2 mmol), EtOAc/*t*-BuOH (1 mL each), 60 % aqueous H_2O_2 (0.2 mmol), reaction temperature (313 K for entries 1–6; 298 K for entries 7–9; 333 K for entries 10–12), under air (1 atm). Yield and selectivity were determined by GC analysis using an internal standard (biphenyl or naphthalene). Yield (%) = products (mol)/initial H_2O_2 (mol) × 100. Selectivity (%) = product (mol)/products (mol) × 100. [b] **1b** (6 atm). [c] Isolated yield of **2g**. [d] 30 % aqueous H_2O_2 (0.1 mmol). [e] Substrate (5 mmol). [f] Substrate (7.5 mmol).

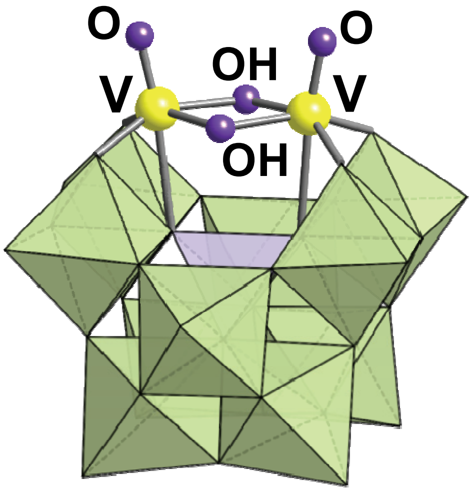


Fig. 1 Molecular structure of PV2. The {WO_6} moieties occupy the green octahedra, and the {PO_4} moiety is shown as the internal gray tetrahedron.

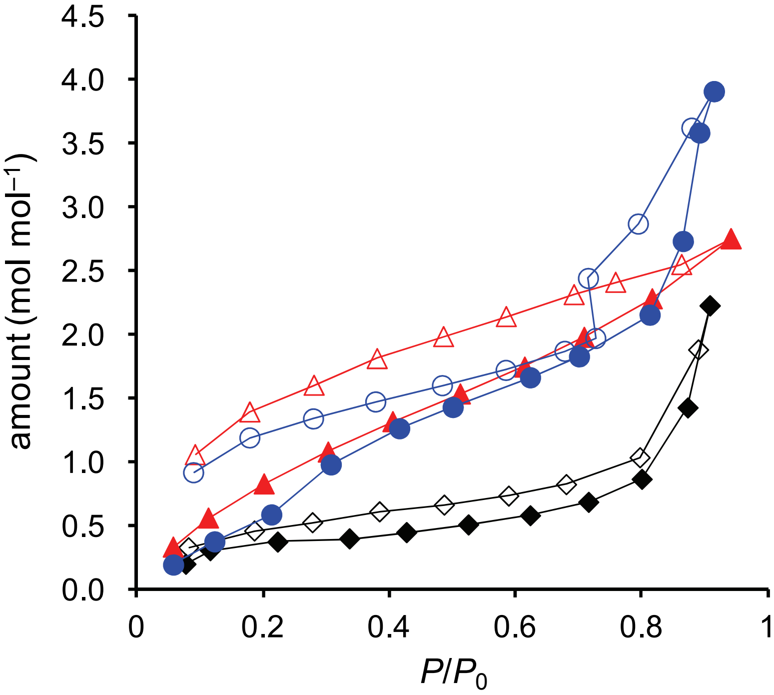


Fig 2 EtOAc vapor sorption-desorption isotherms of TBA salts of PV2-SiW12, PV2, and SiW12 measured at 298 K. Blue circle, red triangle, and black diamond symbols indicate the data for PV2-SiW12, PV2, and SiW12, respectively. Filled and open symbols show the sorption and desorption plots, respectively.

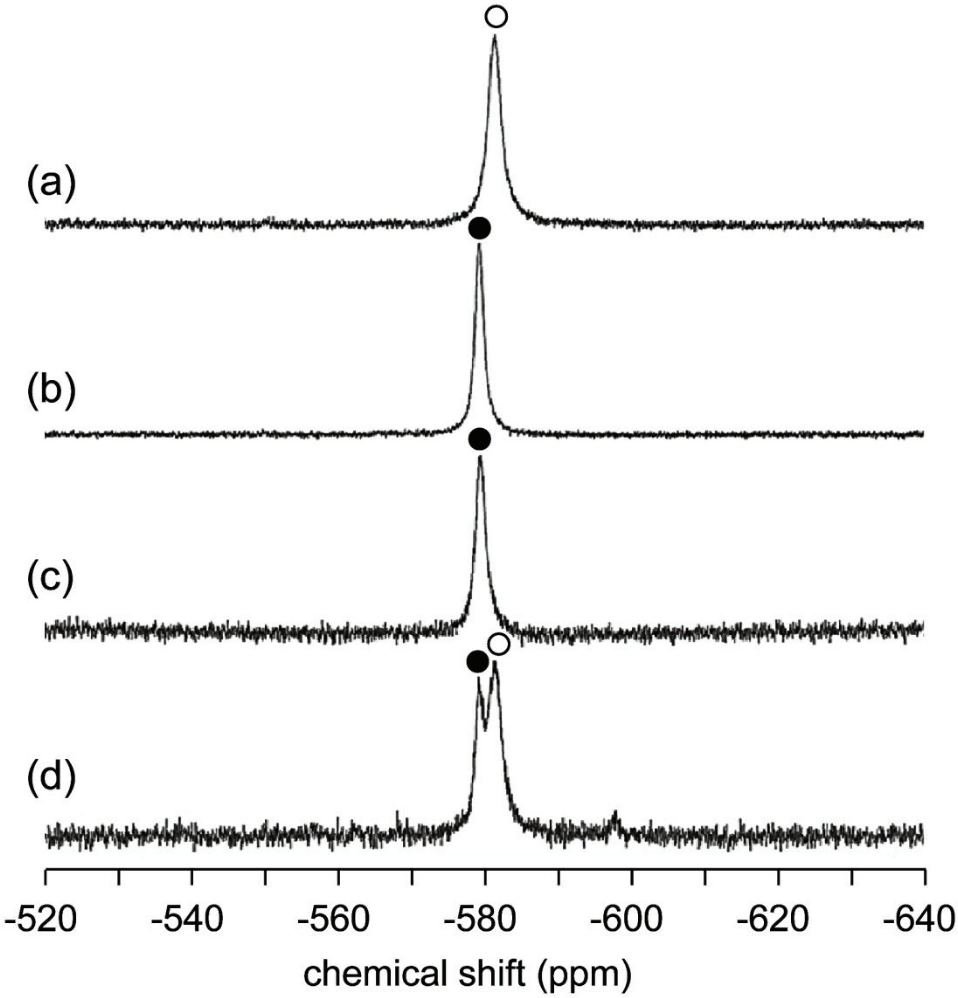


Fig 3 Liquid-phase ^{51}V NMR spectra in CD_3CN: (a) $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$, (b) PV2 ($[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$, TBA salt), (c) vanadium-containing POM supported on the fresh **I**, and (d) vanadium-containing POMs supported on retrieved **I** after the epoxidation of **1a** under the reaction conditions shown in Fig. 7. Open and filled circle symbols indicate the signals due to $[\gamma\text{-}HPV_2W_{10}O_{40}]^{4-}$ and $[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$, respectively.

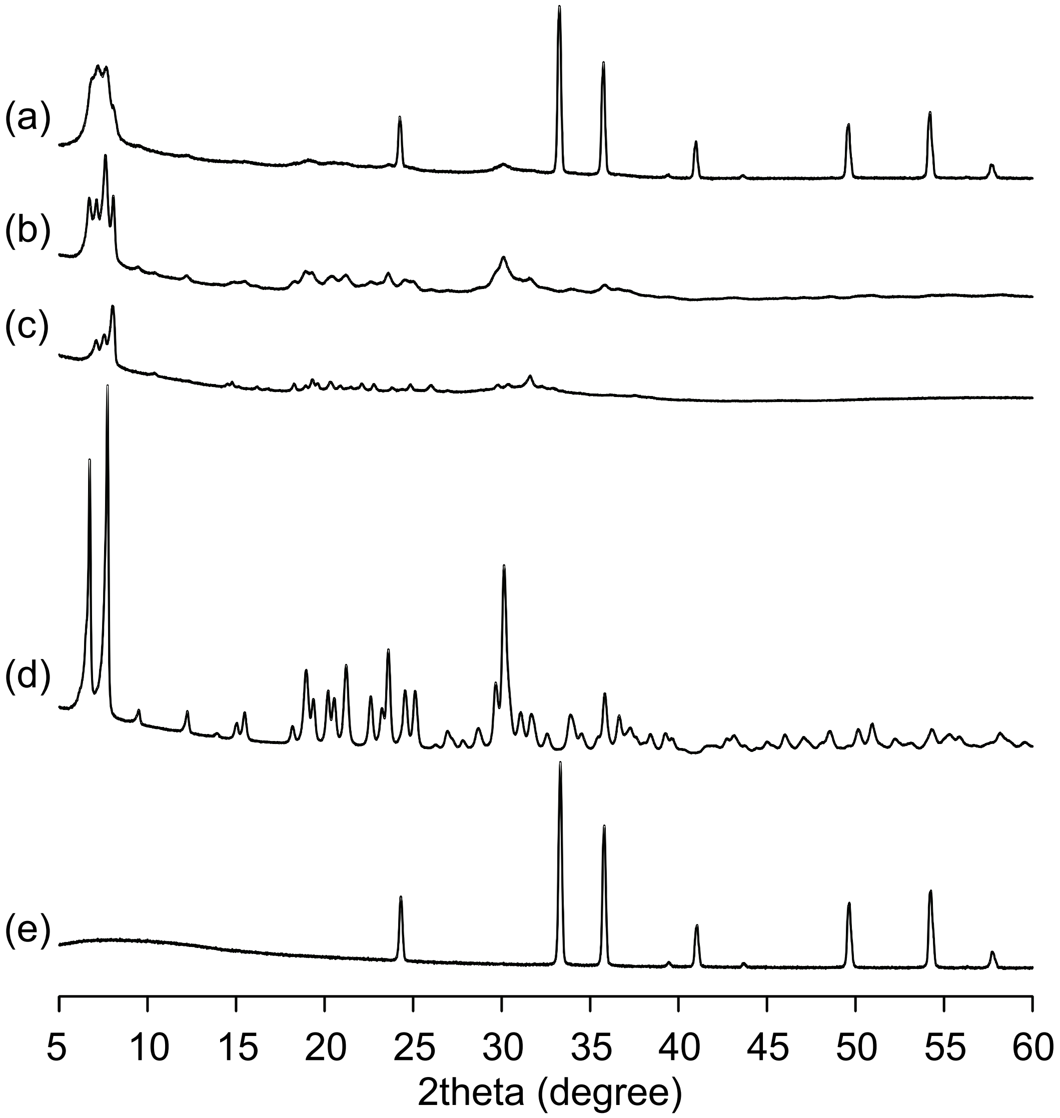


Fig 4 XRD patterns of (a) **I**, (b) PV2-SiW12 (PV2/SiW12 = 1/1, TBA salt), (c) PV2 (TBA salt), (d) SiW12 (TBA salt), and (e) Fe_2O_3.

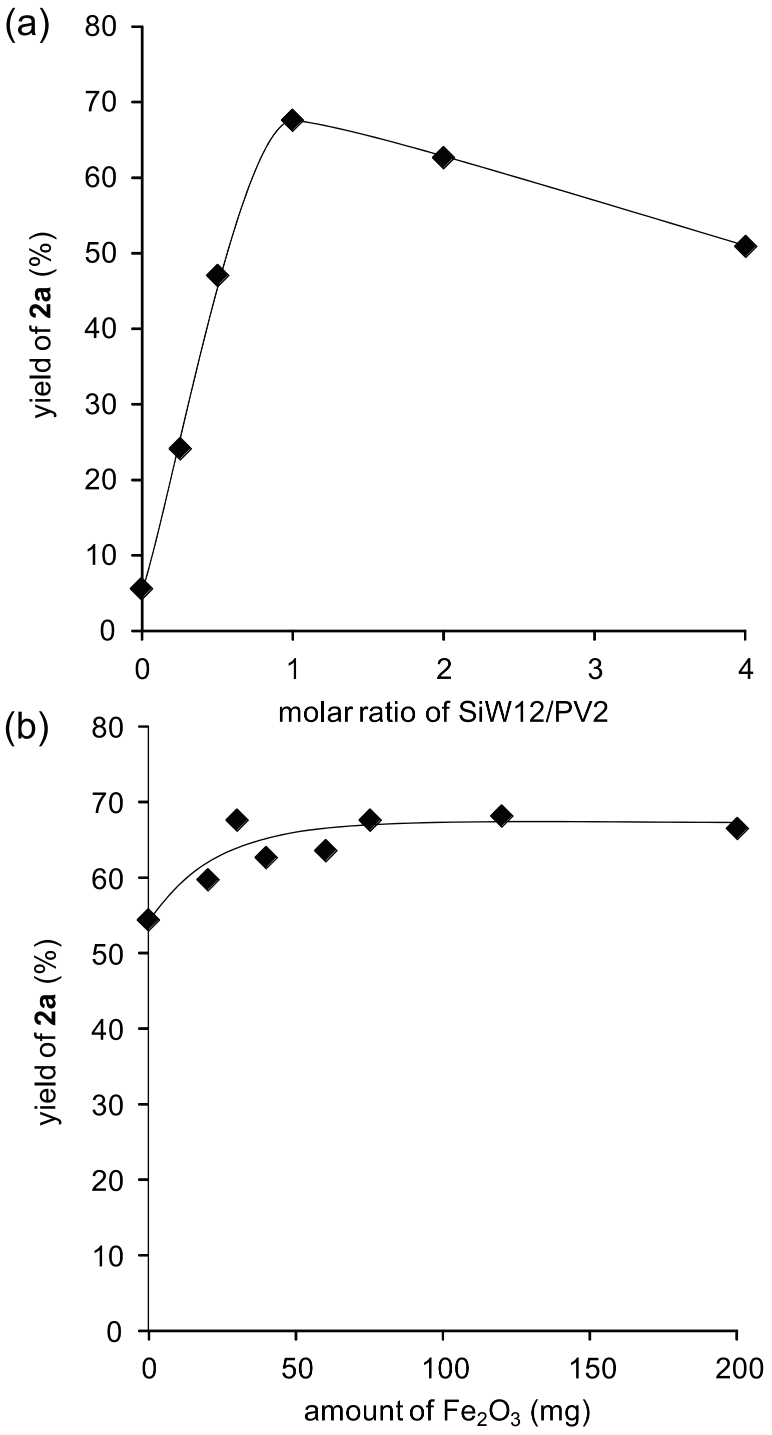


Fig. 5 Plots of yields of **2a** against (a) the molar ratios of SiW12/PV2 and (b) the amounts of Fe_2O_3 used as the support. Reaction conditions: **1a** (0.2 mmol), PV2-SiW12/Fe_2O_3 (PV2: 2 μmol), 60 % aqueous H_2O_2 (0.2 mmol), EtOAc/*t*-BuOH (1 mL each), 313 K, 0.5 h, under air (1 atm).

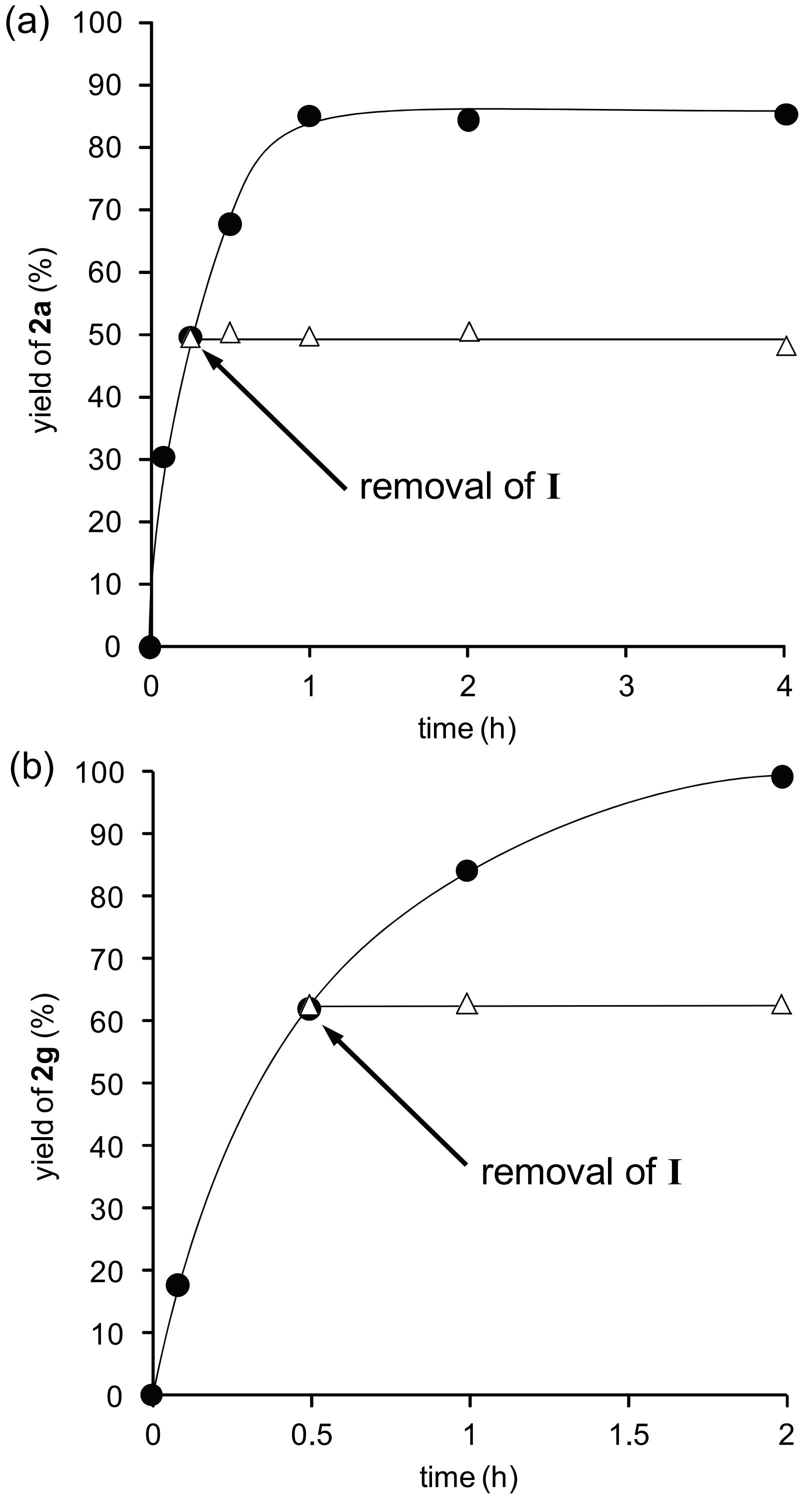


Fig. 6 Effect of removal of **I** on (a) the epoxidation of **1a** and (b) the sulfoxidation of **1g**. Reaction conditions for the epoxidation of **1a**: **1a** (0.2 mmol), **I** (PV2: 2 µmol), 60 % aqueous H_2O_2 (0.2 mmol), EtOAc/*t*-BuOH (1 mL each), 313 K, under air (1 atm). Reaction conditions for the sulfoxidation of **1g**: **1g** (0.2 mmol), **I** (PV2: 2 µmol), 60 % aqueous H_2O_2 (0.2 mmol), EtOAc/*t*-BuOH (1 mL each), 298 K, under air (1 atm).

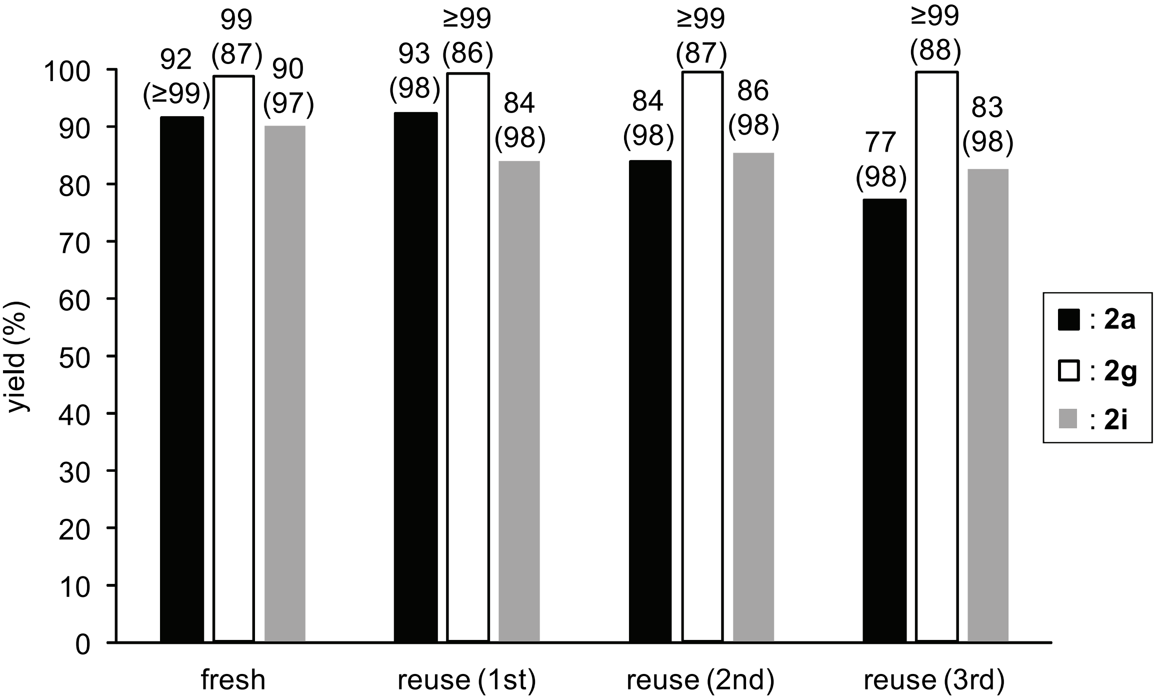


Fig. 7 Recycling of **I** for the oxidation of **1a**, **1g**, and **1i**. Reaction conditions for the epoxidation of **1a**: **1a** (2 mmol), **I** (PV2: 2 μmol), 60 % aqueous H_2O_2 (0.1 mmol), EtOAc/*t*-BuOH (1 mL each), 313 K, 0.5 h, under air (1 atm). $HClO_4$ (1 μmol) was added in each reuse experiment. Reaction conditions for the sulfoxidation of **1g**: **1g** (0.2 mmol), **I** (PV2: 2 μmol), 60 % aqueous H_2O_2 (0.2 mmol), EtOAc/*t*-BuOH (1 mL each), 298 K, 2 h, under air (1 atm). $HClO_4$ (2 μmol) was added in each reuse experiment. Reaction conditions for the hydroxylation of **1i**: **1i** (5 mmol), **I** (PV2: 2 μmol), 60 % aqueous H_2O_2 (0.1 mmol), EtOAc/*t*-BuOH (1 mL each), 298 K, 4 h, under air (1 atm). $HClO_4$ (2 μmol) was added in each reuse experiment. Yield (%) = products (mol)/initial H_2O_2 (mol) × 100. The values in parentheses for the oxidation of **1a**, **1g**, and **1i** are the selectivities to **2a**, **2g**, and **2i**, respectively.