ChemPubSoc Europe

DOI: 10.1002/cctc.201402975

CHEMCATCHEM
Full Papers

Selective Oxidation with Aqueous Hydrogen Peroxide by $[PO_4\{WO(O_2)_2\}_4]^{3-}$ Supported on Zinc-Modified Tin Dioxide

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We prepared supported phosphorus-containing tetranuclear peroxotungstate ($[PO_4\{WO(O_2)_2\}_4]^{3-}$, denoted by PW4) catalysts by using zinc-modified SnO_2 supports with different zinc contents [PW4-Zn(*x*)/SnO_2, in which *x* denotes the zinc content (wt%)]. The supported catalysts, in particular PW4-Zn(0.8)/SnO_2, could act as efficient and reusable heterogeneous catalysts for selective oxidation with aqueous H_2O_2 as the terminal oxidant. The catalytic performance of PW4-Zn(0.8)/SnO_2 was much superior to those of the corresponding homogeneous analogue THA_3PW4 (THA = tetra-*n*-hexylammonium) and the previously reported tungstate-based heterogeneous catalysts such as our W-Zn/SnO_2. In the presence of PW4-Zn(0.8)/SnO_2, various types of organic substrates such as alkenes, amines, silanes, and sulfides could be converted into the corresponding oxygenated products in high to excellent yields by using near-stoichiometric amounts of H_2O_2 with respect to the substrates (typically 1.2 equiv.). The PW4 species interacting with highly dispersed Zn^{2+} species on SnO_2 likely plays an important role in the present oxidation.

Introduction

The oxidative functionalization of organic substrates (alkanes, alkenes, arenes, etc.) to alcohols, carbonyl compounds, epoxides, and phenols is of paramount importance because these oxygenated products have been widely used as starting materials for commodity chemicals and specialty chemicals.[1] The catalytic oxidation with aqueous H_2O_2 as the terminal oxidant has attracted much attention because of its high content of active oxygen species and coproduction of only water.[1,2] Although various effective transition-metal-based catalysts such as titanium,[3] vanadium,[4] manganese,[5] iron,[6] tungsten,[7,8] rhenium,[9] and platinum[10] have been reported for H_2O_2-based oxidation, most of them are homogeneous, and the catalyst separation, recovery, and reuse are difficult in some cases. Therefore, many methodologies (adsorption, covalent linkage, ion exchange, physical entrapment, etc.) for the heterogenization of active homogeneous oxidation catalysts have been developed.[11] Generally, the heterogenized catalysts can be recovered through simple filtration or centrifugation, and the recovered catalysts can be recycled. However, the catalytic activities and selectivities of the parent homogeneous catalysts are decreased by the heterogenization in most cases.[2,11] In this context, the design and development of heterogenized catalysts with their catalytic performances at least comparable to or preferably higher than those of the corresponding homogeneous analogues are one of the most challenging subjects in this research area.

Polyoxometalates (POMs) are a large family of early transition metal–oxygen cluster anions and have been used in many research fields such as catalysis, functional material, and medicine because their physical and chemical properties can be finely controlled by choosing constituent elements.[12] In addition, POMs are thermally and oxidatively stable, and thus they have received much attention, especially as oxidation catalysts.[13] Among the POM-catalyzed oxidation systems with H_2O_2 as the terminal oxidant, the catalytic systems based on a phosphorus-containing tetranuclear peroxotungstate ($[PO_4\{WO(O_2)_2\}_4]^{3-}$, denoted by PW4; Figure 1) and its related compounds have been investigated extensively. Typically, they can homogeneously catalyze H_2O_2-based selective oxidation of alkenes, alcohols, amines, alkynes, and sulfides.[8] Although many heterogeneous catalysts based on PW4 have also been developed (Table S1),[14] they have several disadvantages; for example, 1) the catalytic performances of the previously reported tungstate-based heterogeneous catalysts are (sometimes much) lower than those of the corresponding homogeneous analogues (i.e., alkylammonium salts of PW4),

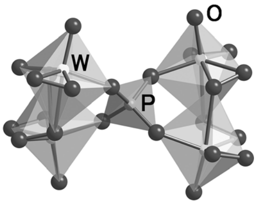

Figure 1. Molecular structure of the anion part of THA_3PW4.[8b]

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402975.

2) their poor stabilities sometimes lead to leaching of the catalytically active tungstate species and difficulty in their recycling without significant loss of their catalytic performances, and/or 3) their application to nonactivated substrates such as terminal alkenes is still limited.[14]

We have previously designed a good anion-exchange support by modifying SnO_2 with zinc (Zn/SnO_2) and created catalytically active polytungstates with dioxo groups on the support.[15] The supported polytungstate catalyst (W-Zn/SnO_2) showed high catalytic performance for the selective oxidation of various organic substrates with aqueous H_2O_2 as the oxidant.[15] Herein, we have developed efficient heterogeneous oxidation catalysts by the immobilization of PW4 onto zinc-modified SnO_2 supports [PW4-Zn(x)/SnO_2, in which x denotes the zinc content (wt %)]. The PW4-Zn(x)/SnO_2 catalysts, in particular PW4-Zn(0.8)/SnO_2, could act as efficient heterogeneous catalysts for the H_2O_2-based oxidation of various types of organic substrates. Notably, the catalytic performance of PW4-Zn(0.8)/SnO_2 was much superior to those of the corresponding homogeneous analogue THA_3PW4 (THA = tetra-*n*-hexylammonium) as well as the previously reported tungstate-based heterogeneous catalysts such as our W-Zn/SnO_2 (Table S1).[14,15] Herein, we also investigated the active species for the present oxidation by using solid-state ^{31}P MAS NMR spectroscopy.

Results and Discussion

Preparation of supported PW4 catalysts

We prepared six types of PW4-Zn(x)/SnO_2 catalysts (x = 0.4, 0.8, 1.2, 1.6, 2.4, and 4.9) by the immobilization of PW4 onto the Zn(x)/SnO_2 supports. Other supported PW4 catalysts (PW4/support or PW4-Zn/support) were also prepared with SnO_2, ZnO, and zinc-modified supports such as Zn/Al_2O_3, Zn/SiO_2, Zn/TiO_2, and Zn/ZrO_2. It has been confirmed by using ^{31}P NMR spectroscopy that alkylammonium salts of PW4 are present as single species in organic media.[16] In contrast, several species such as PW4 and phosphorus-containing mono-, di-, and trinuclear peroxotungstates are observed in aqueous solutions containing $[PO_4]^{3-}$, $[WO_4]^{2-}$, and H_2O_2 owing to the interconversion between PW4 and other peroxotungstates.[16] Therefore, herein, we used THA_3PW4 as the precursor (see the Experimental Section for the synthesis of THA_3PW4), and the supported PW4 catalysts were prepared in CH_3CN (see the Experimental Section for the detailed procedures).

Elemental analyses of PW4-Zn(x)/SnO_2 revealed that the molar ratio of phosphorus/tungsten in each sample was approximately 1:4 (Table S2) and that the carbon and nitrogen contents were almost negligible (e.g., C 0.13 %, N 0.05 % for PW4-Zn(0.8)/SnO_2). The Raman spectra of PW4-Zn(x)/SnO_2 showed two characteristic bands assginable to ν(W=O) (951–959 cm^{-1}) and ν(O–O) (854–859 cm^{-1}),[14] and the bands attributable to THA were hardly observed (Figure S1). The stoichiometric oxidation of triphenylphosphine (250 μmol) with PW4-Zn(0.8)/SnO_2 (W 5.0 μmol) gave 9.2 μmol of triphenylphosphine oxide, which suggested that PW4-Zn(0.8)/SnO_2 has 2 equiv. of active oxygen species with respect to one tungsten atom. These results indicate that PW4 is immobilized onto Zn(x)/SnO_2, likely with the retention of its molecular structure.

Effect of solvents and catalysts on the epoxidation of cyclooctene

The catalytic epoxidation of cyclooctene (**1a**) with 60 % aqueous H_2O_2 (1.2 equiv. with respect to **1a**) was initially performed in dimethyl carbonate (DMC), which was the best solvent for our previously reported W-Zn/SnO_2-catalyzed epoxidation (Table 1).[15] In the presence of PW4-Zn(0.8)/SnO_2, 1,2-epoxycyclooctane (**2a**) was obtained in 99 % yield for only 15 min (Table 1, entry 1), whereas W-Zn/SnO_2 gave **2a** in 22 % yield under the same reaction conditions (Table 1, entry 10). The PW4-Zn(0.8)/SnO_2-catalyzed epoxidation also efficiently proceeded in other polar solvents such as CH_3CN and EtOAc, which gave **2a** in 99 and 96 % yields, respectively (Table 1, entries 7 and 8). Notably, the catalytic activity of PW4-Zn(0.8)/SnO_2 in CH_3CN was much higher than that of the parent homogeneous catalyst THA_3PW4 (Table 1, entry 7 vs entry 9); the reaction rate with PW4-Zn(0.8)/SnO_2 (64.9 mM min^{-1}) was approximately 12 times faster than that with THA_3PW4 (5.2 mM min^{-1}) under the same conditions (Figure 2). Such a significant increase in the reaction rates of homogeneous catalysts by the simple immobilization onto supports has scarcely been reported to date.[14n,17]

Table 1. Effects of catalysts and solvents on the epoxidation of **1a** with H_2O_2.[a]

Entry	Catalyst	Solvent	Yield of **2a** [%]
1	PW4-Zn(0.8)/SnO_2	DMC	99
2[b]	PW4-Zn(0.8)/SnO_2	DMC	99
3[b,c]	PW4-Zn(0.8)/SnO_2	DMC	97
4[b,d]	PW4-Zn(0.8)/SnO_2	DMC	99
5[e]	PW4-Zn(0.8)/SnO_2	DMC	95
6[f]	PW4-Zn(0.8)/SnO_2	DMC	98
7	PW4-Zn(0.8)/SnO_2	CH_3CN	99
8	PW4-Zn(0.8)/SnO_2	EtOAc	96
9	THA_3PW4	CH_3CN	24
10	W-Zn/SnO_2	DMC	22
11	PW4-Zn/Al_2O_3	DMC	13
12	PW4-Zn/SiO_2	DMC	6
13	PW4-Zn/TiO_2	DMC	26
14	PW4-Zn/ZrO_2	DMC	14
15	PW4/SnO_2	DMC	14
16	PW4/ZnO	DMC	1
17[g]	Zn(0.8)/SnO_2	DMC	< 1
18[g]	SnO_2	DMC	1
19	–	DMC	< 1

[a] Reaction conditions: catalyst (W: 3.5 mol % with respect to **1a**), **1a** (0.5 mmol), solvent (1.5 mL), 60 % aqueous H_2O_2 (0.6 mmol), T = 333 K, t = 15 min; yield (%) = [**2a** (mol)/initial **1a** (mol)] × 100. [b] **1a** (1 mmol), solvent (3 mL), 60 % aqueous H_2O_2 (1.2 mmol). [c] First reuse. [d] Second reuse. [e] T = 305 K, t = 3 h. [f] 30 % aqueous H_2O_2 (0.6 mmol), t = 2 h. [g] Catalyst (187 mg).

The epoxidation of **1a** also efficiently proceeded even at the lower temperature (305 K) or with 30 % aqueous H_2O_2, which

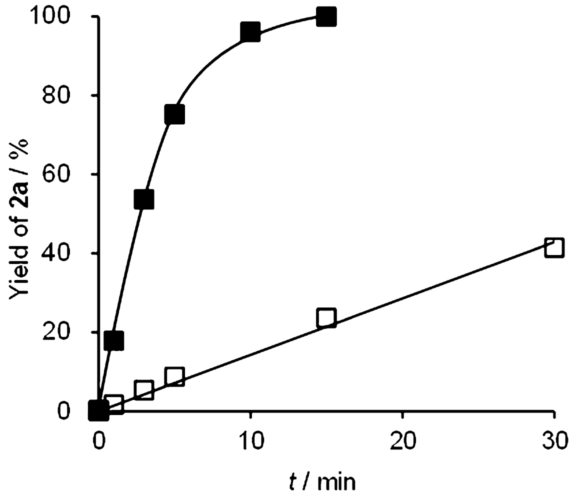


Figure 2. Reaction profiles for the epoxidation of **1 a** with H_2O_2 catalyzed by PW4-Zn(0.8)/SnO_2 (■) and THA_3PW4 (□). Reaction conditions: catalyst (W: 3.5 mol% with respect to **1 a**), **1 a** (0.5 mmol), CH_3CN (1.5 mL), 60% aqueous H_2O_2 (0.6 mmol), $T = 333$ K.

afforded almost quantitative yields of **2 a**, though longer reaction times were required (Table 1, entries 5 and 6). The epoxidation did not proceed at all in the absence of PW4-Zn(0.8)/SnO_2 (Table 1, entry 19) or in the presence of just supports such as SnO_2 and Zn(0.8)/SnO_2 (Table 1, entries 17 and 18). Other supported PW4 catalysts prepared by using zinc-modified supports such as Zn/Al_2O_3, Zn/SiO_2, Zn/TiO_2, and Zn/ZrO_2 were not effective for the epoxidation (Table 1, entries 11–14).[18] The reaction rates for the epoxidation with PW4/SnO_2 and PW4/ZnO were much lower than that with PW4-Zn(0.8)/SnO_2 (Table 1, entries 15 and 16).

Furthermore, we investigated the effect of zinc contents (x values) in PW4-Zn(x)/SnO_2 on the catalytic activities for the epoxidation of **1 a**. As shown in Figure 3 a, the reaction rate increased with an increase in zinc content, reached the maximum at 0.8 wt%, and then decreased. The solid-state ^{31}P MAS NMR spectra of PW4-Zn(x)/SnO_2 ($x = 0.4$, 0.8, 1.2, 1.6, 2.4, and 4.9), PW4/SnO_2 ($x = 0$), and PW4/ZnO are shown in Figure 4. The ^{31}P MAS NMR spectra of PW4/SnO_2 and PW4/ZnO showed single signals at −1.29 and 4.96 ppm, respectively (Figure 4 a and h). The signal position and full-width at half-maximum (FWHM) of PW4-Zn(4.9)/SnO_2 (4.96 ppm; FWHM = 1.69 kHz) (Figure 4 g) were almost the same as those of PW4/ZnO (4.96 ppm; FWHM = 1.48 kHz) (Figure 4 h), which suggests that ZnO is formed on the surface of SnO_2 in the case of PW4-Zn(4.9)/SnO_2 and that PW4 species is mostly immobilized on the support by interaction with ZnO species.

The ^{31}P MAS NMR spectra of PW4-Zn(x)/SnO_2 (except for $x = 4.9$) could not be well reproduced by using only the two deconvoluted signals at −1.29 (PW4 on SnO_2) and 4.96 ppm (PW4 on ZnO). In addition to the two deconvoluted signals, we used the deconvoluted signal at 0.60 ppm and thus could adequately reproduce the ^{31}P MAS NMR spectra of PW4-Zn(x)/SnO_2, as shown in Figure 4. The distributions of each deconvoluted signal (determined from the signal intensities) were plotted against the zinc contents (Figures 3 b and S2). The fraction of the −1.29 ppm signal decreased monotonically and disappeared completely at 1.6 wt% (Figure S2 a). The fraction of the 4.96 ppm signal was not observed at 0.4 wt%, which began to increase at 0.8 wt% and then increased monotonically (Figure S2 c). Zinc species on SnO_2 likely existed as monomerically (or highly) dispersed Zn^{2+} species and started to aggregate to form ZnO at 0.8 wt%. The dependencies of −1.29 and 4.96 ppm fractions on zinc contents were not consistent with the correlation between reaction rates and zinc contents (Figures 3 a, S2 a, and S2 c). The fraction of the 0.60 ppm signal increased with an increase in zinc content, reached the maximum at 1.2 wt%, and then decreased (Figure 3 b). This tendency was quite similar to the relationship between reaction rates and zinc contents (Figure 3 a). Thus, the 0.60 ppm signal corre-

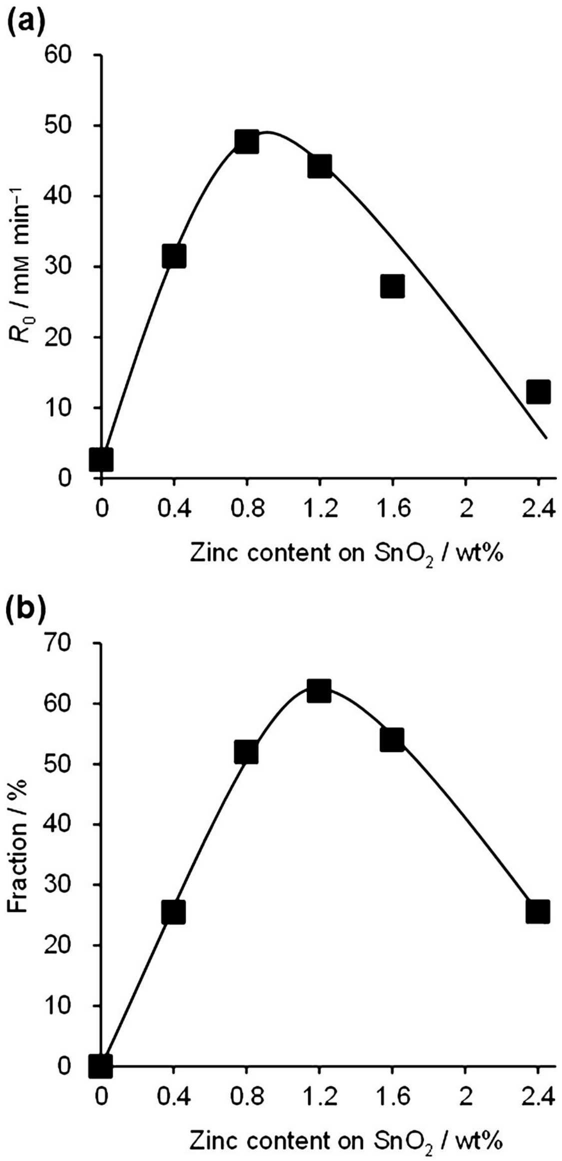


Figure 3. Plots of a) reaction rates and b) fractions of 0.60 ppm signals (PW4 interacting with Zn^{2+} species dispersed on SnO_2) against zinc contents (x values) on PW4/SnO_2 ($x = 0$) and PW4-Zn(x)/SnO_2 ($x = 0.4$–2.4). Reaction conditions: catalyst (W: 3.5 mol% with respect to **1 a**), **1 a** (0.5 mmol), DMC (1.5 mL), 60% aqueous H_2O_2 (0.6 mmol), $T = 333$ K.

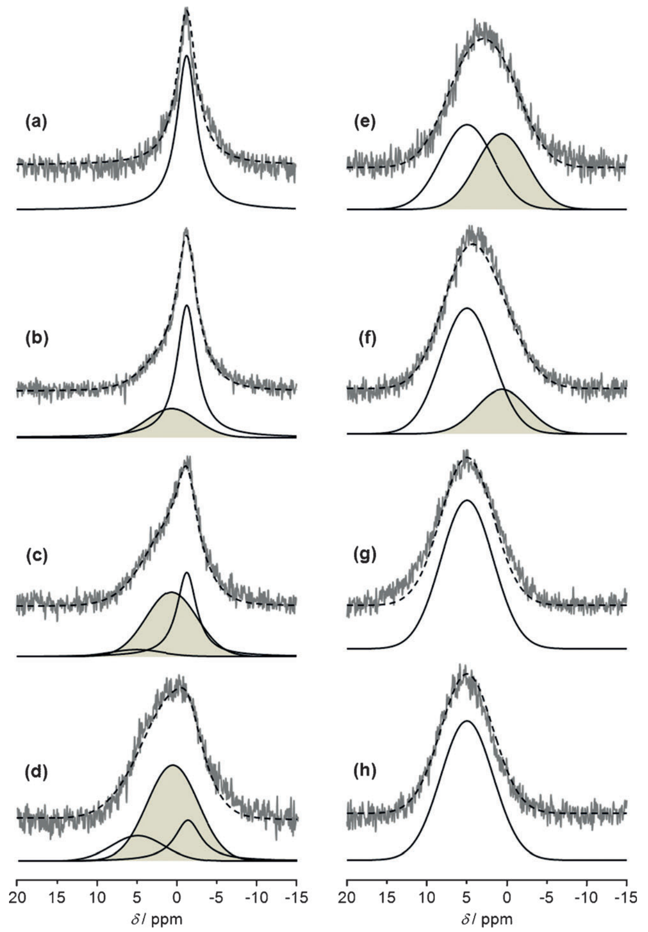


Figure 4. ^{31}P MAS NMR spectra of a) PW4/SnO_2, b) PW4-Zn(0.4)/SnO_2, c) PW4-Zn(0.8)/SnO_2, d) PW4-Zn(1.2)/SnO_2, e) PW4-Zn(1.6)/SnO_2, f) PW4-Zn(2.4)/SnO_2, and g) PW4-Zn(4.9)/SnO_2, and h) PW4/ZnO. Solid and broken lines indicate the deconvoluted signals and the sum of deconvoluted signals, respectively. The deconvoluted 0.6 ppm signals are highlighted.

sponds to that of active species for the present oxidation. In separate experiments, we found that the reaction rates of the homogeneously THA_3PW4-catalyzed epoxidation of **1a** in CH_3CN increased dramatically in the presence of Zn^{2+} species (Table S3). From all the above-mentioned experimental evidences, we conclude that the 0.60 ppm signal is possibly assignable to the PW4 species interacting with Zn^{2+} species dispersed on SnO_2.

Heterogeneous catalysis and catalyst reuse

Hereafter, we mainly used the most active PW4-Zn(0.8)/SnO_2 catalyst for further investigations about the heterogeneous catalysis, catalyst reuse, and substrate scope. First, to verify whether the observed catalysis is derived from solid PW4-Zn(0.8)/SnO_2 or leached tungsten species, the epoxidation of **1a** was performed in DMC under the conditions described in Figure 5, and PW4-Zn(0.8)/SnO_2 was removed from the reaction mixture through hot filtration at approximately 40% conversion of **1a** (at $t=3$ min). Then, the filtrate was heated again at 333 K. In this case, no further production of **2a** was observed (Figure 5). It was confirmed by using inductively coupled plasma combined with atomic emission spectroscopy that the leaching of tungsten species in the filtrate was almost negligible (<0.4% with respect to the tungsten content in the fresh catalyst). In addition, the first-order dependence of the reaction rate on the amount of PW4-Zn(0.8)/SnO_2 (W ≈5 mol%) was observed (Figure S3). These results can rule out any contribution to the observed catalysis of the tungsten species that leached into the reaction solution, and the nature of the observed catalysis is truly heterogeneous.[19] In separate experiments, we also confirmed the heterogeneous catalysis of PW4-Zn(0.8)/SnO_2 even with use of CH_3CN as the solvent.

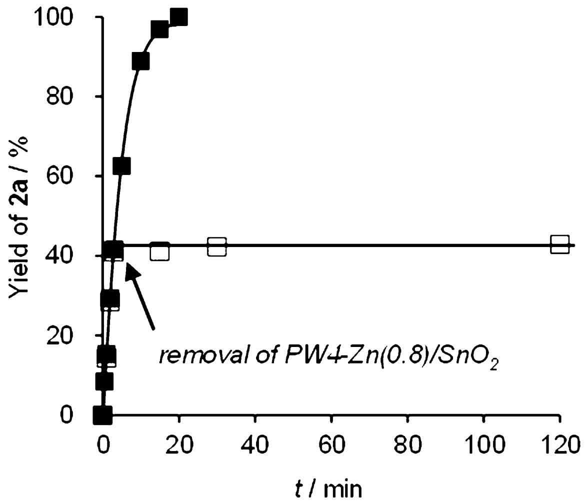


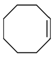
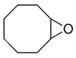
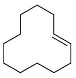
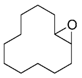
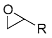
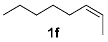
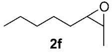
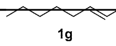
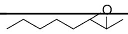
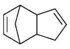
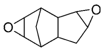
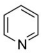
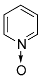
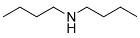
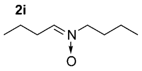
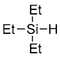
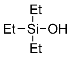
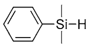
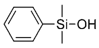
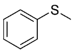
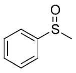
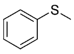
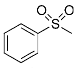
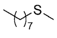
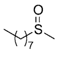
Figure 5. Effect of removal of PW4-Zn(0.8)/SnO_2 on the epoxidation of **1a**. ■, without removal of PW4-Zn(0.8)/SnO_2; □, removal of PW4-Zn(0.8)/SnO_2 as indicated by the arrow. Reaction conditions: PW4-Zn(0.8)/SnO_2 (W: 3.5 mol% with respect to **1a**), **1a** (0.5 mmol), DMC (1.5 mL), 60% aqueous H_2O_2 (0.6 mmol), $T=333$ K.

As mentioned above, PW4-Zn(0.8)/SnO_2 could readily be recovered from the reaction mixture through simple filtration without leaching of the active PW4 species. The Raman spectrum of the recovered PW4-Zn(0.8)/SnO_2 catalyst after the second reuse experiment did not change much in comparison with that of the fresh PW4-Zn(0.8)/SnO_2 catalyst (Figure S4). The recovered PW4-Zn(0.8)/SnO_2 catalyst could be reused at least twice for the epoxidation of **1a** without significant loss of its high catalytic performance; yield of **2a**: 99% (fresh), 97% (first reuse), and 99% (second reuse); the reaction rate: 53.0 mM min^{-1} (fresh), 50.2 mM min^{-1} (first reuse), 48.6 mM min^{-1} (second reuse) (Table 1, entries 2–4).

Substrate scope

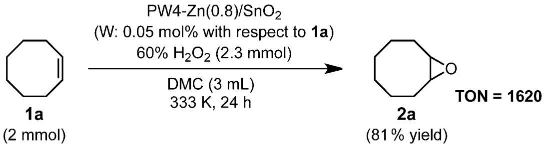
Finally, we investigated the scope of the present PW4-Zn(0.8)/SnO_2-catalyzed system for the oxidation of various types of alkenes, amines, silanes, and sulfides. In all reactions, the catalytic activities of PW4-Zn(0.8)/SnO_2 were much higher than those of our previously reported W-Zn/SnO_2.[15] The results with PW4-Zn(0.8)/SnO_2 as well as W-Zn/SnO_2 are summarized in Table 2. Cyclic internal alkenes such as **1a** and cyclododecene (**1b**) were quantitatively oxidized to give the corresponding epox-

Table 2. Selective oxidation of various substrates with H_2O_2 catalyzed by PW4-Zn(0.8)/SnO_2.[a]

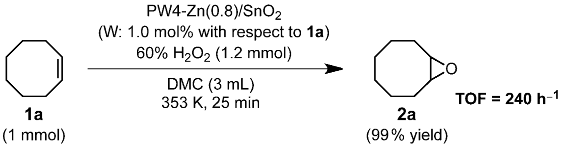
Entry	Substrate	t [min]	Product	Yield [%] (Selectivity [%]) PW4-Zn(0.8)/SnO_2	W-Zn/SnO_2
1	 **1a**	15	 **2a**	99 (99) 47.7 $\mathrm{mM\,min^{-1}}$	22 (99) 5.2 $\mathrm{mM\,min^{-1}}$
2	 **1b**	90	 **2b**	99 (99) 17.7 $\mathrm{mM\,min^{-1}}$	58 (99) 2.5 $\mathrm{mM\,min^{-1}}$
	 **1c-1e**		 **2c-2e**		
3[b,c]	R=CH_3 (**1c**)	60	R=CH_3 (**2c**)	91 (96)	22 (99)
4	R=n-C_6H_{13} (**1d**)	180	R=n-C_6H_{13} (**2d**)	79 (90) 2.8 $\mathrm{mM\,min^{-1}}$	26 (93) 0.5 $\mathrm{mM\,min^{-1}}$
5	R=n-$C_{10}H_{21}$ (**1e**)	240	R=n-$C_{10}H_{21}$ (**2e**)	75 (86)	32 (95)
6	 **1f**	30	 **2f**	97 (94) 24.9 $\mathrm{mM\,min^{-1}}$	18 (99) 7.2 $\mathrm{mM\,min^{-1}}$
7	 **1g**	180	 **2g**	98 (98) 7.1 $\mathrm{mM\,min^{-1}}$	50 (99) 0.9 $\mathrm{mM\,min^{-1}}$
8[d]	 **1h**	60	 **2h**	98 (99)	80 (31)
9	 **1i**	90	 **2i**	99 (99)	32 (99)
10[d]	 **1j**	20	 **2j**	89 (99)	79 (98)
11[e,f]	 **1k**	240	 **2k**	98 (99)	59 (99)
12[e,f]	 **1l**	120	 **2l**	99 (97)	33 (94)
13[c,g]	 **1m**	7	 **2m**	87 (84)	26 (98)
14[f,h]	 **1m**	1	 **3m**	99 (99)	19 (3)
15[c,g]	 **1n**	5	 **2n**	85 (86)	23 (98)

[a] Reaction conditions: catalyst (W: 3.5 mol% with respect to **1**), **1** (0.5 mmol), DMC (1.5 mL), 60% aqueous H_2O_2 (0.6 mmol), $T=333$ K; yield (%)=[sum of oxygenated products (mol)/initial **1** (mol)]×100; selectivity (%)=[desired products (mol)/sum of oxygenated products (mol)]×100. [b] **1c** (6 atm; 1 atm=101.3 kPa), DMC (3 mL); yield was based on the initial H_2O_2. [c] 60% aqueous H_2O_2 (1 mmol). [d] Catalyst (W: 7 mol% with respect to **1**), **1** (0.25 mmol). [e] 60% aqueous H_2O_2 (0.5 mmol). [f] 315 K. [g] Catalyst (W: 0.7 mol% with respect to **1**), **1** (1 mmol), DMC (1 mL), 293 K. [h] 60% aqueous H_2O_2 (1.2 mmol).

ides with 1.2 equiv. of H_2O_2 with respect to the substrates (Table 2, entries 1 and 2). As for the epoxidation of **1a**, the amount of the catalyst could be reduced much; even if the epoxidation was performed with only 0.05 mol% of tungsten, **2a** was obtained in 81% yield [Eq. (1)]. In this case, the turnover number (TON) based on tungsten species reached up to 1620. Moreover, the turnover frequency (TOF) was 240 h^{-1} under the conditions described in Equation (2). These TON and TOF values were the highest among those of the previously reported epoxidation with tungstate-based heterogeneous catalysts such as W-Zn/SnO_2 (TON 19–650; TOF 1–175 h^{-1}; Table S1)[14,15] by using near-stoichiometric amounts of H_2O_2 with respect to **1a** (1.0–1.5 equiv.).



(1)



(2)

In the presence of PW4-Zn(0.8)/SnO_2, the epoxidation of less reactive nonactivated C_3–C_{12} terminal alkenes (**1c–e**) also efficiently proceeded (Table 2, entries 3–5). For the epoxidation of *cis*- and *trans*-2-octenes (**1f** and **g**), the configurations around the C=C moiety were completely retained in the corresponding epoxides (**2f** and **g**) (Table 2, entries 6 and 7), which strongly suggests that the free-radical intermediates are not involved in the present PW4-Zn(0.8)/SnO_2-catalyzed epoxidation. The ratio of the reaction rate of **1f** to that of **1g** was 3.5 and comparable to that of the homogeneous PW4 (3.7).[7a] This result also suggests that the structure of PW4 in the catalyst was preserved. The epoxidation of dicyclopentadiene (**1h**) with 2.4 equiv. of H_2O_2 selectively gave the corresponding diepoxide **2h** in 98% yield, whereas W-Zn/SnO_2 gave a mixture of mono- and diepoxides under the same conditions (Table 2, entry 8).

Pyridine (**1i**) and di-n-butylamine (**1j**) were oxidized to the corresponding N-oxide (**2i**) and nitrone (**2j**) in 99 and 89% yields, respectively (Table 2, entries 9 and 10). Triethylsilane (**1k**) and a more sterically exposed dimethylphenylsilane (**1l**) were selectively oxidized to the corresponding silanols (**2k** and **l**) without the formation of the corresponding disiloxanes through dehydrogenative condensations of the silanols (Table 2, entries 11 and 12). The oxidation of thioanisole (**1m**) and methyl n-octyl sulfide (**1n**) with an equimolar amount of H_2O_2 with respect to the substrates was completed within only 7 min, which results in the selective production of the corresponding sulfoxides (**2m** and **n**) (Table 2, entries 13 and 15). With regard to the oxidation of sulfides, the product selectivity could be controlled by changing the H_2O_2/substrate ratio; for example, if 2.4 equiv. of H_2O_2 was used with respect to **1m**, methyl phenyl sulfone (**3m**) was selectively obtained in 99% yield (Table 2, entry 14).

Conclusions

We have developed efficient heterogeneous catalysts for H_2O_2-based selective oxidation by the immobilization of phosphorus-containing tetranuclear peroxotungstate ($[PO_4\{WO(O_2)_2\}_4]^{3-}$, denoted by PW4) onto the zinc-modified supports (PW4-Zn(*x*)/SnO_2). Most importantly, the catalytic performance of PW4-Zn(0.8)/SnO_2 was much higher than that of the corresponding homogeneous analogue THA_3PW4 (THA = tetra-*n*-hexylammonium). In the presence of PW4-Zn(0.8)/SnO_2, various types of organic substrates such as alkenes, amines, silanes, and sulfides could be converted into the corresponding epoxides, *N*-oxides, silanols, and sulfoxides (or sulfones), respectively, in high to excellent yields. The observed catalysis for the present oxidation was truly heterogeneous, and the recovered catalyst could be reused without significant loss of its high catalytic performance.

Experimental Section

Materials

CH_3CN (Kanto Chemical Co., Inc.) was purified with the Ultimate Solvent System (Glass Contour Company) before use.[20] Substrates were purified according to the reported procedures.[21] Deuterated solvents (CD_3CN, $CDCl_3$, and D_2O) were purchased from Acros Organics and used as received. Tungstic acid (Wako Pure Chemical Industries, Ltd), H_3PO_4 (85 % aqueous solution, Kanto Chemical), tetra-*n*-hexylammonium chloride (Aldrich), H_2O_2 (30 % aqueous solution, Kanto Chemical), zinc nitrate hexahydrate (Kanto Chemical), and solvents [DMC, EtOAc, CH_2Cl_2, and $(C_2H_5)_2O$ (Kanto Chemical)] were purchased and used as received. A solution of 60 % aqueous H_2O_2 was prepared by concentrating 30 % aqueous H_2O_2. SnO_2 (Guaranteed Reagent, >98 %, Kanto Chemical, BET surface area: 51 m^2g^{-1}), SiO_2 (CARiACT G-3CN, Fuji Silysia Chemical Ltd., BET surface area: 335 m^2g^{-1}), γ-Al_2O_3 (NKHD-24, Sumitomo Chemical Co., Ltd., BET surface area: 300 m^2g^{-1}), TiO_2 (ST-01, Ishihara Sangyo Kaisha, Ltd., BET surface area: 129 m^2g^{-1}), ZrO_2 (RC-100, Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 89 m^2g^{-1}), and ZnO (BET surface area: 27 m^2g^{-1}) were used as supports. These supports were pretreated by calcination in air at 673 K for 3 h.

Instruments

The IR spectra were recorded on a JASCO FT/IR-4100 spectrometer Plus using KCl disks. The Raman spectra were recorded on a JASCO NRS 5100 spectrometer with excitation at 531.99 nm. The UV/Vis spectra were recorded on a JASCO V-570 spectrometer. The solution-state NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (^1H NMR: 270.0 MHz; ^{13}C NMR: 67.8 MHz; ^{31}P NMR: 109.3 MHz; ^{183}W NMR: 11.2 MHz) with 5 mm tubes (for ^1H and ^{13}C NMR) or 10 mm tubes (for ^{31}P and ^{183}W NMR) or on a JEOL ECA-500 spectrometer (^1H NMR: 495.1 MHz; ^{13}C NMR: 124.5 MHz) with 5 mm tubes. Chemical shifts were reported as parts per million in the δ scale downfield from $SiMe_4$ (solvent, $CDCl_3$) for ^1H and ^{13}C NMR spectra, 85 % H_3PO_4 for ^{31}P NMR spectra, and 2 M Na_2WO_4 (solvent, D_2O) for ^{183}W NMR spectra. The solid-state ^{31}P MAS (MAS rate = 5 kHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer at 200.4 MHz by using 8 mm zirconia rotor. The 90° pulse width was 8.5 μs. The relaxation time for PW4-Zn(*x*)/SnO_2 (t_1 = 14.4 s) was calculated by using an inversion recovery method. For the quantitative analyses, a single-pulse nondecoupling sequence was used to avoid any effects of incomplete decoupling. The spectra were measured for 1000 scans with a 45° pulse (pulse width = 4.25 μs) and a pulse delay of 60 s. The accumulated flame ionization detector was processed without window functions. Chemical shifts (δ) were reported in ppm downfield from 85 % H_3PO_4. $NH_4H_2PO_4$ (1.00 ppm) was used as an external standard for the calibration of chemical shifts. Inductively coupled plasma combined with atomic emission spectroscopy analyses were performed with a Shimadzu ICPS-8100 spectrometer. The BET surface areas were measured on a Micromeritics ASAP 2010 analyzer and calculated from the N_2 adsorption isotherm by using the BET equation. GC analyses were performed on Shimadzu GC-2014 gas chromatograph equipped with a flame ionization detector and a DB-WAX capillary column (internal diameter: 0.25 mm; length: 30 m) or a TC-1 capillary column (internal diameter: 0.25 mm; length: 30 m). The cold-spray ionization mass (CSI MS) spectra were recorded on a JEOL JMS-T100CS spectrometer. Typical measurement conditions were as follows: orifice voltage 85 V for positive ions; sample flow 0.1 mL min^{-1}; solvent CH_3CN; concentration 0.1 mM; spray temperature 263 K; ion source at RT.

Synthesis and characterization of THA_3PW4

The THA salt of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ (THA_3PW4) was synthesized according to the procedure described in the literature.[8b] Yield: 1.39 g (50 %); ^{31}P NMR (CD_3CN, 298 K): $\delta = 4.5$ ppm ($^2J_{W\text{-}P} = 18.5$ Hz); ^{183}W NMR (CD_3CN, 298 K): $\delta = -588.2$ ppm ($^2J_{W\text{-}P} = 18.4$ Hz, $\Delta\nu_{1/2} = 7.3$ Hz); IR (KCl): $\tilde{\nu} = 977$, 853, 843, 797, 757, 728, 660, 649, 603, 591, 573, 549, 525, 444 cm^{-1}; Raman: $\tilde{\nu} = 990$, 864, 821, 655, 597, 580, 543, 391, 333, 305, 266, 237 cm^{-1}; UV/Vis (CH_3CN) λ_{max} (ε) = 254.2 nm (1268 $mol_W^{-1}\,dm^3\,cm^{-1}$); positive ion MS (CSI, CH_3CN): *m/z*: 2569 $[(THA)_4PO_4\{WO(O_2)_2\}_4]^+$; elemental analysis calcd (%) for $C_{72}H_{156}N_3O_{24}PW_4$ ($(THA)_3[PO_4\{WO(O_2)_2\}_4]$): C 39.05, H 7.10, N 1.90, P 1.40, W 32.22; found: C 38.82, H 6.97, N 1.36, P 1.36, W 33.28.

Preparation of PW4-Zn(0.8)/SnO_2

An aqueous solution (20 mL) of zinc nitrate hexahydrate (38.7 mg, 130 μmol) containing SnO_2 (1.0 g) was stirred vigorously for 1 h at RT. The solution was evaporated to dryness at 323 K, and the resulting solid was calcined in air for 2 h at 473 K, which gave Zn(0.8)/SnO_2. Then, a CH_3CN solution (10 mL) of THA_3PW4 (188 mg, 85 μmol) and 60 % aqueous H_2O_2 (30 μL, 680 μmol) containing Zn(0.8)/SnO_2 was stirred vigorously for 1 h at RT. The resulting solid was collected through filtration, washed with cooled CH_3CN (400 mL), and evacuated to dryness at RT. The pale yellow solid of PW4-Zn(0.8)/SnO_2 was obtained. The contents of phosphorus and tungsten were 0.065 and 1.85 wt %, respectively. The other supported PW4 catalysts were prepared by using the procedure described above.

Procedure for catalytic oxidation

The catalytic oxidation of organic substrates was performed in a 30 mL glass vessel containing a magnetic stir bar. The epoxidation of **1 c** was performed with an autoclave reactor with a Teflon vessel. A typical procedure for catalytic oxidation was as follows: **1 a** (1 mmol), 60 % aqueous H_2O_2 (1.2 mmol), and DMC (3 mL) were charged to the reactor. The reaction was initiated by the addition of PW4-Zn(0.8)/SnO_2 (W 3.5 mol % with respect to **1 a**), and the reaction solution was periodically analyzed by using GC. The remaining H_2O_2 after the reaction was analyzed by performing $Ce^{3+/4+}$ titration.[22] The products were identified by comparing their GC retention times, GC mass spectra, and/or ^{1}H and ^{13}C NMR spectra with the literature data.

Acknowledgements

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)", Grants-in-Aid for JSPS Fellows and Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology of Japan, and Grant for Basic Science Research Projects from The Sumitomo Foundation(No. 130417).

Keywords: epoxidation · heterogeneous catalysis · hydrogen peroxide · peroxotungstate · phosphorus

[1] a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633–639; b) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514; c) *Modern Oxidation Methods* (Ed.: J.-E. Bäckvall), Wiley-VCH, Weinheim, **2004**; d) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329–2363; e) D. Schröder, H. Schwarz, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 18114–18119; f) F. Cavani, J. H. Teles, *ChemSusChem* **2009**, *2*, 508–534.

[2] a) B. S. Lane, K. Burgess, *Chem. Rev.* **2003**, *103*, 2457–2474; b) *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis* (Ed.: S. T. Oyama), Elsevier, Amsterdam, **2008**; c) M. Uyanik, K. Ishihara, *ACS Catal.* **2013**, *3*, 513–520; d) G. B. Shul'pin, *Dalton Trans.* **2013**, *42*, 12794–12818; e) O. A. Kholdeeva, *Catal. Sci. Technol.* **2014**, *4*, 1869–1889.

[3] a) M. G. Clerici, P. Ingallina, *J. Catal.* **1993**, *140*, 71–83; b) Y. Sawada, K. Matsumoto, S. Kondo, H. Watanabe, T. Ozawa, K. Suzuki, B. Saito, T. Katsuki, *Angew. Chem. Int. Ed.* **2006**, *45*, 3478–3480; *Angew. Chem.* **2006**, *118*, 3558–3560; c) O. A. Kholdeeva, *Eur. J. Inorg. Chem.* **2013**, 1595–1605; d) P. Wu, Y. Kubota, T. Yokoi, *ACS Catal.* **2014**, *4*, 23–30.

[4] a) A. Butler, M. J. Clague, G. E. Meister, *Chem. Rev.* **1994**, *94*, 625–638; b) K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara, N. Mizuno, *Nat. Chem.* **2010**, *2*, 478–483; c) V. Conte, B. Floris, *Dalton Trans.* **2011**, *40*, 1419–1436; d) D. Wischang, O. Brücher, J. Hartung, *Coord. Chem. Rev.* **2011**, *255*, 2204–2217; e) K. Kamata, T. Yamaura, N. Mizuno, *Angew. Chem. Int. Ed.* **2012**, *51*, 7275–7278; *Angew. Chem.* **2012**, *124*, 7387–7390.

[5] a) P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy, *J. Am. Chem. Soc.* **1988**, *110*, 8462–8470; b) D. E. De Vos, B. F. Sels, M. Reynaers, Y. V. S. Rao, P. A. Jacobs, *Tetrahedron Lett.* **1998**, *39*, 3221–3224; c) B. S. Lane, M. Vogt, V. J. DeRose, K. Burgess, *J. Am. Chem. Soc.* **2002**, *124*, 11946–11954; d) P. Saisaha, J. W. de Boer, W. R. Browne, *Chem. Soc. Rev.* **2013**, *42*, 2059–2074.

[6] a) M. Costas, K. Chen, L. Que Jr., *Coord. Chem. Rev.* **2000**, *200–202*, 517–544; b) M. C. White, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.* **2001**, *123*, 7194–7195; c) M. S. Chen, M. C. White, *Science* **2007**, *318*, 783–787; d) E. P. Talsi, K. P. Bryliakov, *Coord. Chem. Rev.* **2012**, *256*, 1418–1434.

[7] a) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964–966; b) R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* **2003**, 1977–1986; c) N. Mizuno, K. Yamaguchi, K. Kamata, *Coord. Chem. Rev.* **2005**, *249*, 1944–1956; d) K. Kamata, T. Hirano, S. Kuzuya, N. Mizuno, *J. Am. Chem. Soc.* **2009**, *131*, 6997–7004; e) R. Ishimoto, K. Kamata, N. Mizuno, *Angew. Chem. Int. Ed.* **2012**, *51*, 4662–4665; *Angew. Chem.* **2012**, *124*, 4740–4743.

[8] a) C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* **1983**, *48*, 3831–3833; b) C. Venturello, R. D'Aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Catal.* **1985**, *32*, 107–110; c) Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, *J. Org. Chem.* **1987**, *52*, 1868–1870; d) Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587–3593; e) Y. Ishii, T. Yoshida, K. Yamawaki, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 5549–5552; f) T. Oguchi, Y. Sakata, N. Takeuchi, K. Kaneda, Y. Ishii, M. Ogawa, *Chem. Lett.* **1989**, 2053–2056; g) Y. Ishii, Y. Sakata, *J. Org. Chem.* **1990**, *55*, 5545–5547; h) Y. Sakata, Y. Ishii, *J. Org. Chem.* **1991**, *56*, 6233–6235; i) S. Sakaue, Y. Sakata, Y. Nishiyama, Y. Ishii, *Chem. Lett.* **1992**, 289–292; j) Y. Sakata, Y. Katayama, Y. Ishii, *Chem. Lett.* **1992**, 671–674; k) Y. Ishii, H. Tanaka, Y. Nishiyama, *Chem. Lett.* **1994**, 1–4; l) T. Iwahama, S. Sakaguchi, Y. Nishiyama, Y. Ishii, *Tetrahedron Lett.* **1995**, *36*, 1523–1526; m) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem.* **1996**, *61*, 8310–8311; n) E. Antonelli, R. D'Aloisio, M. Gambaro, T. Fiorani, C. Venturello, *J. Org. Chem.* **1998**, *63*, 7190–7206; o) K. Sato, M. Aoki, R. Noyori, *Science* **1998**, *281*, 1646–1647; p) K. Kamata, K. Sugahara, R. Ishimoto, S. Nojima, M. Okazaki, T. Matsumoto, N. Mizuno, *ChemCatChem* **2014**, *6*, 2327–2332.

[9] a) J. Rudolph, K. L. Reddy, J. P. Chiang, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, *119*, 6189–6190; b) W. A. Herrmann, R. M. Kratzer, H. Ding, W. R. Thiel, H. Glas, *J. Organomet. Chem.* **1998**, *555*, 293–295; c) H. Adolfsson, C. Copéret, J. P. Chiang, A. K. Yudin, *J. Org. Chem.* **2000**, *65*, 8651–8658; d) P. Altmann, M. Cokoja, F. E. Kühn, *Eur. J. Inorg. Chem.* **2012**, 3235–3239; e) M. Crucianelli, R. Saladino, F. De Angelis, *ChemSusChem* **2010**, *3*, 524–540.

[10] a) M. Colladon, A. Scarso, P. Sgarbossa, R. A. Michelin, G. Strukul, *J. Am. Chem. Soc.* **2006**, *128*, 14006–14007; b) M. Colladon, A. Scarso, P. Sgarbossa, R. A. Michelin, G. Strukul, *J. Am. Chem. Soc.* **2007**, *129*, 7680–7689; c) A. N. Vedernikov, *Acc. Chem. Res.* **2012**, *45*, 803–813.

[11] a) D. E. de Vos, B. F. Sels, P. A. Jacobs, *Adv. Catal.* **2001**, *46*, 1–87; b) R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, **2007**; c) *Modern Heterogeneous Oxidation Catalysis* (Ed.: N. Mizuno), Wiley-VCH, Weinheim, **2009**; d) G. J. Hutchings, *J. Mater. Chem.* **2009**, *19*, 1222–1235; e) *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications* (Eds.: M. G. Clerici, O. A. Kholdeeva), Wiley-VCH, Weinheim, **2013**; f) Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, *Chem. Soc. Rev.* **2014**, *43*, 3480–3524.

[12] a) Thematic issue on "POMs" (Ed.: C. L. Hill), *Chem. Rev.* **1998**, *98*, 1–389; 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) A. Proust, R. Thouvenot, P. Gouzerh, *Chem. Commun.* **2008**, 1837–1852; d) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758; *Angew. Chem.* **2010**, *122*, 1780–1803; e) B. S. Bassil, U. Kortz, *Dalton Trans.* **2011**, *40*, 9649–9661.

[13] a) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, *41*, 113–252; b) I. V. Kozhevnikov, *Catalysts for Fine Chemical Synthesis Volume 2, Catalysis by Polyoxometalates*, Wiley, Chichester, **2002**; c) C. L. Hill in *Comprehensive Coordination Chemistry II, Vol. 4* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Pegamon, New York, **2004**, pp. 679–759; d) R. Neumann, *Inorg. Chem.* **2010**, *49*, 3594–3601; e) N. Mizuno, K. Kamata, *Coord. Chem. Rev.* **2011**, *255*, 2358–2370.

[14] a) R. Neumann, H. Miller, *J. Chem. Soc. Chem. Commun.* **1995**, 2277–2278; b) R. Neumann, M. Cohen, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1738–1740; *Angew. Chem.* **1997**, *109*, 1810–1812; c) D. Hoegaerts, B. F. Sels, D. E. de Vos, F. Verpoort, P. A. Jacobs, *Catal. Today* **2000**, *60*, 209–218; d) B. F. Sels, A. L. Villa, D. Hoegaerts, D. E. De Vos, P. A. Jacobs, *Top. Catal.* **2000**, *13*, 223–229; e) T. Sakamoto, C. Pac, *Tetrahedron Lett.* **2000**, *41*, 10009–10012; f) G. Gelbard, T. Gauducheau, E. Vidal, V. I. Parvulescu, A. Crosman, V. M. Pop, *J. Mol. Catal. A* **2002**, *182–183*, 257–266; g) J. Li, G. Zyao, S. Gao, Y. Lv, J. Li, Z. Xi, *Org. Process Res. Dev.* **2006**, *10*, 876–880; h) T. Kovalchuk, H. Sfihi, V. Zaitsev, J. Fraissard, *J. Catal.* **2007**, *249*, 1–14; i) L. T. A. Sofia, A. Krishnan, M. Sankar, N. K. K. Raj, P. Manikandan, P. R. Rajamohanan, T. G. Ajithkumar, *J. Phys. Chem. C* **2009**, *113*, 21114–21122; j) Z. Zhang, W. Zhao, B. Ma, Y. Ding, *Catal. Commun.* **2010**, *12*, 318–322; k) N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin, O. A. Kholdeeva, *Inorg. Chem.* **2010**, *49*, 2920–2930; l) Y. Leng, J. Wang, D. Zhu, M. Zhang, P. Zhao, Z. Long, J. Huang, *Green Chem.* **2011**, *13*, 1636–1639; m) W. Zhao, B. Ma, Y. Ding, W. Qiu, *Reac. Kinet. Mech. Cat.* **2011**, *102*, 459–472; n) S. Doherty, J. G. Knight, J. R. Ellison, D. Weekes, R. W. Harrington, C. Hardacre, H. Manyar, *Green Chem.* **2012**, *14*, 925–929; o) C. Swalus, B. Farin, F. Gillard, M. Devillers, E. M. Gaigneaux, *Catal. Commun.* **2013**, *37*, 80–84; p) M. Craven, R. Yahya, E. Kozhevnikova, R. Boomishankar, C. M. Robertson, A. Steiner, I. Kozhevnikov, *Chem. Commun.* **2013**, *49*, 349–351; q) X. Zuwei, Z. Ning, S. Yu, L. Kunlan, *Science* **2001**, *292*,

1139 – 1141; r) S. Nlate, D. Astruc, R. Neumann, *Adv. Synth. Catal.* **2004**, *346*, 1445 – 1448.

[15] K. Kamata, K. Yonehara, Y. Sumida, K. Hirata, S. Nojima, N. Mizuno, *Angew. Chem. Int. Ed.* **2011**, *50*, 12062 – 12066; *Angew. Chem.* **2011**, *123*, 12268 – 12272.

[16] a) C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, *Inorg. Chem.* **1991**, *30*, 4409 – 4415; b) A. C. Dengel, W. P. Griffith, B. C. Parkin, *J. Chem. Soc. Dalton Trans.* **1993**, 2683 – 2688; c) L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Brégeault, *Inorg. Chem.* **1994**, *33*, 871 – 878; d) D. C. Duncan, R. C. Chambers, E. Hecht, C. L. Hill, *J. Am. Chem. Soc.* **1995**, *117*, 681 – 691.

[17] G. Gelbard, F. Breton, M. Quenard, D. C. Sherrington, *J. Mol. Catal. A* **2000**, *153*, 7 – 18.

[18] In a separate experiment, we confirmed that the nonproductive decomposition of H_2O_2 proceeded significantly in the presence of Al_2O_3, TiO_2, and ZrO_2 under the present reaction conditions. Therefore, Al_2O_3, TiO_2, and ZrO_2 were not suitable supports for the H_2O_2-based oxidation catalysts. Zinc species on SiO_2 were aggregated even at the zinc content of 0.8 wt %, and thus it was difficult to produce highly dispersed Zn^{2+} species on SiO_2. We conclude that SnO_2 was the most suitable support, possibly because of the above-mentioned reasons.

[19] R. A. Sheldon, M. Wallau, I. W. C. E. Arends, U. Schuchardt, *Acc. Chem. Res.* **1998**, *31*, 485 – 493.

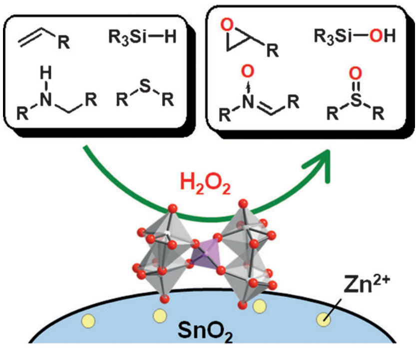
[20] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518 – 1520.

[21] *Purification of Laboratory Chemicals, 5th ed.* (Eds.: D. D. Perrin, W. L. F. Armarego), Pergamon Press, Oxford, **2003**.

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

Received: December 2, 2014

Unconditional support: The supported phosphorus-containing tetranuclear peroxotungstate (PW4) catalyst PW4-Zn(0.8)/SnO_2 can act as an efficient and reusable heterogeneous catalyst for the selective oxidation of various types of organic substrates such as alkenes, amines, silanes, and sulfides with aqueous H_2O_2 as the terminal oxidant. The catalytic performance of PW4-Zn(0.8)/SnO_2 was much higher than those of the corresponding homogeneous analogue and the previously reported tungstate-based supported catalysts.



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Selective Oxidation with Aqueous Hydrogen Peroxide by $[PO_4\{WO(O_2)_2\}_4]^{3-}$ Supported on Zinc-Modified Tin Dioxide