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Molecular design of selective oxidation catalyst with polyoxometalate

Noritaka Mizuno [a,b,*], Shiro Hikichi [a,b], Kazuya Yamaguchi [a,b], Sayaka Uchida [a,b], Yoshinao Nakagawa [a], Kazuhiro Uehara [b], Keigo Kamata [b]

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

[b] *Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

Abstract

Efficient H_2O_2-based oxidation systems with three kinds of polyoxometalates, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (**1**), $[\gamma\text{-1,2-H}_2\text{SiV}_2\text{W}_{10}O_{40}]^{4-}$ (**2**), and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (**3**) are reported. The compound **1** can catalyze epoxidation of various olefins including non-activated terminal olefins such as propylene and 1-octene with $\geq 99\%$ selectivity to epoxide and $\geq 99\%$ efficiency of H_2O_2 utilization. It is notable that **2** shows unique stereospecificity, regioselectivity, and diastereoselectivity for the epoxidation of *cis*/*trans* olefins, non-conjugated dienes, and 3-substituted cyclohexenes, respectively. The epoxidation of various allylic alcohols with only 1 equiv. H_2O_2 in water can be efficiently catalyzed by **3** to give the corresponding epoxy alcohols in high yields. Further, the catalyst **3** can be recycled with the maintenance of the catalytic performance.

Keywords: Allylic alcohols; Hydrogen peroxide; Olefins; Oxidation; Polyoxometalates

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1. Introduction

In the preceding few decades, the use of polyoxometalates (POMs) and POM-based compounds as catalysts has become a very important research area. Especially, POMs have received much attention in the area of acid and oxidation catalysis because their acidic and redox properties can be controlled at the molecular or atomic level [1–8]. The additional attractive and technologically significant aspect of POMs in catalysis is that they are thermally and oxidatively stable compared with organometallic complexes [1–8]. Various types of POMs have been synthesized by the proper selection of the starting components and by the adjustment of pH and temperature, and can act as effective catalysts for oxidations with environmentally friendly O_2 or H_2O_2 [1–8].

A wide variety of hydrocarbons including alkanes, alcohols, amines, and arenes can be oxidized with O_2 in the presence of mixed-addenda POMs $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ [9–17]. The mechanism included one electron oxidation of the substrate by $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ to form the product and the reduced $[PMo_{12-n}V_nO_{40}]^{(4+n)-}$, followed by reoxidation of the reduced catalyst by O_2. In 1986, it was reported for the first time by Hill and Brown that transition-metal-substituted POMs $[PW_{11}O_{39}M'(OH_2)]^{5-}$ ($M' = Mn^{2+}$, Co^{2+}) catalyzed the oxidation of olefins with PhIO [18]. The active sites of transition-metal-substituted POMs can be controlled at the molecular or atomic level. These advantages have been applied to the development of bio-inspired inorganic catalysts relating to the analogues of the heme enzyme, cytochrome P-450, and the non-heme enzymes including methane monooxygenase. Until now, numerous transition-metal-substituted POMs have been reported for catalytic selective oxidations [18–27] and $[WZnRu_2(OH)(H_2O)(XW_9O_{34})_2]^{11-}$ [19], $[\gamma\text{-SiW}_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$ [21], and $[(CH_3CN)_xFe\cdot SiW_9V_3O_{40}]^{5-}$ [22] are examples active for oxidation with O_2.

Tungsten-based POMs and the related compounds show high efficiency of H_2O_2 utilization [28–40]. Ishii et al. have developed effective H_2O_2-based epoxidation of olefins catalyzed by $H_3PW_{12}O_{40}$ combined with cetyl pyridinium chloride as a phase transfer agent [29]. The $[PO_4\{WO(O_2)_2\}_4]^{3-}$ peroxotungstate was isolated and crystallographically characterized by Venturello and co-workers [30,31]. This peroxo anion has been postulated to be catalytically the most active species in the $H_3PW_{12}O_{40}/H_2O_2$ system because $[PO_4\{WO(O_2)_2\}_4]^{3-}$ exhib-

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[*] Corresponding author. Tel.: +81 3 5841 7272; fax: +81 3 5841 7220.
E-mail address: tmizuno@mail.ecc.u-tokyo.ac.jp (N. Mizuno).

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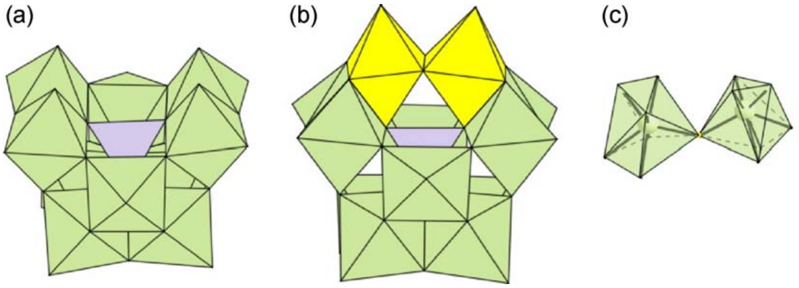

Fig. 1. Polyhedral representations of: (a) $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$, (b) $[\gamma\text{-1,2-H}_2\text{SiV}_2W_{10}O_{40}]^{4-}$, and (c) $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. The WO_6 moieties occupy the green octahedra, and SiO_4 groups are shown as internal gray tetrahedra. In the case of $[\gamma\text{-1,2-H}_2\text{SiV}_2W_{10}O_{40}]^{4-}$, the two vanadium atoms are represented by yellow octahedra.

ited catalytic reactivity similar to that of Ishii-system [32,33]. Recently, Noyori and co-workers reported an H_2O_2-based oxidation system of tungstate and methyltrioctylammonium hydrogensulfate without halides and organic solvents [38–40].

In this paper, we report efficient H_2O_2-based oxidation systems based on three kinds of POMs, a divacant lacunary polyoxotungstate $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (**1**, Fig. 1a) [34,35], a di-vanadium-substituted polyoxotungstate $[\gamma\text{-1,2-H}_2\text{SiV}_2W_{10}O_{40}]^{4-}$ (**2**, Fig. 1b) [41], and a dinuclear peroxotungstate $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (**3**, Fig. 1c) [36,37].

2. Experimental

2.1. Synthesis of tetra-n-butylammonium salt of $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (TBA-1)

$K_8[\gamma\text{-SiW}_{10}O_{36}]\cdot 12H_2O$ [42] (6 g, 2 mmol) was dissolved in 60 mL of water, and the pH of this aqueous solution was carefully adjusted to 2 with HNO_3. After stirring the solution for 15 min at room temperature, an excess amount of $[(n\text{-}C_4H_9)_4N]Br$ (6.46 g, 20 mmol) was added in a single step. The resulting white precipitate of TBA-**1** was collected by the filtration and then washed with an excess amount of water. After the dryness, the crude product was purified twice with the precipitation method. Analytically pure TBA-**1** was obtained as a white powder. Yield 3.4 g (54%). Anal. calcd. for $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]\cdot H_2O$: C, 22.09; H, 4.19; N, 1.64; Si, 0.80; W, 53.24. Found: C, 22.38; H, 4.40; N, 1.63; Si, 0.82; W, 53.53. ^{29}Si NMR (CD_3CN/DMSO (2/1 v/v), 53.45 MHz): −83.5 ppm. ^{183}W NMR (CD_3CN/DMSO (2/1 v/v), 11.20 MHz): −95.7, −98.9, −118.2, −119.6, −195.7 ppm with the integrated intensity ratio of 1:1:1:1:1, respectively. UV–vis (CH_3CN): 275 nm ($\varepsilon = 22{,}000\ M^{-1}\ cm^{-1}$). IR (KBr) ($cm^{-1}$): 999, 958, 920, 902, 877, 784, 745, 691, 565, 544.

2.2. Synthesis of tetra-n-butylammonium salt of $[\gamma\text{-1,2-H}_2\text{SiV}_2W_{10}O_{40}]^{4-}$ (TBA-2)

Aqueous solution of $[\gamma\text{-1,2-H}_2\text{SiV}_2W_{10}O_{40}]^{4-}$ was prepared according to Ref. [43], and the anion was isolated as the tetra-*n*-butylammonium salt. $K_8[\gamma\text{-SiW}_{10}O_{36}]\cdot 12H_2O$ [42] (8 g, 2.7 mmol) was quickly dissolved in 1 M HCl (28 mL). $NaVO_3$ (0.5 M, 11 mL, 5.5 mmol) was added, and the mixture was gently stirred for 5 min. The solution was filtered off followed by the addition of $[(n\text{-}C_4H_9)_4N]Br$ (8 g, 25 mmol) in a single step. The resulting yellow precipitate was collected by the filtration and then washed with an excess amount of water (300 mL). The crude product was purified twice with the precipitation method. Analytically pure TBA-**2** was obtained as a pale yellow powder. Yield: 7.43 g (76%). Anal. calcd. for $[(C_4H_9)_4N]_4[\gamma\text{-1,2-H}_2\text{SiV}_2W_{10}O_{40}]\cdot H_2O$: C, 21.4; H, 4.15; N, 1.56; Si, 0.78; V, 2.83; W, 51.1. Found: C, 21.4; H, 3.91; N, 1.59; Si, 0.79; V, 2.88; W, 51.2. ^{51}V NMR (CD_3CN, 70.90 MHz): −563.6 ppm. ^{29}Si NMR (CD_3CN, 53.45 MHz): −84.0 ppm. ^{183}W NMR (CD_3CN, 11.20 MHz): −82.2, −95.6, −129.7 ppm with an integrated intensity ratio of 2:1:2, respectively. UV–vis (CH_3CN) 240 ($\varepsilon = 36{,}000\ M^{-1}\ cm^{-1}$), 285 ($\varepsilon = 24{,}000\ M^{-1}\ cm^{-1}$), 350 nm ($\varepsilon = 5900\ M^{-1}\ cm^{-1}$). IR (KBr) ($cm^{-1}$): 1151, 1106, 1057, 1004, 995, 966, 915, 904, 875, 840, 790, 691, 550, 519, 482, 457, 405.

2.3. Synthesis of potassium salt of $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (K-3)

The compound K-**3** was synthesized according to the procedure in Ref. [44]. Anal. calcd. for $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$: H, 1.16; K, 11.27; W, 52.99. Found: H, 1.12; K, 11.98; W, 53.19. ^{183}W NMR (D_2O, 11.2 MHz): −704.5 ppm. UV–vis (H_2O): 243 nm ($\varepsilon = 608\ M^{-1}\ cm^{-1}$). IR (KBr) ($cm^{-1}$): 966, 854, 764, 615, 566, 332.

2.4. Catalytic oxidation

The epoxidation of gaseous substrates (propylene and 1-butene) was carried out with a Teflon coated autoclave. For the other substrates, a glass tube reactor was used. Detailed reaction conditions were given in the footnotes of tables. The reaction solution was periodically sampled and analyzed by GC or ^{1}H NMR. The products were identified by the comparison of mass and NMR spectra with those of authentic samples. Remaining H_2O_2 after the reaction was analyzed by the $Ce^{4+/3+}$ titration [45].

3. Results and discussion

3.1. Epoxidation of olefins catalyzed by $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$

The epoxidation of 1-octene with a series of silicotungstates and peroxotungstates in acetonitrile at 305 K was examined

Table 1
Epoxidation of various olefins catalyzed by TBA-**1**

Substrate	Product	Time (h)	Yield (%)
Propylene	Propylene oxide	8	90
1-Butene	1,2-Epoxybutane	8	88
1-Octene	1,2-Epoxyoctane	10	90
cis-2-Octene	*cis*-2,3-Epoxyoctane	3	>99
cis-3-Octene	*cis*-3,4-Epoxyoctane	3	>99
trans-2-Octene	*trans*-2,3-Epoxyoctane	14	91
Cyclopentene	Cyclopentene oxide	3	>99
Cyclohexene	Cyclohexene oxide	6	84
1-Methylcyclohexene	1-Methylcyclohexene oxide	4	95
Cycloheptene	Cycloheptene oxide	4	>99
2-Norbornene	*exo*-2,3-Epoxynorbornane	4	>99
Cyclooctene	Cyclooctene oxide	2	99
Cyclododecene[a]	Cyclododecene oxide	4	97
cis-β-Methylstyrene	*cis*-β-Methylstyrene oxide	4	>99

Reaction conditions: substrate (6 atm for propylene, 3 atm for 1-butene, 5 mmol for the other substrates), TBA-**1** (8 μmol), H_2O_2 (30% aq., 1 mmol), acetonitrile (6 mL), 305 K. Yields are based on H_2O_2. The efficiency of H_2O_2 utilization for each reaction was ≥99%.

[a] Acetonitrile (9 mL).

under the same conditions as those in Table 1. The terta-*n*-butylammonium salt of a divacant lacunary silicodecatungstate $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (TBA-**1**) showed high catalytic activity (90% yield of 1,2-epoxyoctane after 10 h under the conditions in Table 1), whereas $[\alpha\text{-SiW}_{11}O_{39}]^{8-}$ (<1% yield), $[\alpha\text{-SiW}_9O_{34}]^{10-}$ (<1% yield), and $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ (<1% yield) were almost inactive. Compared with the same tungsten loading, the catalytic activity of TBA-**1** for the epoxidation of 1-octene (90% yield) was much higher than those of peroxotungstates of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ (38% yield) and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (25% yield), which have been reported to be effective catalysts for the H_2O_2-based epoxidation [30,31,46–48].

Table 1 shows the results of the TBA-**1**-catalyzed epoxidation of various olefins with H_2O_2 at 305 K. The notable feature of the catalytic epoxidation with TBA-**1** is that non-activated terminal olefins such as propylene, 1-butene, and 1-octene could be transformed to the corresponding epoxides with ≥99% selectivity and ≥99% efficiency of H_2O_2 utilization. Cyclic olefins such as cyclohexene, 1-methylcyclohexene, cyclooctene, cyclododecene, and 2-norbornene were also epoxidized with ≥99% selectivity and ≥99% efficiency of H_2O_2 utilization. For the epoxidation of *cis*- and *trans*-olefins, the configurations around the C=C moieties were completely retained in the corresponding epoxides. Such a stereospecific epoxidation suggests that the free-radical intermediates are not involved in the epoxidation.

Larger-scale experiments (100-fold scaled-up) for propylene and 1-octene showed the same results as for the small-scale experiments in Table 1. Even in the 100-fold scaled-up conditions, the decomposition of H_2O_2 to form O_2 was negligible in the present system, which reduces the risk of building an explosive atmosphere. Thus, the catalytic performance of TBA-**1** raises the prospect of using this type of catalyst for the industrial epoxidation.

3.2. Regio- and diastereoselective epoxidation catalyzed by $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$

It is noted that more accessible, but less nucleophilic double bonds in non-conjugated dienes such as *trans*-1,4-hexadiene, *R*-(+)-limonene, 7-methyl-1,6-octadiene, and 1-methyl-1,4-cyclohexadiene were highly regioselectively epoxidized using terta-*n*-butylammonium salt of $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ (TBA-**2**). The results for the epoxidation of non-conjugated dienes with TBA-**2** are summarized in Table 2. For the *trans*-1,4-hexadiene epoxidation, the [terminal epoxide]/[total epoxide] ratio was >0.99 and much higher than those reported for the sterically hindered porphyrin systems with NaOCl or PhIO [49–52]. In addition, for the (*R*)-(+)-limonene epoxidation, the [8,9-epoxide]/[total epoxide] ratio was 0.99 and the value was much higher than those reported for the epoxidation with H_2O_2 by PhCN/$KHCO_3$ (0.37) [53] and Ti-beta zeolite (0.55) [54]. The regioselectivity for TBA-**2** is higher than the values

Table 2
Regio- and diastereoselective epoxidation of various dienes and 3-substituted cyclohexenes catalyzed by TBA-**2**

Substrate	Product	Time (h)	Yield (%)
trans-1,4-Hexadiene	1,2-Epoxy-*trans*-4-hexene	24	91 (>0.99)[a]
(*R*)-(+)-limonene	8,9-Epoxylimonene	24	89 (0.99)[a]
	Diepoxide		1
7-Methyl-1,6-octadiene	7-Methyl-1,2-epoxy-6-octene	24	77 (0.93)[a]
	7-Methyl-6,7-epoxy-1-octene		5
	Diepoxide		4
1-Methyl-1,4-cyclohexadiene	1-Methyl-4,5-epoxy-1-cyclohexene	24	71 (0.88)[a]
	1-Methyl-1,2-epoxy-4-cyclohexene		5
3-Methylcyclohexene	3-Methylcyclohexene oxide	24	91 (19.0)[b]
3-Ethylcyclohexene	3-Ethylcyclohexene oxide	24	91 (24.0)[b]
2-Cyclohexen-1-ol	2,3-Epoxycyclohexanol	24	87 (7.3)[b]

Reaction conditions: substrate (0.1 mmol), TBA-**2** (5 μmol), H_2O_2 (30% aq., 0.1 mmol), acetonitrile/*tert*-butanol (3 mL, 1/1 v/v), 293 K. Yields are based on substrate.

[a] Values in the parentheses are [less substituted epoxide]/[total epoxide] ratio.

[b] Values in the parentheses are *anti*/*syn* ratios of epoxides.

Table 3
Epoxidation of various allylic alcohols with 1 equiv. H_2O_2 in water catalyzed by K-**3**

Substrate	Product	Time (h)	Yield (%)
Allyl alcohol[a]	Glycidol	10	95
Crotyl alcohol	2,3-Epoxy-1-butanol	2	96
3-Methyl-2-buten-1-ol	2,3-Epoxy-3-methyl-1-butanol	2	97
2-Methyl-2-penten-1-ol	2,3-Epoxy-2-methyl-1-propanol	4	90
2-Hexen-1-ol	2,3-Epoxy-1-hexanol	5	98
Geraniol[b]	2,3-Epoxygeraniol	12	85
4-Methyl-3-penten-2-ol	3,4-Epoxy-4-methyl-2-pentanol	6	85 (15.7)[c]
3-Buten-2-ol[a]	3,4-Epoxy-2-butanol	10	83 (0.32)[c]
(*Z*)-3-methyl-3-penten-2-ol	3,4-Epoxy-3-methyl-2-pentanol	4	77 (0.52)[c]

Reaction conditions: substrate (5 mmol), K-**3** (20 μmol), H_2O_2 (30% aq., 5 mmol), water (6 mL), 305 K. In the case of secondary allylic alcohols, the corresponding ketones were formed as by products (∼9% selectivity). Yields are based on substrate.

[a] K-**3** (100 μmol).

[b] Dodecyltrimethylammonium salt of **3** (20 μmol) was used instead of K-**3**.

[c] Values in the parentheses are *threo*/*erthro* ratios of epoxy alcohols.

reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.62–0.75) [49–52,55,56]. In addition, the regioselectivity value with TBA-**2** for (*R*)-(+)-limonene was much different from those with tungstate catalysts; $[PO_4\{WO(O_2)_2\}_4]^{3-}$ (0.04), $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (0.08), and $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ (0.38).

For the competitive epoxidation of *cis*- and *trans*-2-octenes using TBA-**2** (100 μmol each, the other conditions were the same as those in Table 2), the ratio of the formation rate of *cis*-2,3-epoxyoctane to that of the *trans* isomer was >300 and the value is much larger than those (1.3–11.5) reported for the other stereospecific epoxidation systems including tungstate compounds such as $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ [8]. Further, the epoxidation of 3-substituted cyclohexenes such as 3-methylcyclohexene, 3-ethylcyclohexene, and 2-cyclohexen-1-ol gave the corresponding epoxides with *anti* configuration and highly diastereselective. As far as we know, such unusual stereospecificity, regioselectivity, and diastereoselectivity have never been reported so far [8]. These unusual selectivities would be due to the steric hindrance around the active site(s) [41].

The first-order dependence of the reaction rates on the concentration of TBA-**2** and the fact that the regioselectivity for TBA-**2** was much different from those for tungstate catalysts show that the fragmentation of TBA-**2** does not occur during the catalysis. In fact, it was confirmed by in situ IR and NMR measurements that the tungstate compounds such as $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ were not formed during the catalysis. The IR, UV–vis, and NMR spectra of the catalyst recovered after the completion of the epoxidation were the same as those of the fresh one, also suggesting the maintenance of the structure of **2**. Mono- and tri-vanadium-substituted compounds of $[\gamma\text{-}SiVW_{11}O_{40}]^{5-}$ and $[\alpha\text{-}1,2,3\text{-}SiV_3W_9O_{40}]^{7-}$ were completely inactive for the epoxidation under the present conditions, suggesting that the V–O–W and V=O centers are not the active sites. In addition, the fully occupied silicotungstates of $[\gamma\text{-}SiW_{12}O_{40}]^{4-}$ with the same structure of **2** was inactive, suggesting that the{VO–(μ-OH)$_2$–VO} core in **2** would act as a active site for the present epoxidation.

3.3. Epoxidation of allylic alcohols in water catalyzed by $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$

Table 3 shows the results of the epoxidation of various allylic alcohols with only 1 equiv. H_2O_2 catalyzed by the potassium salt of $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (K-**3**) in water solvent. The pH value of the reaction media was in the range of 4–5 under the present conditions, where the hydrolytic decomposition of epoxy alcohols does not proceed. The epoxidation of simple primary allylic alcohols proceeded almost quantitatively and chemoselectively to afford the epoxy alcohols without formation of the corresponding aldehydes and carboxylic acids. Further, the regioselective epoxidation of geraniol took place at the electron-deficient allylic 2,3-double bond to afford only 2,3-epoxy alcohol in high yield. The epoxidation of the secondary β,β-disubstituted allylic alcohol (1,3-allylic strained alcohol) of 4-methyl-3-penten-2-ol proceeded diastereoselectively to form the *threo*-epoxy alcohol as a main product. On the other hand, the allylic alcohol without the 1,3-allylic strain, 3-penten-2-ol, gave *erythro* rich epoxy alcohol. In addition, the epoxidation of (*Z*)-3-methyl-3-penten-2-ol, in which 1,3- and 1,2-allylic strains compete with each other, was more *erythro* selective. These regio- and diastereoselectivities are similar to those observed for VO(acac)$_2$/TBHP and H_2WO_4/H_2O_2 systems, where metal-alcoholate binding is involved, and different from those of *m*-CPBA and dimethyldioxirane systems, where hydrogen-bonding is involved [57–60]. Thus, it is likely that the present epoxidation proceeds via the metal-alcoholate binding mechanism.

Oxidation products could easily be isolated by simple extraction using dichloromethane after the oxidation since catalyst K-**3** was completely insoluble in dichloromethane. Therefore, the aqueous phase including K-**3** catalyst could be recovered without loss of the tungsten species. It is notable that the recovered aqueous phase including K-**3** catalyst could be reused for the epoxidation of crotyl alcohol at least twice without the loss of the high catalytic performance; 96% yield of 2,3-epoxy-1-butanol for the first run, 97% for the second run, and 97% for the third run.

4. Conclusions

In conclusion, three kinds of polyoxometalates, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$, $[\gamma\text{-1,2-}H_2SiV_2W_{10}O_{40}]^{4-}$, and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ could be used as efficient homogeneous catalysts for liquid phase epoxidations with the environmentally friendly H_2O_2 as a sole oxidant. At present, we are continuing to design functionalized POM catalysts [61–68] toward the development of green selective oxidation processes.

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