Journal of Molecular Catalysis A: Chemical 394 (2014) 224–231

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Editor's Choice paper

Zirconium(IV)- and hafnium(IV)-containing polyoxometalates as oxidation precatalysts: Homogeneous catalytic epoxidation of cyclooctene by hydrogen peroxide

Hiroki Aoto, Keisuke Matsui, Yoshitaka Sakai, Teppei Kuchizi, Hiromi Sekiya, Hironori Osada, Takuya Yoshida, Satoshi Matsunaga, Kenji Nomiya*

Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293, Japan

ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form 8 July 2014
Accepted 12 July 2014
Available online 19 July 2014

Keywords:
Epoxidation
Hafnium(IV)
Zirconium(IV)
Hydrogen peroxide
Polyoxometalates

ABSTRACT

The homogeneous epoxidation of *cis*-cyclooctene with H_2O_2, catalyzed by various Zr/Hf-containing Keggin sandwich polyoxometalates (POMs), i.e., the 1:2 complexes $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ (M = Zr, **1** and M = Hf, **2**), the 4:2 complexes $[[\{M(H_2O)\}_2\{M(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu\text{-}OH)_2](\alpha\text{-}1,2\text{-}PW_{10}O_{37})_2]^{7-}$ (M = Zr, **3** and M = Hf, **4**), the 2:2 complexes $[\{M(\mu\text{-}OH)(H_2O)\}_2(\alpha\text{-}PW_{11}O_{39})_2]^{8-}$ (M = Zr, **5** and M = Hf, **6**), and the 3:2 complex $[Zr_3(\mu_2\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (**7**), was examined. At least two different reaction types exist: (1) one brought about by the highly catalytically active Venturello complex $[PO_4\{WO(O_2)_2\}_4]^{3-}$, which was generated by reactions of the Zr/Hf-containing POMs with hydrogen peroxide, and (2) the reaction with active species formed on Zr/Hf clusters in the POMs. In the first type, the original sandwich structures are not maintained during the reactions (as shown in **1**, **2**, **3**, and **4**), but in the second type, the sandwich structures are maintained (as seen in **5** and **6**). **7** was inactive. The reaction, (**5** + *cis*-cyclooctene) + H_2O_2, was explicitly influenced by changing the reaction time of 5 and olefin, before addition of H_2O_2, indicating a significant interaction between **5** and olefin, such as coordination of olefin to the POM. Thus, for homogeneous olefin epoxidation by hydrogen peroxide catalyzed by di-Zr/Hf clusters, a new mechanism is proposed through olefin-coordinated species to di-Zr/Hf centers.

1. Introduction

In academic and industrial fields, the selective catalytic epoxidation of alkenes with an environmentally friendly oxidant, aqueous hydrogen peroxide, is an interesting objective [1–5]. Transition-metal-substituted polyoxometalates (POMs) have attracted considerable attention as oxidation catalysts because they are resistant to oxidative degradation. Furthermore, the "active sites" of their transition metals and countercations can undergo extensive synthetic modifications. The most commonly studied types of reaction are H_2O_2-based epoxidation and sulfoxidation catalyzed by metal-substituted POMs [6–18].

Several H_2O_2-based oxidation reactions catalyzed by titanium(IV)-substituted POMs have been extensively investigated [19], e.g., the monomeric Keggin monotitanium(IV)-substituted POM $[\alpha\text{-}PW_{11}TiO_{40}]^{5-}$ [20–23] and its conjugated acid $[\alpha\text{-}P(TiOH)W_{11}O_{39}]^{4-}$ [21,23]; the dimeric Keggin monotitanium(IV)-substituted POM $[(\alpha\text{-}PTiW_{11}O_{39})_2O]^{8-}$ [23], and the monomeric Keggin 1,5-dititanium(IV)-substituted POM $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$ [22,24,25].

With regard to the catalytic activities of the dimeric mono-, di-, and tri-titanium(IV)-substituted α-Keggin polyoxotungstates $[(\alpha\text{-}PTiW_{11}O_{39})_2O]^{8-}$ (**Ti1**), $[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2O_2]^{10-}$ (**Ti2**), and $[(\alpha\text{-}1,2,3\text{-}PTi_3W_9O_{37})_2O_3]^{12-}$ (**Ti3**) in alkene epoxidation with H_2O_2, it has been reported that the structure around the titanium centers has a strong influence on the catalytic activities [26]. The formation of catalytically active peroxo- and hydroperoxo-titanium(IV) species has been confirmed [26–29]. Previous studies of H_2O_2-based oxidation catalyzed by Ti-substituted POMs have also indicated that the protons in countercations and/or reaction solutions are crucial for the catalytic activities and the formation of active hydroperoxo–titanium and/or protonated peroxo species [23,26,30–35]. In alkene epoxidation with H_2O_2 catalyzed by Ti-substituted POMs, homolytic O—O cleavage of the Ti–hydroperoxo species, followed by oxygen transfer to the alkene [radical mechanism], has been proposed

---

* Corresponding author at: Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293, Japan. Tel.: +81 463 59 4111; fax: +81 463 58 9684.
E-mail address: nomiya@kanagawa-u.ac.jp (K. Nomiya).

http://dx.doi.org/10.1016/j.molcata.2014.07.020
1381-1169/

[33]. For example, it is generally accepted that in oxidation catalyzed by dititanium-containing 19-tungstodiarsenate(III), $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$, the Ti–hydroperoxo groups are the active oxygen-donating intermediates for alkene epoxidation [32].

In contrast, only a few examples of H_2O_2-based oxidation catalyzed by Zr-containing POMs have been reported, by Kholdeeva's group, e.g., oxidation catalyzed by 2:2 complexes of Zr in dimeric Keggin POMs such as $(Bu_4N)_7H[\{PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]$, $(Bu_4N)_8[\{PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]$, and $(Bu_4N)_9[\{PW_{11}O_{39}Zr\}_2(\mu\text{-}OH)(\mu\text{-}O)]$ [36]. Kholdeeva's group proposed that the active species for cyclohexene oxidation was an unstable Zr–peroxo species (^{31}P NMR at δ −12.3 ppm) generated by ligand exchange of the coordinating water ligands of the monomeric POM, $(Bu_4N)_{3+n}[PW_{11}O_{39}Zr(OH)_n(H_2O)_{3(2)-n}]$ ($n = 0$ and 1), with the peroxo (H_2O_2) ligand. They also suggested that the acid proton is crucial for catalysis by Zr-containing POMs. With respect to catalysis by Zr-containing POMs, Kortz's group reported the stoichiometric oxidation of L-methionine by the side-on peroxo species (i.e., μ-η^2-peroxo-containing Zr_2 species) of the dimeric Keggin POM $K_{12}[Zr_2(O_2)_2(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 25H_2O$ [37].

In this work, we focused on epoxidation of *cis*-cyclooctene with aqueous hydrogen peroxide catalyzed by various structurally characterized Zr/Hf-containing Keggin sandwich POMs, i.e., $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ (M = Zr, **1** and M = Hf, **2**), $[[\{M(H_2O)\}_2\{M(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu\text{-}OH)_2](\alpha\text{-}1,2\text{-}PW_{10}O_{37})_2]^{7-}$ (M = Zr, **3** and M = Hf, **4**), $[\{M(\mu\text{-}OH)(H_2O)\}_2(\alpha\text{-}PW_{11}O_{39})_2]^{8-}$ (M = Zr, **5** and M = Hf, **6**), and $[Zr_3(\mu_2\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (**7**). In the reactions with **5** and **6**, the original sandwich structures were kept after the reactions and the active species were formed on the Zr/Hf centers, whereas in the reactions with **1**–**4**, the reaction was brought about by the highly active Venturello complex [38–46], which was generated during the reaction. No catalytic activity was observed for **7** and the side-on peroxo species with heteroatom P $[\{Zr(\mu\text{-}\eta^2\text{-}O_2)\}_2(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ (**8**), the latter of which was synthesized from a reaction between **5** and aqueous H_2O_2 [see Supporting Information].

In this paper, we report full details of homogeneous *cis*-cyclooctene epoxidation with hydrogen peroxide catalyzed by Zr/Hf-containing Keggin sandwich POMs (**1**–**8**), and propose that a significant interaction between olefin and POMs (**5** and **6**), i.e., an olefin coordination process is present before attack of hydrogen peroxide.

2. Experimental

2.1. Materials

The following reactants were used as received: 30% aqueous H_2O_2 (Wako), Bu_4NCl (TCI), and CD_3CN and D_2O (Isotec). $H_3[PW_{12}O_{40}]\cdot 3H_2O$ was prepared by a traditional method and identified using FTIR spectroscopy, thermogravimetry (TG) and differential thermal analysis (DTA), and ^{31}P NMR spectroscopy. Venturello complex $(Bu_4N)_3[PO_4\{WO(O_2)_2\}_4]$ was synthesized using a modified version of the reported method [38] and characterized by elemental analysis, ^{31}P and ^{183}W NMR spectroscopy (see Supporting Information). $(Et_2NH_2)_8[\{\alpha\text{-}PW_{11}O_{39}Zr(\mu\text{-}OH)(H_2O)_2\}_2]\cdot 6H_2O$ (**EtN-5**) and the lithium salt (**Li-5**) were prepared using a modified version of the reported method [47], and identified by CHN analysis, FTIR spectroscopy, TG/DTA, and ^{31}P NMR spectroscopy. The side-on peroxo dinulcear Zr complex $(Et_2NH_2)_{10}[\{Zr(\mu\text{-}\eta^2\text{-}O_2)\}_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 11H_2O$ (**EtN-8**) was synthesized by a reaction of **EtN-5** with 30% aqueous H_2O_2 using a modified version of the reported method [37], and characterized by elemental analysis, TG/DTA, FTIR, ^{31}P NMR and x-ray crystallography (also see Supporting Information). Other precatalysts were prepared according to the reported methods or modified versions of these [47–52], and identified by elemental analysis, FTIR spectroscopy, TG/DTA, and ^{31}P NMR spectroscopy. The precatalysts and their abbreviations are shown in Table 1. The abbreviation consists of a combination of the countercation and polyoxoanion (**EtN-** and **BuN-** represent Et_2NH_2 and Bu_4N countercations, respectively). The polyoxoanion moieties are denoted as complexes, by a combination of the number of metal centers and the two lacunary POMs, i.e., 1:2 complexes of one metal center (Zr/Hf) and two monolacunary POMs (**EtN-1** and **EtN-2**) [49], 4:2 complexes of four metal centers (Zr/Hf) and two dilacunary POMs (**BuN-3** and **BuN-4**) [51,52], 3:2 complexes of three Zr centers and two trilacunary POMs (**BuN-7**) [50], and several types of 2:2 complexes such as (i) 2:2 complexes consisting of two hydrated metal centers (Zr/Hf) and two monolacunary POMs with a P heteroatom (**BuN-5**, **BuN-6**, and **Li-5**) [47], and (ii) 2:2 complexes consisting of a Zr_2 center with two side-on peroxo groups and two monolacunary POMs with a P heteroatom (**EtN-8**). Instrumentation/analytical procedures are described in Supporting Information.

2.2. Catalytic reactions

Homogeneous reactions of *cis*-cyclooctene, catalyzed by several POMs as Et_2NH_2, Bu_4N, or Li salts (Table 1), were carried out in round-bottomed flasks. *cis*-Cyclooctene (1.0 mL, 7.70 mmol), 30% aqueous H_2O_2 (1.0 mL, 12.72 mmol), and a POM (0.01–0.02 mmol) in a mixed solvent (30 mL) consisting of CH_3CN and CH_2Cl_2 (15/15 v/v), a mixed solvent (31 mL) consisting of CH_3CN and water (30/1 v/v), or a mixed solvent (33 mL) consisting of CH_3CN and water (30/3 v/v) were mixed at 25 °C under air. The reaction solution was sampled after 0.0, 0.5, 0.75, 1.0, 1.5, 2.0, 2.25, 2.5, 3.0, 4.0, 5.0, 6.0, and 24 h and analyzed using Shimadzu GC-17AAT and Shimadzu GC-2010 Plus gas chromatographs (TCD) and a DB-FFAP capillary column (0.53 mm × 15 m). The catalytic activities of POMs **1**–**8**, evaluated as turnover numbers (TON) and/or turnover frequencies per second (TOF), were compared with those of the Venturello complex and several previously reported Ti-containing Keggin POMs.

Table 1
Compositions, formulas, and abbreviations of precatalysts.

M: lacunary POM ratio	Formula	Abbreviation	Ref.
1:2 complex	$(Et_2NH_2)_{10}[Zr(\alpha\text{-}PW_{11}O_{39})_2]\cdot 7H_2O$	**EtN-1**	[49]
	$(Et_2NH_2)_{10}[Hf(\alpha\text{-}PW_{11}O_{39})_2]\cdot 8H_2O$	**EtN-2**	[49]
4:2 complex	$(Bu_4N)_7[[\{Zr(H_2O)\}_2\{Zr(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu_3\text{-}OH)_2](\alpha\text{-}1,2\text{-}PW_{10}O_{37})_2]\cdot 3H_2O$	**BuN-3**	[51,52]
	$(Bu_4N)_7[[\{Hf(H_2O)\}_2\{Hf(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu_3\text{-}OH)_2](\alpha\text{-}1,2\text{-}PW_{10}O_{37})_2]\cdot 2H_2O$	**BuN-4**	[51,52]
2:2 complex	$(Bu_4N)_7H[\{Zr(\mu\text{-}OH)(H_2O)\}_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 3H_2O$	**BuN-5**	[47]
	$(Bu_4N)_7H[\{Hf(\mu\text{-}OH)(H_2O)\}_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 3H_2O$	**BuN-6**	[47]
	$Li_8[\{Zr(\mu\text{-}OH)(H_2O)\}_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 20H_2O$	**Li-5**	[47]
	$(Et_2NH_2)_8[\{Zr(\mu\text{-}OH)(H_2O)\}_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 6H_2O$	**EtN-5**	[47]
	$(Et_2NH_2)_{10}[\{Zr(\mu\text{-}\eta^2\text{-}O_2)\}_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 11H_2O$	**EtN-8**	This work
3:2 complex	$(Bu_4N)_{6.5}H_{2.5}[Zr_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]$	**BuN-7**	[50]

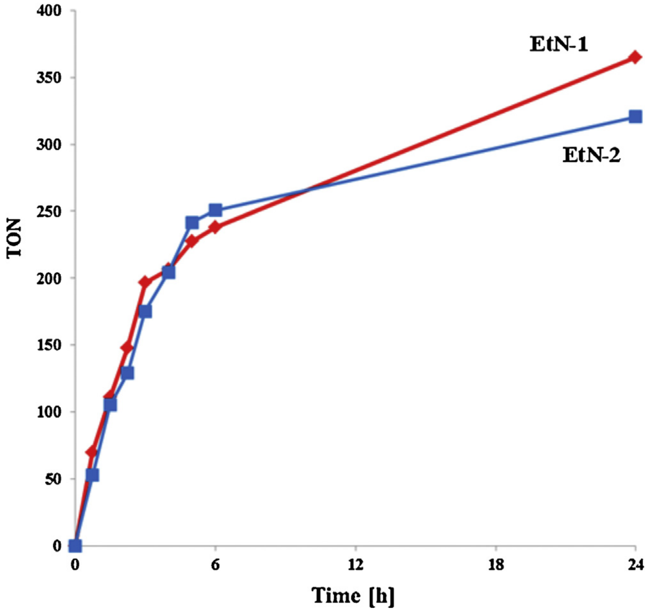


Fig. 1. TON–time curve of *cis*-cyclooctene epoxidation with 30% aqueous H_2O_2 catalyzed by POMs (**EtN-1** and **EtN-2**). Reaction conditions: catalysts 0.02 mmol, substrate 7.70 mmol, 30% H_2O_2 *aq.* 12.72 mmol, under air at 25 °C.

3. Results and discussion

3.1. *Zr/Hf-containing POMs as precatalysts for cis-cyclooctene epoxidation by H_2O_2: Catalysis by **1–4** and Venturello complex*

Homogeneous epoxidation of *cis*-cyclooctene with hydrogen peroxide catalyzed by various Zr/Hf-containing POMs was examined under the conditions of POM (0.02 mmol), *cis*-cyclooctene (7.70 mmol) and 30% aqueous H_2O_2 (12.72 mmol) in a mixed solvent (30 mL) consisting of CH_3CN:CH_2Cl_2 (15/15 v/v), at 25 °C in air. The POMs used were 1:2 complexes (**EtN-1** and **EtN-2**), 4:2 complexes (**BuN-3** and **BuN-4**), and the freshly prepared Venturello complex, $(Bu_4N)_3[PO_4\{WO(O_2)_2\}_4]$. The time course versus TON plots of epoxide formation are shown in Figs. 1 and 2.

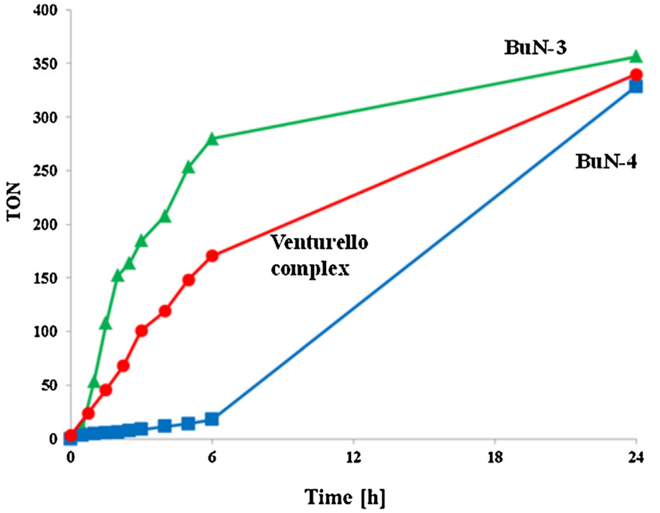


Fig. 2. TON–time curve of *cis*-cyclooctene epoxidation with 30% aqueous H_2O_2 catalyzed by POMs (freshly prepared Venturello complex, **BuN-3**, and **BuN-4**). Reaction conditions: catalysts 0.02 mmol, substrate 7.70 mmol, 30% H_2O_2 *aq.* 12.72 mmol, under air at 25 °C.

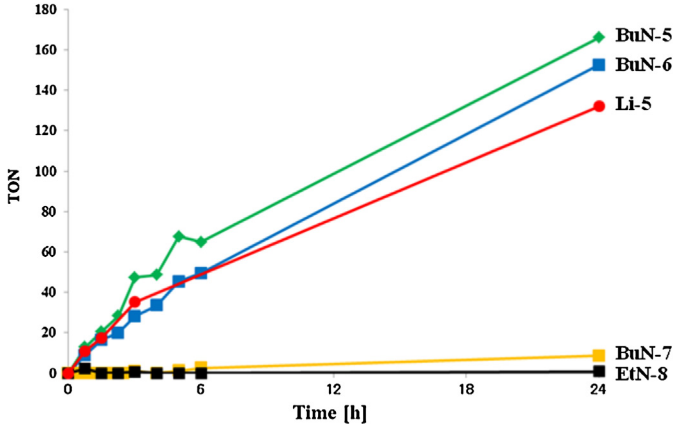


Fig. 3. TON–time curve of *cis*-cyclooctene epoxidation with 30% aqueous H_2O_2 catalyzed by POMs (**Li-5**, **BuN-5**, **BuN-6**, **BuN-7**, and **EtN-8**). Reaction conditions: catalysts 0.02 mmol, substrate 7.70 mmol, 30% H_2O_2 *aq.* 12.72 mmol, under air at 25 °C.

The conversions of *cis*-cyclooctene after 24 h-reactions were more than 83–95% for both **EtN-1** and **EtN-2**, and more than 77–95% for both **BuN-3** and **BuN-4**. **BuN-4** shows a rapid increase in activity after an induction period of more than 6 h and the final TON was almost the same as that of **BuN-3** after 24 h-reaction. The TONs after 24 h-reactions for **EtN-1** and **EtN-2** (Fig. 1) and those for **BuN-3** and **BuN-4** (Fig. 2) reached more than 300.

The reactions by **EtN-1**, **EtN-2**, **BuN-3** and **BuN-4** (Figs. 1 and 2) are quite different from those by **BuN-5** and **BuN-6** (Fig. 3). In the solutions of the 24 h-reactions of **EtN-1** and **EtN-2** (6.35 and 6.27 μmol, respectively) and H_2O_2 (0.636 mmol), formation of the Venturello complex was confirmed by ^{31}P NMR as signals at 3.57 ppm (from **EtN-1**) and 3.54 ppm (from **EtN-2**). In fact, the highly active reaction by the Venturello complex has been well known [38–46]. In Figs. 1 and 2, it should be noted that the TONs after 6 h-reactions for **EtN-1**, **EtN-2**, and **BuN-3** were about two times of the TON after 6 h-reaction for the separately prepared, fresh Venturello complex, indicating that the POMs (**EtN-1**, **EtN-2**, and **BuN-3**) generate 2 mol of the Venturello complex during the reactions.

Thus, the catalysis by **EtN-1**, **EtN-2**, **BuN-3**, and **BuN-4** was actually due to the Venturello complex, which was derived by direct reaction with hydrogen peroxide.

3.2. *Homogeneous epoxidation of cis-cyclooctene with hydrogen peroxide catalyzed by POMs **5–8***

The 2:2 complexes **BuN-5** and **BuN-6**, and the 3:2 complex **BuN-7** (POMs 0.02 mmol) were used in a mixed solvent (30 mL) consisting of CH_3CN/CH_2Cl_2 (15/15 v/v) as homogeneous catalysts for epoxidation of *cis*-cyclooctene. The 2:2 complex of Zr as a Li salt (**Li-5**, 0.01 mmol) and the separately prepared, side-on peroxo–Zr_2 species **EtN-8** (0.02 mmol), both of which were water soluble, but insoluble in organic solvents, were also used as homogeneous catalysts in a mixed solvent (31 mL) consisting of CH_3CN/water (30/1 v/v). The TON–time course curves are shown in Fig. 3.

In the reactions by **5** and **6** in the presence of 30% aqueous H_2O_2, a color change was not observed, i.e., the original colorless, clear, homogeneous solution was maintained during the course of the reaction. This is in contrast to the oxidation reactions with 30% aqueous H_2O_2 catalyzed by mono-, di-, and tri-titanium(IV)-substituted Keggin POMs (**Ti1**, **Ti2**, and **Ti3** as Bu_4N salts), in which the colors of all the POMs changed from colorless to yellow or orange as a result of formation of peroxotitanium(IV)

Table 2
Epoxidation of olefins (*cis*-cyclooctene, cyclohexene, 1-octene, and styrene) with 30% aqueous H_2O_2 catalyzed by **BuN-5** and **Li-5**.

Precatalyst	Substrate	Epoxide	TON[c]	Selectivity (%)[c]	Other products
BuN-5[a]	*cis*-cyclooctene	cyclooctene oxide	166	99	–
	cyclohexene	*trans*-cyclohexane-1,2-diol	101	37	2-hydroxycyclohexanone
	1-octene	1,2-epoxyoctane	23	–	heptanal
	styrene	styrene oxide	7	–	benzaldehyde
Li-5[b]	*cis*-cyclooctene	cyclooctene oxide	132	99	–
	cyclohexene	*trans*-cyclohexane-1,2-diol	38	62	2-hydroxycyclohexanone
	1-octene	1,2-epoxyoctane	23	–	heptanal

[a] Solvent 15:15 (v/v) CH_2Cl_2/CH_3CN, 30 mL.
[b] Solvent 30:1 (v/v) CH_3CN/H_2O, 31 mL.
[c] After 24 h.

Reaction conditions: catalyst 0.02 mmol, substrate *cis*-cyclooctene 7.70 mmol, cyclohexene 9.86 mmol, 1-octene 6.37 mmol, or styrene 8.70 mmol, 30% H_2O_2 aq. 12.72 mmol, under air, at 25 °C.

Table 3
Epoxidation of mixed olefins (*cis*-cyclooctene and cyclohexene) with 30% aqueous H_2O_2 catalyzed by **BuN-5** and **Li-5**.

Precatalysts	Mixed substrate (mmol)	Total conversion (%)[c]	Products (mmol)[c]	TON[c]	Selectivity (%)[c]
BuN-5[a]	*cis*-cyclooctene (1.54)	92	cyclooctene oxide (1.4)	71	99
	cyclohexene (4.62)	68	*trans*-cyclohexane-1,2-diol (1.2)	58	37
	cis-cyclooctene (4.62)	61	cyclooctene oxide (2.8)	138	97
	cyclohexene (1.54)	58	*trans*-cyclohexane-1,2-diol (0.2)	11	25
Li-5[b]	*cis*-cyclooctene (1.54)	53	cyclooctene oxide (0.8)	41	99
	cyclohexene (4.62)	23	*trans*-cyclohexane-1,2-diol (0.5)	31	58
	cis-cyclooctene (4.62)	51	cyclooctene oxide (2.4)	118	99
	cyclohexene (1.54)	23	*trans*-cyclohexane-1,2-diol (0.2)	9	51

Reaction conditions: catalyst 0.02 mmol, mixed substrate *cis*-cyclooctene and cyclohexene, 30% H_2O_2 aq. 12.72 mmol, under air, at 25 °C.
[a] Solvent 15:15 (v/v) CH_2Cl_2/CH_3CN, 30 mL.
[b] Solvent 30:1 (v/v) CH_3CN/H_2O, 31 mL.
[c] After 24 h.

and/or hydroperoxotitanium(IV) intermediates [26,27]. The catalytic activities of **BuN-5** and **BuN-6** at 25 °C were monitored by GC during 24 h-reactions. Cyclooctene oxide was the major product (selectivity > 99%), and no induction period was observed for these reactions. The ratio of the activity with **BuN-5** to that of the Venturello complex was about 38% after 6 h and 49% after 24 h. Also, the ratio of the activity with **BuN-6** to that of the Venturello complex was about 29% after 6 h and 45% after 24 h.

In comparing **Li-5** and **BuN-5** as precatalysts for cyclooctene epoxidation, it should be noted that the catalytic activity was **BuN-5** > **Li-5** (see Tables 2 and 3, Section 3.5. (4)), whereas the catalytic stability was **Li-5** > **BuN-5**. Powder samples of **BuN-5** and **BuN-6**, recovered after 24 h-reactions by evaporating the reaction solutions and reprecipitating with excess diethyl ether, were characterized using FTIR and ^{31}P NMR spectroscopies. The original sandwich structures were maintained during and after the reactions. However, the recovered sample of the Bu_4N salt was contaminated with saturated Keggin POM species $[PW_{12}O_{40}]^{3-}$ as minor species, which was confirmed by ^{31}P NMR signal at -14.40 ppm in CD_3CN, whereas that of the Li salt was not. Repeated reuse of the Bu_4N salt resulted in increased amounts of the saturated Keggin $[PW_{12}O_{40}]^{3-}$ species. Thus, with regard to catalyst stability, it appears that the Li salt is superior to the Bu_4N salt.

BuN-7 was inactive for epoxidation of *cis*-cyclooctene. The side-on coordinated peroxo–Zr_2 species (**EtN-8**) did not show any activity (Fig. 3); the TON after 24 h was 0.8 without addition of trifluoromethanesulfonic acid (TFSA) and 17.3/19.0 with addition of TFSA 1:2/1:4, respectively. Kortz et al. reported that the side-on peroxo species of a dimeric Zr complex with Si heteroatom was active in the stoichiometric oxidation of L-methionine, but the reaction was not catalytic [37]. In the POM with P heteroatom, the side-on peroxo species (**EtN-8**) is probably formed during the course of reaction from the active, end-on hydroperoxo species Zr–OOH, which will be formed at the early stage of the reaction of POM **5** with aqueous H_2O_2 (Fig. S3).

3.3. *Homogeneous epoxidation of olefins with hydrogen peroxide catalyzed by **BuN-5** and **Li-5**: selection of cis-cyclooctene as a test substrate*

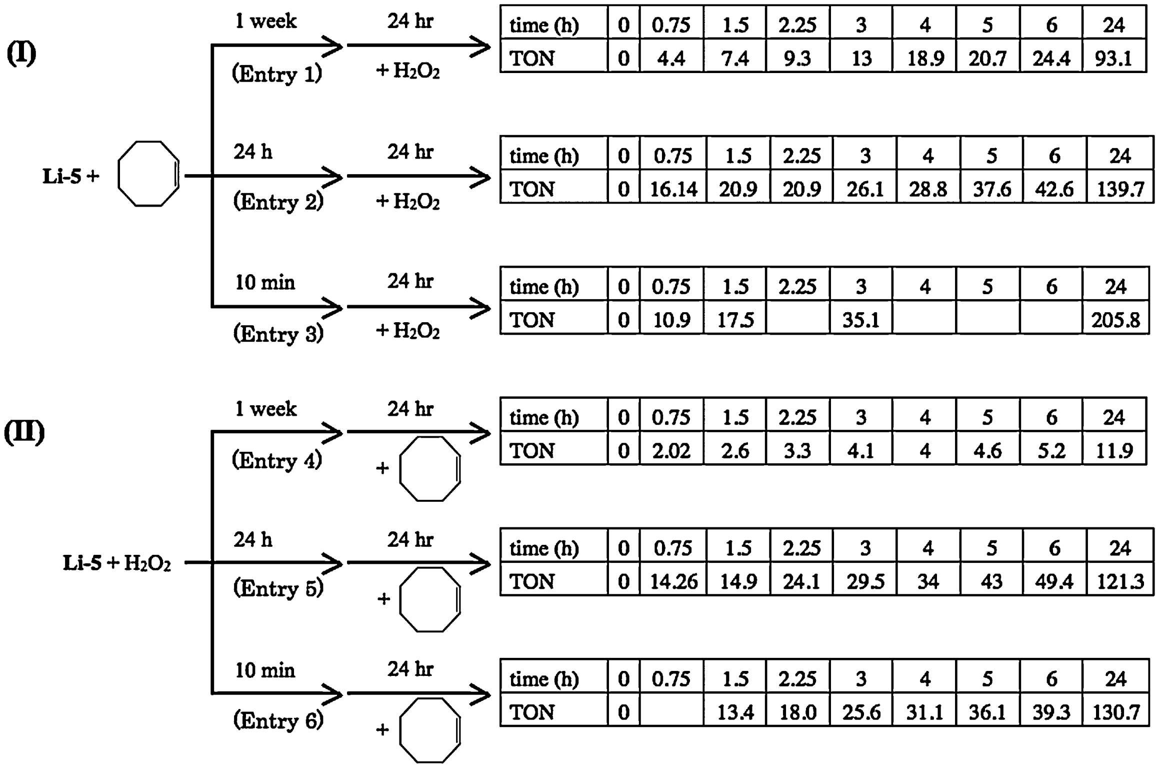
The epoxidations of olefins (*cis*-cyclooctene, cyclohexene, 1-octene, and styrene) with 30% aqueous H_2O_2 catalyzed by **BuN-5** and **Li-5** were examined at 25 °C under air in a mixed solvent (30 mL) consisting of CH_3CN and CH_2Cl_2 (15/15 v/v) and a mixed solvent (31 mL) consisting of CH_3CN and water (30/1 v/v), respectively.

Cyclohexene has been known as a useful test substrate that allows one to distinguish between homolytic and heterolytic oxidation mechanism [35]. It has been said that formation of allylic oxidation products, 2-cyclohexene-1-ol, 2-cyclohexene-1-one, cyclohexene oxide is an indication of a homolytic oxidation by hydrogen peroxide (radical mechanism), whereas the selective formation of *trans*-cyclohexane-1,2-diol (major product) and cyclohexene oxide (minor product) suggests a heterolytic mechanism (ionic mechanism) [35]; distribution of products containing cyclohexene oxide depends on the reaction mechanism. Our results of cyclohexene oxidation suggest the ionic mechanism, i.e., heterolytic mechanism (Table 2), in which 2-hydroxycyclohexanone as other products is derived by further oxidation of *trans*-cyclohexane-1,2-diol.

In this work, we selected *cis*-cyclooctene as a test substrate for further studying the reaction in detail rather than cyclohexene, because *cis*-cyclooctene gave the best results in the viewpoints of the sole product of oxidation, i.e., highest selectivity for the epoxide, and the highest TON of the epoxide (Table 2).

3.4. *Results from changing reaction times between **Li-5** and cis-cyclooctene before addition of H_2O_2 and between **Li-5** and H_2O_2 before addition of cis-cyclooctene (Control experiments #1)*

Control experiments (Fig. 4) consisting of the reactions (**I**) (**Li-5** + *cis*-cyclooctene) + H_2O_2 (Entries 1–3) and (**II**)



time (h)	0	0.75	1.5	2.25	3	4	5	6	24
TON	0	4.4	7.4	9.3	13	18.9	20.7	24.4	93.1

time (h)	0	0.75	1.5	2.25	3	4	5	6	24
TON	0	16.14	20.9	20.9	26.1	28.8	37.6	42.6	139.7

time (h)	0	0.75	1.5	2.25	3	4	5	6	24
TON	0	10.9	17.5		35.1				205.8

time (h)	0	0.75	1.5	2.25	3	4	5	6	24
TON	0	2.02	2.6	3.3	4.1	4	4.6	5.2	11.9

time (h)	0	0.75	1.5	2.25	3	4	5	6	24
TON	0	14.26	14.9	24.1	29.5	34	43	49.4	121.3

time (h)	0	0.75	1.5	2.25	3	4	5	6	24
TON	0		13.4	18.0	25.6	31.1	36.1	39.3	130.7

Fig. 4. Results of control experiments consisting of two types of reaction: (**I**) (**Li-5** + olefin) + H_2O_2 and (**II**) (**Li-5** + H_2O_2) + olefin, which were examined by changing the addition times of the second additive (olefin or H_2O_2) to **Li-5**. Reaction conditions for (I) and (II): catalysts 0.02 mmol, substrate 7.70 mmol, 30% H_2O_2 *aq.* 12.72 mmol, under air at 25 °C. Reaction product in (**I**) and (**II**): cyclooctene oxide.

(**Li-5** + H_2O_2) + *cis*-cyclooctene (Entries 4–6) were carefully carried out by changing the reaction times of the second additive (*cis*-cyclooctene in (**I**) or H_2O_2 in (**II**)) to **Li-5**. GC analysis was performed during 24 h-reactions after addition of H_2O_2 in (**I**) or *cis*-cyclooctene in (**II**). In the reaction (**I**), the highest activity (TON 205.8) was observed for Entry 3, in which hydrogen peroxide was added on 10 min after **Li-5** and *cis*-cyclooctene were mixed, and the final solution was analyzed after 24 h-reaction. As the reaction time of **Li-5** and *cis*-cyclooctene increased, the activity decreased (Entries 1 and 2). This indicates that there is a significant interaction between the POM and *cis*-cyclooctene before addition of H_2O_2. An olefin coordination as such an interaction is proposed. Based on theoretical and experimental studies containing x-ray crystallography, several Zr^{IV} ion (d^0)–olefin bonding complexes have been reported in the literature [53–57]. The longest reaction time (one week) between **Li-5** and *cis*-cyclooctene resulted in the lowest activity (Entry 1). The reason may be attributable to polymerization such as ring-opening metathesis of *cis*-cyclooctene coordinated to **Li-5** [58]. The coordinated olefin can undergo the nucleophilic attack of free and/or coordinated hydrogen peroxide. Thus, the reaction (**I**) is due to the ionic oxidation mechanism by hydrogen peroxide rather than the radical oxidation mechanism.

In contrast, the similar control experiments were also carried out using a dimeric trititanium(IV)-substituted Keggin POM (**Ti3**) that has been known as epoxidation catalysis via radical mechanism [26]. The reaction times between **Ti3** and *cis*-cyclooctene were changed (1 h and one week), followed by adding H_2O_2, and analysing the products after 24 h-reactions. The TONs of epoxide produced during different reaction times (1 h and one week) were almost unchanged (~150). These results are quite different from the results using **Li-5**.

On the other hand, in (**II**), the reaction times between **Li-5** and H_2O_2 were changed. TONs (130.7 and 121.3) of epoxide produced on 24 h-reactions after addition of *cis*-cyclooctene (Entries 5 and 6, respectively) were much higher than that (TON 11.9) of Entry 4. TONs by changing reaction times of catalyst + H_2O_2, i.e., 24 h and 10 min indicate that decomposition of H_2O_2 does not occur. Entry 4 also shows that the lowest activity results from the formation of side-on peroxo species (POM **8**) during the prolonged mixing time (see Fig. S3). Entries 5 and 6 are probably due to the active, end-on coordinated hydroperoxo species, which are alive at the early stage.

Since the activities in (**I**) are higher than those in (**II**), in the case of that **Li-5**, olefin and H_2O_2 are simultaneously coexistent, the process based on (**I**), i.e., olefin coordination and subsequent nucleophilic attack of free and/or coordinated hydrogen peroxide, will be proposed as plausible reaction scheme (Fig. 5).

*3.5. Catalytic epoxidation of mixed substrates by **Li-5** and **BuN-5** (Control experiments #2)*

Epoxidations of mixed substrates (*cis*-cyclooctene and cyclohexene in molar ratios of 1:3 and 3:1) with aqueous H_2O_2 catalyzed by **BuN-5** and **Li-5** were examined for 24 h. The results are shown in Table 3.

(1) In cyclohexene oxidation, the products were cyclohexene epoxide as the minor product and *trans*-cyclohexane-1,2-diol as the major product. *trans*-Cyclohexane-1,2-diol was derived from cyclohexene epoxide in an acidic environment, based on dissociation of the coordinated water molecules in the Zr centers. The selectivity for cyclohexene epoxide is therefore actually the same as that for *trans*-cyclohexane-1,2-diol. The selectivity

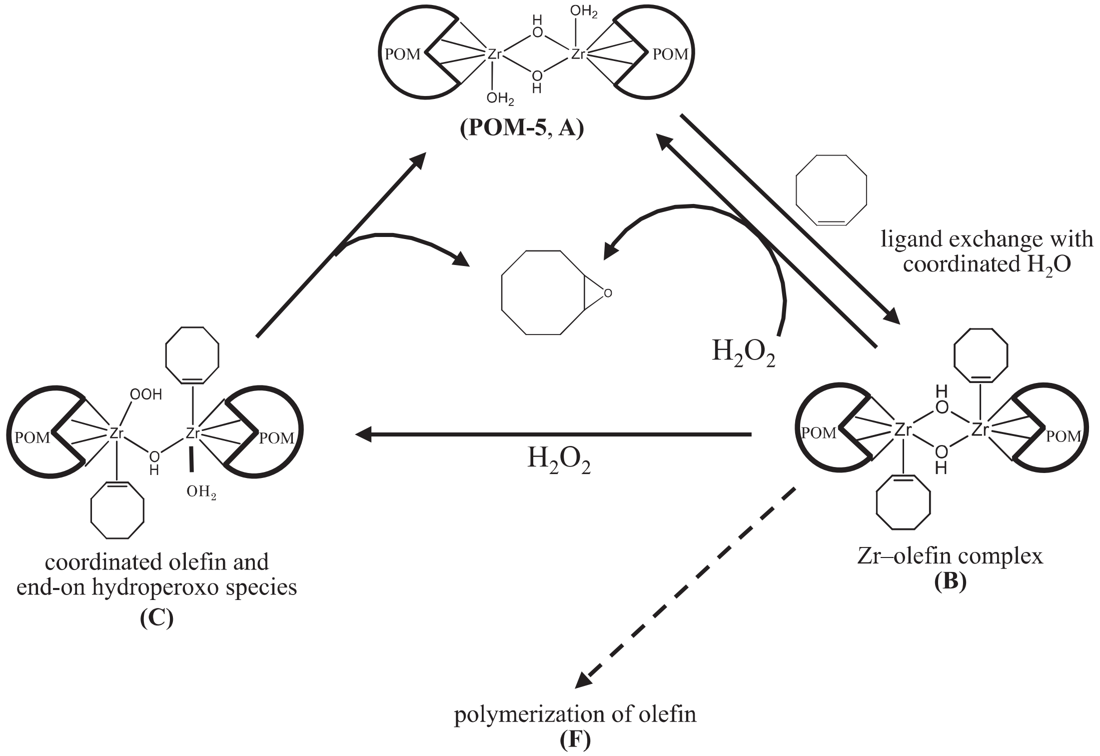


Fig. 5. Proposed reaction scheme.

after 24 h-reaction for *trans*-cyclohexane-1,2-diol was evaluated as

$$[trans-\text{cyclohexane}-1,2-\text{diol}]/([\text{cyclohexene}]_{t=0} - [\text{cyclohexene}]_{t=24}).$$

(2) Despite the different starting molar ratios of the mixed substrates, *cis*-cyclooctene was oxidized more than cyclohexene by either **BuN-5** or **Li-5**, showing strong substrate dependence of these precatalysts. This fact suggests that coordination ability of *cis*-cyclooctene to Zr centers is higher than that of cyclohexene. The coordination of cyclohexene and subsequent epoxidation will begin after the *cis*-cyclooctene has been almost consumed.

(3) The selectivity for *trans*-cyclohexane-1,2-diol in oxidation with **BuN-5** is lower than that with **Li-5**. The present reaction is significantly influenced by the solvent system. **BuN-5** in CH_3CN/CH_2Cl_2 (15/15 v/v, 30 mL) is much more active than **Li-5** in CH_3CN/H_2O (30/1 v/v, 31 mL). Thus, in catalysis by **BuN-5**, further oxidation products of *trans*-cyclohexane-1,2-diol such as 2-hydroxycyclohexanone can be also formed, resulting in lower selectivity.

(4) Difference between catalytic activities of **BuN-5** and **Li-5**: although the order of the catalyst stability is **Li-5** > **BuN-5**, that of the catalytic activity is **BuN-5** > **Li-5**. Both reactions proceed in homogeneous systems. The solubilities of **BuN-5** and **Li-5** are different in the constituent solvents: **Li-5** is soluble in H_2O, but insoluble in CH_3CN, whereas **BuN-5** is soluble in CH_3CN, but insoluble in CH_2Cl_2. The substrates are soluble in both CH_3CN and CH_2Cl_2. Since the present reaction is significantly influenced by the solvent systems, the different activities are attributable to the different reaction systems; the system consisting of **Li-5** in H_2O and CH_3CN becomes a "homogeneous biphasic" system, whereas that consisting of **BuN-5** in CH_3CN and CH_2Cl_2 becomes a "homogeneous monophasic" system.

3.6. ^{31}P NMR spectra of POM **5** in the presence of mixed or single substrate (cis-cyclooctene and/or cyclohexene) and aqueous H_2O_2

Solution ^{31}P NMR spectra of **5** are strongly dependent on solvents and countercations; **BuN-5** in CD_3CN shows a signal at −2.00 ppm, **EtN-5** in D_2O at −3.59 ppm, **Li-5** in D_2O at −3.53 ppm together with minor peaks at −4.47 and −4.58 ppm, and **Li-5** in CD_3CN at −2.07 ppm (Table S2). The ^{31}P NMR spectrum of **Li-5** in CD_3CN in the presence of aqueous H_2O_2 showed a signal at −2.80 ppm as a broad peak after 1 h-mixing and at −2.57 ppm after 216 h-mixing. The latter signal was in good agreement with that of the separately prepared, side-on peroxo species **EtN-8** in CD_3CN (−2.55 ppm). Thus, the broad signal at −2.80 ppm is attributable to the end-on hydroperoxo species. The ^{31}P NMR spectrum of **Li-5** in CD_3CN on 1 h after excess *cis*-cyclooctene or cyclohexene was added showed signals at −2.11 ppm or −2.14 ppm, respectively; the signals on 168 h after the addition were observed at −2.14 ppm for *cis*-cyclooctene and at −2.16 (main) and −2.60 ppm (minor) for cyclohexene. The signals at −2.11 ppm and −2.14 ppm are assignable to the olefin-coordinated species of *cis*-cyclooctene and cyclohexene, respectively. The ^{31}P NMR signal at −2.08 ppm for **L-5** (2 mmol) in CD_3CN solution containing olefin mixtures of *cis*-cyclooctene (154 mmol) and cyclohexene (462 mmol) was the same as the signal for olefins mixed in a different ratio, i.e., *cis*-cyclooctene (462 mmol) and cyclohexene (154 mmol), even after 1 h and/or longer (Table S2). These facts are consistent with that the coordination ability of *cis*-cyclooctene is higher than that of cyclohexene. Thus, it is suggested that under the co-existence of *cis*-cyclooctene, neither cyclohexene coordinated species nor mixed coordinated species are formed. These results are also consistent with those for epoxidation of mixed substrates with different molar ratios (see Section 3.5).

3.7. Comparison of present work with catalysis by Ti-containing POMs and Zr-containing POMs reported in the literature

(1) The 2:2 complexes (**5** and **6**) and the 1:2 complexes $[M(PW_{11}O_{39})_2]^{10-}$ (M = Zr **1** and Hf **2**) underwent mutual interconversion under appropriate pH conditions [47], suggesting that these complexes are not rigid, but flexible. However, they showed quite different catalytic behaviors in the epoxidation of *cis*-cyclooctene with H_2O_2; the 2:2 complexes formed active species on dinuclear Zr/Hf centers in sandwich structures, whereas the 1:2 complexes generated the highly active Venturello complex.

(2) The active species formed by **5** and **6** are substantially different from those formed by Ti-substituted POMs. In the latter case, homolytic O—O cleavage of the Ti–hydroperoxo species, followed by oxygen transfer to the alkene, has been considered [33]. It is generally accepted that Ti–hydroperoxo groups are the active oxygen-donating intermediates for the epoxidation of alkenes, but the alkene-coordinating species have never been considered.

(3) The active species formed by **5** and **6** are also different from that derived from the Zr_2-containing POMs reported by Kholdeeva's group [36], which has been proposed as an unstable Zr–peroxo species (^{31}P NMR, δ −2.3 ppm) formed by a ligand exchange of the monomeric species $(Bu_4N)_{3+n}[PW_{11}O_{39}Zr(OH)_n(H_2O)_{3(2)-n}]$ (n = 0 and 1) with a peroxo (H_2O_2) ligand.

4. Conclusion

Two different types of *cis*-cyclooctene epoxidation with hydrogen peroxide were found in catalysis by Zr/Hf-based sandwich-structured POMs **1–8**. The reactions with **1–4**, which gave very high activities, were brought about by the Venturello complex $[PO_4\{WO(O_2)_2\}_4]^{3-}$ [38–46], which was generated by reactions with hydrogen peroxide, whereas the reactions with **5** and **6**, which gave moderate activities (about 45% those of **1**–**4**), proceeded via active species formed on dimeric Zr/Hf clusters in the sandwich structure. The 2:2 complex containing side-on peroxo species on the Zr_2 centers (**8**) and the 3:2 complex (**7**) showed almost no activities. Two control experiments (#1 and #2) suggest that the reactive species of **5** is formed as the dimeric species containing *cis*-cyclooctene coordinated to Zr atom. Thus, for homogeneous olefin epoxidation by hydrogen peroxide catalyzed by di-Zr/Hf clusters, a new mechanism is proposed through olefin-coordinated species to di-Zr/Hf centers. The epoxidation of olefin with H_2O_2 catalyzed by **5** probably proceeds via nucleophilic attack of free and/or coordinated hydrogen peroxide to the coordinated olefin (the ionic mechanism), which is contrasted to the catalysis by the Ti-substituted POMs via radical mechanism.

Acknowledgements

This work was supported by JSPS KAKENHI Grant number 22550065, and also by the Strategic Research Base Development Program for Private Universities of the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.07.020.

References

[1] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981 (Chapter 3).
[2] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, 2nd ed, Wiley, New York, 1992, pp. 151.
[3] K.S. Suslick, in: C.L. Hill (Ed.), Activation and Functionalization of Alkenes, Wiley, New York, 1989, p. 219.
[4] K.A. Jorgensen, Chem. Rev. 89 (1989) 431–458.
[5] B. Meanier, Chem. Rev. 92 (1992) 1411–1456.
[6] N. Mizuno, K. Kamata, K. Yamaguchi, Top. Catal. 53 (2010) 876–893.
[7] N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944–1956.
[8] A.C. Estrada, I.C.M.S. Santos, M.M.Q. Simoes, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, Appl. Catal. A 392 (2011) 28–35.
[9] N. Mizuno, K. Yamaguchi, K. Kamata, Catal. Surv. Asia. 15 (2011) 68–79.
[10] N. Mizuno, K. Yamaguchi, Chem. Rec. 6 (1) (2006) 12–22.
[11] N. Mizuno, S. Hikichi, K. Yamaguchi, S. Uchida, Y. Nakagawa, K. Uehara, K. Kamata, Catal. Today 117 (2006) 32–36.
[12] C. Jahier, S.S. Mal, U. Kortz, S. Nlate, Eur. J. Inorg. Chem. (2010) 1559–1566.
[13] M. Carraro, N. Nsouli, H. Oelrich, A. Sartorel, A. Soraru, S.S. Mal, G. Scorrano, L. Walder, U. Kortz, M. Bonchio, Chem. Eur. J. 17 (2011) 8371–8378.
[14] M. Craven, R. Yahya, E. Kozhevnikova, R. Boomishankar, C.M. Robertson, A. Steiner, I. Kozhevnikov, Chem. Commun. 49 (2013) 349–351.
[15] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, E. Shams, N. Rasouli, Appl. Catal. A: Gen. 334 (2008) 106–111.
[16] R. Hajian, S. Tangestaninejad, M. Moghadam, V. Mirkhani, A. Reza Khosropour, C. R. Chimie 15 (2012) 975–979.
[17] Z. Karimi, A.R. Mahjoub, S.M. Harati, Inorg. Chim. Acta 376 (2011) 1–9.
[18] P.A. Shringarpure, A. Patel, Ind. Eng. Chem. Res. 50 (2011) 9069–9076.
[19] K. Nomiya, Y. Sakai, S. Matsunaga, Eur. J. Inorg. Chem. (2011) 179–196.
[20] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, L.A. Kovaleva, M.A. Fedotov, React. Kinet. Catal. Lett. 66 (1999) 311–317.
[21] O.A. Kholdeeva, R.I. Maksimovskaya, G.M. Maksimov, L.A. Kovaleva, Kinet. Catal. 42 (2001) 217–222.
[22] T. Yamase, E. Ishikawa, Y. Asai, S. Kanai, J. Mol. Catal. A: Chem. 114 (1996) 237–245.
[23] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, L.A. Kovaleva, M.A. Fedotiv, V.A. Grigoriev, C.L. Hill, Inorg. Chem. 39 (2000) 3828–3837.
[24] E. Ishikawa, T. Yamase, J. Mol. Catal. A: Chem. 142 (1999) 61–76.
[25] F. Gao, T. Yamase, H. Suzuki, J. Mol. Catal. A: Chem. 180 (2002) 97–108.
[26] C.N. Kato, S. Negishi, K. Yoshida, K. Hayashi, K. Nomiya, Appl. Catal. A: Gen. 292 (2005) 97–104.
[27] K. Hayashi, C.N. Kato, A. Shinohara, Y. Sakai, K. Nomiya, J. Mol. Catal. A: Chem. 262 (2007) 30–35.
[28] K. Hayashi, M. Takahashi, K. Nomiya, Dalton Trans. (2005) 3751–3756.
[29] C.N. Kato, K. Hayashi, S. Negishi, K. Nomiya, J. Mol. Catal. A: Chem. 262 (2007) 25–29.
[30] O.A. Kholdeeva, T.A. Trubitsina, R.I. Maksimovskaya, A.V. Golovin, W.A. Nelwert, B.A. Kolesov, X. López, J.M. Poblet, Inorg. Chem. 43 (2004) 2284–2292.
[31] O.A. Kholdeeva, T.A. Trubitsina, G.M. Maksimov, A.V. Golovin, R.I. Maksimovskaya, Inorg. Chem. 44 (2005) 1635–1642.
[32] F. Hussain, B.S. Bassil, U. Kortz, O.A. Kholdeeva, M.N. Timofeeva, P. de Oliveira, B. Keita, L. Nadjo, Chem. Eur. J. 13 (2007) 4733–4742.
[33] N.S. Antonova, J.J. Carboí, U. Kortz, O.A. Kholdeeva, J.M. Poblet, J. Am. Chem. Soc. 132 (2010) 7488–7497.
[34] Y. Matsuki, Y. Mouri, Y. Sakai, S. Matsunaga, K. Nomiya, Eur. J. Inorg. Chem. (2013) 1754–1761.
[35] O.A. Kholdeeva, Eur. J. Inorg. Chem. (2013) 1595–1605.
[36] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, M.P. Vanina, T.A. Trubitsina, D.Y. Naumov, B.A. Kolesov, N.S. Antonova, J.J. Carbo, J.M. Poblet, Inorg. Chem. 45 (2006) 7224–7234.
[37] S.S. Mal, N.H. Nsouli, M. Carraro, A. Sartorel, G. Scorrano, H. Oelrich, L. Walder, M. Bonchio, U. Kortz, Inorg. Chem. 49 (2010) 7–9.
[38] C. Aubry, G. Chottard, N. Platzer, J-M. Bregeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem. 30 (1991) 4409–4415.
[39] L.I. Kuznetsova, N.I. Kuznetsova, R.I. Maksimovskaya, G.I. Aleshina, O.S. Koscheeva, V.A. Utkin, Catal. Lett. 141 (2011) 1442–1450.
[40] L. Liu, C. Chen, X. Hu, T. Mohamood, W. Ma, J. Lin, J. Zhao, New J. Chem. 32 (2008) 283–289.
[41] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681–691.
[42] G. Roelfes, M. Lubben, R. Hage, L. Que Jr., B.L. Feringa, Chem. Eur. J. 6 (2000) 2152–2159.
[43] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175–187.
[44] C. Venturello, R. D'Aloisio, J. Org. Chem. 53 (1988) 1553–1557.
[45] Z. Zhang, W. Zhao, B. Ma, Y. Ding, Catal. Commun. 12 (2010) 318–322.
[46] R. Ishimoto, K. Kamata, N. Mizuno, Eur. J. Inorg. Chem. (2013) 1943–1950.
[47] K. Nomiya, Y. Saku, S. Yamada, W. Takahashi, H. Sekiya, A. Shinohara, M. Ishimaru, Y. Sakai, Dalton Trans. (2009) 5504–5511.
[48] H. Osada, A. Ishikawa, Y. Saku, Y. Sakai, Y. Matsuki, S. Matsunaga, K. Nomiya, Polyhedron 52 (2013) 389–397.
[49] C.N. Kato, A. Shinohara, K. Hayashi, K. Nomiya, Inorg. Chem. 45 (2006) 8108–8119.

[50] Y. Saku, Y. Sakai, A. Shinohara, K. Hayashi, S. Yoshida, C.N. Kato, K. Yoza, K. Nomiya, Dalton Trans. (2009) 805–813.

[51] K. Nomiya, K. Ohta, Y. Sakai, T. Hosoya, A. Ohtake, A. Takakura, S. Matsunaga, Bull. Chem. Soc. Jpn. 86 (2013) 800–812.

[52] K. Nomiya, N.C. Kasuga, S. Matsunaga, Y. Sakai, T. Hasegawa, T. Kimura, Sci. J. Kanagawa Univ. 21 (2010) 43–46.

[53] H. Zhao, A. Ariafard, Z. Lin, Inorg. Chim. Acta 359 (2006) 3527–3534.

[54] J.-F. Carpentier, Z. Wu, C.W. Lee, S. Strömberg, J.N. Christopher, R.F. Jordan, J. Am. Chem. Soc. 122 (2000) 7750–7767.

[55] M. Dahlmann, G. Erker, K. Bergander, J. Am. Chem. Soc. 122 (2000) 7986–7998.

[56] S. Kuroda, F. Dekura, Y. Sato, M. Mori, J. Am. Chem. Soc. 123 (2001) 4139–4146.

[57] E. Negishi, F.E. Cederbaum, T. Takahashi, Tetrahedron Lett. 27 (1986) 2829–2832.

[58] H. Martinez, N. Ren, M. Matta, M. Hillmyer, Polym. Chem. (2014), http://dx.doi.org/10.1039/C3PY01787G.