Catalytic properties of holmiumdecatungstate modified with cetylpyridinium cation [{C$_5$H$_5$N(CH$_2$)$_{15}$CH$_3$}$_7$H$_2$Ho(III)W$_{10}$O$_{36}$; Cetyl-HoW10] for H$_2$O$_2$-oxidation of alcohols and olefins and its working states under an organic-solvent-free condition

Ryuji Siozaki [a], Atushi Inagaki [a], Hiroshi Kominami [a], Shunro Yamaguchi [b], Junko Ichihara [b], Yoshiya Kera [a,*]

[a] *Faculty of Science and Engineering, Department of Applied Chemistry, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577, Japan*

[b] *The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567, Japan*

Abstract

Catalytic properties of holmiumdecatungstate modified with cetylpyridinium cations [Cetyl-Ho(III)W10] for H$_2$O$_2$-oxidations of alcohols and olefins were investigated under various organic solvents–aqueous H$_2$O$_2$ biphasic conditions. Generally, secondary alcohols and benzyl alcohols and internal olefins such as cyclooctene were efficiently catalyzed by Cetyl-Ho(III)W10, while primary alcohols and terminal olefins were almost not. The activity for 2-octanol grew much by using a smaller amount of nonpoler solvents such as CHCl$_3$. Especially, in an organic-solvent-free condition as a limited case, Cetyl-Ho(III)W10 was elucidated to be workable as a highly active but quite mild catalyst in comparison with the other heteropolyoxometalates well known. A schematical model on the working states was successfully presented. The present H$_2$O$_2$–Cetyl-Ho(III)W10 catalyst system will be insisted, finally, to be responsible for industrial oxidation processes such as being performed in a non-organic solvent system as environmental concerns.

Keywords: Holmiumdecatungstate; Catalytic properties; H$_2$O$_2$-oxidation; Alcohols; Olefins; Working states; Environmental concerns

1. Introduction

The chemistry of heteropoly- and isopolyoxometalates has been developed covering a wide scope [1]. Application to catalysts for partial oxidation and acid–base reactions has been attempted (Refs. [2] and references therein, [3,4]): Peroxo complexes of molybdenum and

* Corresponding author.

tungsten have been reported to be stabilized by pyridine carboxylato ligands and to be also utilized as good catalysts for oxidation of secondary alcohols to ketones by hydrogen peroxide [5]. Hydrogen peroxide epoxidation of olefinic alcohols was also catalyzed by tungstic acid in buffered protic media [6,7]. Allylic alcohols were shown to be very reactive by the uses of H$_2$O$_2$ and a catalytic amount of a quarternary phosphonium and ammonium per-

tungstate [8]. Venturello and co-workers [9–12] found that quaternary ammonium tetrakis(oxodiperoxo–tungstato) phosphates, $\{(n\text{-}C_6H_{13})_4N\}_3PO_4[WO(O_2)_2]_4$, acted as highly effective and versatile oxidation catalysts in conjunction with H_2O_2 as the primary oxidant in an aqueous/organic biphasic system. Ishii and co-workers (Refs. [13–16] and references therein) have reported that tris(cetylpyridinium)12-molybdophosphate, $[C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$, prepared from 12-molybdo–phosphoric acid (PMo12) and cetylpyridinium chloride (CPC) catalyzes the regio-selective epoxidation of allylic alcohols with dilute hydrogen peroxide in chloroform. The similar complex, prepared from 12-tungstophosphoric acid (PW12) and CPC, efficiently catalyzed the oxidations of the secondary alcohols and diols with H_2O_2.

Griffith and co-workers have recognized such heteropoly-peroxometalates as $R_3[XO_4\{MO(O_2)_2\}_3]$ derived from XM12 and H_2O_2, in which $[AsO_4\{MO(O_2)_2\}_4]^{3-}$ is the most effective for the epoxidations of cyclic and linear alkenes with H_2O_2 [17]. A new type peroxo-complex: $WO_3(O_2)_4$ was comparable with the $PO_4WO(O_2)_4$ species in the activity for alcohol oxidations, although less reactive in alkene epoxidations [18]. They have proposed recently a hexanuclear species: $(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4$, which catalyzes the epoxidation of a number of cyclic and linear alkenes [19]. Aubry and co-workers [20,21] recognized the formation of a dinuclear species, $[HPO_4\{MO(O_2)_2\}_2]$, besides the tetranuclear species, $[XO_4\{MO(O_2)_2\}_4]$. Both species containing W stoichiometrically epoxidized (R)-(+)-limonene 30-times more actively than the Mo-containing species. They suggested that these differences can be related to the observed $\nu(O–O)$ frequency of the peroxo-group in IR and Raman [20,21]. Hill and co-workers [22] thoroughly investigated the reactivity and stability of the species derived from PW12 and H_2O_2. The rate of epoxide formation from 1-octene by a dinuclear compound,

$\{[WO(O_2)_2(H_2O)]_2O\}$ which was formed by the decomposition of PW12 by H_2O_2, was at least two orders of magnitude slower than that observed for the tetra-nuclear compound, $PO_4\{WO(O_2)_2\}_4$.

We have been interested in the catalytic properties of heteropoly-oxometalates other than the Keggin type ones [23]. In fact, cerium decatungstate $(Ce(IV)W_{10}O_{36}^{8-})$ modified with cetylpyridinium cations was found to be an active and selective catalyst for the oxidation of secondary alcohols to ketones with hydrogen peroxide (H_2O_2) [24]. The catalyst, however, exhibited only a quite low activity for primary alcohols, except for benzylic alcohols which were easily oxidized to aldehydes. A kind of peroxo-species formed was observed in $H_2O_2–$Na–Ce(IV)W10 reacting system by FT-Raman, FT-IR, and [183]W-NMR spectrometries: A unique structure of the peroxospecies, which was not largely degraded from the original LnW10 structure, in contrast to the cases of the Keggin type ones mentioned above [9–12,17–22], was proposed [25,26]. The peroxo-species behaved quite reversibly, suggesting that it may also be an intermediate species in the alcohol oxidation reaction.

Recently, a series of Ln(III)W10 [Ln: La–Yb] was synthesized and characterized by various spectroscopic measurements. Their spectroscopic data were found to be correlated well to the physicochemical parameters of lanthanide elements, such as the ionic radii (r) and theoretical magnetic moments ($\mu_{(theor)}$) (Ref. [27] and references therein). Furthermore, the activities of the series of Cetyl-LnW10 for H_2O_2-oxidation of benzyl alcohol correlated well with the spectroscopic and physicochemical parameters of Ln(III)W10, suggesting that the $4f^n$-electron in the lanthanide ions would participate directly in the catalytic steps [28]. A working mechanism in the catalyses has been discussed favorably based on the peroxo complex model proposed on the $H_2O_2–Ce(IV)W10$ reacting system [26].

In the present paper, in order to clarify the

catalytic features of such Ln(III)W10 in comparison with the common Keggin type heteropoly oxometalates, we investigated the effects of the kinds and amounts of organic solvents on the catalytic activity for the H_2O_2-oxidation of alcohols in detail mainly on HoW10 as a test catalyst. In an organic-solvent-free system as a limited case, an extremely high activity (TOF) was found in a quite low concentration of Ho(III)W10 modified with cetylpyridinium. The present lanthanide-containing polytungstates were quite active, but it suppressed almost completely the further oxidation of the primary products (aldehydes and ketones), in contrast to the catalysts derived from Keggin type tungstate and H_2O_2. The working states of the catalyst under a specific condition such as being free from organic solvent will be successfully discussed. As an environmental concern, a possibility of an application of Cetyl-LnW10 to the H_2O_2-oxidation of alcohols and olefins will be proposed as a new type catalyst workable under an organic-solvent-free reaction condition.

2. Experimental

2.1. Materials and preparation procedures

$Na_7H_2Ln(III)W_{10}O_{36} \cdot nH_2O$ (Na–LnW10; Ln = Ho, Gd, La) were synthesized according to Refs. [27,29]. $H_3PMo_{12}O_{40} \cdot nH_2O$ (PMo12) and $H_3PW_{12}O_{40} \cdot nH_2O$ (PW12) were presented from Nippon New Metal, and $H_4SiW_{12}O_{40} \cdot 24H_2O$ (SiW12) was purchased from Kanto Chemical. They were used without further treatments. $Na_2BW_{12}O_{40}$(BW12) and $K_6P_2W_{18}O_{66} \cdot 10H_2O$ (P_2O_{18}) were synthesized according to Refs. [30,31], respectively. Those samples except for SiW12 were successfully modified with cetylpyridinium cations according to Refs. [13–16,24]: Typically, to a stirred solution of those samples (ca. 1 g) in distilled water (5 ml), an aqueous solution of cetylpyridinium chloride monohydrate (ca. equivalent amounts corre-

sponding to the anion charge; 2–9) was dropwise added at room temperature (ca. 20°C). After 2 h, the resulting precipitate was filtered, washed with distilled water, and dried in vacuo. The samples thus modified are listed in Table 1. The other samples modified with quaternary alkyl ammonium in Table 3, $[(C_4H_9)_4N]_4W_{10}O_{32}]$ and $[(C_6H_{13})_4N]_3\{PO_4[WO(O_2)_2]_4\}$, were synthesized according to Refs. [17,32], respectively.

2.2. Analyses and characterization

The samples thus prepared were characterized by UV-vis, FT-IR, FT-Raman, [183]W-NMR, ^{13}C-NMR, ICP, and CHN-elemental analyses, as described on the previous papers [24,27]. For $[C_5H_5N(CH_2)_{15}CH_3]_7H_2HoW_{10}O_{36}$ (Cetyl-HoW10), anal. calcd.: C, 37.46; H, 5.74; N, 2.08, and found: C, 37.78; H, 5.95; N, 2.06. FT-IR(KBr): 956, 853, 790, 694, 581, 549, 488 cm^{-1}. For $(Cetyl)_7H_2LaW_{10}O_{36}$, anal. calcd.: C, 37.66; H, 5.77; N, 2.09, and found: C, 37.96; H, 5.72, N, 2.17. FT-IR: 948, 844, 790, 705, 570, 541, 483 cm^{-1}. For $(Cetyl)_7H_2GdW_{10}O_{36}$, anal. calcd.: C, 36.62; H, 5.63; N, 2.03, and found: C, 36.80; H, 5.64, N, 2.11. FT-IR: 935, 846, 704, 587, 544, 486 cm^{-1}. For $(Cetyl)_3PMo_{12}O_{40}$, anal. calcd.: C, 27.66; H, 4.21; N, 1.54, and found: C, 27.27; H, 4.13, N, 1.48. FT-IR: 1065, 965, 870, 787, 597, 507 cm^{-1}. For $(Cetyl)_3PW_{12}O_{40}$, anal. calcd.: C, 19.96; H, 3.04; N, 1.11, and found: C, 20.38; H, 3.13, N, 1.08. FT-IR: 1081, 985, 892, 802, 596, 524 cm^{-1}. For $H_4SiW_{12}O_{40}$, FT-IR: 1090, 1021, 981, 927, 880, 780, 539, 479 cm^{-1}. For $(Cetyl)_5BW_{12}O_{40}$, anal. calcd.: C, 29.0; H, 4.4; N, 1.6, and found: C, 29.0; H, 4.4, N, 1.6. FT-IR: 1003, 968, 911, 812, 634, 510 cm^{-1}. For $(Cetyl)_6P_2W_{18}O_{62}$, anal. calcd.: C, 24.5; H, 3.7; N, 1.4, and found: C, 24.5; H, 3.7, N, 1.3. FT-IR: 1093, 961, 913, 789, 599, 565, 531, 476 cm^{-1}. For $[(C_4H_9)_4N]_4W_{10}O_{32}$(TBA–$W_{10}O_{32}$), anal. calcd.: C, 23.1; H, 4.3; N, 1.7, and found: C, 23.2; H, 4.3, N, 1.6. FT-IR: 995, 959, 891, 800, 582 cm^{-1}. For [(n-

$C_6H_{13})_4N]_3\{PO_4[WO(O_2)_2]_4\}$, anal. calcd.: C, 39.1; H, 7.1; N, 1.9, and found: C, 39.1; H, 7.0, N, 1.8. FT-IR: 1097, 1057, 1034, 978, 854, 844, 650, 592, 574, 549, 525 cm^{-1}. All FT-IR data exhibit those of the corresponding anions.

2.3. Catalytic reactions and procedures

The organic reagents (special grade), which were purchased from Kanto Chemical, E. Merck, and Tokyo Kasei, were used without further treatments. H_2O_2 aqueous solution (30%), produced by Mitsubishi Chemical, was used. The oxidation reactions were carried out according to the previous paper [24]: Typically, in a three-necked round bottom flask (100 ml), a catalyst (0.5 g, 0.1 mmol), a substrate (5 mmol), and CHCl$_3$ (2 and 10 ml) were introduced. After ca. 10 min of preheating the mixture at 60°C under N$_2$ atmosphere, the reaction was started by the addition of H$_2$O$_2$ (30%, 10–20 g). At the end of the reaction, the solution was cooled and extracted with CHCl$_3$. The product
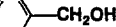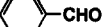
yields were determined by GC (0.25 mm × 30 m DBWax Capillary column) using the internal standard method (GC yield) and by a chromatographic separation using silica gel column (CHCl$_3$) (isolated yield).

3. Results and discussion

3.1. Catalytic features of Cetyl-HoW10 for the H$_2$O$_2$-oxidations of typical alcohols and olefins in a biphasic CHCl$_3$–aqueous H$_2$O$_2$ system

The catalytic activities of Cetyl-HoW10 for the H$_2$O$_2$-oxidation of alcohols and olefins as test reactions were examined in a biphasic CHCl$_3$–aqueous H$_2$O$_2$ system. The reaction condition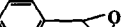s and the results analyzed are summarized in Table 1. At first, it should be noted that only 1.5 equivalent of H$_2$O$_2$ as the oxidant was required in Cetyl-Ho(III)W10, in contrast to the case of Cetyl-Ce(IV)W10 [24]. In the oxidations of alcohols and cyclooctene, the H$_2$O$_2$–Cetyl-

Table 1
Oxidation of alcohols and alkenes catalyzed by Cetyl-HoW10/H$_2$O$_2$ catalyst system.

run	substrate	temp /°C	time /h	product	yield /%[1]
1	∿∿∿OH	60	6	∿∿∿CHO	trace
2	∿∿∿(OH)	60	6	∿∿∿(=O)	59
3	⬡—CH₂OH	60	6	⬡—CHO	94
4	∿∿∿	60	6	∿∿∿◁(O)	trace
5	⬡=	60	6	⬡—◁(O)	trace
6	⬡	60	3	⬡▷=O	95

Substrate + H2O2 (1.5eq.) →[0.5mol% Cetyl-HoW10 / CHCl₃] Products

[1] GC yield using the internal standard method. Reaction conditions: Substrates, 20 mmol; H$_2$O$_2$, 30 mmol; catalyst, 0.1 mmol; CHCl$_3$, 10 ml.

HoW10 catalyst system seems to have higher activity than the peroxo-species derived from tungstic and molybdic acids, but in the oxidation of the terminal olefins, it may be rather less active [5–8]. On the other hand, heteropoly peroxometalates derived from 12-tungsto- and molybdo-phosphates (PW12 and PMo12) and H_2O_2 have been known to be generally a quite active catalyst for the oxidations of alcohols and olefins; especially the tetranuclear tungstate linked with a phosphate ion; $PO_4\{WO(O_2)_2\}_4$, is the most active [9–12,22]. Hexanuclear species, $[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2-(H_2O)]^{3-}$ is also workable as an active catalyst [19]. The activities of Cetyl-HoW10 for benzyl alcohol and cyclooctene listed in Table 1 may be comparable to those of such heteropoly peroxometalates.

3.2. Variation of catalytic activity of Cetyl-HoW10 for the H_2O_2-oxidation of 2-octanol with amounts of $CHCl_3$-organic solvent

In order to understand in further detail the catalytic features of Cetyl-HoW10, the H_2O_2-oxidation of 2-octanol as a test reaction were investigated under various reaction conditions. The results are summarized in Table 2: The conversion grows much with decreasing the amounts of the solvent used from 10 ml to zero as runs 1–6. However, below 2 ml of the organic solvent, the selectivity decreased much

in almost 100% conversion (runs 4, 5, and 6). This might occur apparently due to the volatility of the product. When the reaction time was shortened and more reactant (20 mmol) was introduced, such a low conversion as 47% was obtained and the selectivity was recovered to 100% (run 7). On raising the temperature up to 90°C, the conversion was improved to 94% without degrading the selectivity (run 8). It is noteworthy that the high conversion and selectivity were kept even though the least amount of 0.02 mmol of the catalyst was used (run 9). Thus, as an adequate reaction condition, the ratio of

$$\frac{catalyst/substrate(alcohol)}{oxidant(H_2O_2)/organic-solvent}$$

is described to be 1/1000/1500/0.

3.3. Variation of the catalytic activity of Cetyl-HoW10 with the kinds and amounts of organic solvent used: A consideration on the working states and mechanisms

The H_2O_2-oxidation of 2-octanol on the catalyst was further examined in various organic solvents–aqueous H_2O_2 systems. The results are summarized in Fig. 1. The hatched and dotted columns denote the results in 10 and 2 ml of the solvents used, respectively. The blanc column corresponds to the results in the or-

Table 2

H_2O_2 oxidation of 2-octanol to 2-octanone by Cetyl-HoW10/H_2O_2 catalyst system under the various reaction conditions

$$\text{OH} \quad \xrightarrow[\text{CHCl}_3]{\text{Cetyl-HoW10}} \quad \text{O}$$
$$+ H_2O_2$$

Run	Catal. (mmol)	Sub. (mmol)	H_2O_2 (mmol)	Solvn. (ml)	Time (h)	Temp. (°C)	Conv. (%)	Selec. (%)
1	0.1	5	35	10	6	60	59	> 98
2	0.1	5	35	5	6	60	81	> 98
3	0.1	5	35	3	6	60	96	> 98
4	0.1	5	35	2	6	60	> 98	95
5	0.1	5	35	1	6	60	> 98	79
6	0.1	5	35	0	6	60	> 98	68
7	0.1	20	30	0	2	60	47	> 98
8	0.1	20	30	0	2	90	94	> 98
9	0.02	20	30	0	2	90	94	> 98

ganic-solvent-free system as a reference. In 10 ml of the solvents used, the activity decreases greatly with reducing the polarity of solvent $(CH_3CN > t\text{-}BuOH > CHCl_3 > C_6H_6)$. The activity increases greatly by reducing the amount of the solvent $(10 \rightarrow 2$ ml) in the nonpolar solvents, while it is not so largely affected in the polar solvents. Especially, it is noted that the yield in 2 ml of $CHCl_3$ used is very close to that in the organic-solvent-free system.

In the polar organic solvent–aqueous H_2O_2 system, that is, only a small effect of the amount of the solvent on the conversion yield was resulted as in Fig. 1. In the case of CH_3CN, especially at 10 ml, the reacting system was apparently uniphasic, in which the catalyst and the substrate might be homogeneously dissolved in a mixed solvent of $CH_3CN-H_2O(H_2O_2)$. In such a CH_3CN-H_2O mixing solvent the polarity is generally regarded to be high rather than that of pure CH_3CN. In such a situation, the OH-group of 2-octanol molecules, which were introduced in the interspace of the CH_2-chains of the Cetyl-group, would be oriented at random to the center of active sites on LnW10 and opposite to the solvent molecules, as an interacting model postulated in Fig. 2 illustrates. Thus, the activity may be rather low and may not largely depend upon the amount of the solvents.
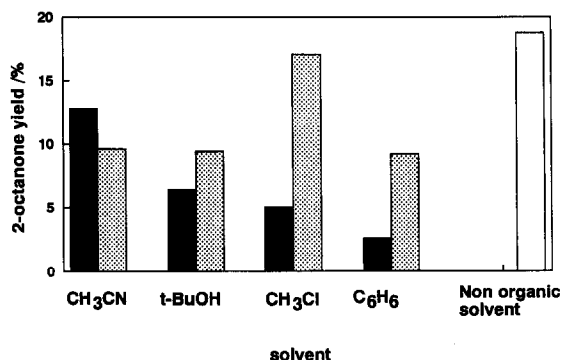

Fig. 2. A schematic illustration of working states of the H_2O_2 /Cetyl-Ln(III)W10 catalyst.

In the nonpolar solvent systems, not only the substrates but also the solvent molecules come into the hydrophobic space so that the chance of the close and encounter of the substrate molecules to the active sites becomes relatively low, that is, the amount of the coexisting solvent should affect the activity. The supply of the H_2O_2 molecules to the peroxo-HoW10 species should also be interrupted by the coexistence of the nonpolar solvent molecules. Thus the activity may be rather high at least with the lower amounts of the solvents.

In the solvent having a medium polarity such as $CHCl_3$, since the substrate and solvent molecules are dissolved competitively into the hydrophobic CH_2-chains of the modified catalyst, the amounts of the solvent should greatly affect the activity. The acceleration in the activity would be caused by an increase in the efficiency of an encounter of the substrates to an active site in the peroxo-HoW10 complex anion in the organic-solvent-free system. That is, the substrate is attractively taken into the CH_2-chains of the Cetyl-group surrounding the peroxo-HoW10 complex and thus the OH-group is closed easily to the hydrophilic active sites, as referred in Fig. 2.

Fig. 1. 2-octanone yield from 2-octanol on the Cetyl-HoW10/H_2O_2 catalyst system under various kinds and amounts of organic solvents. Reaction conditions: 2-octanol, 20 mmol; H_2O_2, 30 mmol; Cetyl-Ho(III)W10, 0.02 mmol; temperature, 55°C; time, 2 h. Amounts of solvents: 10 ml (hatched column); 2 ml (dotted column); 0 ml (blanc column).
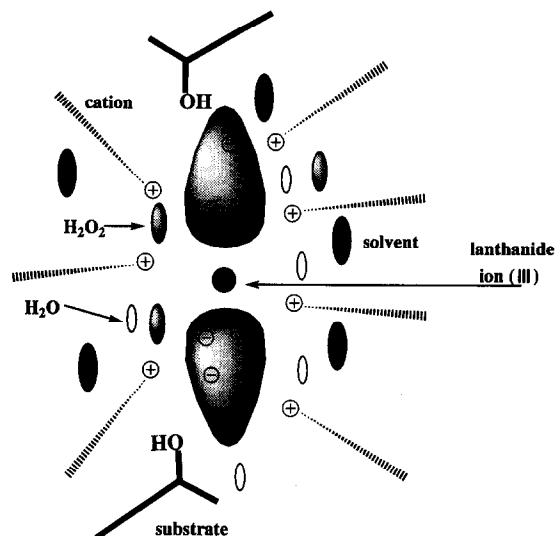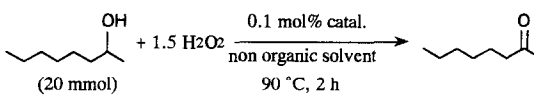
3.4. Comparisons of the catalytic activity between Cetyl-Ln(III)W10[Ln: La, Gd, Ho] and the other heteropoly oxometalates modified with alkyl ammonium cations under an organic-solvent-free condition

The catalytic activities of the other heteropoly acids (HPA) well-known for the H_2O_2-oxidation of 2-octanol were measured in the organic-solvent-free system to compare their catalytic features with that of LnW10. The reaction conditions and the results are summarized in Table 3. In any LnW10 catalyst containing light, medium, and heavy lanthanide elements (runs 1, 2, and 3), a high activity was found. Any of the well-known Keggin type HPA, except for PW12, were not workable as the catalyst for the H_2O_2-oxidation in the non-organic solvent system. TBA–$W_{10}O_{32}$ also did not work in the H_2O_2-oxidation, suggesting an important role of a Ln(III) ion that is inserting into the center of $W_{10}O_{32}$ units such as (W_5O_{18})–Ln–(W_5O_{18}) [29]. The tetrahexylammonium salt of the tetranuclear polyoxometalate, THA–$PO_4[WO(O_2)_2]_4$, which has been regarded as a precursor for an oxidation catalyst derived from PW12 and an excess amount of H_2O_2 [9–16], shows excellent activity.

Such low activities in the catalyst systems, other than PW12 and THA–$PO_4[WO(O_2)_2]_4$, might be caused from an instability and/or an extremely degraded form in their corresponding peroxo-species as the intermediates under such a specific condition as being organic-solvent-free. In contrast to those, the high activities in the Cetyl-Ln(III)W10 catalysts might arise from the peroxo-complex kept in a bulky form such as previously postulated in the H_2O_2–Ce(IV)W10 reacting system (see Fig. 4 in Ref. [26]). Based on such peroxo-complex model, an inverse correlation found between the activities of the series of the Cetyl-Ln(III)W10 catalysts[Ln: La–Yb] for the H_2O_2 oxidations of benzyl alcohol and cyclooctene, in fact, has been favorably understood [28]. A representation for the working states of the Cetyl-

Table 3

Comparison of catalytic activities for H_2O_2 oxidation of 2-octanol among the various polyoxometalates

OH $\quad\quad$ 0.1 mol% catal. $\quad\quad$ O
⌃⌃⌃⌃⌃ + 1.5 H2O2 ————————→ ⌃⌃⌃⌃⌃⌃
$\quad\quad$ non organic solvent
(20 mmol) $\quad\quad$ 90 °C, 2 h

Run	Catalysts	Yield (%)
1	Cetyl-$HoW_{10}O_{36}$ [a]	94
2	Cetyl-$LaW_{10}O_{36}$	94
3	Cetyl-$GdW_{10}O_{36}$	94
4	Cetyl-$PMo_{12}O_{40}$	0
5	Cetyl-$PW_{12}O_{40}$	72
6	Cetyl-$SiW_{12}O_{40}$ [b]	trace
7	Cetyl-$BW_{12}O_{40}$	trace
8	Cetyl-$P2W_{18}O_{62}$	trace
9	TBA–$W_{10}O_{32}$ [c]	trace
10	THA–$[PO_4\{WO(O_2)_2\}_4]$ [d]	> 98

[a] Cetylpyridinium salt.
[b] 4 equivalent Cetyl was added to $H_4SiW_{12}O_{40}$.
[c] Tetrabutylammonium salt.
[d] Tetrahexylammonium salt.

Ln(III)W10 catalyst under the various conditions, as schematically illustrated in Fig. 2, will be favorable for such bulky peroxo-complex model.

Cetyl-HoW10 also possessed a quite high activity and selectivity for the oxidations of cyclohexanol and benzyl alcohol to the corresponding ketone and aldehyde in the organic-solvent-free system exit as shown in Table 4. With the oxidation of benzyl alcohol, on the other hand, THA–$PO_4[WO(O_2)_2]_4$ is less active and selective than Cetyl-HoW10, in which the lower selectivity is caused from the further oxidation to benzoic acid (run 4). In the $PO_4[WO(O_2)_2]_4$ catalyst modified with the other alkyl ammonium cations (run 5), benzyl alcohol is oxidized less selectively [12]. In the organic-solvent-free system, internal olefins are efficiently oxidized to epoxides at 30°C: Especially, it is noted that allylic alcohols such as 2-octen-1-ol are quite rapidly and quantitatively oxidized to 2,3-epoxy-1-octanol (run 7). The terminal olefinic group in 1-octen-3-ol is preferentially oxidized to 1,2-epoxy-3-octanol (run 8), while that in 1-octene is never oxidized by using the Cetyl-HoW10 catalyst. From comparison of the data, runs 8 and 9, Cetyl-HoW10

Table 4

H_2O_2 oxidation of alcohols and olefins catalyzed by Cetyl-HoW10

$$\text{Substrate} + H_2O_2{}^a \xrightarrow[\substack{\text{non-organic} \\ \text{solvent}}]{\text{Cetyl-HoW10 }^b} \text{Product}$$

Run	Substrate (mmol)	Temp. (°C)	Time (h)	Product	Conv. (%)	Yield (%) [c]
1	2-octanol (20)	90	2.0	2-octanone	94	94
2	cyclohexanol (20)	90	0.75	cyclohexanone	94	94
3	benzylalcohol (20)	90	0.75	benzaldehyde	96	96
4 [d]	benzylalcohol (20)	90	0.75	benzaldehyde	84	74
5 [e,f]	benzylalcohol (25)	90	0.75	benzaldehyde	91	77
6	cyclooctene (8.0)	30	24	epoxycyclooctane	73	73
7	2-octen-1-ol (8.0)	30	1.0	2,3-epoxy-1-octanol	81	81
8	1-octen-3-ol (8.0)	30	6.0	1,2-epoxy-3-octanol		55
				1-octen-3-one		21
				1,2-epoxy-3-octanone		1
9 [e,f]	1-octen-3-ol (25)	70	2.0	1,2-epoxy-3-octanol		64
				1-octen-3-one		18
				1,2-epoxy-3-octanone		6

[a] Run 1–4: 30 mmol, run 6–8: 99.1 mmol of 30% aqueous H_2O_2, run 5: 37.5 mmol, run 9: 27.5 mmol of 40% aqueous H_2O_2.
[b] Catalyst: run 1–4: 0.02 mmol, run 6–8: 0.04 mmol.
[c] Run 1–5: GC yield, run 6–9: isolated yield.
[d] Catalyst: $THA-PO_4[W(O)(O_2)_2]_4$.
[e] Catalyst: $[(n-C_8H_{17})_3NCH_3]\{PO_4[W(O)(O_2)_2]_4\}$: 0.125 mmol.
[f] Ref. [12].

may be evaluated to be almost equivalent or more active than Venturello's $PO_4[WO(O_2)_2]_4$ catalyst. Thus, an excellent potentiality of Cetyl-HoW10 as the H_2O_2 oxidation catalyst for alcohols and olefins, especially under an organic-solvent-free condition, should be emphasized.

The various 'transition-metal-substituted polyoxometalates' based on Keggin structure have been well-known as the excellent catalysts for the selective oxidations of various organic substrates (Refs. [33–35] and references therein, [36–42]). However, we have no data at present about their catalytic behaviors in the organic-solvent-free system, which should be compared with those of the Cetyl-Ln(III)W10 catalysts.

4. Conclusion

In conclusion, Cetyl-HoW10 was elucidated to behave as a highly active but quite mild catalyst for the H_2O_2-oxidation of alcohols; that is, retarding the further oxidation to acids. The working states of the catalysts were discussed

successfully in the various organic solvents–aqueous H_2O_2 biphasic systems, and also the behavior as an excellent catalyst under the organic-solvent-free condition was favorably explained on the basis of the schematical model on the working states proposed (Fig. 2). Finally, it is pointed out that the present H_2O_2–Cetyl-LnW10 catalyst systems should be applied quite efficiently to syntheses of aldehydes, ketones, and epoxides, especially in a specific reaction condition such as being free from organic solvents.

An industrial process such as being performed in non-organic solvent systems, i.e., in aqueous reacting systems, has been required recently as environmental concerns (for instance Refs. [43–45]). It will be insisted that the present H_2O_2–Cetyl-LnW10 catalyst systems are responsible for such a request.

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