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Participation of new active species in epoxidation with cetylpyridinium dodecatungstate/FAp/urea–H_2O_2 system

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Abstract

We have developed an efficient catalytic solid-phase system for epoxidations that uses cetylpyridinium dodecatungstate ((Cetyl-Py)$_{10}$[$H_2W_{12}O_{42}$]) catalyst/fluorapatite (FAp) disperse phase with a solid urea–hydrogen peroxide complex (urea–H_2O_2). The solid system was reusable and retained its high catalytic activity, although the catalyst was not fixed on the solid-phase. The reaction rate was first-order with respect to substrate concentration and amount of the catalyst. The solid-phase activation of polyoxometalates with urea–H_2O_2 was studied using FT-IR and solid-state NMR spectroscopy, and no known degraded peroxo-species was observed to form. Based on these kinetic and spectroscopic studies, we propose that the active species is a new, stable peroxo-species with the framework of the parent dodecatungstate, of which the terminal W(=O)$_2$ site is specifically transformed to peroxo-type of W=O(O_2), in the system. Much higher efficiency of the dodecatungstate compared with the phsphotungstate or the decatungstate is considered to be due to the non-degraded, site-specific peroxo-species.

Keywords: Polyoxometalate; Dodecatungstate; Fluorapatite; Epoxidation; Urea–H_2O_2; Recyclable catalyst; Non-degraded peroxo-species

1. Introduction

Clean, selective oxidations with hydrogen peroxide have been increasingly required from a viewpoint of green sustainable chemistry. Polyoxometalates have recently attracted much attention as environmentally benign catalysts for such reactions because of their high selectivities and high stabilities towards heating and oxidation [1,2]. It is well-known that heteropolyoxometalates, especially Keggin-type phosphotungstates $[PW_{12}O_{40}]^{3-}$, efficiently catalyze the H_2O_2-epoxidation of alkenes and allylic alcohols and the oxidation of sulfides [3,4]. In the reactions, the heteropolytungstates are precursors, which react with H_2O_2 to form an active tetrameric peroxo-catalyst, $\{(PO_4)[W(O)(O_2)_2]_4\}^{3-}$ (PW4), in situ [5]. In the case of isopolytungstate catalysts, the active species is considered to be the degraded dimeric peroxide $[W_2O_3(O_2)_4]^{2-}$ (W_2O_{11}) [6,7]. The structure of the peroxo-catalyst PW4 is similar in part to that of dimeric peroxide W_2O_{11} and four WO_6 groups are joined via a phosphorous group. As the reaction of heteropolytungstates with aqueous H_2O_2 afforded other complexed peroxo-polytungustates in addition to PW4 and W_2O_{11}, involvement of other active species in the oxidation process could not be ruled out [5,8]. We previously reported that the reaction rates and selectivities of $[PW_{12}O_{40}]^{3-}$ in H_2O_2-epoxidation of allylic alcohols under conventional biphasic conditions (chloroform/water) are the combined rates and selectivities of PW4 and W_2O_{11}, which are significantly different [9]. Because of requirement of higher reactivity and selectivity, more recently, the previous preparation and use of the degraded peroxo-catalysts such as PW4 and W_2O_{11} have been of great interest rather than the use of precursor of polyoxometalates [10–12]. As the non-degraded catalysts, the transition-metal-substituted polyoxometalates have been developed but the clusters are used not as a catalyst but as a ligand that supports active transition metals [2]. So far the diversity of the cluster structures of common polyoxometalates has not been used satisfactorily in H_2O_2-catalytic oxidation system. To make use of the structural diversity of the polyoxometalates, involvement of non-degraded peroxo-species that retains the parent cluster in oxidation process is needed.

In order to develop a new H_2O_2-catalytic oxidation system with peroxo-type non-degraded polyoxometalates, we have

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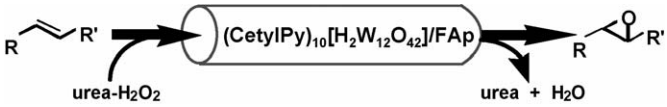


Scheme 1. $CetylPy_{10}$ $[H_2W_{12}O_{42}]$/FAp solid-phase epoxidation system.

attempted at solid-phase H_2O_2-oxidations with polyoxometalates dispersed on apatite [13–18]. Our first example of peroxo-type non-degraded polyoxometalate, tetrabutylammonium phosphomolybdate on fluorapatite ($(Bu_4N)_3[PMo_{12}O_{40}]$/FAp) is an effective, selective and reusable catalyst for sulfide oxidation with urea–hydrogen peroxide (urea–H_2O_2) [17,18]. We have also developed an efficient solid-phase epoxidation system using dodecatungstate ($CetylPy_{10}[H_2W_{12}O_{42}]$)/FAp/urea–$H_2O_2$ as shown in Scheme 1 [15,16]. Uniquely, the solid disperse phase does not fix the catalyst but is simply mixed with its powder; the oxidations are carried out at powdery solid-state without organic solvents. The unique reaction conditions brought about the formation of the non-degraded peroxo-species. Apatite was superior in this system to commonly used solid supports such as silica gel or clays, perhaps, owing to no active sites inducing side reactions on the apatite surface [13]. We also found that the catalytic activity was enhanced by using a large amount of apatite, which efficiently dispersed the active catalyst on its surface [16].

In this paper, we report details of the dodecatungstate-catalyst/FAp-disperse phase epoxidation system and of our spectroscopic studies of catalyst activation that allowed us to propose the active species in the reaction.

2. Experimental

2.1. Preparation of materials

FAp ($Ca_{10}(PO_4)_6F_2$) powder (particle size 5–20 μm; specific surface area 8–12 m^2/g) was used as obtained from Sekisui Kasei Co. Ltd.

Cetylpyridinium dodecatungstate ($CetylPy_{10}[H_2W_{12}O_{42}]$) was prepared in water from commercially available ammonium dodecatungstate and cetylpyridinium chloride. Other cetylpyridinium polyoxometalates ($CetylPy_3[PMo_{12}O_{40}]$ and $CetylPy_4[W_{10}O_{32}]$) were prepared using previously reported procedures [16]. The peroxo-species $CetylPy_2[W_2O_3(O_2)_4]$ (W_2O_{11}), $CetylPy_2[Mo_2O_3(O_2)_4]$ (Mo_2O_{11}) and $CetylPy_3\{(PO_4)[Mo(O)(O_2)_2]_4\}$ (PMo4) were prepared using previously reported procedures [9]. Identities were confirmed with FT-IR spectroscopy and the organic cations were estimated by CHN elementary analyses.

2.2. Catalytic activities

The activities of the solid catalysts for the epoxidations of cyclooctene and 3-octen-2-ol were examined using urea–H_2O_2 and FAp disperse phase. FAp powder (0.5 g), urea–H_2O_2 powder (2.5 mmol) and 1 mol% of the catalyst powder were mixed in a test tube equipped with a teflon-coated screw-cap, and then permeated by liquid substrate (1.0 mmol). After mixing, the reaction was left at 25 °C without stirring.

Product yields were periodically measured by capillary gas chromatography using Shimazu GC14B with a capillary column TC-70 (GL Sciences Inc., Ø0.25 mm × 30 m) with an internal standard.

2.3. Spectroscopic studies of catalyst activation

For the spectroscopic studies, solid-phase catalyst activation was carried out under the following conditions: catalyst (0.10 mmol), CaF_2 (0.20 g), urea–H_2O_2 (1.0 mmol) at 25 °C. CaF_2 was used in place of FAp because, while it is also effective as a solid-disperse phase for epoxidations, its spectra can be observed without overlap by PO_4^{3-}. The activation process was monitored as follows: FT-IR spectra were recorded as KBr disks on a JEOL WINSPEC 1000 FT-IR spectrometer; solid-state ^{31}P NMR spectra were recorded on a JEOL GX-270 W NMR spectrometer.

3. Results and discussion

3.1. Catalytic activities of cetylpyridinium polyoxometalates/FAp phase

In the solvent-free, solid-phase epoxidation of cyclooctene with urea–H_2O_2, the catalytic activities of the polyoxometalates increased in the presence of the FAp disperse phase; the degree of increase was affected not only by the polyoxometalate-cluster anion but also by the counter cation [19]. Fig. 1 summarizes the catalytic activities of a series of cetylpyridinium polyoxometalates on FAp. The activities were greatly influenced by the cluster structures; the order of activity was $(CetylPy)_{10}[H_2W_{12}O_{42}] \gg (CetylPy)_3[PMo_{12}O_{40}] > (CetylPy)_3[PW_{12}O_{40}] > (CetylPy)_4[W_{10}O_{32}]$. This order is different from that in the conventional liquid-biphasic system [3]; the Keggin-type phosphotungstate, $(CetylPy)_3[PW_{12}O_{40}]$, which is known to be the most effective catalyst in the liquid system, was less effective than phosphomolybdate, $(CetylPy)_3[PMo_{12}O_{40}]$, in

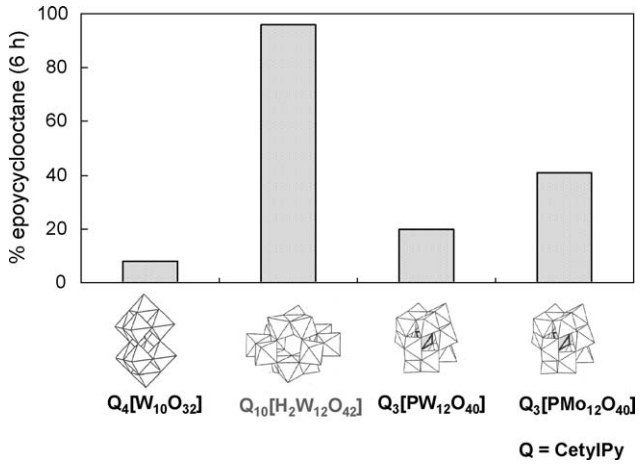


Fig. 1. Catalytic activities of polyoxometalates/FAp in the epoxidation of cyclooctene with urea–H_2O_2.

our system. Isopolytungstate, $(CetylPy)_4[W_{10}O_{32}]$, showed the lowest catalytic activity. The catalytic activity of dodecatungstate, $(CetylPy)_{10}[H_2W_{12}O_{42}]$, was outstandingly high.

3.2. Solid-phase epoxidation using cetylpyridinium dodecatungstate/fluorapatite phase

The epoxidation of cyclooctene was kinetically studied in the dodecatungstate catalyst/urea–H_2O_2/FAp phase system. Over 95% yield of epoxide product was formed after 6 h at 25 °C in the presence of 1 mol% catalyst. The natural logarithms of substrate concentration showed a first-order decrease with reaction time, as shown in Fig. 2 (solid circles). The observed reaction rate (k_{obs}), which was calculated from the slope of the line, was 0.55 h^{-1}. The linearity showed from the start to about 95% conversion with no initial induced time. In the absence of FAp phase, dodecatungstate catalyzed the epoxidation under similar reaction conditions (78% yield after 6 h at 25 °C). The decrease in substrate concentration was not linear after 6 h and the reaction rate slowed. The rate in the presence of the catalyst/FAp was about twice as fast as that with catalyst alone (Fig. 2, open circles).

Compared with H_2WO_4/urea–H_2O_2/FAp phase system as previously reported, there are two different points; in the H_2WO_4/FAp phase system, the kinetic plots showed the linearity with some initial induced time and in the absence of FAp the epoxidation did not substantially proceed [16]. Thus, the dodecatungstate/FAp system is a reactive system to form the active species smoothly in the initial step.

When the amount of the dodecatungstate catalyst was changed in the range 0.25–2.00 mol%, the kinetic plots showed linear to determine the observed reaction rate k_{obs} in all the cases. The reaction rate increased linearly with increasing amount of the catalyst, as shown in Fig. 3. The results showed

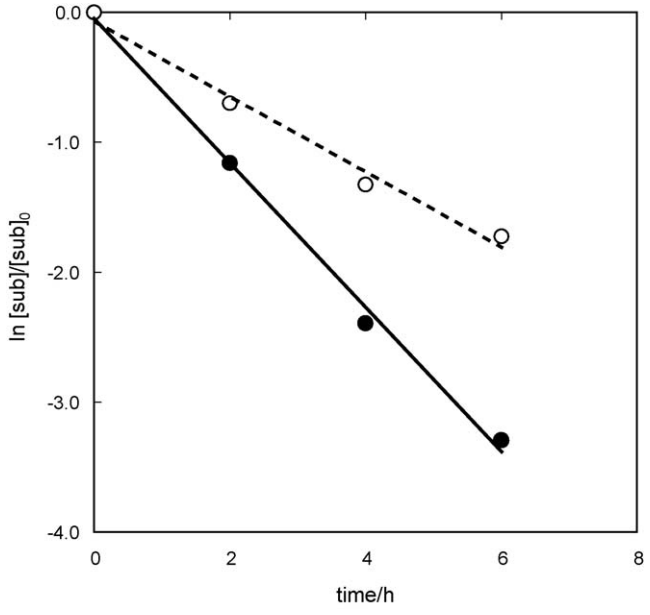


Fig. 2. Kinetic plots in CetylPy $[H_2W_{12}O_{42}]$-catalyzed epoxidation of cyclooctene with urea–H_2O_2 at 25 °C in the presence of FAp (●) and in the absence of FAp (○).

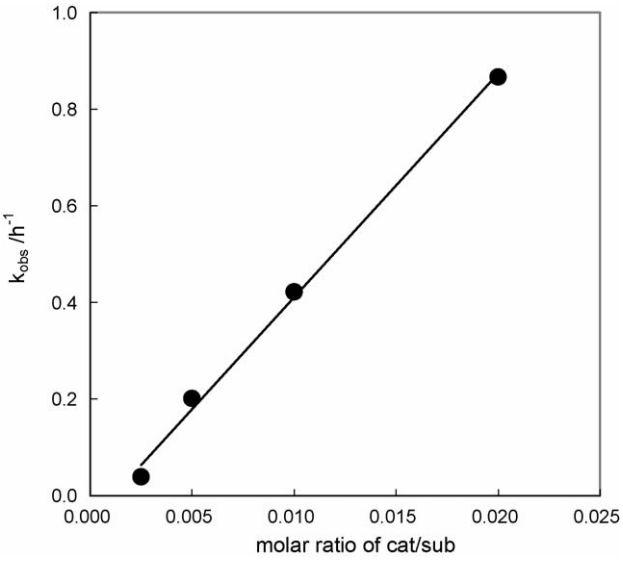


Fig. 3. Relationship between the molar ratio of $CetylPy_{10}$ $[H_2W_{12}O_{42}]$ to cyclooctene and the reaction rate k_{obs}.

that the epoxidation rate was first-order not only with respect to the substrate concentration but also with respect to the amount of catalyst. Thus, the bimoleclular reaction of cyclooctene and the active catalyst formed proportionally to the amount of the used catalyst proceeds even in the solid-phase epoxidation.

From these kinetic studies, the following important informations for the active catalyst were obtained; the initial formation of the active catalyst from the crystalline dodecatungstate catalyst with H_2O_2 is faster than the epoxidation; a constant amount of the active catalyst regenerates in the catalytic cycle. Accordingly, the active catalyst on apatite can be stable and not be further degraded in the epoxidation.

3.3. The formation of novel active species on solid disperse phase

In order to elucidate the active species, the activation of cetylpyridinium dodecatungstate with urea–H_2O_2 was followed using FT-IR spectroscopy. After the reaction of $(CetylPy)_{10}[H_2W_{12}O_{42}]/CaF_2$ (Fig. 4a) with urea–H_2O_2 at 25 °C for 24 h, four absorption bands assigned to the parent cluster had not changed, but a new band assigned to a peroxo group, ν(O–O), had appeared at 835 cm^{-1} (Fig. 4b) [16,20]. $(CetylPy)_2[W_2O_3(O_2)_4]$ (W_2O_{11}) is known to be an active species in the isopolytungstate-catalyzed reaction in aqueous solution [7]. Comparing spectrum b (activated $(CetylPy)_{10}[H_2W_{12}O_{42}]$) with that of previously prepared W_2O_{11}/CaF_2 (Fig. 4c), showed that only the ν(O–O) band was common to both: thus, the structure of the active species does not resemble W_2O_{11} but retains the structure of the parent cluster.

In our precedent paper, we concluded that the peroxo-species formed from the phosphomolybdate which reacts with hydrogen peroxide easier than the corresponding tungstate maintains the parent cluster structure in the solid-phase system, based on solid-state ^{31}P NMR and FT-IR spectroscopic studies [18]. After activation at 25 °C for 24 h, no new signal appeared

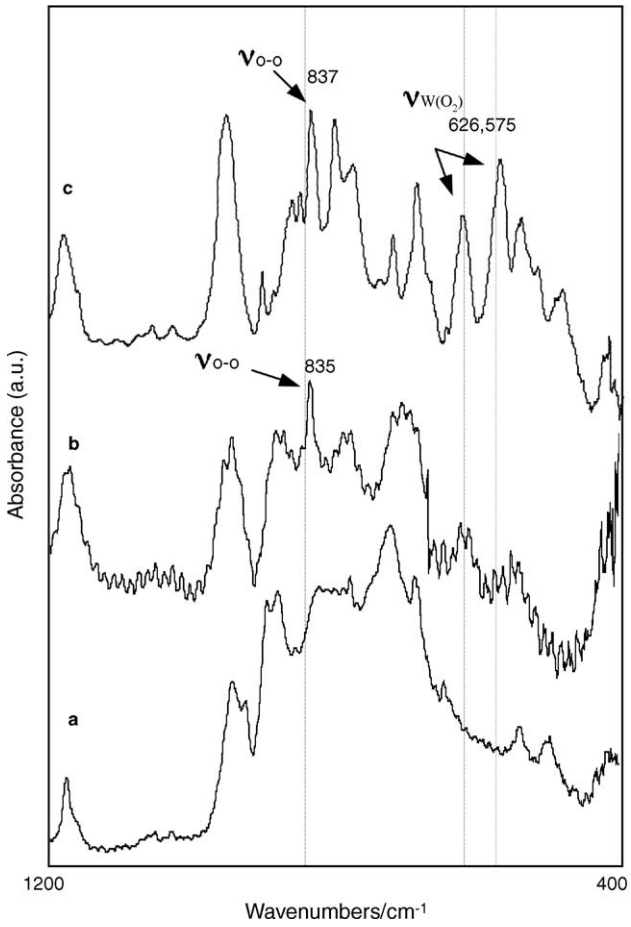


Fig. 4. FT-IR spectra of active species in $CetylPy_{10}$ $[H_2W_{12}O_{42}]$-solid-phase system. (a) $CetylPy_{10}$ $[H_2W_{12}O_{42}]/CaF_2$, (b) $CetylPy_{10}$ $[H_2W_{12}O_{42}]/CaF_2$/urea–H_2O_2 solid-phase system, 25 °C, 24 h and (c) peroxotungstate $CetylPy_2[W_2O_3(O_2)_4]/CaF_2$.

in the solid-state ^{31}P NMR spectrum besides the parent cluster signal at −3.85 ppm. The expected signal at 8.09 ppm, corresponding to the degraded species $(CetylPy)_3\{(PO_4)[Mo(=O)(O_2)_2]_4\}$ (PMo4), which is well-known as an active species in the liquid-phase system, was not detected after the continued activation. In the FT-IR spectrum of the same sample, the four absorption bands in the range of 700–1100 cm^{-1}, indicative of a Keggin-cluster structure, did not change and a new broad band appeared at 590 cm^{-1}. This new band may correspond to $\nu(Mo(-O)_2)$ of a newly formed peroxo group. These results suggest that the peroxo-species of the phosphomolybdate maintains the structure of the parent cluster.

In the present peroxidation of $(CetylPy)_{10}[H_2W_{12}O_{42}]$, although the solid-state NMR spectrum was not obtained, similar changes among FT-IR spectra of $(CetylPy)_{10}[H_2W_{12}O_{42}]$ and the phosphomolybdate were observed. As the active species of labile phosphomolybdate maintains the parent cluster structure, the active species of $(CetylPy)_{10}[H_2W_{12}O_{42}]$ differs from the degraded structure of W_2O_{11} and keeps the parent cluster structure.

In addition to these spectroscopic data, the peroxo-species without drastic degradation may be suggested by the following two findings on the epoxidations.

The dodecatungstate catalyst was more effective than the equivalent tungsten-amount of the peroxo-catalyst W_2O_{11} in the apatite-phase epoxidations. With the use of $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp, higher product yields in the epoxidations of cyclooctene and 3-octen-2-ol were obtained than with W_2O_{11}/FAp (Fig. 5). Taking into account such higher activity of $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp, non-detectable amount of the degraded peroxo-species formed on the surface of the parent dodecatungstate may not be involved. In the use of the phosphomolybdate catalyst/FAp, the non-degraded peroxo-species showed higher catalytic activity than the degraded peroxo-catalyst, PMo4/FAp or $(CetylPy)_2[Mo_2O_3(O_2)_4]$ (Mo_2O_{11})/FAp [17].

$(CetylPy)_{10}[H_2W_{12}O_{42}]$ /FAp is an efficient, reusable solid catalyst in spite of the simplicity of mixing of the catalyst with the solid disperse phase [15,21]. The recovered solid catalyst retained its activity for the urea–H_2O_2 epoxidation of cyclooctene over more than five reaction cycles. In general, the activity of a catalyst fixed on a solid support tends to decrease with repeated use, owing to loss of the soluble catalyst separated from the support. In our system, the insoluble solid catalyst mixed with the solid disperse phase may be hardly leaked from the system as long as the catalyst is not degraded. Thus, the solid catalyst may not be drastically degraded in the recycled system.

3.4. Site-specific peroxidation of polytungstates with urea–H_2O_2

In the solid-phase system, the rate of initial formation of the active catalyst is an important factor contributing to the catalytic activity, because the solid-phase reaction of catalyst with solid hydrogen peroxide proceeds much slower than the liquid-phase

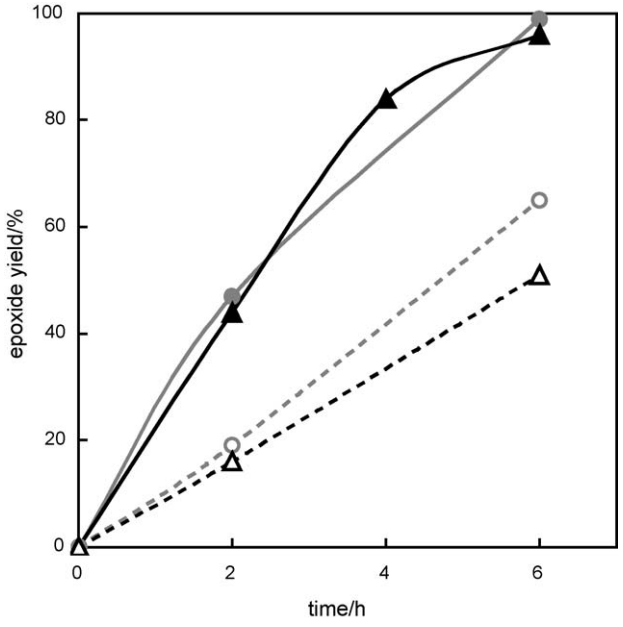
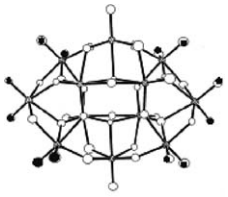
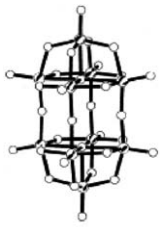
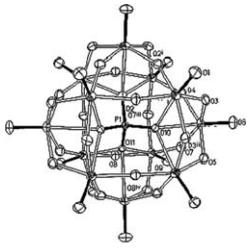
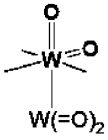
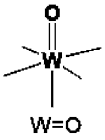


Fig. 5. Comparison of the catalytic activity of $CetylPy_{10}$ $[H_2W_{12}O_{42}]$/FAp with that of peroxotungstate $CetylPy_2$ $[W_2O_3(O_2)_4]$/FAp in the epoxidations of cyclooctene (circle) and 3-octen-2-ol (triangle) $CetylPy_{10}$ $[H_2W_{12}O_{42}]$/FAp (solid line); $CetylPy_2$ $[W_2O_3(O_2)_4]$/FAp (dotted line).

Table 1
The influence of cluster structures of polyoxometalates on catalytic activities

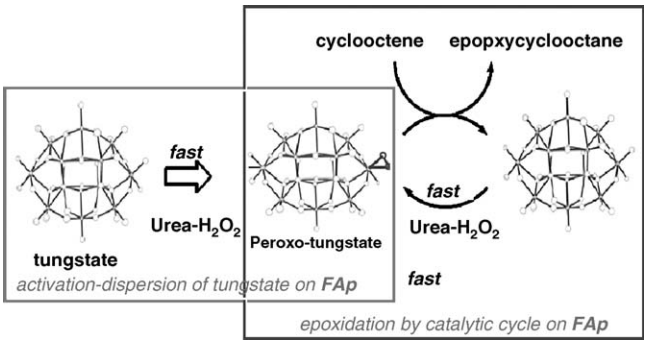
Terminal oxygen structure	 $[H_2W_{12}O_{42}]^{10-}$	 $[W_{10}O_{32}]^{4-}$	 $[PW_{12}O_{40}]^{3-}$
 $W(=O)_2$	6	0	0
 W=O	6	10	12
Catalytic activity[a]	96	8	20

[a] % epoxycyclooctane at 25 C for 6 h.

reaction. In the case of phosphotungstate and decatungstate, the formation of peroxo-species was not detected after the long time of the activation. In contrast, in the case of the dodecatungstate catalyst, the formation of the peroxo-species was spectroscopically observed as described above.

To form peroxo-species, terminal W=O groups of the polyoxometalate framework are attacked by hydrogen peroxide. The dodecatungstate cluster structure [22] comprises six octahedra with one terminal oxygen (W=O type) and six with two terminal oxygens ($W(=O)_2$ type) (Table 1). The other two clusters, not only decatungstate but also phosphotungstate, have only W=O type terminal oxygens. Their different activities must result from the different reactivities of $W(=O)_2$ and W=O sites. The $W(=O)_2$ site in the cluster framework would be more easily attacked by hydrogen peroxide than the W=O site to form the peroxo structure of $W(=O)(O_2)$ on the following supposition. The $M(=O)(O_2)$ structure is considered to be easily constructed and stable, as the structure can been seen as a partial structure in the degraded peroxo-species PM4 and M_2O_{11} and also in the peroxo-type of polyoxometalates crystallized from the solution, for examples, diperoxo-heptatungstate [23–25]. If W=O site reacts with hydrogen peroxide to form the same peroxo structure of $W(=O)(O_2)$, another W–O bond of the cluster framework must be broken. Thus, the transformation of W=O site to $W(=O)(O_2)$ would not occur easily. Therefore, the formation of $W(=O)(O_2)$ would occur specifically at the terminal $W(=O)_2$ site of the cluster framework, in comparison with the terminal W=O site.

Accordingly, we propose that the terminal $W(=O)_2$ site of $(CetylPy)_{10}[H_2W_{12}O_{42}]$ is site-specifically attacked by hydrogen peroxide to form a new active species, $(CetylPy)_{10}[H_2W_{11}O_{40}W{=}O(O_2)]$, in the FAp disperse phase system. The



Scheme 2. Peroxotungstate-catalyzed epoxidation in the apatite disperse phase system.

proposed active species-catalyzed epoxidation system is summarized in Scheme 2, taking into account the obtained kinetic results: the initial formation of the active catalyst with no induced time and fast regeneration of the active catalyst in the epoxidation. The proposed non-degraded, site-specific active species is easily formed on apatite in the initial activation step by hydrogen peroxide. In the epoxidation of cyclooctene the formed peroxo-species transfers oxygen to epoxidise cyclooctene, converting to the inactive parent cluster structure, which is easily regenerated by hydrogen peroxide. In the system, FAp disperse phase will be effective not only for dispersion of the active species but also for stabilization of the active species.

In our solid-phase system, the polytungstate clusters having terminal $W(=O)_2$ groups may be expected to show high catalytic activities. Lacunary phosphotungstates and heptatungstate, etc., are candidates for effective catalysts in our system. The studies on the line are in progress.

4. Conclusions

$(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp was the most efficient, reusable solid catalyst for the solvent-free epoxidation of cyclooctene with urea–H_2O_2. The kinetic studies suggest that the active catalyst was easily formed in the initial activation step and easily regenerated by hydrogen peroxide in the catalytic cycle and that the active catalyst was not degraded in the epoxidation process. Spectroscopic studies suggest the formation of the active catalyst with the parent cluster. Based on the obtained kinetic and spectroscopic results, we propose that the terminal $W(=O)_2$ site of $(CetylPy)_{10}[H_2W_{12}O_{42}]$ is specifically activated by hydrogen peroxide to form a new peroxo-species that retains the framework of the parent cluster, $(CetylPy)_{10}[H_2W_{11}O_{40}W{=}O(O_2)]$: the peroxo-species carries out the epoxidation reaction, cycling back to the inactive parent cluster, in the FAp disperse phase system. Much higher efficiency of the dodecatungstate compared with the phsphotungstate and the decatungstate in the solid-phase system is considered to be due to easy formation of the non-degraded, site-specific peroxo-species.

Acknowledgements

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References

[1] I.W.C.E. Arends, R.A. Sheldon, Top. Catal. 19 (2002) 133.
[2] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[3] Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, J. Org. Chem. 52 (1987) 1868.
[4] C. Venturello, R. D'Aloiso, J. Org. Chem. 53 (1988) 1553; C. Venturello, R. D'Aloiso, J.C. Bart, M. Ricci, J. Mol. Catal. 32 (1985) 107.
[5] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681.
[6] C. Aubry, G. Chottard, N. Platzer, J.-M. Bregeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem. 30 (1991) 4409.
[7] N.J. Campbell, A.C. Dengel, C.J. Edwards, W.P. Griffith, J. Chem. Soc., Dalton Trans. (1989) 1203.
[8] L. Salles, C. Aubry, R. Thouenot, F. Robert, C. Doreiux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Bregeault, Inorg. Chem. 33 (1994) 871.
[9] Y. Sasaki, T. Nomoto, S. Yamaguchi, J. Ichihara, Phosphorus Res. Bull. 9 (1999) 87.
[10] X. Zuwei, Z. Ning, S. Yu, L. Kunlan, Science 292 (2001) 1139.
[11] K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno, J. Am. Chem. Soc. 127 (2005) 530.
[12] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, Science 300 (2003) 964.
[13] J. Ichihara, Tetrahedron Lett. 42 (2001) 695.
[14] J. Ichihara, S. Yamaguchi, T. Nomoto, H. Nakayama, K. Iteya, N. Naitoh, Y. Sasaki, Tetrahedron Lett. 43 (2002) 8231.
[15] J. Ichihara, A. Kambara, K. Iteya, E. Sugimoto, T. Shinkawa, A. Takaoka, S. Yamaguchi, Y. Sasaki, Green Chem. 5 (2003) 491.
[16] J. Ichihara, K. Iteya, A. Kambara, Y. Sasaki, Catal. Today 87 (2003) 163.
[17] J. Ichihara, K. Iteya, H. Kawaguchi, Y. Sasaki, H. Nakayama, S. Yamaguchi, J. Ceram. Pro. Res. 4 (2003) 42.
[18] Y. Sasaki, K. Ushimaru, K. Iteya, H. Nakayama, S. Yamaguchi, J. Ichihara, Tetrahedron Lett. 45 (2004) 9513.
[19] Y. Sasaki, J. Ichihara, K. Sakamoto, S. Yamaguchi, Phosphrous Res. Bull. 17 (2004) 211.
[20] It was confirmed that FT-IR spectrum of urea–H_2O_2/CaF_2 showed no clear absorption bands in a range of 400–1200 cm^{-1} because of amorphous solid. In FT-IR spectra of $(CetylPy)_{10}[H_2W_{12}O_{42}]$/$CaF_2$/urea–$H_2O_2$ system, a new absorption band of 835 cm^{-1} was observed more clearly with the reaction time [16].
[21] Recycled procedures: after the reaction the solid catalyst phase is easily recovered with the following simple procedures [16]. From the solid reaction mixture the product is separated by pentane-extraction and filtration. Next the urea-complexes are removed by washing with acetone-water and filtration. Then the residue solid catalyst phase is dried under vacuum over P_2O_5, and reused to the reaction by mixing with the substrate and urea–H_2O_2.
[22] V.R. Allmann, Acta. Cryst. B27 (1971) 1393.
[23] O.W. Howarth, Dalton Trans. (2004) 476.
[24] I. Larking, R. Stomberg, Acta Chem. Scand. 26 (1972) 3708.
[25] H. Suzuki, M. Hashimoto, S. Okeya, Eur. J. Inorg. Chem. (2004) 2632.