Pergamon

Tetrahedron Letters 43 (2002) 8231–8234

TETRAHEDRON
LETTERS

Keggin-type polyacid clusters on apatite: characteristic catalytic activities in solvent-free oxidation

Junko Ichihara,[a,]* Shunro Yamaguchi,[a] Takuya Nomoto,[a] Hirokazu Nakayama,[b] Katsuma Iteya,[c] Nozomu Naitoh[c] and Yoh Sasaki[c,]*

[a]*Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[b]*Kobe Pharmaceutical University, Motoyama-kitamachi, Higashinada, Kobe, Hyogo 658-8558, Japan*
[c]*Faculty of Science and Engineering, Kinki University, Kowakae, Higashiosaka, Osaka 577-8502, Japan*

Received 7 August 2002; revised 17 September 2002; accepted 18 September 2002

Abstract—We found that Keggin-type phosphometalates are effective catalysts for solvent-free oxidation with urea–H_2O_2 by dispersing on fluorapatite solid phase. In the solid phase system the phosphomolybdate $(NH_4)_3PMo_{12}O_{40}$ was more effective than the phosphotungstate $(NH_4)_3PW_{12}O_{40}$, whereas the latter was much superior to the former in the liquid-phase reaction with aqueous H_2O_2. In situ formation of novel peroxo-type species from $(NH_4)_3PMo_{12}O_{40}$/FAp and urea–H_2O_2, which may lead to the high catalytic activity in the solid phase system, was observed by ^{31}P solid-state NMR. © 2002 Published by Elsevier Science Ltd.

A solid phase-assisted reaction system without organic solvent has been attracted as an environmentally benign catalyzed organic reaction system.[1,2] We have developed new catalytic reaction systems using apatite as a solid phase. Apatites, $Ca_{10}(PO_4)_6X_2$, which form the mineral component of bones and teeth, are handled as a harmless solid to environment.[3] Importantly, they have both ion exchange ability and organic compound-affinity. Recently, we have found that apatites are effective as a solid disperse phase for assisting tungstic acid (H_2WO_4)-catalyzed epoxidation of alkenes and allylic alcohols with solid urea–H_2O_2 without solvent.[4] In homogeneous or heterogeneous liquid-phase oxidation with aqueous H_2O_2–organic solvent, it has been so far recognized that Keggin-type heteropolytungstic acid, $PW_{12}O_{40}{}^{3-}$, is the most effective catalyst among a variety of polyoxometalates, and that its active species is phosphoperoxotungstate $[PW_4O_8(O_2)_8]^{3-}$ (PW_4), formed via degradation by aqueous H_2O_2.[5–12] In the aqueous H_2O_2 solution, however, the PW_4-catalyzed epoxidation reaction does not efficiently proceed without organic solvent and a phase transfer catalyst. We thought that the reaction of the heteropoly acid with urea–H_2O_2 on apatite solid phase must proceed in a different way to form another active species. We now report that the combinations of solid urea–H_2O_2 and Keggin-type heteropoly-tungstates or molybdates on apatites have their characteristic activities for solvent-free organic oxidation reactions.

The salts of Keggin type-heteropolyacids ($M_3PW_{12}O_{40}$, $M_4SiW_{12}O_{40}$, and $M_3PMo_{12}O_{40}$) and the salts of isopolyacids ($M_{10}H_2W_{12}O_{42}$, $M_6Mo_7O_{24}$) were used as solid catalysts. Hydroxyapatite (HAp, X = OH) or fluorapatite (FAp, X = F) was used as a solid disperse phase.[13] The poly-tungstates or molybdates on apatites were not previously prepared by impregnating in solution but simply mixed in powders.[4] Activities of the solid catalysts were examined based on the epoxidation of cyclooctene with urea–H_2O_2 as follows. A solid catalyst (0.01 mmol, 1.0 mol%), apatite (1.0 g), and solid urea–H_2O_2 (2.5 mmol) were simply mixed, and the solid mixture was permeated by liquid cyclooctene (1.0 mmol). Then the mixture was left without stirring at room temperature. The reaction was followed by gas chromatography using the internal standard method.

The catalytic activities in the epoxidation of cyclooctene at rt were summarized in Fig. 1. All the polyacids except for $H_4SiW_{12}O_{40}$ showed positive activities for the epoxidation in the presence of HAp or FAp. The catalytic activities in the solid-phase system were not greatly affected by using either the heteropoly- or isopoly-acids and either tungstates or molybdates, and also by using either HAp or FAp solid phase. Thus, the employed polyacids on apatites were found to

---

Keywords: epoxidation; phosphomolybdates; fluorapatite; urea–H_2O_2; environmentally benign catalyst; peroxo species.

* Corresponding authors. Fax: +81-6-6879-8469; e-mail: ichihara@sanken.osaka-u.ac.jp; sasaki@meta.kindai.ac.jp

0040-4039/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4039(02)02033-6

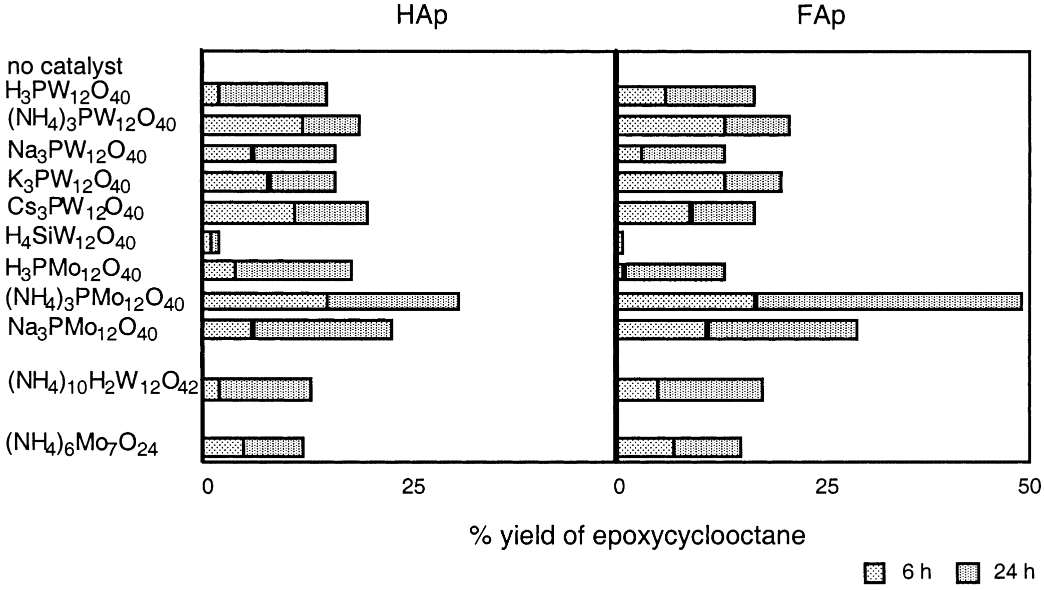


Figure 1. Catalytic activities of polyoxometalates on apatites in the solvent-free epoxidation of cyclooctene with urea–H_2O_2.

catalyze the epoxidation of C=C double bond without solvent, whereas in the absence of apatite the catalytic reaction proceeded slightly.

Among them $(NH_4)_3PMo_{12}O_{40}$ on FAp had the highest activity for the solvent-free reaction. As shown in Table 1, $(NH_4)_3PMo_{12}O_{40}$ on FAp catalyzed the solvent-free oxidations of some alkenes, sulfides and sulfoxides with urea–H_2O_2.[14] The selective oxidation of aryl methyl sulfide to the corresponding sulfoxide was accomplished by using a small excess of urea–H_2O_2. The reaction of cyclic alkenes afforded the epoxides, and acyclic *cis*-alkenes were oxidized to give the diols. *trans*-Alkene slightly oxidized under the same reaction conditions to form the epoxide. Our system of phosphomolybdate without organic solvent and a phase transfer catalyst provided comparable catalytic activity to the phase-transfer catalyzed system using aq. H_2O_2–chloroform biphase.[15]

Remarkably, the phosphomolybdates, $PMo_{12}O_{40}^{3-}$, were more effective than the phosphotungstates, $PW_{12}O_{40}^{3-}$, in the solid phase reaction system. In liquid-phase reactions, in contrast, it has been reported that the phosphotungstates are much more effective for oxidation of organic compounds than the phosphomolybdates.[6,8,15] For their active peroxo-type species, it has been reported by J.-M. Bregeault that the peroxo-type tungsten catalysts (PW4) prepared previously are about 30 times more active than the molybdenum analog (PMo4) in water–chloroform biphase.[10,11] The catalytic activities orders in the two reaction systems are different as described below.

The order of catalytic activities in the solid phase system:

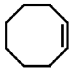
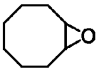
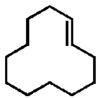
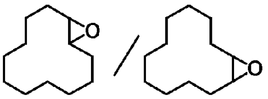
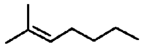
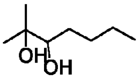
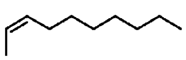
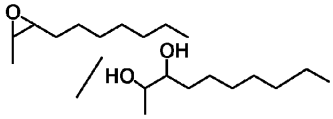
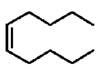
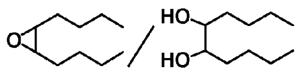
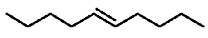
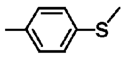
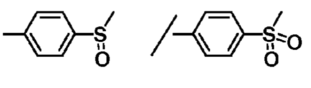
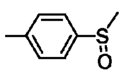
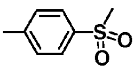
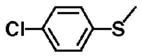
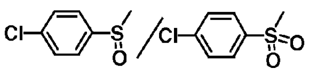
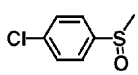
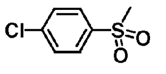
$PMo_{12}O_{40}^{3-}$/apatite > $PW_{12}O_{40}^{3-}$/apatite ≫ $SiW_{12}O_{40}^{4-}$/apatite

The order of catalytic activities in the liquid-phase system:

$PW_{12}O_{40}^{3-} \gg PMo_{12}O_{40}^{3-} > SiW_{12}O_{40}^{4-}$

The higher activity of $(NH_4)_3PMo_{12}O_{40}$/FAp than that of $(NH_4)_3PW_{12}O_{40}$/FAp in our reaction system might be attributed to the formation of a new active species or stability of the known active species (PM4 type) on apatite solid phase. In order to search the catalytic active species, the reactions of $(NH_4)_3PMo_{12}O_{40}$/FAp and $(NH_4)_3PW_{12}O_{40}$/FAp with urea–H_2O_2 were directly followed by ^{31}P solid-state NMR. The reaction was carried out under the following conditions: catalyst/FAp or CaF_2/urea–H_2O_2 = 0.10 mmol/0.19 mmol/1.0 mmol) at rt for 3 days. NMR spectra behavior of catalysts with CaF_2 was similar to that with FAp, while the PO_4^{3-} signal of FAp overlapped in the latter case. Fig. 2 shows the NMR spectra in the reaction of $(NH_4)_3PMo_{12}O_{40}/CaF_2$ by urea–H_2O_2. In the case of $(NH_4)_3PMo_{12}O_{40}$ new signals together with the parent one were observed immediately after mixing the solid powders. NMR spectra after 24 h (Fig. 2b) clearly demonstrated that $(NH_4)_3PMo_{12}O_{40}$ reacted with H_2O_2 on solid phase to form several new species. These species were different from PMo4-type species (δ ~7.5 ppm).[11] In this case the presence of the peroxo group (M–O–O–) was confirmed from ATR method of FT-IR. In contrast to $(NH_4)_3PMo_{12}O_{40}$, in the case of $(NH_4)_3PW_{12}O_{40}$ NMR spectra did not have any variation for 3 days. These results showed that the activation of $(NH_4)_3PMo_{12}O_{40}$/FAp to the new peroxo species by urea–H_2O_2 proceeded faster than that of $(NH_4)_3PW_{12}O_{40}$/FAp. The faster formation of the active species may lead to the higher catalytic activity of $(NH_4)_3PMo_{12}O_{40}$/FAp in the solid-phase reaction system.

Table 1. Solvent-free oxidation using $(NH_4)_3PMo_{12}O_{40}$/FAp[a]

Substrate	Reaction conditions	Product	Yield/%[c]	(Conversion)
	rt, 24 h		85	(91)
 (69/31)[d]	rt, 24 h		23 / 11	(34)
	rt, 48 h		99	(100)
	rt, 24 h		6 / 76	(83)
	rt, 72 h		19 / 71	(90)
	rt, 72 h		8	(8)
	4 °C, 30 h[b] rt, 5 h[b]		91 / 9 74 / 19	(100) (93)
	rt, 24 h[b]		92	(92)
	4 °C, 30 h[b] rt, 2 h[b] rt, 5 h[b]		74 / 14 72 / 0 53 / 46	(88) (72) (99)
	rt, 24 h[b]		94	(94)

[a] $(NH_4)_3PMo_{12}O_{40}$/FAp/urea-H_2O_2/substrate= 0.075 mmol/ 1.25 g/ 6.25 mmol/ 2.5 mmol.

[b] $(NH_4)_3PMo_{12}O_{40}$/FAp/urea-H_2O_2/substrate= 0.067 mmol/ 1.25 g/ 2.90 mmol/ 2.5 mmol.

[c] Isolation procedure is noted in ref. 14. Determined by GC and/or ^{1}H NMR.

[d] The ratio of *trans to cis*.

Although the activation process of $(NH_4)_3PW_{12}O_{40}$/FAp was not confirmed from solid state NMR, $(NH_4)_3PW_{12}O_{40}$/FAp showed positive activity in our solid phase system. This might be promoted by another peroxo-type species without significant degradation. The further studies on the line are under way.

In our system, Keggin-type structure of $(NH_4)_3$-$PMo_{12}O_{40}$ was an effective catalyst for the solvent-free epoxidation with urea–H_2O_2 by dispersing on FAp solid phase. FAp disperse phase can play an important role to assist the formation of novel active species from $(NH_4)_3PMo_{12}O_{40}$ and the species-catalyzed organic oxidation.

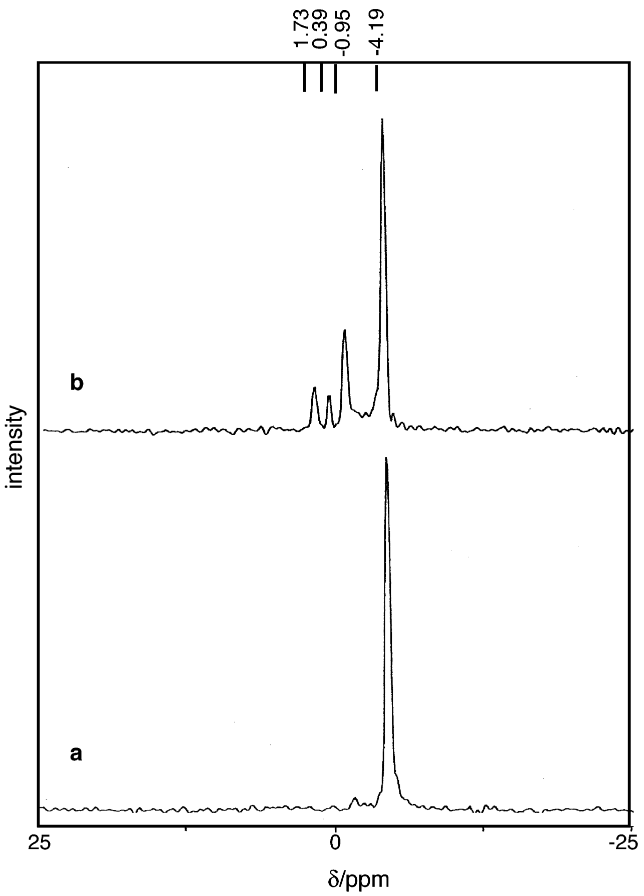


Figure 2. ^{31}P solid-state NMR spectra of $(NH_4)_3PMo_{12}O_{40}$ (a) and the solid mixture of $(NH_4)_3PMo_{12}O_{40}$/CaF_2/urea–H_2O_2 after 24 h (b).

References

1. (a) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199–217; (b) Misono, M. *J. Chem. Soc., Chem. Commun.* **2001**, 1141–1152.
2. Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171–198.
3. Elliott, J. C. In *Studies in Inorganic Chemistry*; Structure and Chemistry of the Apatites and Other Calcium Orthophosphates; Elsevier: Amsterdam, 1994; Vol. 18.
4. Ichihara, J. *Tetrahedron Lett.* **2001**, *42*, 695–697.
5. (a) Venturello, C.; D'Aloiso, R. *J. Org. Chem.* **1988**, *53*, 1553–1557; (b) Venturello, C.; D'Aloiso, R.; Bart, J. C.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107–110.
6. Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587–3593.
7. Ishii, Y.; Yamawaki, K.; Yoshida, T.; Ura, T.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 1868–1870.
8. Duncan, D. C.; Chambers, C.; Hecht, E.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 681–691.
9. Aubry, C.; Chottard, G.; Platzer, N.; Bregeault, J.-M.; Thouvenot, R.; Chauveau, F.; Huet, C.; Ledon, H. *Inorg. Chem.* **1991**, *30*, 4409–4415.
10. Salles, L.; Aubry, C.; Thouenot, R.; Rober, F.; Doreiux-Morin, C.; Chottard, G.; Ledon, H.; Jeannin, Y.; Bregeault, J.-M. *Inorg. Chem.* **1994**, *33*, 871–878.
11. Dengel, C.; Griffith, W. P.; Parkin, B. C. *J. Chem. Soc., Dalton Trans.* **1993**, 2683–2688.
12. (a) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 8310–8311; (b) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Panyella, D.; Noyori, R. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905–915.
13. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and fluorapatite $Ca_{10}(PO_4)_6F_2$ were presented by Sekisui Kasei Co., Ltd.
14. The reactions were carried out under the conditions described in Table 1. The solid reaction mixture was extracted with pentane. Conversions were determined by GC or ^{1}H NMR analysis of the pentane solution. In most cases, after evaporating the solvent, the mixture of the starting materials and the described products were obtained without loss of weight. The yields of the products were estimated without separation by GC and/or ^{1}H NMR.
15. (a) Ichihara, J.; Yamaguchi, S. *Phosphorus Res. Bull.* **1998**, *8*, 143–146; (b) Sasaki, Y.; Nomoto, T.; Yamaguchi, S.; Ichihara, J. *Phosphorus Res. Bull.* **1999**, *9*, 87–90; (c) Yasuhara, Y.; Yamaguchi, S.; Ichihara, J.; Nomoto, T.; Sasaki, Y. *Phosphorus Res. Bull.* **2000**, *11*, 43–46.