

Characteristics of apatites as a disperse phase for solid-phase organic oxidation system

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In the novel solid phase system consisting of cetylpyridinium dodecatungstate (CetylPy₁₀[H₂W₁₂O₄₂]) catalyst/ solid oxidant (urea-H₂O₂)/ apatite disperse phase, the O-insertion reaction (epoxidation) of C=C double bond of cyclooctene proceeds at powdery solid state in the absence of organic solvents without stirring at room temperature. In the system, the formation of the epoxide was affected by various forms of hydroxyapatite powders (HAPs) used as a solid disperse phase. The high crystallinity and low surface area of HAP and the uniform size of spherical particles of HAP were found to be important factors as an effective solid disperse phase for assisting the epoxidation. The factors were quite different from those of common solid supports used for fixing the catalyst in liquid-solid heterogeneous reactions. Taking account of the kinetic behavior in the solid-phase-epoxidation system, key points for promoting the reaction are considered to be the diffusion of liquid reactant and its proximity to the active catalyst. The effective forms of apatites might have advantages in these points.

Key words: apatite, solid disperse phase, epoxidation, polyoxometalate, hydrogen peroxide, green chemistry.

Introduction

Apatites (Ca₁₀(PO₄)₆X₂, X=OH, F) are well-known as the mineral component of bones and teeth, and also are widely distributed in minerals [1, 2]. So far the apatites, which are synthesized from calcium and phosphate components or from the related calcium phosphates, have been mainly used as biocompatible materials for repairing bones and teeth. The chemical and physical properties of apatites are known to be as follows; cation & anion exchange abilities; the formation of unstoichiometric apatite; solubility in acidic conditions; the conversion to another structure of calcium phosphate in acidic conditions; affinity for amino acids. From the view of recent ecology, the apatites as harmless materials have increasingly attracted much attention in a variety of fields and the applications have been rapidly extended to adsorbents, deodorants, column chromatograph packing or photocatalysts.

Towards environmentally benign organic syntheses, the inorganic ceramics have been frequently used as reaction fields and as supports of catalysts because of eco-materials and recyclability [3]. However, there have been few reports on the use of apatites; apatites have been used in solution as a solid support for impregnating the catalysts [4, 5]. We used the apatite powder

as a 'harmless solid-disperse-phase' for the organic reaction process instead of organic solvents. We have recently developed an efficient reusable solid-phase-oxidation system using solid urea-hydrogen peroxide (urea-H₂O₂)/tungstate catalyst/fluorapatite (FAP) [6-12]. Unique points in the system are as follows; the solid-disperse-phase does not fix the catalyst but is simply mixed with the powdery catalyst and the other reactants; if a liquid reactant, it permeates the solid-disperse-phase to keep the powdery state of the solid phase; the reactions are carried out in the powder solid state in the absence of organic solvents. In such a solid-phase system, the powder forms of the solid-disperse phase must affect the reactions in a different manner from the conventional liquid-solid heterogeneous system using solid-supported catalysts and solvents. In this paper, we studied the effect of various forms of hydroxyapatites (HAPs) on the tungstate-catalyzed epoxidation in order to understand the apatite-assisted mechanism and to find a suitable disperse phase for our green reaction system.

Experimental Procedures

Several hydroxyapatites (Ca₁₀(PO₄)₆(OH)₂, HAP) were obtained from Sekisui Kasei Co. Ltd., PENTAX Corporation and Taihei Chemical Industrial Co. Ltd and used without treatment. Powdery forms and sizes of HAPs were observed by an optical microscope (Olympus BH2-TR30 and BH2-DP12) and scanning electron microscopy (SEM, Hitachi S-2250N) [7]. Crystal structures

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and crystallinities were analyzed by powder X-ray diffractometry (PXD) with a Rigaku RINT 2000. Specific surface area was determined by a N_2 -BET method with Shimadzu FLOWSORB 2300.

Cetylpyridinium dodecatungstate (CetylPy₁₀[H₂W₁₂O₄₂]) was used as a solid catalyst. The catalyst was prepared from the commercially available ammonium dodecatungstate ((NH₄)₁₀[H₂W₁₂O₄₂]) and cetylpyridinium chloride in water, as reported previously [6]. The catalyst was identified with Fourier transform infrared spectroscopy (JASCO FT/IR-4100); Absorbances corresponding to the paradodecatungstate cluster were observed at 891, 845, 779, 717 cm^{-1} . The substitution of the catalyst by the cetylpyridinium cation was calculated by elementary analyses of carbon, hydrogen and nitrogen. The catalyst was found to be 0.5-2.0 μm sized flat plate-forms by scanning electron microscope [8].

Urea- H_2O_2 [13] was the commercially available solid oxidant from Aldrich Co., and the particle sizes were in a wide range from 50 to 500 μm .

Apatite-assisted epoxidation: solvent-free H_2O_2 -epoxidation of cyclooctene using the solid catalyst/ apatite disperse phase was carried out in the powdery solid-state in the absence of organic solvent as follows. Apatite powder (0.25 g) was simply mixed with a 1 mol% of the solid catalyst, solid urea- H_2O_2 (1.25 mmol) in a test tube with a Teflon-coated screw cap, and the solid mixture was permeated with the liquid substrate (0.5 mmol). After a short mixing, the resulting solid mixture was left without stirring at 25 $^{\circ}\text{C}$. The epoxidation was periodically followed by capillary gas chromatography using an internal standard method.

Decomposition of hydrogen peroxide on apatite: apatite powder (0.25 g) was simply mixed with solid urea- H_2O_2 (1.25 mmol) in a test tube with a teflon-coated screw cap, and left without stirring at 25 $^{\circ}\text{C}$. After 24 h the amount of H_2O_2 remaining in the solid mixture was determined by iodometry.

Results and Discussion

Characteristics of HAp disperse phases

Table 1. Characteristics of HAp-1-8

No.	Volume ^a cm^3/g	Crystallinity $\beta_{1/2}^{-1}$ (002) ^b	Specific surface area, m^2/g	Particle size, μm	Secondary particle form	Manufacturer
HAp-1	0.469	6.6	6	< 5	—	TAIHEI
HAp-2	0.372	4.1	42	< 5	—	TAIHEI
HAp-3	0.392	3.7	74	10-70	—	TAIHEI
HAp-4	0.392	4.5	55	20-150	—	TAIHEI
HAp-5	0.339	4.1	39	70-75	spherical	PENTAX
HAp-6	0.343	4.0	41	15-20	spherical	PENTAX
HAp-7	0.365	3.6	45	10-30	spherical	TAIHEI
HAp-8	0.375	3.5	74	10-60	spherical	SEKISUI

^acalculated by density. ^bin text

A variety of forms of HAp are prepared by various methods and calcinations conditions, and are available for artificial bones, adsorbents or column packings. Eight species of HAp used in this study were classified into 2 groups of unformed particles of HAp-1-4 and spherically formed particles of HAp-5-8, which showed a variety of crystallinity, specific surface area and particle size as summarized in Table 1. Powder X-ray diffraction patterns of HAp-1-8 showed crystal structures of apatite in a wide range from partially amorphous to high crystallinity (Fig. 1). The crystallinities of HAp were evaluated from the reciprocal number ($\beta_{1/2}^{-1}$) of the half-value width of (002) diffraction in powder X-ray diffraction patterns [2]. Specific surface areas determined by the N_2 -BET method roughly corresponded to the crystallinities but varied more greatly. Particle sizes of HAp were in a wide range from < 5 μm to 150 μm . Spherical particle sizes of HAp-5 and 6 are controlled in a 10% width for column chromatography.

Solid-phase epoxidation on HAp disperse phases

We have previously reported that the solid phase system consisting of cetylpyridinium dodecatungstate (CetylPy₁₀[H₂W₁₂O₄₂]) catalyst/solid oxidant (urea-

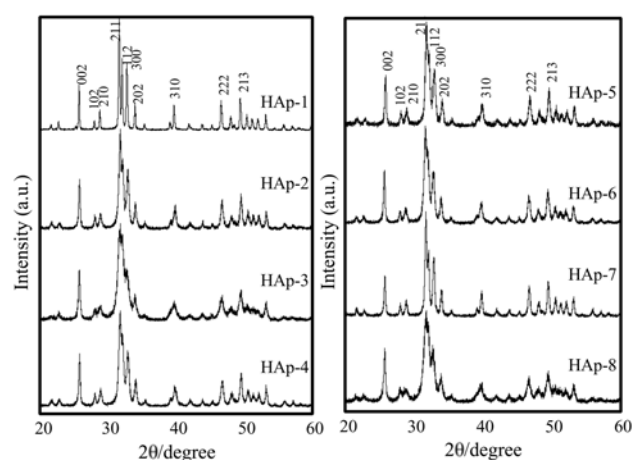


Fig. 1. Powder XRD patterns of HAp-1-8.

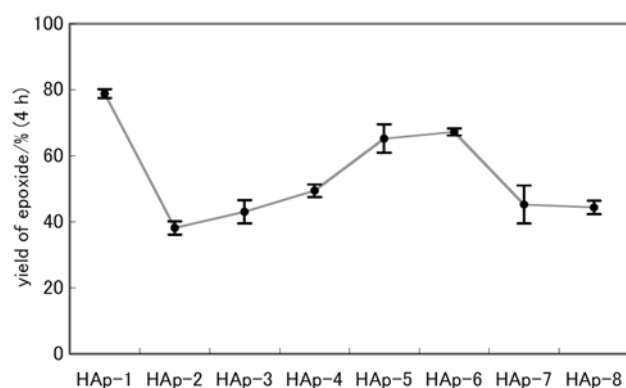


Fig. 2. Solid-phase epoxidations with HAp-1-8.

H₂O₂/Fap disperse phase is an efficient and reusable system for solvent-free epoxidation [9]. The solvent-free epoxidation of cyclooctene with CetylPy₁₀[H₂W₁₂O₄₂] and urea-H₂O₂ was selected as a reference reaction. The epoxidation of cyclooctene with urea-H₂O₂ does not occur in the absence of the catalyst, and the solid disperse phase does not catalyze the reaction but is needed to accelerate the reaction. HAp-1-8 were used as a solid disperse phase for the reaction. A reaction mixture of HAp powder, urea-H₂O₂ powder, a 1 mol% of the catalyst powder and liquid cyclooctene kept the powder solid-state through the epoxidation. In all cases, the solid-phase-epoxidations proceeded at 25 °C without stirring, but gave various yields of the epoxide after 4 h. As the yields of the epoxide are shown as the average of 4 runs with the average deviation in Fig. 2, the solid-phase reactions had high reproducibility. Thus, it was clear that the forms of HAp affected the catalytic epoxidation. HAp-1 was the most effective disperse phase among them, and HAp-5 and HAp-6 were next effective. Next, the factors in the form of HAp for accelerating the reaction were analyzed in each group of unformed and spherically formed HAp.

Influences of forms of HAp disperse phases on epoxidation

Figure 3 shows the influence of particle sizes of unformed HAp-1-4 on the epoxidation. With the use of fine powders (< 5 μm) of HAp-1, the epoxidation proceeded smoothly to form an 80% yield of the epoxide at 25 °C after 4 h. HAp-2, which is a fine powder similar to HAp-1, was less effective and the epoxide yield was 39% yield under the same conditions. In the cases of HAp-3 and HAp-4 with larger and wider particle sizes, the yields of the epoxide were also lower than that in the case of HAp-1 (40 and 51% yields). The change of about 1 to 150 μm in particle sizes of HAp was not related to the yields of the epoxide, and thus the particle size was not an important factor.

The crystallinities and surface areas of HAp-1-4 are shown with dot plots of the yields of the epoxide in Fig. 4. HAp-1 shows a strikingly high crystallinity,

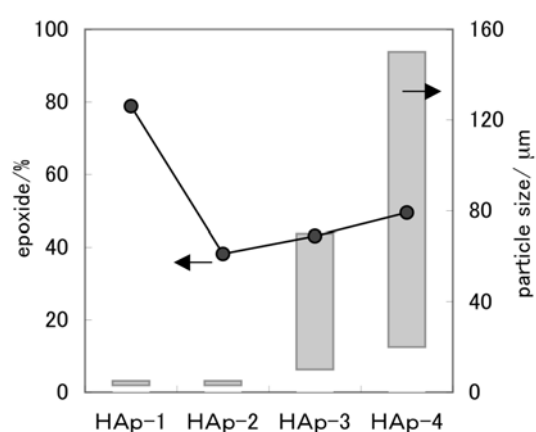


Fig. 3. Influence of particle sizes of HAp-1-4.

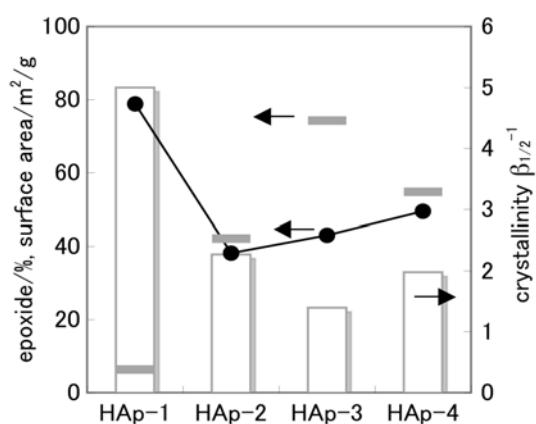


Fig. 4. Influences of crystallinities and surface areas of HAp-1-4.

whereas the others have similarly low crystallinities (a bar chart). On the other hand, specific surface areas of HAp-1-4 greatly changed (a bar plot –). The change in the crystallinities was more closely correlated to the yields of the epoxide rather than that in the surface areas. The use of HAp-1 with a high crystallinity resulted in a high yield of the epoxide. In addition to the crystallinity, HAp-1 has a lower surface area and somewhat higher bulkiness, which is different from the other HAp. As such a characteristic of HAp-1 is similar to that of Fap, HAp-1 acts as an effective disperse phase for the epoxidation next to Fap.

Spherically formed HAp-5-8 have similar crystallinities and surface areas except for the surface area of HAp-8, and they were evaluated as a disperse phase for the epoxidation (Fig. 5). In the uses of spherical HAp-7 and HAp-8, the yields of the epoxide were similar to those in the uses of the unformed HAp-2-4 with similar crystallinities (41 and 44% yields at 25 °C after 4 h). By contrast, in the uses of HAp-5 having approximately 70 μm particle size as well as HAp-6 having approximately 15 μm particle size, higher yields of the epoxide (65 and 67% yields) were obtained. In the cases of HAp-5 and HAp-6, the particle sizes are nearly uniform, whereas HAp-7 contains two main particle

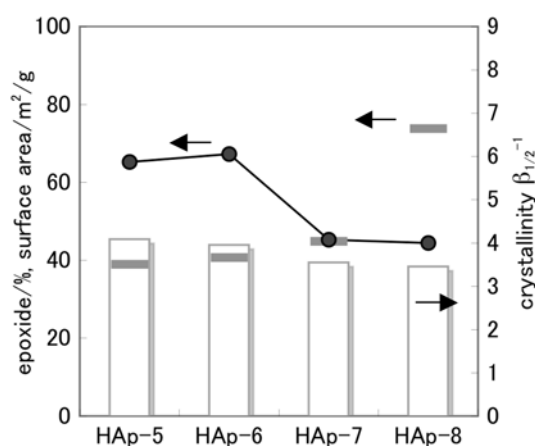


Fig. 5. Influences of crystallinities and surface areas of HAp-5-8.

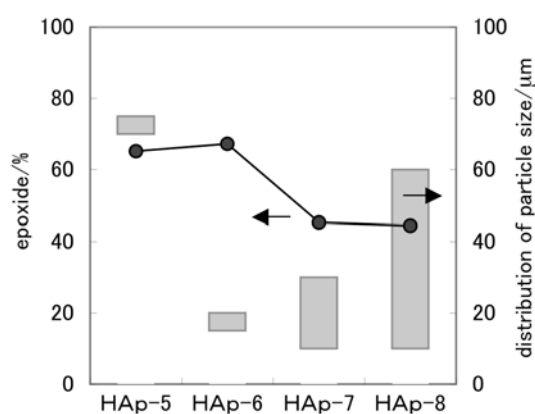


Fig. 6. Influence of distributions of particle sizes of HAp-5-8.

sizes (10 and 30 μm) and HAp-8 has different particle sizes over a wide range of 10 to 60 μm (Fig. 6). Thus, a uniform of particle size is more important than the particle size itself for an apatite disperse phase to assist the epoxidation.

High crystallinity and low surface area in HAp-1, and uniform particle sizes in spherical HAp-5 and 6 were found to be important factors as an effective solid phase for assisting the epoxidation.

Surface chemical properties of HAp disperse phase

It is first desired that a disperse phase does not work negatively for reactants such as hydrogen peroxide and the active catalyst in the reaction. Urea- H_2O_2 is a stable and easy to handle solid oxidant at room temperature. But HAp with weakly basic OH groups might induce the decomposition of urea- H_2O_2 . In the presence of HAp-2-8 except for HAp-1, the decomposition of urea- H_2O_2 was observed to occur slightly after 4 h but to some extent after a longer reaction time (24 h) under similar conditions to the oxidation. On the other hand, HAp-1, which has a form nearer to FAp, scarcely promoted the decomposition. Thus, HAp-1 was found to be an effective disperse phase for the stability of hydrogen peroxide, next to FAp.

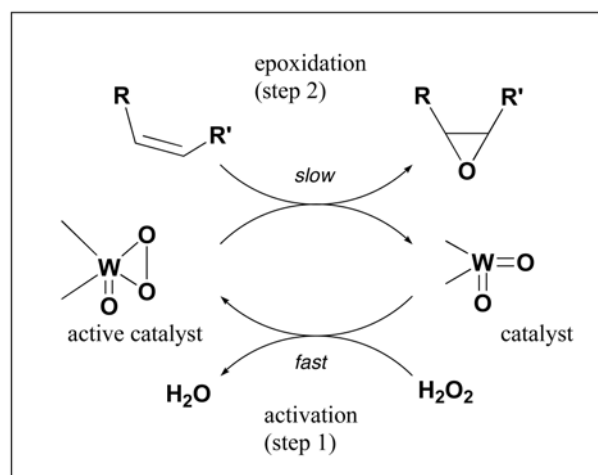


Fig. 7. Schematic catalytic cycle by tungstate catalyst.

Assistance of HAp disperse phase in catalytic epoxidation cycle

As previously reported from kinetic studies on the solid-phase-epoxidation system, the FAp-assisted reaction proceeds at a pseudo first order rate both with respect to substrate concentration and with respect to amount of the catalyst, respectively [6]. Similarly, in all cases of HAp, the catalytic reaction proceeded at about a pseudo first order at least in terms of a half-life period. Taking account of the kinetic behavior, the solid-phase epoxidation on HAp similarly to FAp proceeds through a similar catalytic cycle mechanism to that in general liquid-phase catalytic reactions (Fig. 7); The insertion of oxygen to the substrate with the active catalyst (step 2 in Fig. 7) is a rate-determining step in the cycle. Thus, the reactivity difference by HAp (Fig. 2) is considered to be the difference in assistance of HAp for the reaction step. In the solid-phase reaction key points for promoting the reaction step are the diffusion of liquid organic reactant and its proximity to the active solid catalyst on the apatite surface. The effective forms of apatites: high crystallinity and low surface area and a uniform of particle size might provide a smooth surface and loose packing for the epoxidation to have advantages in these points.

The effective forms of apatites in our system are quite different from those of common solid supports for fixing the catalyst in liquid-solid heterogeneous reactions; In the latter case, amorphous solids with high surface areas and macropores are generally used. Such a difference in effective forms of solids between the two reaction systems comes from the difference in function for assisting the reaction. In the case of the liquid-solid heterogeneous reactions adsorption of organic reactant from the solution on a surface is necessary for proximity of reactants in the same reaction step. In our system, in contrast, a weaker interaction of the organic reactant on the solid surface is preferred to such adsorption in order to gently move the reactant on the

surface to the proximity to the other reactant.

Although a continued study on the roles of apatite-disperse-phase in the epoxidation, especially, the interaction with the organic substrate and its diffusion on the surface is needed, a liquid substrate-permeated solid-phase reaction system using apatites with high crystallinities and low surface areas can be expected to be a new simple eco-process system.

Conclusions

In the solid-phase-epoxidation system using CetylPy₁₀-[H₂W₁₂O₄₂]/urea-H₂O₂, it was required that apatites had a high crystallinity and a low surface area or were a uniform of particle size in spherical forms. From the results it is considered that in the solid-phase system the smooth surface of apatite crystals and loose packing with a uniform size of apatite particles facilitate the diffusion of the liquid organic reactant and the proximity of the reactant and the catalyst to assist the epoxidation.

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References

1. J.C. Elliott, *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*, Studies in Inorganic Chemistry 18, Elsevier, Amsterdam, 1994.
2. M. Okazaki, *Chemistry of Apatites*, Tokai University, Tokyo, 1992 (in Japanese).
3. *Handbook of Green Chemistry & Technology*, ed. By J. Clark, Blackwell, Oxford, 2002; J.H. Clark, *Catalysis of Organic Reactions Using Supported Inorganic Reagents*, VCH, New York (1994); T. Ando, J. Ichihara, T. Hanafusa, *Kagaku Sosetsu* 47 (1985) 166-175 (in Japanese); A. McKillop, D.W. Young, *Synthesis* (1979) 401, 481.
4. The use of apatites as catalyst supports; K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.* 122 (2000) 7144-7145.
5. The use of apatites as catalyst supports; A. Crosmana, G. Gelbard, G. Poncelet, V.I. Parvulescu, *Appl. Catal. A*: 264 (2004) 23-32.
6. J. Ichihara, and Y. Sasaki, *Catal. Today* 117 (2006) 120-125.
7. K. Iteya, Y. Sasaki, S. Itoh, and J. Ichihara, *Phosphorus Res. Bull.* 19 (2005) 142-146.
8. Y. Sasaki, J. Ichihara, K. Sakamoto and S. Yamaguchi, *Phosphorus Research Bull.* 17 (2004) 215-218.
9. J. Ichihara, A. Kambara, K. Iteya, E. Sugimoto, T. Shinkawa, A. Takaoka, S. Yamaguchi, and Y. Sasaki, *Green Chem.* 5 (2003) 491-493.
10. J. Ichihara, K. Iteya, A. Kambara, and Y. Sasaki, *Catal. Today* 87 (2003) 163-169.
11. J. Ichihara, S. Yamaguchi, T. Nomoto, H. Nakayama, K. Iteya, N. Naitoh, and Y. Sasaki, *Tetrahedron Lett.* 43 (2002) 8231-8234.
12. J. Ichihara, *Tetrahedron Lett.* 42 (2001) 695-697.
13. C. Lu, E.W. Hughes and P. Giguere, *J. Am. Chem. Soc.* 63 (1941) 1507-1513.