EFFECTIVE FORMS OF HYDROXYAPATITE DISPERSE PHASE IN SOLVENT-FREE EPOXIDATION SYSTEM

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Abstract In CetylPy10[H₄W₁₂O₄²]-catalyzed epoxidation solid-phase-system, high crystallinity of apatite and a uniform size of apatite particle were found to be important factors as a solid disperse phase.

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.¹² 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. From the view of recent ecology, the apatites as harmless materials have been increasingly attracted in a variety of fields and the applications have been rapidly extended to phosphors, adsorbents, deodorants, or photocatalysts.

In green organic syntheses, improvement over the conventional organic reaction process has been of great significance.³ In the field 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 We first introduced the apatite powder as a harmless solid-disperse-phase to the organic reaction process instead of organic solvents. Recently we have developed an efficient reusable solid-phase-epoxidation system using urea-hydrogen peroxide (urea-H₂O₂)/ tungstate catalyst/ fluorapatite (FAp).⁵⁻⁹ In the solid-phase-system the solid-forms of apatite powders might directly influence epoxidations on the solid surface. In this paper, we studied the effect of various forms of hydroxyapatites (HAps) on the tungstate-catalyzed epoxidation of cyclooctene in order to find a suitable disperse phase.

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EXPERIMENTAL

Several hydroxyapatites (Ca_{10}(PO_4)_6(OH)_2, HAp) were obtained from Sekisui Kasei Co. Ltd., PENTAX Corporation and Taihei Chemical Industrial Co. Ltd. Powdery forms of HAp's were observed by an optical microscope and SEM, and their crystallinities were analyzed by powder X-ray diffractometry. Cetylpyridinium dodecatungstate (CetylPy_{10}[H_2W_{12}O_{42}]) were prepared from the commercially available ammonium dodecatungstate ((NH_4)_{10}[H_2W_{12}O_{42}]) and cetylpyridinium chloride in water, as reported previously. The catalyst was identified with FT-IR. The substitution of the catalyst by cetylpyridinium cation was calculated by CHN elementary analyses.

Apatite-assisted epoxidation

Solvent-free H_2O_2-epoxidation of cyclooctene using the solid catalyst/apatite disperse phase was carried out under the powdery solid-state as follows. Apatite powder (0.5 g) was simply mixed with a 1 mol% of the solid catalyst, solid urea-H_2O_2 (2.5 mmol) and the liquid substrate (1.0 mmol) in a test tube with a teflon-coated screw cap. After shortly mixing, the resulting solid mixture was left without stirring at 25 °C. The epoxidation was periodically followed by capillary gas chromatography with an internal standard method.

RESULTS AND DISCUSSION

Cetylpyridinium dodecatungstate (CetylPy_{10}[H_2W_{12}O_{42}]) was the most effective catalyst in solvent-free epoxidation using urea-H_2O_2/FAp solid-phase system. In the CetylPy_{10}[H_2W_{12}O_{42}]-catalyzed epoxidation of cyclooctene, various HAp's were used instead of FAp and the effectiveness as a solid disperse phase was studied. In all cases, solid-phase epoxidations occurred at 25 °C without solvent; A reaction mixture of HAp powder, urea-H_2O_2 powder, a 1 mol% of the catalyst powder and liquid cyclooctene kept the powdery solid state through the epoxidation.

Fig.1 shows the results of the epoxidation using various particle sizes of HAp's. In the use of fine powders (> 5 μm) of HAp-1, the epoxidation smoothly proceeded to form an 80 % yield of the epoxide at 25 °C after 4 h. HAp-2, which is fine powders similarly 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 having larger and wider particle sizes, the epoxide yields were also lower than that in the case of HAp-1 (40 and 51 % yields). Apparently, the epoxide yield was not affected by the particle sizes of HAp's, and HAp-1 was the most effective disperse phase among them.
The crystallinities of HAp's used were evaluated with reciprocal number ($\beta_{1/2}^{-1}$) of the half-value width of (300) diffraction in powdery X-ray diffraction patterns. The crystallinities of HAp's 1-4 are shown as a bar chart with plots of the epoxide yields in Fig. 2. HAp-1 only shows strikingly high crystallinity, whereas the others have nearly the same lower crystallinities. The only use of HAp-1 having high crystallinity resulted in high yield of the epoxide. Therefore, the crystallinities of HAp's may affect the yields of the epoxide in the solid-phase system. In addition to the crystallinity, HAp-1 has lower surface area and higher bulkiness, differently from the other HAp's. As such characteristic of HAp-1 is similar to that of FAp, HAp-1 acts as an effective disperse phase for the epoxidation next to FAp.

Four spherical HAp's prepared as secondary particles with various sizes, which have similar crystallinities, were compared as a disperse phase in the epoxidation (Fig. 3). HAp-5 having ca. 70 μm of particle size as well as HAp-6 having ca. 15 μm of particle size promoted the reaction to form the epoxide in 67% yields at 25 °C after 4 h. The other spherical forms of HAp-7 and HAp-8 having a wider range of particle sizes were...
less effective (41 and 44 % yields). In the cases of HAp-5 and HAp-6, the particle sizes are nearly uniform, whereas HAp-7 contains two main particle sizes (10 and 30 µm) and HAp-8 has different particle sizes in the wide range of 10 to 60 µm (Fig 4). Thus, as apatite disperse phase for promoting the epoxidation, a uniform of particle size is more important than particle size itself.

In the solid-phase-epoxidation system using CetylPy$_{10}$[H$_2$W$_{12}$O$_{42}$]/urea-H$_2$O$_2$, it was effective as a solid disperse phase that apatites had high crystallinity and were a uniform of particle size. From the results it is considered that in the solid-phase system smooth surface of apatite crystals and loose packing with a uniform size of apatite particles facilitate diffusion of the reactants, dispersion of the catalyst, and proximity of the reactants with the catalyst to promote the epoxidation.

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