

The catalytic activities of nanoclusters dispersed on apatite

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Cetylpyridinium phosphomolybdates ($Q_3[PMo_{12}O_{40}]$, Q =CetylPy) dispersed on apatite catalyzed H_2O_2 -oxidations of organic compounds under solid-phase conditions without organic solvent. FT-IR and ^{31}P solid-state NMR spectroscopic studies showed the formation of peroxo species in our solid-phase system, which was different from the peroxo type of $CetylPy_3\{PO_4[Mo(O)(O_2)_2]_4\}$ (PMo4) known as an active species in the conventional liquid-biphase system. The catalytic activities of them were compared in the solid-phase system.

Key words: nanocluster catalyst, apatite, organic oxidation, urea- H_2O_2 , solid disperse phase.

Introduction

We have developed solid-phase-assisted organic reaction systems without organic solvent as an environmentally benign catalyzed reaction system. Apatites, which form the mineral component of bones and teeth, are handled as a harmless solid to environment, and have their ion exchange ability and affinity for organic compounds. Recently, we found that tungstic acid catalyst dispersed on apatite solid phase (H_2WO_4 /apatite) is effective as the environmentally benign solid catalyst for the epoxidation of alkenes and allylic alcohols with solid urea-hydrogen peroxide complex (urea- H_2O_2) [1]. And nano-sized Keggin structure of heteropolyacids were found to be also effective catalysts in our apatite solid phase system [2]. We further investigated the catalytic activities of Keggin-type of phosphomolybdates ($Q_3[PMo_{12}O_{40}]$) dispersed on apatite phase.

Experimental

Fluorapatite powder $Ca_{10}(PO_4)_6F_2$ (particle size, 5-20 μm ; specific surface area, 8-12 m^2/g) were purchased from Taihei Chemical Industrial Co. Ltd and used. Cetylpyridinium phosphomolybdate ($Q_3[PMo_{12}O_{40}]$, Q : CetylPy) was prepared from $Na_3[PMo_{12}O_{40}]$ and cetylpyridinium chloride in water. The peroxo species $CetylPy_3\{PO_4[Mo(O)(O_2)_2]_4\}$ (PMo4) and $CetylPy_2-[Mo_2O_3(O_2)_4]$ (Mo_2O_{11}) were prepared by previously reported procedures [3]. These catalysts were confirmed with FT-IR and ^{31}P NMR. The substitution of the catalysts by the organic cation was confirmed by CHN

elementary analysis.

The catalytic activities of phosphomolybdates were examined for H_2O_2 -epoxidations of cyclooctene on apatite solid phase. Typical heterogeneous catalytic reaction was carried out as follows. A solid mixture of apatite powder (0.5 g), urea- H_2O_2 powder (2.5 mmol) and a 1 mol% of catalyst powder was mixed sufficiently in a test tube with a teflon-coated screw-cap, and then permeated by a liquid cyclooctene (1.0 mmol). After mixing the solid reaction mixture was left without stirring at room temperature. The yields of the product were periodically measured by capillary gas chromatography using Shimadzu GC14B with an internal standard method.

The activation process of phosphomolybdates with urea- H_2O_2 on solid phase was observed by the following spectrometers; FT-IR spectra were recorded as KBr disks on a JEOL WINSPEC 1000 FT-IR spectroscopy; Solid state ^{31}P NMR spectra were recorded on a JEOL GX-270W NMR.

Results and Discussion

In the epoxidation of cyclooctene using apatite disperse phase and solid urea- H_2O_2 oxidant without organic solvent, the catalytic activities of phosphomolybdates ($Q_3[PMo_{12}O_{40}]$) were higher than those of phosphotungstates ($Q_3[PW_{12}O_{40}]$) [2]. In contrast, it is known that $Q_3[PW_{12}O_{40}]$ is superior to $Q_3[PMo_{12}O_{40}]$ in the liquid-liquid biphasic reaction with aqueous H_2O_2 and halogeno-organic solvent. In the combination of $Q_3[PMo_{12}O_{40}]$ and urea- H_2O_2 on apatite disperse phase, the epoxidation of cyclooctene proceeded to give epoxycyclooctane in good yields after about 2 days at 25°C. In the combination of $Q_3[PMo_{12}O_{40}]$ and urea- H_2O_2 without apatite, the epoxidation proceeded sluggishly under similar

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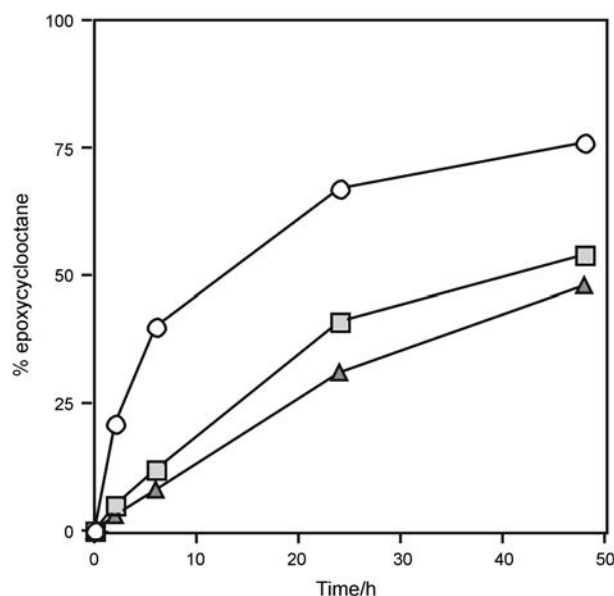


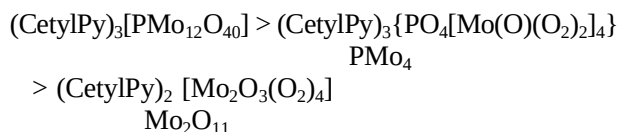
Fig. 1. Catalytic activities in the epoxidation of cyclooctene with urea-H₂O₂ on apatite.

—○— (CetylPy)₃[PMo₁₂O₄₀], —■— (CetylPy)₃{PO₄[Mo(O)(O₂)₂]₄}, —▲— (CetylPy)₂[Mo₂O₃(O₂)₄]

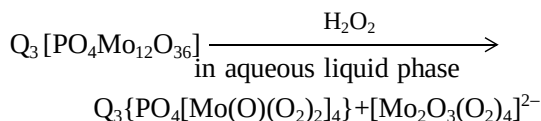
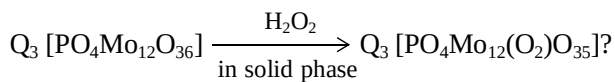
reaction conditions. The combination of apatite and urea-H₂O₂ without the catalyst did not promote the epoxidation; apatite had no catalytic activity in the epoxidation. Thus, the combination of three components, Q₃[PMo₁₂O₄₀], urea-H₂O₂, and apatite, is important for promoting the organic reactions.

In the conventional liquid-liquid biphasic reaction with aqueous H₂O₂, the peroxo species, {PO₄[Mo(O)(O₂)₂]₄}³⁻ and [Mo₂O₃(O₂)₄]²⁻, have been recognized as active species of phosphomolybdates and isopolyoxomolybdates, respectively [3-7]. In apatite solid phase system, catalytic activities of cetylpyridinium phosphomolybdate (CetylPy)₃[PMo₁₂O₄₀] and the previously prepared peroxo species, (CetylPy)₃{PO₄[Mo(O)(O₂)₂]₄} and (CetylPy)₂[Mo₂O₃(O₂)₄], were studied. Figure 1 shows the results in the epoxidation of cyclooctene. (CetylPy)₃[PMo₁₂O₄₀] was the most effective among

them under the apatite phase system without solvent. The order of the catalytic activities was described as below.



In order to understand the high catalytic activity of (CetylPy)₃[PMo₁₂O₄₀] in our solid system, we studied on the active species by use of FT-IR and ³¹P solid-state NMR. The solid-phase-activation process of (CetylPy)₃[PMo₁₂O₄₀] with urea-H₂O₂ on apatite was able to be directly followed using both the spectrometers. From the analyses it was found that (CetylPy)₃[PMo₁₂O₄₀] reacted with H₂O₂ to give a peroxo species. The observed peroxo species was different from the degradation species (CetylPy)₃{PO₄[Mo(O)(O₂)₂]₄} which serves as the active species in the liquid-liquid biphasic system [3-7], as described below.



The conceptual idea of our reaction system is shown in Fig. 2. In this system activation with urea-H₂O₂ and successive dispersion on the solid phase is essential for effective catalytic oxidation. The reaction rate in the solid phase system, generally, is controlled by diffusion of reactants and decreased. Nevertheless, our solid phase system has high catalytic activities comparable to the conventional liquid-phase system [3, 8]. Spectroscopic studies suggest the formation of nano-sized structure of peroxo species in our solid system, which was different from the degradation species of PMo4 in the liquid-phase system. Based on our conceptual idea, we concluded that in our system as the activation

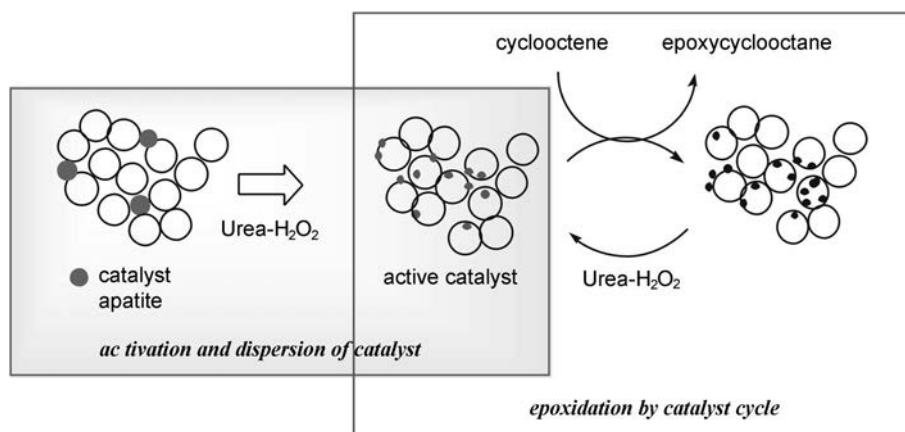


Fig. 2. The conceptual scheme of our epoxidation system on apatite solid phase.

reaction of the phosphomolybdate with hydrogen peroxide proceeded, the nano-sized structures of peroxo species were formed and dispersed on apatite to give high activities for the oxidations.

Our solid phase system is convenient and a green process. As the active species have enough catalytic activities and are expected to have unique structures, our system may provide an effective and selective oxidation process.

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