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New approach to environmentally benign epoxidation: the solid-phase-system using urea–H_2O_2 and recyclable dodecatungstate on apatite

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Abstract

On the basis of new concept using a solid disperse phase we have developed an efficient catalytic solid-phase-system for epoxidations of alkenes using urea–hydrogen peroxide (urea–H_2O_2) complex and cetylpyridinium dodecatungstate ($(CetylPy)_{10}[H_2W_{12}O_{42}]$) catalyst on fluorapatite (FAp). The recovered solid catalyst phase was reused to keep the catalytic activity after several times. In the conceptual idea it is a key point that in situ solid-phase-activation of the catalyst with urea–H_2O_2 proceeds to form microcrystals of the active species dispersed on the solid phase. The dispersion of the catalyst on FAp in the case of tungstic acid (H_2WO_4) was suggested by EPMA analysis. We proposed the peroxo type of species keeping the parent polyoxometalate framework as novel active species from FT-IR spectroscopic studies. FAp phase plays important roles of dispersing the active species on its surface to have high catalytic activity and of stabilizing the active species to lead to high reusability.

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1. Introduction

The search for environmentally benign alternatives to the conventional reaction process using organic solvents has been of great significance in green, sustainable chemistry [1]. Recently, a number of novel solid catalysts and solid-supported catalysts have been developed for basic and important oxidation reactions of organic compounds [2]. Use of oxygen gas or aqueous hydrogen peroxide solution has been desired as the oxygen donor, which has economic and environmental advantages. In most cases, the reactions have been carried out in heterogeneous system with liquid phase, and solvent-free reactions using solid phase have been rarely reported.

We have developed a new type of solid-phase-assisted epoxidation reaction using a solid urea–hydrogen peroxide (urea–H_2O_2) complex and a solid polyoxometalate catalyst [3–5]. In our system, apatite phase is used as a harmless solid disperse phase instead of organic solvents. Practically, apatite was simply mixed with a catalyst, urea–H_2O_2 and a substrate. The resulting solid mixture appeared dry powdery state, and the epoxidation proceeded in the solid state. So far development of a lot of solid catalysts and solid-supported catalysts have been focused in the following points; how to efficiently impregnate the catalyst on the solid support and how to

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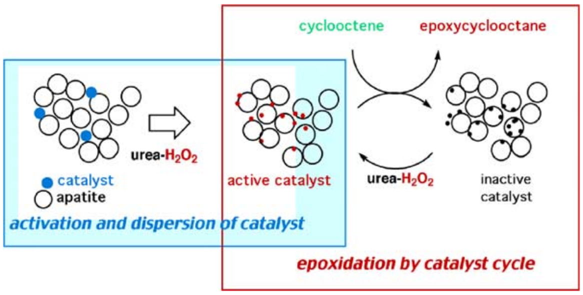

Fig. 1. Conceptual idea using apatite as a solid disperse phase.

chemically incorporate the catalyst into the surface of solid support [6,7]. Compared with these common solid-supported catalysts, in our system apatite surface can interact not rigidly but loosely with the catalyst by simply mixing. The conceptual idea of our reaction system is shown in Fig. 1. The loose interaction arising from the simple mixing facilitates the contact between the catalyst crystals and the urea–H_2O_2 crystals to assist the solid-phase-activation of the catalyst. As the activation proceeds, the catalyst crystals are more easily destroyed to microcrystals and the resulting peroxo-species must be finely dispersed on apatite. In this system it is a key point that in situ solid-phase-activation of the catalyst with urea–H_2O_2 proceeds to form and disperse microcrystals of the active species on the solid phase.

We studied the reaction profile in detail on the line of the proposed idea, and found a more efficient and recyclable solid catalyst.

2. Experimental

2.1. Catalysts and solid disperse phase

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 (CetylPy) polyoxometalates were prepared from the inorganic salts of polyoxometalates and cetylpyridinium chloride in water. These catalysts were confirmed with FT-IR and ^{31}P NMR. The substitution of the catalysts by the organic cation was estimated by CHN elementary analyses.

2.2. Studies on the catalytic activities of polyoxometalates/FAp

The catalytic activities of polyoxometalates 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 being shortly mixed by use of a vibrator, the reaction mixture was left without stirring at 25 °C. The yields of the product were periodically measured by capillary gas chromatography using Shimadzu GC14B with an internal standard method.

2.3. Spectroscopic studies on the activation process of the catalyst

The activation process of polyoxometalates with urea–H_2O_2 on solid phase was observed by the following analytical method: FT-IR spectra were recorded as KBr disks on a JEOL WINSPEC 1000 FT-IR spectrometer; EPMA for element distribution of the catalyst/FAp was carried out using Shimadzu EMX-2A electron prove microanalyzer. For IR analyses the reaction conditions were changed as follows: catalyst/FAp or CaF_2/urea–H_2O_2 = 0.10 mmol/0.2 g/1.0 mmol at 25 °C. CaF_2 was not so effective for the catalytic activity as FAp, but spectra behavior in the catalyst-activation using CaF_2 showed similar to that using FAp. Fig. 8 shows the spectra using CaF_2, which were clear without absorption of solid disperse phase.

2.4. Recycling epoxidation using $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp solid phase

To the solid mixture of $(CetylPy)_{10}[H_2W_{12}O_{42}]$ (0.074 mmol, 3.2 mol%) and FAp (2.50 g) in a test tube with screw-cap, was added solid urea–H_2O_2 (5.10 mmol), and the solid mixture was permeated by liquid cyclooctene (2.3 mmol). Then, in the closed test tube, the mixture was left without stirring at 25 °C for 6 h. The solid reaction mixture was extracted with pentane and the solvent was evaporated. A colorless solid of epoxycyclooctane was obtained in 85% yield.

The g.c. purity was about 99% without purification. The solid moiety remained after the isolation of the epoxide was washed with a small amount of 5% water–acetone solution to remove the urea-complexes, and dried under vacuum over P_2O_5. To the recovered solid-catalyst-phase was added cyclooctene and urea–H_2O_2, and the reaction was carried out at 25 °C for 6 h in a similar way. After the same experimental procedures (isolation and recovery) the reaction was repeatedly carried out.

3. Results and discussion

3.1. A new type of apatite-assisted H_2O_2-epoxidation

The catalytic epoxidation of cyclooctene with urea–H_2O_2 without an organic solvent was examined under various reaction conditions. A heterogeneous epoxidation of cyclooctene using urea–H_2O_2 and the tungstic acid catalyst (H_2WO_4, 10 mol%) on fluorapatite (FAp) smoothly proceeded at 25 °C to afford epoxycyclooctane in 90% yield after 48 h. When tungstic acid was used alone without FAp, in contrast, the reaction sluggishly proceeded, as shown in Fig. 2. Since no reaction occurred with the use of only FAp, FAp had no catalytic activity for the oxidation with urea–H_2O_2. FAp facilitates the tungstate-catalyzed reaction with urea–H_2O_2 under solid phase conditions.

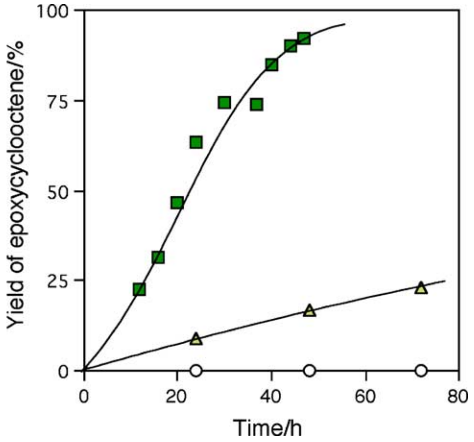

Fig. 2. Tungstate-catalyzed epoxidation of cyclooctene with urea–H_2O_2 at 25 °C.

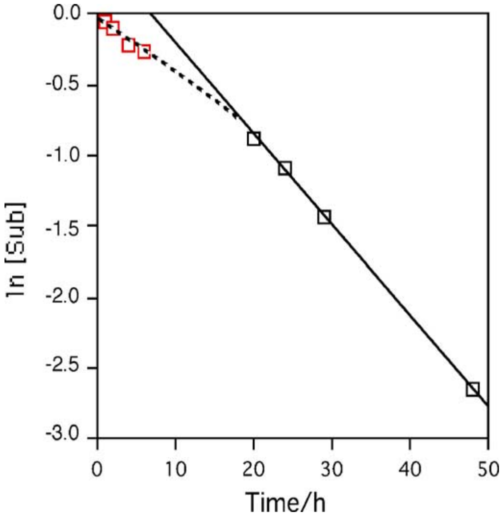

Fig. 3. Kinetic plot in H_2WO_4/FAp-catalyzed epoxidation of cyclooctene with urea–H_2O_2 at 25 °C. $\ln[\mathrm{Sub}] = -0.0639\,t + 0.4259$ ($r = 0.9997$) and $k_{obs} = 6.4 \times 10^{-2}$/h.

Fig. 3 shows the kinetic plot in the epoxidation of cyclooctene using H_2WO_4 on FAp. Although the reaction contained an initial induced time, the logarithms of the substrate concentrations linearly decreased with the reaction time. The linearity shows that the concentration of the active catalyst is constant. Thus, regeneration of the active catalyst from the resulting inactive ones with urea–H_2O_2 should be fast. In the heterogeneous solid phase system, generally, the observed reaction rate is controlled by the diffusion rate of mass transfer. Therefore, the rate should decrease compared with one in liquid homogeneous reaction. On the contrary, the observed reaction rate (k_{obs}) which was calculated from the slope of the line was comparable to homogeneous reactions [8] and showed linear to the substrate concentration as described above. At the points, our reaction seems to have similar behavior to common catalytic liquid-phase reactions. The reactants, the substrate and hydrogen peroxide in urea-complexes, might have mobility in the solid phase system.

3.2. Effect of apatite disperse phase on the catalytic activities

Fig. 4 shows influence of FAp amount on the rate k_{obs} of the tungstate-catalyzed epoxidation. When FAp

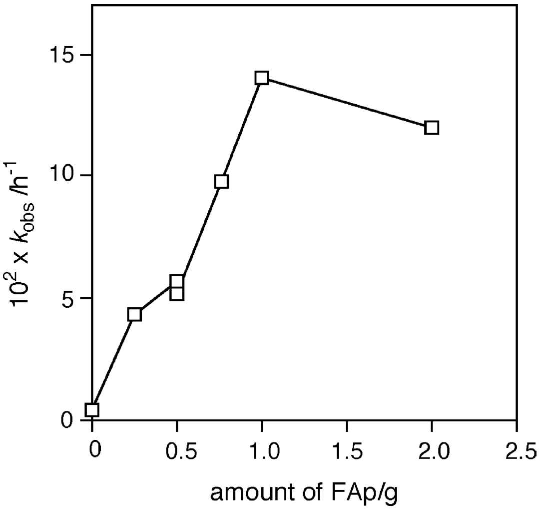

Fig. 4. Influence of FAp amount on the reaction rate in the tungstate-catalyzed epoxidation. Reaction conditions: cyclooctene (1.0 mmol); H_2WO_4 (0.1 mmol); urea–H_2O_2 (2.5 mmol); FAp (x g) at 25 °C.

amount was in a range 0.75–2.00 g per 0.1 mmol of H_2WO_4 or 1 mmol of cyclooctene, the reaction rate increased much higher. The rate showed a maximum at about 1.00 g of FAp. Such phenomenon has not been observed when the amount of organic solvents increases in homogeneous reactions. Our system required considerable amount of FAp to give the highest catalytic activity. Accordingly, it is considered that FAp plays an important role of dispersing the catalyst on its surface.

The efficient dispersion of the tungstic acid on FAp was experimentally suggested by EPMA analyses. Fig. 5 shows calcium and tungsten distribution on the solid mixtures of H_2WO_4/FAp before and after the activation with urea–H_2O_2. Distribution of tungsten element was clearly observed at the different position from that of calcium element in the simply mixed mixture of H_2WO_4 and FAp. After the activation at 25 °C for 7 days the presence of tungsten element was not detected. After the activation the

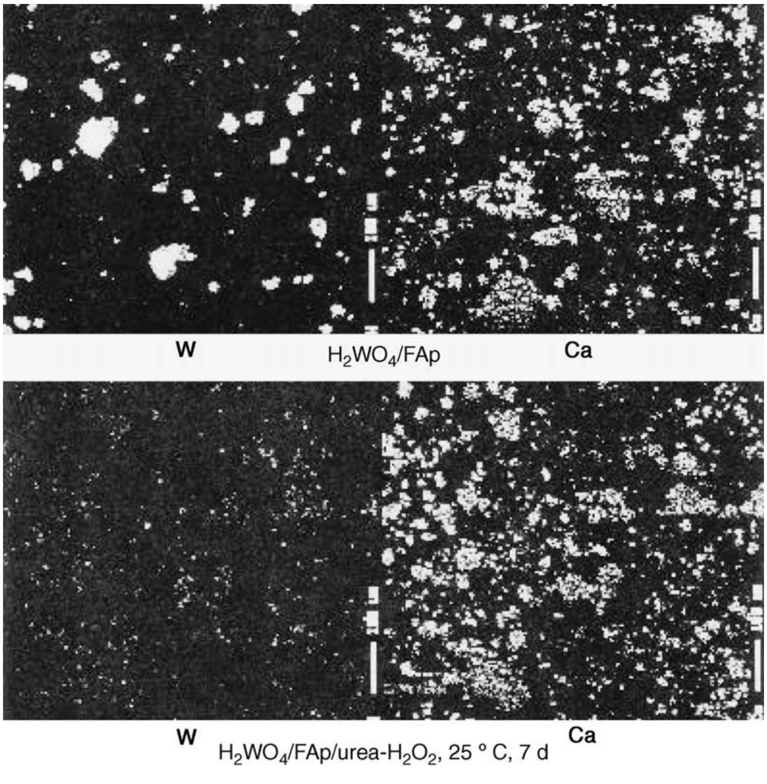

Fig. 5. Tungsten and calcium distribution in the activation of H_2WO_4/FAp by EPMA analyses.

concentration of tungsten was lower than the limit of detection, which suggested that the tungstate crystals were finely crushed by the solid-phase-activation and widely dispersed on apatite phase.

3.3. Development of efficient and recyclable solid polyoxometalate catalysts

In our solid-phase-system, catalytic activities of a variety of clusters of polyoxometalates such as hetero/iso forms of polytungstates and polymolybdates were examined and enhancement of their catalytic activities by FAp was also found [2]. Taking into account the stabilities of the solid catalysts for the reuse, modification of polyoxometalates by cetylpyridinium cation was carried out and the catalytic activities were examined in the solid-phase-system. As shown in Fig. 6, the catalytic activities of cetylpyridinium tungstates and molybdates greatly varied by the cluster structures, compared with those of the ammonium salts. In the liquid–liquid biphase reaction it is well-known that cetylpyridinium phosphotungstate $(CetylPy)_3[PW_{12}O_{40}]$ is the most efficient catalyst [9,10]. In our solid phase system, in contrast, $(CetylPy)_3[PW_{12}O_{40}]$ was not effective. Among them cetylpyridinium dodecatungstate $(CetylPy)_{10}[H_2W_{12}O_{42}]$ showed outstandingly high catalytic activity in the solid-phase-system. The corresponding epoxide was formed in over 90% yield after 6 h at 25 °C. Such high activity of dodecatungstate has rarely been reported to the best of our knowledge [11–14].

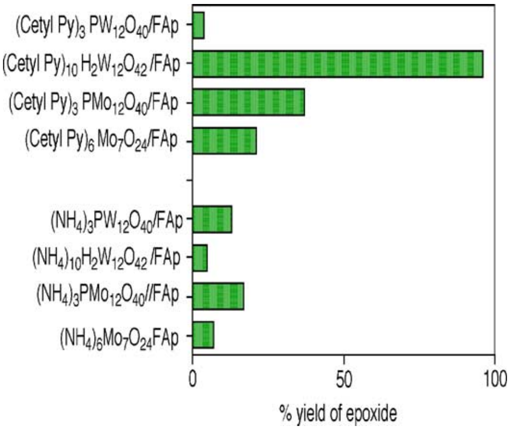

Fig. 6. Catalytic activities of polyoxometalates/FAp in the epoxidation of cyclooctene (at 25 °C after 6 h).

The use of the most effective $(CetylPy)_{10}[H_2W_{12}O_{42}]$ on FAp was applicable to the epoxidations of various alkenes and allylic alcohols under mild reaction conditions [5]. By simple procedures the corresponding epoxides were isolated in good to excellent yields. $(CetylPy)_{10}[H_2W_{12}O_{42}]$ is easily prepared by the ion exchange of commercially available ammonium paratungstate with cetylpyridinium chloride.

For our solid reaction system using $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp and urea–$H_2O_2$, it is important that the solid catalyst phase was repeatedly usable. The repeated epoxidations using the solid-catalyst-phase recovered after the reaction were carried out under the simple procedures as shown in the flowchart (Fig. 7). The product was easily isolated by pentane-extraction. The remained solid-catalyst-phase was recovered by washing for removal of the urea-complexes and drying. $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp was reused for the epoxidation of cyclooctene with urea–H_2O_2 over five times to keep high catalytic activity. Urea–H_2O_2 can be easily prepared from 30% aq. H_2O_2 and the urea-complexes removed by washing [15]. By recycling use of urea, atom efficiency is 87.5% in our cyclooctene-epoxidation.

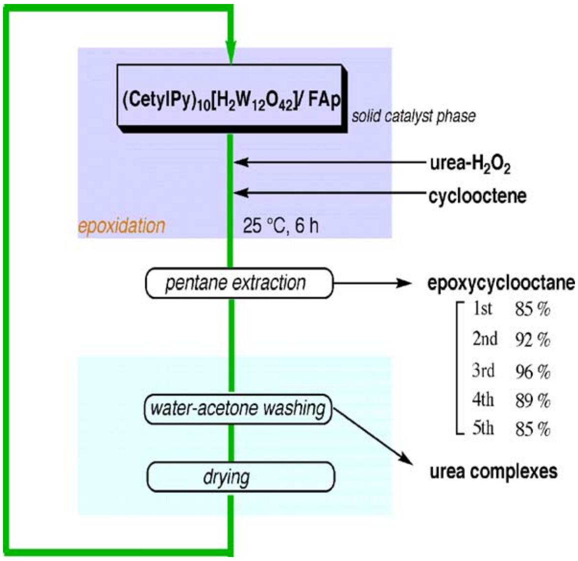

Fig. 7. Recycling system of cyclooctene-epoxidation using $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp.

3.4. The formation of novel active species in the solid phase system

In H_2O_2 aqueous solution the dodecatungstate immediately reacts with a lot of hydrogen peroxide being surrounding it to form the completely degraded peroxo species $Q_2[M_2O_3(O_2)_4](M_2O_{11})$ [12]. On the other hand, in solid phase reaction a tungstate group on the surface of the dodecatungstate crystals reacts with the urea–H_2O_2 crystals; one cluster of the dodecatungstate reacts with at most one molecule of hydrogen peroxide. Therefore, the peroxo-type of species keeping the cluster framework is expected in the solid-phase-reaction. In FT-IR spectra in the activation of $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp with urea–$H_2O_2$, four absorption bands corresponding to the parent cluster structure did not have much variation, although a new absorption band corresponding to a peroxo group appeared at 835 cm^{-1} after 6 h (Fig. 8). In the case of certain polyoxometalate, the active species without degradation was suggested from FT-IR and solid-state NMR spectroscopic studies. Accordingly, we propose the dodecatungstate cluster containing one peroxo group as novel active species in the solid phase system. The peroxo species keeping the cluster framework can be expected to be stable in the catalytic epoxidation cycle, which leads to high recyclability. We considered that high activity and high reusability in our solid phase system using $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp was due to the proposed active species.

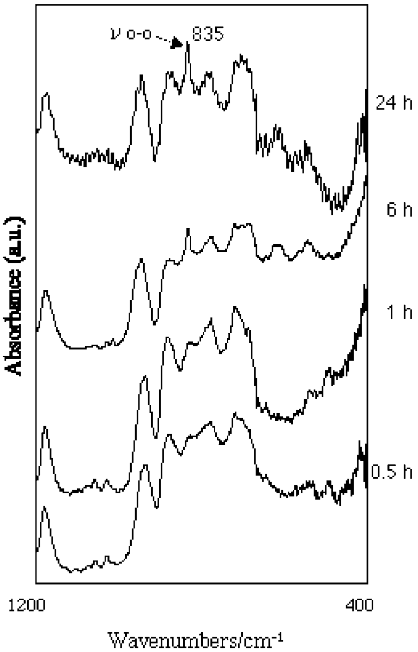

Fig. 8. FT-IR spectra in the solid-phase-activation of $(CetylPy)_{10}$ $[H_2W_{12}O_{42}]$.

4. Conclusions

We have developed an efficient, reusable solid catalyst, $(CetylPy)_{10}[H_2W_{12}O_{42}]$/FAp, for the epoxidations with urea–H_2O_2 without solvent. Our solid phase system is convenient and a green process in the following points: solvent-free, catalytic reaction, using a harmless solid disperse phase and reusable solid catalyst phase, without heating or cooling, without special apparatus.

We concluded that high catalytic activities in our system are due to the activation–dispersion of the catalyst on apatite phase and that reusability of $(CetylPy)_{10}$ $[H_2W_{12}O_{42}]$/FAp is due to the stability of the active species keeping a dodecatungstate framework in epoxidations.

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