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Tetrahedronylammonium phosphomolybdate on fluorapatite: an efficient solid catalyst for solvent-free selective oxidation of sulfides

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Abstract—A new synthetic method of sulfoxides and sulfones using solvent-free oxidations of sulfides with urea–hydrogen peroxide complex (urea–H_2O_2) and tetrabutylammonium phosphomolybdate catalyst on fluorapatite ($(Bu_4N)_3[PMo_{12}O_{40}]$/FAp). In the solid-phase system the oxidations of aromatic and alkyl sulfides proceeded at 4–25 °C and the corresponding sulfoxides or sulfones were selectively obtained in good yields by controlling the amount of urea–H_2O_2.

A solid-phase-assisted reaction system without organic solvent has been increasingly attracted as an environmentally benign organic reaction system.[1,2] Recently, we have developed a new solvent-free catalytic reaction system using apatite as a harmless solid disperse-phase. A tungstic acid dispersed on fluorapatite solid phase (H_2WO_4/FAp) catalyzed epoxidation of alkenes and allylic alcohols with solid urea–H_2O_2 without solvent under ordinary temperature and pressure.[3–5] We have also found the effectiveness of Keggin-type of ammonium phosphomolybdate ($(NH_4)_3[PMo_{12}O_{40}]$) in the solvent-free epoxidations with urea–H_2O_2 by dispersing on fluorapatite solid phase.[4] In the solid-phase system the phosphomolybdate was superior to the phosphotungstate, in contrast to the conventional liquid-biphase-system.[6,7] In the related studies, we now report that the combination of solid urea–H_2O_2 and tetrabutylammonium phosphomolybdate on fluorapatite ($(Bu_4N)_3[PMo_{12}O_{40}]$/FAp) promotes the selective oxidation of sulfides to the sulfoxides and the sulfones.

Several inorganic and organic salts of Keggin-type of phosphomolybdates on fluorapatite ($M_3[PMo_{12}O_{40}]$/FAp) were examined in the solvent-free oxidation of *p*-tolyl methyl sulfide with urea–H_2O_2. The solvent-free reaction was carried out under solid phase conditions as follows. A solid catalyst phase of $M_3[PMo_{12}O_{40}]$/FAp (0.005 mmol/0.25 g, 1.0 mol%) was not previously prepared by impregnating in solution but prepared by simple mixing in the powders.[5,8] The solid catalyst phase was permeated by the liquid sulfide (0.5 mmol). After the resulting solid mixture was cooled at 4 °C for 30 min, solid urea–H_2O_2 (1.25 mmol) cooled at 4 °C was added and sufficiently mixed. Then, the solid mixture was left without stirring at 4 °C. The reaction proceeded in powdery state, which was followed by gas chromatography using the internal standard.

In the oxidation of *p*-tolyl methyl sulfide, the phosphomolybdates modified by organic cations such as tetrabutylammonium or cetylpyridinium cation were much more effective than the salts of inorganic cations such as ammonium or sodium. For example, in the use of $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp the conversion of the sulfide to the sulfone was over 99% at 4 °C after 6 h. Under the mild conditions, the sulfide was not oxidized with urea–H_2O_2 without additives, and FAp itself did not catalyze the reaction.

Keywords: Oxidation; Sulfides; Phosphomolybdate; Fluorapatite; Urea–H_2O_2; Solvent-free reaction; Solid NMR; Sulfoxides; Sulfones.

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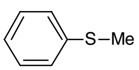
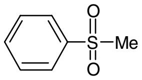
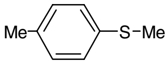
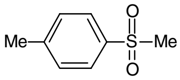
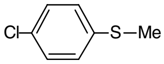
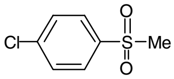
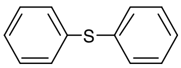
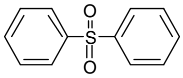
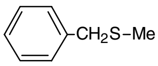
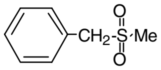
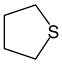
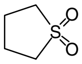
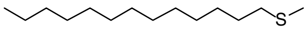
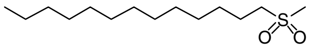
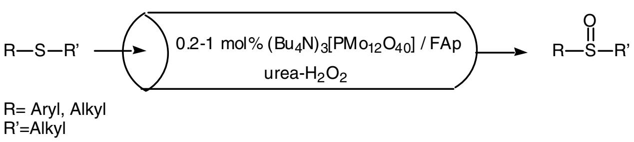
Table 1. The oxidation of sulfides to sulfones using $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp and urea–$H_2O_2$

Substrate	Reaction conditions[a] Temp/°C, time/h	Product	Yield/% (selectivity/%)[c]
	25, 24		93 (93)
	25, 24		99 (100)
	25, 48		93 (95)
	25, 72		62 (64)
	4, 48[b]		87 (97)
	4, 48[b]		89 (100)
	4, 31[b]		81 (99)

[a] $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp/urea–$H_2O_2$/substrate = 0.025 mmol/2.5 g/6.25 mmol/2.5 mmol.
[b] 0.005 mmol of $(Bu_4N)_3[PMo_{12}O_{40}]$ was used.
[c] The selectivity was determined by GC or ^1H NMR. The other component was the sulfoxide. See Ref. 9.

The solid-phase system using $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp/urea–$H_2O_2$ was effectively used for the solvent-free oxidations of some aromatic and aliphatic sulfides. As shown in Table 1, when 2.5 times amount of urea–H_2O_2 to a substrate was used, the oxidation of the sulfide to the corresponding sulfone proceeded under the mild conditions (at 4–25 °C for 24–72 h). The sulfones were obtained in good to excellent yields by the simple isolation procedure described in Ref. 9. The oxidation of sulfides is a consecutive reaction via sulfoxides to sulfones. The selective oxidation of the sulfides to the corresponding sulfoxides was accomplished by using 1.05 times amount of urea–H_2O_2 to the substrate at 4 °C (Table 2). Aromatic and aliphatic sulfoxides were mostly obtained with over 85% of the selectivity. The use of smaller amount of the catalyst (0.2 mol%) was more effective for the oxidation of aliphatic sulfides.



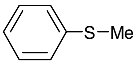
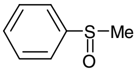
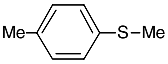
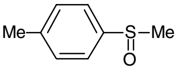
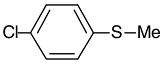
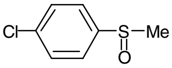
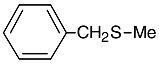
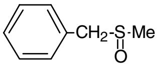
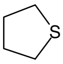
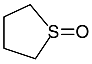
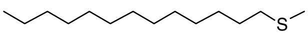
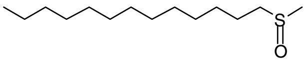
In the oxidation of aryl methyl sulfides to the sulfoxides, methyl substitution to *para*-position of phenyl ring did not affect the reactivity and the selectivity, while *p*-chloro substitution decreased the selectivity to afford the sulfoxide in a lower yield. The electron-withdrawing substituent such as Cl may be favorable for the second nucleophilic oxidation of the sulfoxide. Except for the *p*-chloro sulfide, the rate of electrophilic oxygen transfer to the sulfides was over ten times faster than that of nucleophilic oxygen transfer to the sulfoxides to lead to the high selectivities. In our system the peroxo-species derived from $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp had electrophilicity to preferentially attack the sulfides leading to the selective synthesis of the sulfoxides.

In order to elucidate the peroxo-species, we carried out the analysis of ^{31}P solid-state NMR on the solid-phase-activation of $(Bu_4N)_3[PMo_{12}O_{40}]$ catalyst. NMR spectra did not change after the activation at 25 °C for 24 h (Fig. 1).[10] In the NMR spectra on the solid-phase-activation of $(NH_4)_3[PMo_{12}O_{40}]$, the formation of the active species with partial degradation of the framework was observed.[4] Therefore, the Keggin-cluster structure of $(Bu_4N)_3[PMo_{12}O_{40}]$ was not degraded through the activation and a novel peroxo-species having the parent framework could be formed. In contrast to the solid-phase reactions, the degraded peroxo-species of $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (PMo_4) is formed in the biphasic reaction of $CetylPy_3[PMo_{12}O_{40}]$ with aq H_2O_2.[6] Further degraded species may be formed, which would cause the poor catalytic activity of the phosphomolybdate.

In our system urea–H_2O_2 was quantitatively used for the sulfide oxidation without loss; when the excess amount of the substrate to urea–H_2O_2 was used, the sulfoxide and sulfone were formed over 99% yield based on the urea–H_2O_2 amount. In the system, probably, the peroxo-species with the parent framework has not been degraded during the repeated catalytic cycle, which can lead to the high H_2O_2 efficiency and the high activity obtained above.

In conclusion, the simple solid-phase system, Keggin-type of $(Bu_4N)_3[PMo_{12}O_{40}]$ dispersed on FAp phase, is effective for the selective oxidation of the sulfides with urea–H_2O_2. In the system the reaction can be carried

Table 2. The oxidation of sulfides to sulfoxides using $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp and urea–$H_2O_2$[a]

Substrate	Time/h	Product	Yield/% (selectivity/%)[c]
	72		85 (4/88/8)
	72		89 (1/89/10)
	24		49 (26/56/18)
	49[b]		93 (0/93/7)
	48[b]		77 (0/89/11)
	51[b]		77 (7/86/7)

[a] $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp/urea–$H_2O_2$/substrate = 0.025 mmol/2.5 g/2.63 mmol/2.5 mmol at 4 °C.

[b] 0.005 mmol of $(Bu_4N)_3[PMo_{12}O_{40}]$ was used.

[c] The selectivity of sulfide/sulfoxide/sulfone was determined by GC and ^1H NMR. See Ref. 9.

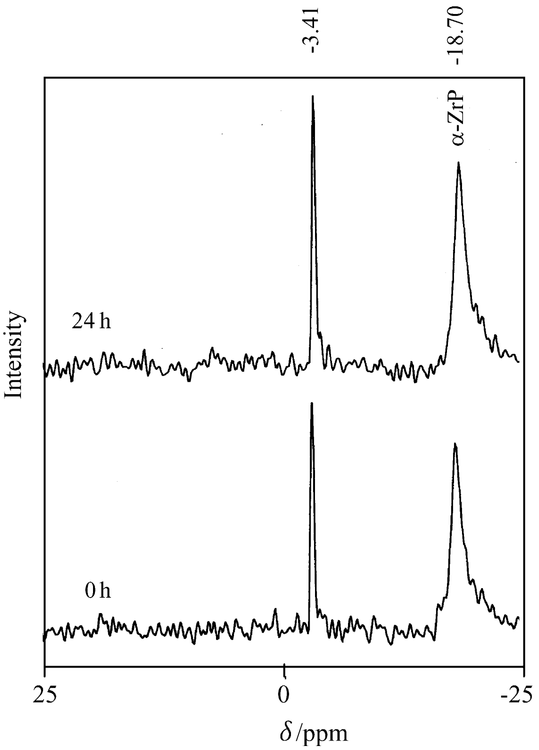


Figure 1. ^{31}P solid-state NMR spectra on the activation of $(Bu_4N)_3$-$[PMo_{12}O_{40}]$/CaF_2 with urea–H_2O_2; immediately after mixing (0 h) and after 24 h at 25 °C using α-zirconium phosphate (α-ZrP) as an internal standard.

out under solvent-free, neutral, and mild reaction conditions with easy isolation procedure.[11–13] In addition to the effectiveness and the convenience, it is notified that the simple Keggin-type of phosphomolybdates exceptionally catalyzed the oxidation in this system.

References and notes

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8. Fluorapatite powder $Ca_{10}(PO_4)_6F_2$ (particle size, 5–20 μm; specific surface area. 8–12 m^2/g) were purchased form Taihei Chemical Industrial Co. Ltd and used.
9. The reactions were carried out under the conditions described in Tables 1 and 2. The solid reaction mixture was extracted with *n*-hexane–ethyl acetate. 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 calculated without further separation and purification of the extracts by means of GC and/or ^1H NMR.
10. In NMR spectra the behavior of the catalyst on CaF_2 disperse phase was similar to that on FAp disperse phase. Since the PO_4^{3-} signal of FAp overlapped in the latter case, the NMR spectra in the reaction of the former $(Bu_4N)_3[PMo_{12}O_{40}]$/$CaF_2$ with urea–H_2O_2 were shown.
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