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Oxidation of Cyclopentene with Hydrogen Peroxide Catalyzed by 12-Heteropoly Acids

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12-Heteropoly acids exhibited high performance for selective oxidation of cyclopentene to glutaraldehyde with hydrogen peroxide. Especially, heteropoly acids with mixed addenda atoms of Mo and W, $H_3PMo_{12-x}W_xO_{40}$(x=1-9), showed excellent results.

There have been very few studies on the selective oxidation with hydrogen peroxide catalyzed by heteropoly acids, though combinations of molybdates or tungstates with H_2O_2 are known as selective oxidation catalysts.[1] It has recently been reported that epoxidation of olefins proceeded selectively with alkylpyridinium 12-molybdophosphate.[2] Some patents[3] disclose that catalysts such as $MoO_2(acac)_2$-B_2O_3 are effective for the oxidation of cyclopentene to glutaraldehyde using hydrogen peroxide in a non-aqueous system, but its performance is not sufficient for practical applications. We attempted to apply heteropoly acids, which are unique bifunctional catalysts possessing both acidic and oxidizing properties, and found much improved performance.[4] We report here that 12-heteropoly anions containing both Mo and W are very active and selective for this reaction.

Heteropoly acids (HPA) with Keggin structure were synthesized by the conventional method[5] and evacuated at room temperature before use. The heteropoly anions with mixed addenda atoms thus prepared were probably mixtures of several different compositions. The water contents of the HPA are estimated to be about 6 molecules per anion.[6)] This amount is negligible as compared with that in the system (see below). A non-aqueous H_2O_2-TBP (tributyl phosphate) solution was prepared by removing most of water from a mixture of 30% H_2O_2 aqueous solution and TBP by vacuum distillation. About 3 wt% of water remained in the H_2O_2-TBP solution thus prepared. The reaction was conducted using a 200-ml four-necked flask equipped with a reflux condenser, a thermometer, a stirrer, and a dropping funnel. The products were analyzed with gas chromatography and titration.

Table 1. Oxidation of Cyclopentene with Hydrogen Peroxide using Various Heteropoly Acids[a)]

Catalyst	Amount of catalyst mmol	Yield / mol% on H_2O_2		
		Glutaraldehyde[b)]	1,2-Cyclopentanediol	Cyclopentene oxide
$MoO_2(acac)_2$	2.8	21.7	0.7	0.6
$MoO_2(acac)_2$[c)]	2.8	30.9	1.3	1.1
$H_3PMo_{12}O_{40}$	0.59	46.5	6.2	0.5
$H_4SiMo_{12}O_{40}$	0.59	1.3	1.8	0.2
$H_4GeMo_{12}O_{40}$	0.59	20.6	2.3	0.6
$H_3PW_{12}O_{40}$	0.59	5.4	6.5	0.2
$H_3PMo_{10}W_2O_{40}$	0.21	60.6	13.9	0.8
$H_3PMo_{10}V_2O_{40}$	0.59	6.3	5.6	0.3

a) Reaction temp: 35 °C, Time: 3 h, Cyclopentene: 0.21 mol H_2O_2: 0.14 mol (H_2O_2 was used as 10 wt% solution in TBP).

b) Glutaraldehyde yield based on cyclopentene corresponds to one third of the value based on H_2O_2 given in this table.

c) B_2O_3 (4.2 mmol) was added as cocatalyst.

Table 1 shows the results of the reaction using various heteropoly acids. The yields of glutaraldehyde, 1,2-cyclopentanediol and cyclopentene oxide were calculated on the basis of H_2O_2 by the following equations:

$$\text{Glutaraldehyde yield (mol\%)} = \frac{\text{Glutaraldehyde produced (mol)} \times 2}{H_2O_2 \text{ fed (mol)}} \times 100$$

$$\text{Diol or Oxide yield (mol\%)} = \frac{\text{Diol or Oxide produced (mol)}}{H_2O_2 \text{ fed (mol)}} \times 100$$

12-Molybdophosphoric acid showed fairly good performance without any co-catalyst such as B_2O_3. This result is much better than the results obtained by using greater amounts of $MoO_2(acac)_2$ catalyst. Phosphorus was the most suitable heteroatom among $H_3XMo_{12}O_{40}$ (X=P, Si, Ge) tested. As for the addenda atom, 12-tungstophosphoric acid indicated much lower activity than 12-molybdophosphoric

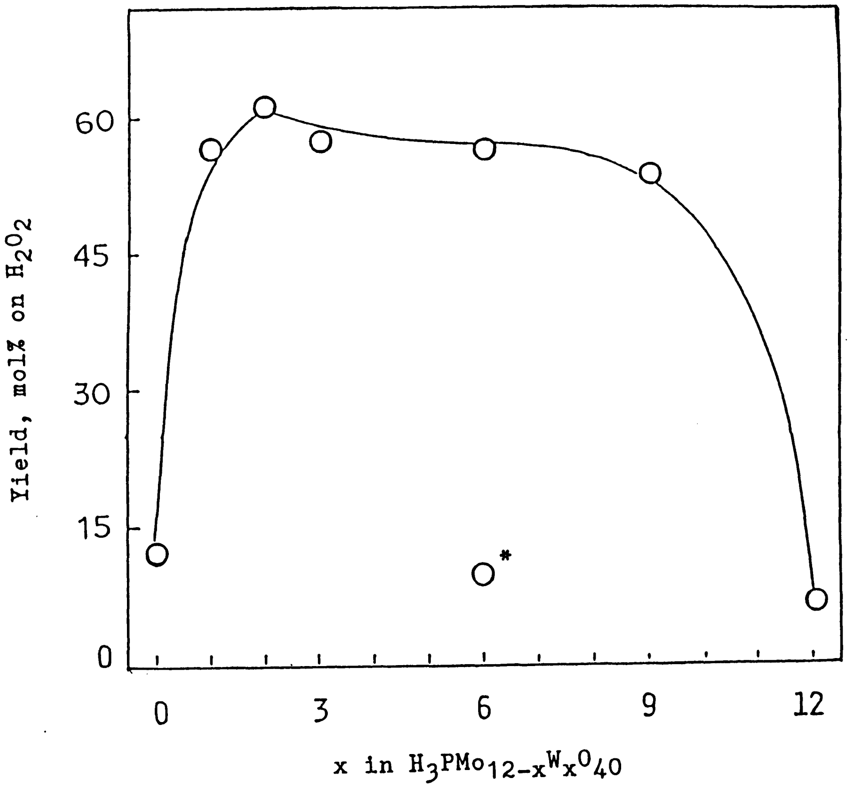

Fig. 1. Yield of glutaraldehyde in the oxidation of cyclopentene with hydrogen peroxide using Mo-W mixed-coordinated heteropoly acids. The mark, *, indicates the result obtained by using a mixture of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$.
Reaction temp: 35 °C, Time: 3 h, HPA: 0.21 mol
Cyclopentene: 0.21 mol, H_2O_2: 0.14 mol (H_2O_2 was used as 10 wt% solution in TBP).

acid. Increased activity was observed when a part of molybdenum atoms of the 12-molybdophosphoric acid were replaced by tungsten atoms. However, the replacement of molybdenum to vanadium atoms caused undesirable decomposition of hydrogen peroxide and resulted in a low yield of glutaraldehyde.

Figure 1 shows the effect of Mo-W mixed addenda atoms on the catalytic activity. The activity increased markedly by the mixed coordination. The yields for $H_3PMo_{12-x}W_xO_{40}$ (x=1-9) were more than five times greater than those for $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, so that it was possible to reduce the amount of catalysts to about one-third of that in the standard conditions (cf. Table 1). Judging from the low activity of simple mixture of 12-molybdophosphoric acid and 12-tungstophosphoric acid as plotted in Fig. 1, the formation of polyanions with Mo-W mixed addenda atoms is essential for the excellent performance. It has been reported that redox potential and catalytic performance change by the Mo-W mixed coordination ($H_3PMo_{12-x}W_xO_{40}$).[7] Therefore, the improved catalytic activity of heteropoly acid is likely to be associated with the change in the redox properties of polyanions.

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