

Catalysis by Heteropoly Compounds

IV. Oxidation of Methacrolein to Methacrylic Acid over 12-Molybdophosphoric Acid

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Oxidation of methacrolein over heteropoly acid catalysts (mainly 12-molybdophosphoric acid) at 300°C was investigated by use of a flow method. Primary (Keggin) and secondary structures of the catalyst were rather stable upon heat treatment at 250–350°C, and reproducible data of the oxidation reaction were obtained by the pretreatment at 350°C in a N₂ + O₂ + H₂O stream. Effects of oxygen in the feed gas demonstrated that oxygen atoms of polyanions or steam were directly involved in the reaction and the reduced polyanions were reoxidized by gaseous oxygen. Presence of steam had a remarkable effect both on the rate and selectivity. Rate equation, ESR study, and the comparison between the catalytic oxidation (flow method) and noncatalytic oxidation (pulse method) indicated that the reduction of catalysts was rate-determining in a redox mechanism and the catalysts were in a highly oxidized state under the present reaction conditions. Effects of metal salt formation and silica support were also examined. On the basis of these results, a possible reaction mechanism with an ester- or diol-type intermediate has been proposed.

INTRODUCTION

Application of heteropoly acids as oxidation catalysts has been attempted for many years (1, 2). Recently, the oxidation of methacrolein to methacrylic acid catalyzed by heteropoly compounds has become of major industrial importance. Quite a few studies have been published in patents (3) and some also in scientific papers (4, 5). It was suggested from ir spectra of catalysts that the polyanion structure (Keggin structure) of 12-heteropoly acid (mainly of molybdenum) was the effective component for the reaction (7).

Besides the application to industrial processes, heteropoly acids are suitable materials for fundamental research on catalysis by the following reasons. First, their structure can be defined at the "molecular

level" of heteropoly anion. Second, their acidic and oxidizing properties can be modified by changing the constituting elements (heteroatom, polyatom, and counteranion). By the control of acid and redox properties, it would be also possible to develop new synthetic processes by use of heteropoly acid catalysts.

However, although the structure of heteropoly acids in the crystalline state and their acid or redox properties in solution have been well clarified (8), there is little information on those properties in the solid state at elevated temperatures. For example, the reduction process of 12-molybdophosphoric acid is likely different in solution and in the solid state, since ESR signal at 77 K became extraordinary broad and isotropic when reduced in solution (9), while an anisotropic signal with hyperfine structure was observed at the same temperature when reduced at 250°C (10). As for the acidic properties, it was suggested from

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color change of an indicator that 12-tungstophosphoric acid was an acid stronger than $H_0 = -8.2$ (6). However, it was quite recent that 12-heteropoly acids were demonstrated to be purely protonic and very strong in the solid state at high temperatures (1, 11). Moreover, if one considers the thermal instability and its strong tendency to be hydrolyzed, it is uncertain whether or not the structure of heteropoly anion itself was maintained under the reaction conditions of earlier studies.

It appears therefore very important in the study of heteropoly acid catalysts to ensure the structure and to measure directly their acid and redox properties. With sufficient care paid to this, it would be possible to elucidate the relationships between catalyst properties and structure, and further to describe the reaction path at a molecular level, by taking advantage of "well-definable" structure of heteropoly acids.

We have been studying the acid and redox properties of 12-heteropoly acids in relation to their catalytic function, as summarized in our recent reviews (12). We studied previously the oxidation of methacrolein over several heteropoly compounds and proposed a reaction mechanism in which acidity functions in the pre-equilibrium step and the oxidizing ability plays roles in the rate-determining second step (4). In the present study, we examined in more detail the oxidation reaction over 12-molybdophosphoric acid, on the basis of reaction kinetics, structural changes by heat treatment or use for reaction, and the effects of oxygen and steam supply, as well as ESR measurement.

EXPERIMENTAL

XRD and ir. X-Ray diffraction (XRD) patterns were determined by a X-ray diffractometer (Rigaku Denki, Rotaflex) using $CuK\alpha$ radiation. In order to minimize rehydration, in most cases samples were very quickly covered by a Mylar film on a sample holder after various treatments. Infra-

red (ir) spectra were recorded after pressed into a KBr disk with the aid of a Fourier-transform ir spectrometer (JEOL JIR-10).

Reaction procedure. Oxidation of methacrolein (MCN) was carried out under continuous flow conditions in a tubular glass made reactor (10 mm in diameter) at 1 atm total pressure. The standard procedure was as follows. About 1 g of catalyst (unsupported; powder) was loaded in the reactor and the temperature was raised slowly in a N_2 (22 cm^3/min) + O_2 (3 cm^3/min) stream to 100°C in about 1 hr. Water (25 cm^3 —steam/min) was added to the N_2 + O_2 stream by use of a microfeeder when the temperature exceeded 100°C. Then the temperature was raised to 350°C within about 1.5 hr, and the catalyst was kept at 350°C for 2 hr. After it was cooled to 300°C, MCN was introduced to the gas stream by passing a part of the stream (N_2 only) through an evaporator-saturator. The standard reactant gas mixture was $MCN : O_2 : H_2O : N_2 = 0.015 \text{ atm} : 0.06 \text{ atm} : 0.5 \text{ atm} : \text{balance}$. The total flow rate was 50 cm^3 (STP)/min. Carbon balance was ordinarily better than about 90%.

Analyses. Products of flow experiments were analyzed by gas chromatographs. Products in the gas phase of the outlet gas (CO , CO_2 , and MCN) were sampled by use of a microsyringe and analyzed by a Chromosorb 101 or Porapak Q column kept at 160°C, a molecular sieve column (1.2 m), and an activated charcoal (1.2 m) both kept at 80°C. After a stationary state of the catalytic oxidation was confirmed by the gas phase composition (usually it took about 40–60 min), liquid products were collected by a condenser kept at 0°C. Liquid products (MCN, methacrylic acid, and acetic acid) were analyzed by a Porapak Q or Chromosorb 101 column (both 1.5 m) kept at 160°C. The latter was superior in life and product separation. Sensitivity of gas chromatographs was frequently calibrated.

Catalysts and reagents. Two 12-molybdophosphoric acid samples ($H_3PMo_{12}O_{40} \cdot 19-22H_2O$; abbreviated as PMo_{12} hereafter) were used; one was prepared as de-

scribed previously following the literature (1), and the other was kindly donated by Climax Molybdenum Co. (Japan) Ltd. There was little difference between the two samples in the flow experiments, so that no distinction was made in the following description. $H_3PW_xMo_{12-x}O_{40}$ (PW_xMo_{12-x}) was prepared from $Na_2WO_4 \cdot 2H_2O$, $Na_2MoO_4 \cdot 2H_2O$, and $Na_2HPO_4 \cdot 2H_2O$ as described previously (1). Na and Cs salts of $H_3PMo_{12}O_{40}$ (for example, $Na_2HPMo_{12}O_{40}$ will be abbreviated as Na_2H) were prepared by adding alkali carbonates to $H_3PMo_{12}O_{40}$ (both aqueous solutions) and subsequent evaporation to dryness.

Methacrolein and acrolein were GR reagents obtained commercially (Tokyo Kasei and Yoneyama Chemicals). Methacrolein was used after adding a small amount of hydroquinone to prevent polymerization.

RESULTS

Structural Changes by Heat Treatment and by Uses for Catalytic Oxidation

Figure 1 shows the examples of XRD patterns of PMo_{12} which had been treated in a stream of $N_2 + O_2$ or $N_2 + O_2 + H_2O$ gas at various temperatures. In most cases, samples were covered with a Mylar film after they were quickly placed on sample holders, in order to avoid rehydration. By this procedure, the variation of XRD patterns

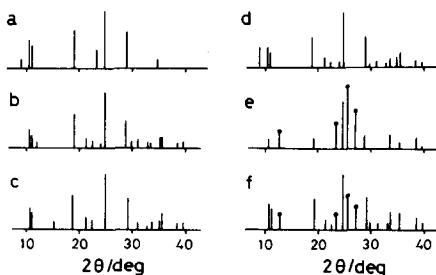


FIG. 1. Examples of XRD patterns of $H_3PMo_{12}O_{40}$ after heat treatments. Heated for 2 hr at (a) 110°C, (b) 250°C, and (c) at 300°C in $N_2 + O_2$ stream; at (d) 350°C and (e), (f) at 400°C in $N_2 + O_2 + H_2O$ stream. Mylar films were used except for (f). Peaks due to MoO_3 are marked by open circles.

during the measurement did not occur. The intensity of XRD lines was not very accurate at $2\theta \sim 25^\circ$ due to the broad diffraction peak of the Mylar film when it was used.

Heat treatment below 100°C gave rather broad XRD lines and the XRD patterns were not reproducible, owing to the variation of water content (which causes changes in the secondary structure) (1) and poor crystallinity.

Samples after heat treatments at 200–350°C gave rather similar XRD patterns. Broad lines with a very low S/N ratio were obtained after treatment in $N_2 + O_2$ at 400°C, indicating poor crystallinity. Samples after this treatment were yellow-brown, but turned to yellow-green or green when kept in air without a Mylar film. The other samples were yellow or greenish yellow after heat treatments and the color did not apparently change in the air. Treatment at 400°C in $N_2 + O_2 + H_2O$ gave rather sharp lines. The samples treated at 400°C exhibited lines due to MoO_3 (labeled by open circles in the figure). The MoO_3 lines increased in intensity as the period of treatment was extended. After the treatment at 450°C, lines due to MoO_3 were predominant.

Figure 2 shows the XRD patterns and ir spectra of PMo_{12} after it was used for oxidation of methacrolein for 2 hr at 300°C under the standard conditions. The catalysts were quickly taken out of the reactor after the feed gas was replaced by dry nitrogen. The XRD patterns were very similar with one another and to those before the reaction (see Fig. 1), except for the lines at $2\theta < 10^\circ$. It was noted that the MoO_3 lines which appeared after the treatment at 400°C (Figs. 1e and f) were often smaller after the use as catalyst. This fact together with the change in ir spectrum described below (Fig. 2a) indicates that part of MoO_3 reacted with phosphoric acid to re-form 12-molybdophosphoric acid under the reaction conditions.

Infrared spectra (taken as KBr disks) re-

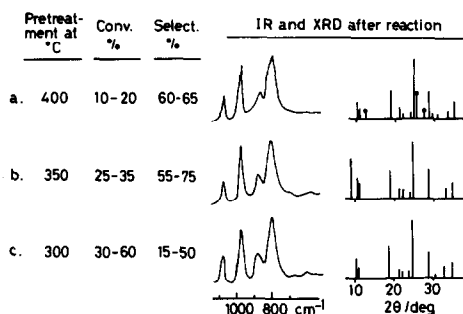


FIG. 2. Infrared spectra and XRD patterns of $H_3PMo_{12}O_{40}$ after use as catalysts for 2 hr at 300°C. $H_3PMo_{12}O_{40}$ samples were pretreated at (a) 400, (b) 350, and (c) 300°C for 2 hr in $N_2 + O_2 + H_2O$ stream. Conversion of methacrolein and selectivity to methacrylic acid obtained in the subsequent reaction are also given. XRD was measured for the samples covered by Mylar films. XRD peaks due to MoO_3 are marked by open circles.

sembled one another. They were in close agreement with that of Keggin structure ($PMo_{12}O_{40}^{3-}$ or $PW_{12}O_{40}^{3-}$) (4, 13). There were few changes before and after the reaction in the cases of the 300 and 350°C pretreatment. However, the ir spectrum after treatment at 400°C indicated partial decomposition of the Keggin structure, but there was little indication of the decomposition after the reaction (Fig. 2a).

The effects of heat treatment on catalytic properties were examined to choose appropriate pretreatment conditions, since our previous studies indicated that the structure and catalytic properties of PMo_{12} were sensitive to these treatments. Steam was added to the $N_2 + O_2$ mixture to promote the effect of pretreatment by accelerating the rearrangement of the secondary structure. Results are given in Fig. 2. Reproducible data (conversion, 25–35%; selectivity to methacrylic acid, 55–75%) were obtained by the pretreatment at 350°C. XRD and ir did not change before and after the reaction as described above. Furthermore, variations of the conversion and selectivity during the time course of reaction (4 hr) were small in this case. After 300°C treatment XRD and ir of the catalyst were similar to those after the 350°C treatment, but

the data of catalytic oxidation were not reproducible. Sometimes, a high conversion with a low selectivity was obtained at the initial stage and the conversion gradually decreased and the selectivity increased during the reaction period, both approaching the ordinary values of 25–35% conversion and 55–75% selectivity. Therefore, the 300°C pretreatment was presumably not sufficient. Treatment at 400°C which caused partial decomposition of PMo_{12} gave an ordinary value of selectivity, but the conversion was lower. Thus pretreatment at 350°C in a stream of $N_2 + O_2 + H_2O$ for 2 hr was chosen as the standard pretreatment. Reaction data were obtained after this standard pretreatment unless otherwise described.

Oxidation of Methacrolein over



Rate equation. The following pressure dependencies were found at 280–300°C, in the range of the partial pressure of methacrolein (MCN), 0.004–0.03 atm; oxygen, 0.004–0.1 atm; and steam, 0.1–0.8 atm (4).

$$-d[MCN]/dt = k p_{MCN}^{0.6-1} p_{O_2}^{0-0.2} p_{H_2O}^0 \quad (1)$$

Conversion was kept below 10% for the determination of the pressure dependency. At higher conversions, the dependency on MCN tended to decrease. Pressure dependencies of the formation of each product are summarized in Table 1. Dependency on the partial pressure of steam is shown in Fig. 3. As reported previously (4), the rate and the product composition little changed above $p_{H_2O} = 0.1$ atm; they varied in the pressure range of 0 ~ 0.1 atm. In this pressure range the conversion increased with p_{H_2O} , but the production of acetic acid, CO, and CO_2 was high, resulting in a low selectivity to methacrylic acid. The dependency of the rate on p_{O_2} in the absence of water was higher (e.g., 0.3 th for consumption of MCN and 0.6 th for CO_2 formation).

Dependency on W/F. Figure 4 shows the data obtained under the standard conditions with different amounts of catalyst.

TABLE 1
Dependencies of the Rate on Partial Pressure^a

	Reaction order on ^b		
	MCN (0.004-0.03)	O ₂ (0.004-0.1)	H ₂ O (0.1-0.8)
Consumption of MCN	0.6-1.0	0	-0.2
Formation of Methacrylic acid	0.5-1.0	0.1-0.2	~0
Acetic acid	0.4-0.8	0	-0.3
CO	0.3-0.9	0	-0.2
CO ₂	~1.1	0.1-0.3	~0

^a Catalyst, H₃PMo₁₂O₄₀; temperature, 300°C.

^b Pressure ranges (in atm) are given in parentheses.

With the increase in the amount of catalyst (W/F), the conversion increased almost linearly, but the selectivity of methacrylic acid slightly decreased. Among the by-products, the content of acetic acid increased with W/F, while the ratio of CO plus CO₂ remained almost constant. It was noted that the ratio of methacrylic acid : acetic acid : CO + CO₂ was reproducible, but the CO to CO₂ ratio varied considerably in the reaction products when different lots of PMo₁₂ were used (the reason is not clear at present). When methacrylic acid was fed in place of MCN under the same conditions, acetic acid, CO, and CO₂ were produced in the ratio of 2 : 1 : 2.

Effects of oxygen and steam in the gas phase. The composition of products varied as given in Table 2, when the supply of oxygen was stopped at the stationary state in

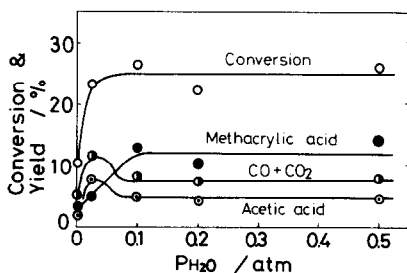


FIG. 3. Dependency of conversion and yields on the partial pressure of steam for methacrolein oxidation over H₃PMo₁₂O₄₀ at 300°C.

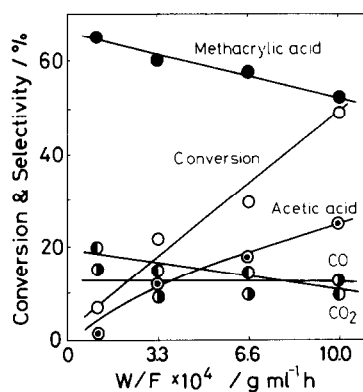


FIG. 4. Conversion and selectivity vs W/F plots for methacrolein oxidation over H₃PMo₁₂O₄₀ at 300°C. Only the amount of catalyst was changed.

flow experiments. Data in this table are for the products collected and analyzed after the concentration of oxygen in the outlet gas decreased to a very low level. Within 5 min after the stop of the oxygen supply, the concentration became lower than 0.01 ~ 0.03%. The variation of the products given in the table was very similar to the previous results (4); the oxidation reaction continued for a prolonged period, although the rate decreased significantly. As for the selectivities it is noted that the selectivity to methacrylic acid remained rather constant. The formation of acetic acid relatively increased and that of CO and CO₂ decreased. The number of oxygen incorporated into the products, that is, methacrolein, acetic acid, CO, CO₂, and H₂O (H₂O was estimated from the other products), in the period of 5-170 min after the stop of the oxygen supply amounted to 8.7×10^{-4} g-atom/g-catalyst which is about 5% of the total number of oxygen in the catalyst, or about two oxygen atoms per polyanion in the whole bulk. This amount is more than 10 times greater than the amounts of the oxygen impurity and adsorbed oxygen.

When the supply of steam was stopped and restarted at the stationary state of flow experiments, the products varied reversibly in a short period (less than 10 min) as shown in Fig. 5. In this experiment, total

TABLE 2
Effect of Oxygen Supply on the Oxidation of Methacrolein^a

	Conversion (%)	Selectivity (%) to			
		Methacrylic acid	Acetic acid	CO	CO ₂
(A) In the presence of O ₂	16.6	74.4	2.3	11.9	11.4
(B) After O ₂ supply was stopped					
5-60 min	6.3	72.5	6.8	8.2	12.5
60-170 min	2.3	70.1	19.6	3.9	6.4
(A) In the presence of O ₂	33.0	68.0	1.8	15.1	15.1
(B) After O ₂ supply was stopped					
5-60 min	9.8	80.1	6.1	7.0	6.8
60-100 min	2.1	71.2	17.1	2.4	9.3

^a Catalyst, H₃PMo₁₂O₄₀; temperature, 300°C. Feed for (A), MCN/O₂/H₂O/N₂ = 0.015/0.06/0.5/ balance.

flow rate was kept constant by changing the flow rate of nitrogen. Obviously the presence of steam increased both the conversion and selectivity (to methacrylic acid) as expected from Fig. 3 and the previous data (4). After the stop of the steam supply, the formation of methacrylic acid decreased greatly, the selectivity to it becoming about one-half (68 → 21%, 71 → 32%, and 78 → 40% in three different runs).

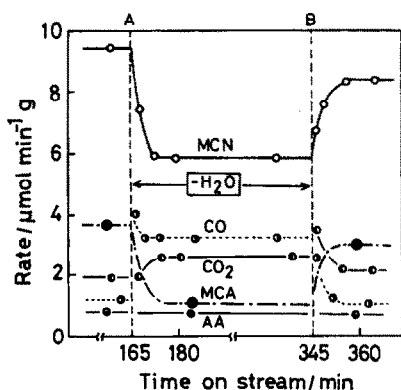


FIG. 5. Variation of composition by the stop of steam supply. Catalyst, H₃PMo₁₂O₄₀; temperature, 300°C. MCN, Methacrolein; MCA, methacrylic acid; AA, acetic acid. Steam (0.5 atm) was replaced by nitrogen for the period from A to B.

A similar trend was observed for the Cs salt of PMo₁₂, but the extent of variation was smaller (20 ~ 30% relative decrease by the stop of steam supply). Rapid and reversible variation of products also took place for Cu salt. However, in this case, the conversion increased 1.5 times in the absence of steam. This increase was mainly due to the increased formation of CO, CO₂, and acetic acid.

Silica-supported PMo₁₂. Figure 6 shows the results of MCN oxidation over PMo₁₂ supported on silica gel. At the loading level of 20-60 wt% the rate normalized to the weight of PMo₁₂ was nearly constant and was 10-15 times greater than that for unsupported PMo₁₂.

ESR of PMo₁₂. After the oxidation reactions in the presence of steam (standard conditions) and in its absence, the catalysts were cooled in a N₂ stream and placed in ESR tubes. ESR signals of these samples measured at 25°C are shown in Fig. 7. Both samples showed signals due to Mo⁵⁺ which are similar to those reported in the literature for PMo₁₂ reduced at a high temperature (10). However, the signal intensity (approximately calculated by the integration

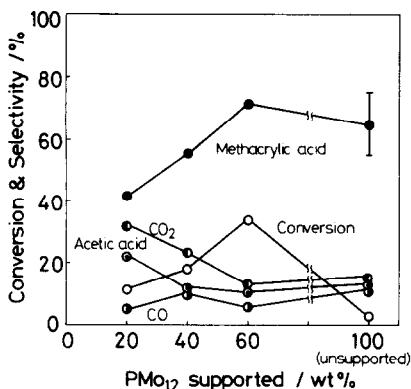


FIG. 6. Oxidation of methacrolein over silica-supported $H_3PMo_{12}O_{40}$ (100 mg) at $300^\circ C$.

on graphs) of the sample used for the reaction in the absence of steam was at least ca. 10 times greater than the sample used for the reaction in the presence of steam. The color of the former was greenish yellow, while the latter was more greenish.

In Fig. 7, the ESR signals of PMo_{12} samples which were reduced to different extents in a closed circulating system by H_2 (100 Torr) at $250^\circ C$ after O_2 treatment at the same temperature are also shown. These ESR signals were not the same as those of PMo_{12} used for reaction, but some similarities are found between the samples which had been reduced by H_2 to lesser extents

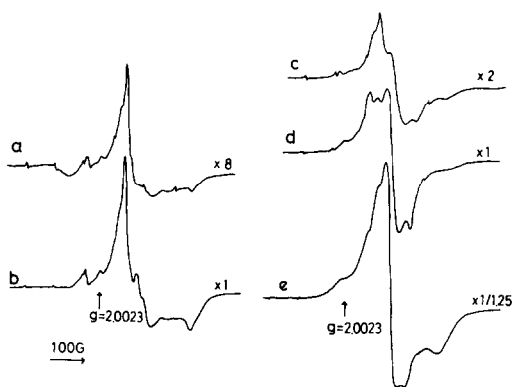


FIG. 7. ESR signals of $H_3PMo_{12}O_{40}$. (a) and (b) correspond to (a) and (b) in Table 3. (c)–(e) correspond to (d)–(f) in Table 3. Small hfs signals of a Mn marker are superimposed. Positions of free electron signal ($g = 2.0023$) are indicated by arrows.

TABLE 3

Intensity of ESR Signal and Color of $H_3PMo_{12}O_{40}$ Which Had Been Used for Methacrolein Oxidation at $300^\circ C$ or Reduced by Hydrogen at $250^\circ C$

	Relative ESR intensity	Color
After use for reaction		
a. In the presence of steam	1	Yellow green
b. In the absence of steam ^a	11	Yellow green -green
Reduction by H_2		
$H_2/\text{anion} =$		
c. 0	0	Yellow
d. 0.11	8	Green
e. 0.32	16	Blue
f. 1.25	32	Dark Blue

^a Steam in the standard conditions was replaced by nitrogen.

and the samples after use for reaction. Variation of the signals with the extent of reduction (Figs. 7c–e) indicates that there are two or more Mo^{5+} species in PMo_{12} reduced by H_2 . The ESR intensity of the reduced PMo_{12} is summarized in Table 3 together with its color. The intensity increased with the extent of reduction. By use of this correlation, the extent of reduction of PMo_{12} used for the reaction may be estimated to be ca. 0.01 electrons/anion and ca. 0.2 electrons/anion for the samples used for the reaction in the presence and absence of steam, respectively (Table 3). It was confirmed that the ESR signal of sample d in Table 3 decreased only by 20% when it was kept for 30 min in a stream of oxygen at room temperature.

Oxidation of Methacrolein over $H_3PW_xMo_{12-x}O_{40}$ and Alkali Salts of $H_3PMo_{12}O_{40}$

Oxidation of methacrolein was carried out over 12-molybdophosphoric acid, in which part or all of the Mo atoms are replaced by W atoms. As the results in Fig. 8

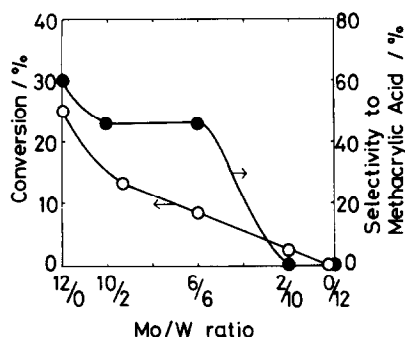


FIG. 8. Effect of the substitution by W for Mo of $H_3PMo_{12}O_{40}$ on methacrolein oxidation (300°C).

show, the conversion decreased with increase in the W to Mo ratio. The selectivity to methacrylic acid changed little up to the substitution of six atoms, but the selectivity became very small when 10 or more atoms were replaced. It was confirmed previously that PMo_6W_6 was not a simple mixture of PMo_{12} and PW_{12} , although PMo_6W_6 probably contained PMo_5W_7 , PMo_7W_5 , etc. to some extent (1).

The effect of alkali-salt formation on the catalytic activity and selectivity was preliminarily examined. In the case of Na salts, the catalytic activity decreased gradually as the extent of neutralization increased ($H_3 > NaH_2 > Na_2H > Na_3$, the activity of Na_3 was a half of H_3). The selectivity varied much less: from 60% for H_3 to 53% for Na_3 . As for Cs salts, the catalytic activity normalized to catalyst weight and the selectivity changed only slightly with the extent of neutralization. In both cases, if the alkali was in excess by 10%, the activity was almost null (4). No structural change was detected by ir and XRD in the case of the Cs salts, while considerable decomposition of Keggin structure was indicated after reaction for the Na salt containing Na in excess.

DISCUSSION

Structural Changes

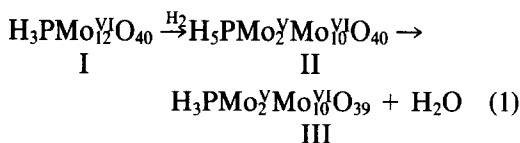
As previously pointed out (1, 4), it is necessary, for the understanding of the ca-

talysis of heteropoly acids, to distinguish between the primary structure (polyanion: Keggin structure in the case of 12-heteropoly acid (A series)) and the secondary structure (three-dimensional arrangement of polyanion, counteraction, and water of crystallization). The secondary structure is usually very variable, so that water, alcohols, etc. readily penetrate into and come out of the bulk by changing the interstitial distance, that is, the rearrangement of the secondary structure (note that this is not diffusion in micropores). By this effect, heteropoly acids behave in some respects very like that in solution. The behavior like solution may allow us to call the solid state of these compounds "pseudoliquid phase" (4, 14). Reactions like dehydration of alcohols actually take place in the bulk not only on the BET surface (15).

In the present study the primary structure was inferred by ir and the secondary structure by XRD. It is seen in Fig. 1 that very similar XRD patterns were obtained after treatments at 250–350°C in $N_2 + O_2$ or $N_2 + O_2 + H_2O$ and after use for reaction. These XRD patterns also resemble those of K and Cs salts, which are close to those given in ASTM cards (9–408(K), 412 (NH₄)). Slight differences were observed at $2\theta \div 10^\circ$ and for the position of main peaks. The highest peak appears at $2\theta = 26.6^\circ$ for K salt and 26.0° for Cs salt, while it is at $2\theta = 24.8^\circ$ in Fig. 1. The XRD pattern of hexahydrate of $H_3PW_{12}O_{40}$ was also similar, the highest peak being at $2\theta = 25.5^\circ$. Infrared spectra of the samples after the above treatments are of typical Keggin structure of 12-heteropoly anion (4, 13). Therefore, it may be concluded that both the primary and secondary structures are rather stable at about 300°C. Since the rehydration process is very rapid, the possibility of rehydration during the XRD measurement cannot be totally eliminated, but it may be stated that the secondary structure at high temperatures is at least closely related to the structure of hexahydrate (16) and the salts of K, Cs, etc.

Oxidation State of $H_3PMo_2O_{40}$ under the Reaction Conditions

XRD and ir indicated that there were no significant structural changes before and after the reaction. According to the previous studies, the reduction of PMo_{12} proceeds by the following scheme (4, 17):



At low temperatures, the reduction to II is predominant (reduction beyond or less than two electrons/anion is possible in some cases), and at high temperatures the reduction to III prevails. The presence of water vapor has an influence on the rate of reduction (17), and probably also on the relative ratio of reduction to II and to III, as the second step is a dehydration process. The reduction to II may cause only a small change in ir spectrum, since the structure of anion is retained (4).⁴ However, the reduction to III (for example, reduction at 300°C) resulted in a significant decrease of P–O and Mo–O–Mo bands (18). Therefore, the few changes in ir spectra after use as catalyst (Fig. 2) suggest either that the oxidation state was high or that the reduction mostly remained at the stage of II (not transformed to III).

According to the ESR measurement of PMo_{12} reduced electrochemically (9), the Keggin structure is maintained and an unpaired electron migrates rapidly in the 12 Mo atoms in a polyanion, so that ESR becomes very broad and unmeasurable at room temperature. It was further suggested that reduction by two electrons per polyanion causes reduction of ESR intensity (measured at low temperature) by electron

pairing. On the other hand, ESR signals with hfs were observed in the present study as in the literature (10). In the latter cases, PMo_{12} was reduced at 250–300°C. If one takes into account Eq. (1) and Pope's results on electrochemical reduction (9), it is probable that the reduction with H_2 proceeded mainly to III at high temperatures, but the electrochemical reduction only to II. In the structure III, unpaired electrons would be localized on Mo atoms which are deficient of coordinated oxygen. Therefore, ESR measurement given in Table 3 probably have detected considerable portion of Mo^{5+} species present in the samples.⁵

Provided that most of Mo^{5+} was detected by ESR, the data in Table 3 indicate that the degree of reduction at the working state is very low. Greater ESR intensity after use for the reaction in the absence of steam suggests that steam accelerated the reoxidation of PMo_{12} .

The above argument that the oxidation state is very high at the working state is supported by the observation of the color of the catalyst (Table 3). The color was always greenish yellow after the reaction under standard conditions. The color was green after the reduction (with H_2) of only 0.2 electrons/polyanion and turned to dark blue by the reduction of 0.6 electrons/polyanion (Table 3).

Reaction Mechanism

Oxygen atoms incorporated into the oxidation products after the cessation of the oxygen supply amounted to a considerable amount as described above, so that the oxygen atoms did not originate directly from gaseous or adsorbed oxygen but from the oxygen of polyanions or steam. The small difference observed in the selectivity to me-

⁴ Recently, it was reported that the P–O and Mo–O–Mo bands decreased considerably upon electrochemical reduction, where probably the anion skeleton remained essentially unchanged (26). Therefore, this statement ought to be reexamined by further study.

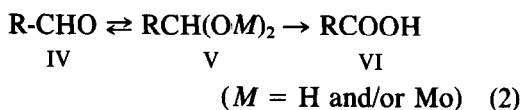
⁵ In fact, the heat treatment in vacuum of the sample which had been prerduced at 25°C increased the ESR signal intensity more than 10 times in agreement with the reaction from II to III in Eq. (1). ESR measurement at 77 K which would furnish the evidence of this argument is now being planned.

thacrylic acid before and after the cessation of the oxygen supply indicates that the oxygen atoms used in the oxidation reaction did not change regardless of the presence of gaseous oxygen. The composition of the other products changed considerably, but this change is probably due to the decrease in the secondary reactions.

Based on the effects of gaseous oxygen discussed above, it may be concluded that lattice oxygen (oxygen of polyanion) or oxygen from steam is involved directly in the present oxidation reaction as in the case of allylic oxidation over Bi-Mo oxide (19) and γ -Fe₂O₃ (20) or oxidation of propene to acetone over Sn-Mo oxide (21). In these cases, catalysts are reduced by the reactant and the reduced catalysts are reoxidized by oxygen in the gas phase ("redox" mechanism).

We previously reported that the steam supply greatly enhanced the rate and selectivity (4) of PMo₁₂. The rather short transient period as seen in Fig. 5 indicates that considerable change in the catalyst structure by H₂O, which would take a longer time, did not occur. ESR measurements suggest as discussed above that the reoxidation step is accelerated by steam. Direct involvement in the reaction and promotion of the removal of products are other possible roles of steam. Steam may also affect the state of the "pseudoliquid phase," since water-insoluble Cs salt exhibited a much smaller effect of steam. As for the latter idea no direct evidence has been obtained so far. Enhanced formation of CO and CO₂ over Cu salt in the absence of steam may be attributed to the reaction over Cu which changed in state.

On the basis of the above discussion, the following reaction scheme (Eq. (2)) proposed before (4) appears most probable. By the combined pulse-mass spectrometer technique as applied previously to acrolein, rapid ¹⁸O exchange between either two of H₂O, PMo₁₂, and methacrolein was confirmed (18a). Therefore, the first step is rapid, and does not require strong acidity.



A fair relationship between the catalytic activity and the rate of reduction of catalysts by H₂ led us to propose that the second step is rate-determining and the catalysts are reduced in this step as given in Eq. (1) (4). The reaction order which was high in MCN and low in O₂ is consistent with this mechanism. This idea was confirmed by the agreement between the order observed for the catalytic activity in flow experiments and the order in the stoichiometric reaction obtained by pulse method, that is, PMo₁₂ > PW₂Mo₁₀ > PW₆Mo₆ > PW₁₀Mo₂ > PW₁₂ (22).

Reaction intermediates similar to V (gem-diol or ester of molybdate) have been postulated for oxidation of alcohols and aldehydes with chromic acid or permanganate in a homogeneous system (23). It is very interesting in relation to the present reaction mechanism that complexes of aldehydes coordinated to an isopoly acid of Mo have recently been prepared (24a). A complex of carboxylic acid with an isopoly acid, which may be a model compound of an intermediate formed between V and VI, was recently reported (24b). An ester-type intermediate has been postulated also in the allylic oxidation of olefin over Bi-Mo oxides (25).

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