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Factors Controlling the Selectivity of the Oxidation of Acetaldehyde over Heteropoly Compounds[1]

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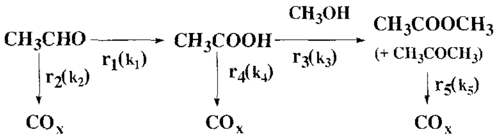
The catalytic oxidation of acetaldehyde over various heteropoly compounds (alkali salts of 12-molybdophosphoric acid) was investigated in relation to the redox and acidic properties of the heteropoly compounds based on the reaction scheme proposed:



where r_i's (i = 1–5) and k_i's are the rates and rate constants of respective steps, respectively. It was found that r_1 (or k_1), r_2 (k_2), and r_4 (k_4) were primarily determined by the oxidizing ability of catalysts measured by the rate of the reduction of the catalysts by CO and r_5 (k_5) was very small. On the other hand, r_3 (k_3) was mainly controlled by the acidic property of the catalyst (the amount of Brønsted acid site measured by pyridine uptake). The present results suggest that the heteropoly compounds having high oxidizing abilities and low Brønsted acidity are desirable for obtaining high yield of acetic acid.

INTRODUCTION

We previously reported that there are two extreme cases in the catalytic oxidations over heteropoly compounds; surface-type (e.g., oxidations of acetaldehyde and CO) and bulk-type (II) (e.g., oxidations of H_2 and cyclohexene) (*1–4*). The rates of the latter reactions depended little on the specific surface area of catalyst, owing to the rapid migration of the redox carriers in the catalyst bulk, while those of the surface-type reactions (the ordinary type) were proportional to the surface area. It is remarkable that two industrially interesting oxidation reactions to produce methacrylic acid, that is, oxidative dehydrogenation of isobutyric acid and oxidation of methacrolein, belong to the bulk (II)- and the surface-type, respectively (*5*).

The presence of correlation between catalytic performance and chemical properties of catalysts such as acidity and redox property are helpful both for the catalyst design and for the elucidation of reaction mechanism. Thus, several attempts have also been made to find out the correlations for heteropoly compounds as described in Ref. (*5*).

In order to elucidate the correlations for the heteropoly compounds, it is necessary to make clear whether the catalytic reaction belongs to the surface-type or the bulk-type.

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[1] Catalysis by Heteropoly Compounds, XVII. Part XVI: Mizuno, N., Watanabe, T., Mori, H., and Misono, M., *J. Catal.* **123**, 157 (1990).

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This is because the catalytic activity for a surface-type oxidation reaction is correlated with the surface redox property, while that for a bulk-type reaction is correlated with the bulk property (*4*). For example, a good correlation exists between the rates of the catalytic oxidation of acetaldehyde (a surface-type catalysis) and the reducibility of catalysts by CO. The reducibility represents the oxidizing ability of the catalyst surface, since, as we reported previously (*2, 4*), the noncatalytic (stoichiometric) reduction of heteropoly compounds by CO takes place only near the surface and the rate is proportional to the surface area.

In the present work, we chose the oxidation of acetaldehyde, a typical surface-type reaction (*4, 5*), and the mechanism was examined. Then based on the mechanism the factors controlling each step of the acetaldehyde oxidation were investigated.

EXPERIMENTAL

Catalysts and materials. 12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$, abbreviated as PMo_{12}) was commercially obtained from Kanto Chemical Co., Inc. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated as PW_{12}) was obtained commercially from Nippon Inorganic Colour and Chemical Co., Ltd. and recrystallized from water after purification by extraction with diethyl ether. The infrared spectra were the same as those of standard sample (*6*). The salts of Na and Cs ($M_xH_{3-x}PMo_{12}O_{40}$, M = Na, Cs, x = 1–3, abbreviated as M_xPMo_{12}) were prepared from Na_2CO_3 and Cs_2CO_3 by the method described previously (*2*).

Acetaldehyde (Merck–Schuchardt, >99%) was stored at ca. 253 K after distillation. Acetic acid (Tokyo Kasei Chem. Co.) was used without further purification. No impurities were detected in them by gas chromatography.

Reactions. Catalytic oxidations of acetaldehyde and acetic acid were carried out at 573 K with a conventional flow reactor.

The standard procedure was as follows: Catalysts (0.015–2 g) were loaded in a reactor and the temperature was raised at a rate of 10 $K \cdot min^{-1}$ in a mixture of N_2 (ca. 63 $cm^3 \cdot min^{-1}$) and O_2 (ca. 7 $cm^3 \cdot min^{-1}$) streams up to 573 K and kept for 1 h. Then acetaldehyde or acetic acid was introduced by passing a part of the stream (N_2 only) through an evaporator saturator. The reactant gas composition for the standard conditions was acetaldehyde : O_2 : N_2 = 2% : 10% : 88% for the oxidation of acetaldehyde, and acetic acid : O_2 : N_2 = 2% : 10% : 88% for the conversion of acetic acid. The total flow rate for each reaction was ca. 70 $cm^3 \cdot min^{-1}$ and the carbon balance of each reaction was usually more than 90%. The reaction was carried out at 573 K. It was confirmed that the conversion of acetaldehyde in the blank run without catalyst was less than 2%.

Analysis. Products of flow experiments were analyzed by gas chromatography. Products in the gas phase at the outlet of the reactor were sampled by use of a stainless-steel sampler kept at 413 K. Products were analyzed by Porapak Q and Molecular Sieve 5A columns, as described previously (*4*). Each peak assignment in GC spectrum was confirmed by MS.

Other measurements. Most of the amount of irreversible absorption or adsorption of pyridine at 403 K and the rate of the reduction by CO were cited from Refs. (*1, 7*) and Ref. (*2*), respectively, and are used as a measure of the amount of Brønsted acid site and that of the reducibility (or oxidizing ability) of catalyst, respectively. The rate of reduction of PW_{12} by CO and the amount of pyridine adsorbed on $Cs_{2.85}PMo_{12}$ were measured according to the literature (*1, 2, 7*).

RESULTS

Oxidation of acetaldehyde. Figure 1a shows the time course of the oxidation of acetaldehyde over PMo_{12}. The conversion and selectivity reached almost constant after 2 h. The main products were acetic acid, methyl acetate, CO, and CO_2. A very small amount of methanol or formaldehyde was observed for PMo_{12} above the conver-

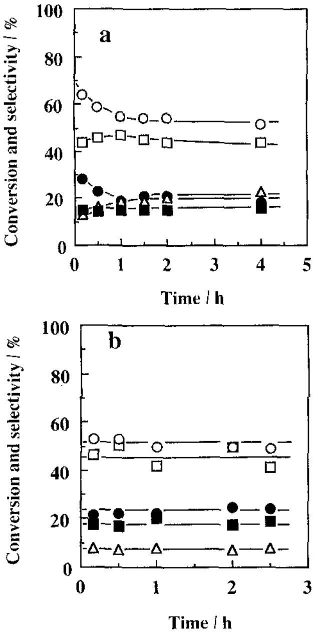


FIG. 1. Time courses of the oxidation of acetaldehyde over $H_3PMo_{12}O_{40}$ and $Cs_{2.85}H_{0.15}PMo_{12}O_{40}$. Figures 1a and 1b correspond to the time courses of the oxidation over $H_3PMo_{12}O_{40}$ and $Cs_{2.85}H_{0.15}PmO_{12}O_{40}$, respectively. (○) conversion. Selectivities (□) to acetic acid, (△) to methyl acetate, (●) to CO, and (■) to CO_2. Catalyst weight: 500 mg and 300 mg for $H_3PMo_{12}O_{40}$ and $Cs_{2.85}H_{0.15}PMo_{12}O_{40}$, respectively. Reaction temperature: 573 K.

sion of 30%. The same products were observed for M_xPMo_{12} (M = Na, Cs; x = 1–3) and PW_{12}. In the case of $Cs_{2.85}PMo_{12}$, the conversion and selectivity changed little with time (Fig. 1b). Na_xPMo_{12} (x = 1, 2), Cs_xPMo_{12} (x = 1, 2, 2.5, 3), and PW_{12} showed time courses similar to those of PMo_{12}, while Na_3PMo_{12} was similar to $Cs_{2.85}PMo_{12}$.

The pressure dependencies were as in Eq. (12) at 573 K for PMo_{12}, in the range of the partial pressures of acetaldehyde, 0.004–0.05 atm and oxygen, 0.1–0.3 atm. Conversion was kept below 30% for the determination of the pressure dependency. The pressure dependencies are similar to those observed for the oxidation of methacrolein (*8*).

$$-d[CH_3CHO]/dt = k \cdot P^{0.9}_{CH_3CHO} P^{0.1}_{O_2}. \quad (1)$$

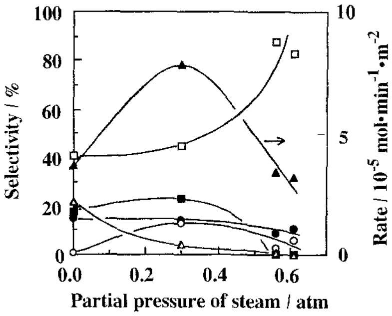


FIG. 2. Dependencies of the rates and selectivities on the partial pressure of steam for the acetaldehyde oxidation over $H_3PMo_{12}O_{40}$ at 573 K. Selectivities (□) to acetic acid, (△) to methyl acetate, (○) to methanol, (●) to CO, and (■) to CO_2. (▲) rate of the conversion of acetaldehyde. Catalyst weight: 0.2–0.5 g.

Dependency of the rates and selectivities on the partial pressure of steam is shown in Fig. 2. Conversions of acetaldehyde in these experiments were between 41 and 54%. The rate and the selectivities to CO, methanol, and methyl acetate increased by the addition of 0.3 atm of steam. Further addition of steam decreased the rates of formations of CO, methanol, and methyl acetate and increased the selectivity to acetic acid up to ca. 80%.

Dependency of selectivity on conversion. Figure 3 shows the selectivity vs conversion relationship for PMo_{12} obtained under the

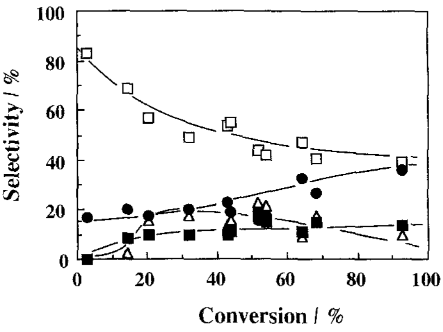


FIG. 3. Conversion dependency of the selectivity of acetaldehyde oxidation over $H_3PMo_{12}O_{40}$. Catalyst weight: 0.015–2.0 g. Reaction temperature: 573 K. Symbols are the same as those in Fig. 2.

TABLE 1

Oxidation of Acetaldehyde at 573 K

Catalysts	Surface area ($m^2 \cdot g^{-1}$)	Conv. (%)	Overall rates[a] ($= r_1 + r_2$)	Selectivity (%)				Rates and ratio estimated		
				Acetic acid	Methyl acetate	CO	CO_2	R_s[b]	R_c[b]	R'_s[b]
$H_3PMo_{12}O_{40}$	1.8 (0.16[c])	20	5.9	57	16	18	10	5.5	0.4	0.36
$NaH_2PMo_{12}O_{40}$	1.4 (0.46)	39	4.3	49	10	15	26	3.5	0.8	0.29
$Na_2HPMo_{12}O_{40}$	2.1 (0.47)	30	3.6	44	19	24	13	3.2	0.4	0.46
$Na_3PMo_{12}O_{40}$	2.9 (0.47)	16	1.6	47	9	15	30	1.3	0.3	0.28
$CsH_2PMo_{12}O_{40}$	0.4 (1.40)	26	0.9	58	4	8	30	0.7	0.2	0.12
$Cs_2HPMo_{12}O_{40}$	0.4 (1.48)	24	0.6	56	7	23	13	0.5	0.1	0.20
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	18.8 (0.29)	37	27.7	43	3	12	42	18.2	9.5	0.12
$Cs_{2.85}H_{0.15}PMo_{12}O_{40}$	91.8 (0.26)	38	8.2	46	4	25	25	5.8	2.4	0.15
$Cs_3PMo_{12}O_{40}$	82.2 (0.97)	28	1.6	56	2	18	24	1.2	0.4	0.07
$H_3PW_{12}O_{40}$	4.7 (1.30)	18	0.5	38	27	19	16	0.5	0.03	0.56

[a] Steady-state rates. Unit: $10^{-5} \cdot mol \cdot min^{-1} \cdot g^{-1}$.

[b] Unit: $10^{-5} \cdot mol \cdot min^{-1} \cdot g^{-1}$ for R_s and R_c and arbitrary unit for R'_s. Rates and the ratio estimated according to Eqs. (5), (6), and (9). $R_s = r_1 - r_4 - r_5$; $R_c = r_2 + r_4 + r_5$; $R'_s = r_3/r_1$ (estimated by $(r_3 - r_5)/R_s$); see text.

[c] The number in parenthesis is catalyst weight.

standard conditions (573 K) with different amounts of PMo_{12}.

The selectivity to acetic acid monotonously decreased with increase in conversion. As for byproducts, the formation of methyl acetate started to increase when the conversion exceeded 10%, and then slightly decreased with increase in conversion. The formation of CO and CO_2 increased with conversion. CO was significantly formed even at low conversion. Above the conversion of 30%, a small amount of methanol or formaldehyde, which is not shown in Fig. 3, was observed. Similar variations of the selectivity with conversion were observed for the other 12-molybdophosphates. In the case of PW_{12}, the selectivity to methyl acetate was considerably higher (27% at 18% conversion).

Effect of alkali salt formation. The effects of alkali salt formation on the catalytic activity and selectivity were examined. The results are summarized in Table 1, and the overall rates and the selectivities to acetic acid at the conversion level of 20–40%, where the selectivities did not change much, are shown in Fig. 4. Linear correlations between the conversion and W (weight of catalyst)/F (flow rate) were confirmed for PMo_{12}, Na_3PMo_{12}, $Cs_{2.85}PMo_{12}$, and Cs_3PMo_{12} up to the conversion level of ca. 50%. Therefore, the rates were calculated from the slopes. The rate divided by the surface area (the surface area measured after the reaction) decreased with increase in the alkali contents, while the selectivity to acetic acid did not change much.

A similar monotonous decrease of the catalytic activity is also found when the rate after 5 min, a measure of the initial rate, was plotted against the alkali content.

Conversion of acetic acid. When the acetic acid was fed over heteropoly compounds at 573 K, methyl acetate, acetone, and CO_x ($= CO + CO_2$) were produced as shown in Table 2. Only a little acetone was detected over less acidic Na_3PMo_{12} and Cs_3PMo_{12}, while it was the main product for PW_{12}. The overall rate was proportional to $P_{CH_3COOH}^{0.4-0.9}$ for PMo_{12}, Na_3PMo_{12}, Cs_3PMo_{12}, and PW_{12}, while the dependencies were small on P_{O_2}. The rate was a little smaller than

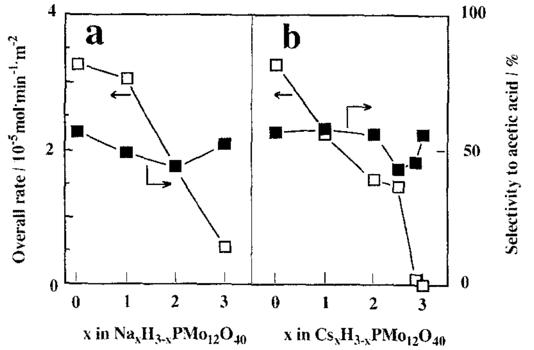


FIG. 4. Effect of alkali salt formation on the catalytic activity and selectivity of acetaldehyde oxidation. (□) the rate per surface area, and (■) the selectivity to acetic acid at 20–40% conversion. Reaction temperature: 573 K.

approximately half the rate of the oxidation of acetaldehyde for 12-molybdophosphates. The order of the rate per surface area was as follows: $PMo_{12} > PW_{12} > Na_2PMo_{12} \gg Na_3PMo_{12} > Cs_{2.85}PMo_{12} > Cs_3PMo_{12}$. In one experiment with PMo_{12}, the rate and selectivity of acetic acid conversion were measured by changing the feed gas from acetaldehyde to acetic acid after the oxidation of acetaldehyde was carried out. The rate and selectivity obtained in this experiment were similar to those in Table 2.

DISCUSSION

Reaction scheme. First, possible effects of steam on the acetaldehyde oxidation (Fig. 2) are discussed. The increase in rate caused by the addition of 0.3 atm steam may be explained by the acceleration of the diffusion of oxide ions (redox carrier) (*2*), the direct involvement in the reaction (*8*), and/or the promotion of the removal of products (*8*). The decrease in rate by the further addition of steam may be due to the inhibition of acetaldehyde absorption by steam. The effects on the selectivity would be explained by the different extents of these effects on each step in Eq. (3) as discussed later in this section.

The partial pressure of steam formed by the oxidation reactions is estimated to be less than 0.01 atm at the conversion of 50% over PMo_{12}. With this low level of pressure of steam, the steam formed during the reaction does not affect the rate of the selectivity very much (see Fig. 2).

As shown in Fig. 3 for PMo_{12}, the selectiv-

TABLE 2

Conversion of Acetic Acid at 573 K

Catalysts	Overall rates[a]	Selectivity[b] (%)				Rates[c]	
		Methyl acetate	Acetone	CO	CO_2	Methyl acetate + acetone	$CO + CO_2$ ($= R_c'$)
$H_3PMo_{12}O_{40}$	87	16	11	17	56	62	25
$Na_2HPMo_{12}O_{40}$	47	9	16	17	58	32	15
$Na_3PMo_{12}O_{40}$	13	6	0	22	72	3	10
$Cs_{2.85}H_{0.15}PMo_{12}O_{40}$	4[d]	10	7	18	65	2	1.7
$Cs_3PMo_{12}O_{40}$	1[d]	7	0	28	65	0.3	0.7
$H_3PW_{12}O_{40}$	60[d]	0	45	0	45	~60	~0

[a] Steady-state rates. Unit: $10^{-7} \cdot mol \cdot min^{-1} \cdot m^{-2}$.

[b] Conversion was kept 4–28%, in which the selectivity of each catalyst changed only a little.

[c] Unit: $10^{-7} \cdot mol \cdot min^{-1} \cdot m^{-2}$. Rates of the acetic acid conversion into methyl acetate + acetone and $CO + CO_2$ estimated similarly to R_s and R_c, respectively.

[d] Rates estimated by the extrapolation of the respective log (rate) vs log (concentration of acetic acid) linear plots to the concentration of acetic acid of 2%.

ity to methyl acetate increased as that to acetic acid decreased with increase in conversion from 15 to 30%. Further, a large amount of methyl acetate was formed in the acetic acid conversion. Therefore, methyl acetate is most probably formed according to Eqs. (2-1) and (2-2):

$$2CH_3COOH \rightarrow CH_3COOCH_3 + CO + H_2O \quad (2)$$

$$CH_3COOH \rightarrow CH_3OH + CO \quad (2\text{-}1)$$

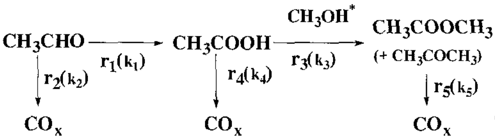
$$CH_3OH + CH_3COOH \rightarrow CH_3COOCH_3 + H_2O. \quad (2\text{-}2)$$

Ready CO elimination from carboxylic acid has been observed in the acid-catalyzed reaction of isobutyric acid over heteropoly acid (*9*). Akimoto *et al.* have also reported the formation of acetone by the CO elimination in the oxidative dehydrogenation of isobutyric acid (*10*). Formation of methanol and formaldehyde, the latter being an oxidation product of the former, also indicates that the elimination of CO from acetic acid (Eq. (2-1)) actually took place. The formation of methanol is clearer in the presence of steam (○, Fig. 2). Only a small amount of methanol or formaldehyde was observed for the oxidation of acetaldehyde probably because the methanol formed rapidly reacts with acetic acid to form methyl acetate; that is, Eq. (2-2) is very rapid.

The decrease of acetic acid at high conversions is mainly due to the successive oxidation of acetic acid because the amounts of CO and CO_2 increased in parallel. The reduction of the selectivity to methyl acetate is mainly due to the decrement of the amount of acetic acid (see Eq. (2)). It was confirmed that methyl acetate is much less reactive than acetic acid.

The selectivities to acetic acid and CO_x extrapolated to 0% conversion were 85 and 15%, respectively. This shows that there are two paths in the first steps: one is the selective oxidation; $CH_3CHO \rightarrow CH_3COOH$, and the other is complete oxidation; $CH_3CHO \rightarrow CO_x$.

Therefore, the reaction scheme of acetaldehyde oxidation is proposed as



(3)

where k_i's (i = 1–5) are the rate constants and r_i's are the rates of the respective reactions. (*Methanol was formed from acetic acid according to Eq. (2-1).) For example, r_1 is defined as the rate of the reaction $CH_3CHO \rightarrow CH_3COOH$. Note that this is not the rate of the formation of acetic acid (or the increase of its amount) which is $r_1 - r_3 - r_4$. Hereafter, r_i's are expressed on the C_2 (= acetaldehyde)-basis.

The ketonization of aliphatic acid has been considered to proceed involving acyl carbenium ion (11–13) or acid anhydride (*17*). At present, the former is more probable for the formation of acetone because of reactivity of acetic anhydride much lower than that of acetic acid (*13*). So, we assume that acetone is formed according to Eqs. (4-1), (4-2), and (4-3), as was reported for

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O \quad (4)$$

$$CH_3COOH \rightarrow CH_3CO^+ + OH^- \quad (4\text{-}1)$$

$$CH_3COOH \rightarrow CH_3COO^- + H^+ \quad (4\text{-}2)$$

$$CH_3CO^+ + CH_3COO^- \rightarrow CH_3COCH_3 + CO_2 \quad (4\text{-}3)$$

Cr_2O_3, Fe_2O_3, and ZrO_2-Al_2O_3 (*11–13*). All of these catalysts have been reported to be acidic (*14–16*), so that acetone observed in the present study is likely produced from acetic acid on the acidic site. By contrast, acetone was little formed in the oxidation of acetaldehyde. This may be due to the lower concentration of acetic acid or due to the suppression of the adsorption of acetic acid by coexisting acetaldehyde in the case of the oxidation of acetaldehyde.

Correlation between catalytic properties (activities and selectivities) and chemical properties (oxidizing ability and acidity).

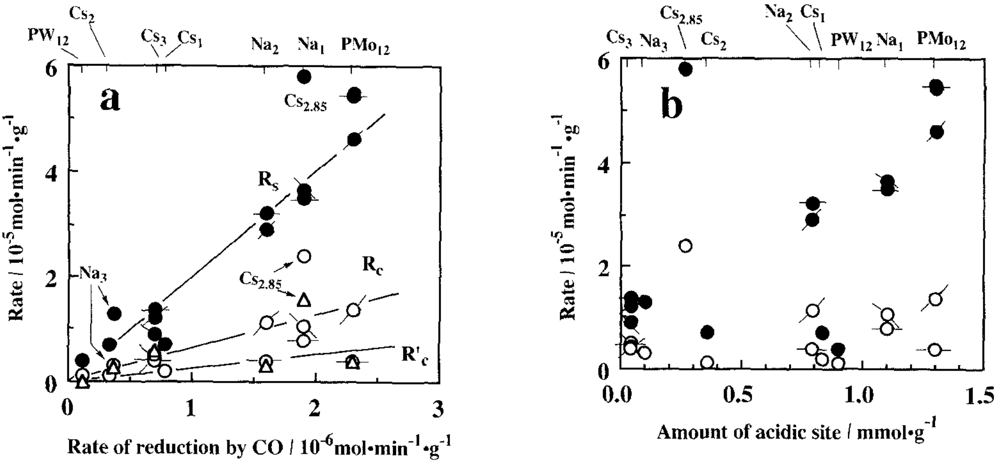


FIG. 5. Correlations between the rates (R_s, R_c, and R'_c) and the reducibilities or the amount of acid of heteropoly compounds. (●) R_s (= $r_1 - r_4 - r_5$), (○) R_c (= $r_2 + r_4 + r_5$), and (△) R'_c; see Tables 1 and 2. Figure 5a shows the correlation between the rates (R_s, R_c, and R'_c) and the rate of reduction by CO. Figure 5b shows the correlation between the rates (R_s and R_c) and the amount of acid sites measured by pyridine uptake. Flags attached indicate different lots. M_x denote $M_xH_{3-x}PMo_{12}O_{40}$.

We have previously reported (*4*) that the oxidation of acetaldehyde is an ordinary surface-type reaction as is usually observed in heterogeneous catalysis: The overall rate of acetaldehyde oxidation ($r_1 + r_2$) was proportional to the specific surface area of the catalyst and linearly correlated with the oxidizing ability of catalyst surface, which was measured by the reduction of catalyst by CO.

In the present study, factors controlling the selectivity of acetaldehyde oxidation, that is, the correlations between each of the k_i's or r_i's and the redox or acidic properties of catalysts, are discussed.

Here, let us define R_s and R_c. R_s is the sum of the rates of formation of acetic acid, methyl acetate, and acetone on the C_2-basis. R_s is the measure of the rate of the selective oxidation and can be estimated by the equation

$$\begin{aligned} R_s &\equiv r_1 - r_4 - r_5 \\ &= \text{rate [acetic acid formation]} \\ &\quad + 2 \times \text{rate [methyl acetate} \\ &\qquad \text{(+ acetone) formation]}. \end{aligned} \tag{5}$$

In Eq. (5), it is taken into account that one molecule of methyl acetate or acetone is formed from two molecules of acetic acid, according to Eqs. (2) and (4). Note again that, for example, the rate of acetic acid formation is not r_1, but $r_1 - r_3 - r_4$.

R_c is the measure of the complete oxidation and can be estimated by subtracting the amounts of methyl acetate and acetone from the whole amounts of CO_x as in Eq. (6), since an equimolecular amount of CO is formed with methyl acetate (Eq. (2)) and an equimolecular amount of CO_2 is formed with acetone (Eq. (4)).

$$\begin{aligned} R_c &\equiv r_2 + r_4 + r_5 \\ &= \tfrac{1}{2} \times \{\text{rate } [CO_x \text{ formation}] \\ &\quad - \text{rate [methyl acetate} \\ &\qquad \text{(+ acetone) formation]}\}. \end{aligned} \tag{6}$$

The values of R_s and R_c thus calculated are shown in Table 1.

Figure 5 shows the correlation between the oxidizing abilities of the catalysts measured with CO (a surface redox property (*2, 4*)) and $R_s \equiv r_1 - r_4 - r_5$ or $R_c \equiv r_2 + r_4 + r_5$. R_s and R_c increased linearly with the increase in the oxidizing ability, except for $Cs_{2.85}PMo_{12}$ and Na_3PMo_{12}, which deviated a little. A similar linear correlation was observed when those values were normalized to the surface areas of catalysts. On the other hand, correlations are hardly found when R_s or R_c (per either weight or surface area) is plotted against the amount of acidic sites measured by the pyridine uptake. The infrared spectra of pyridine held by catalysts showed that they were essentially of Brønsted type (*1, 18*) (Fig. 5b).

The reason for the high R_s and R_c values for $Cs_{2.85}PMo_{12}$ and Na_3PMo_{12} (Fig. 5a) may be its higher oxidation state under the reaction conditions. The color of $Cs_{2.85}PMo_{12}$ and Na_3PMo_{12} after having been used as catalysts was more yellowish than the other catalysts and the selectivity and conversion changed little with time as shown in Fig. 1b. All other catalysts showed deactivation for the first 1–2 h (Fig. 1a) accompanied by the color change to dark green, indicating greater extents of catalyst reduction. The fact that $Cs_{2.85}PMo_{12}$ and Na_3PMo_{12} were more highly oxidized may be explained by their small rate of reduction by acetaldehyde and relatively great rate of reoxidation by O_2 based on the redox cycle as described previously (*1, 2*). Dependencies of R_s and R_c on the partial pressure of CH_3CHO determined for PMo_{12} were quite different ($P^{1.5}_{CH_3CHO}$ for R_s and $P^{0.5}_{CH_3CHO}$ for R_c), while they were both small on P_{O_2}. The dependencies suggest that acetaldehyde weakly adsorbed is more selectively converted to acetic acid, and those strongly adsorbed mainly to CO_x.

r_3, r_4, and r_5 of acetaldehyde oxidation (Eq. (3)) may be discussed based on the results of acetic acid conversion. For example, rates of the conversion of acetic acid into CO_x for the latter reaction (denoted by R_c'), can be estimated by subtracting the amounts of methyl acetate plus acetone from the entire amount of CO_x. We regard R_c' to be the measure of $r_4 + r_5$ in Eq. (3). R_c', thus estimated, is shown in Table 2. R_c' increased with the increase of the oxidizing ability of catalysts (Fig. 5a, △). The change in the selectivity was very small in the conversion range of 4–28%, indicating that r_5 is much smaller than r_4. So, $R_c' = r_4$ and the linear correlation shown in Fig. 5a (△) indicates that r_4 is controlled by the oxidizing ability of the catalysts. R_c' and the rate of formation of methyl acetate plus acetone ($r_3 - r_5$) for the conversion of acetic acid were proportional to $P^{0.6\pm0.3}_{CH_3COOH}$ in the acetic acid conversion over each catalyst. k_4's approximately estimated by assuming $R_c' = r_4 = k_4 \cdot P^{0.6}_{CH_3COOH}P^{0}_{O_2}$ are given in Table 3.

R_c' was smaller than R_s and R_c as seen in Fig. 5a. Moreover, the value of $r_4 + r_5$ during the oxidation of acetaldehyde was probably much smaller than R_c', since the concentration of acetic acid during the oxidation of acetaldehyde (acetaldehyde: 2%) was much lower than that during the conversion of acetic acid (2%) and the overall rate of acetic acid conversion was proportional to [acetic acid]$^{0.4-0.9}$.

Therefore, $r_4 + r_5$ may be much smaller than R_s and R_c. By neglecting $r_4 + r_5$ in Eqs. (5) and (6), Eqs. (7) and (8) are obtained, respectively.

$$R_s \cong r_1 \qquad (7)$$

$$R_c \cong r_2. \qquad (8)$$

Consequently, linear correlations as shown in Fig. 5a (● and ○) indicate that r_1 and r_2 increase with the increase in the oxidizing ability of the catalyst. k_1 and k_2 of each catalyst were estimated from Eqs. (7) and (8) on the assumption that $r_1 = k_1 \cdot P^{1.5}_{CH_3CHO}P^{0}_{O_2}$ and $r_2 = k_2 \cdot P^{0.5}_{CH_3CHO}P^{0}_{O_2}$, as observed for PMo_{12}. The values are collected in Table 3.

Next, the factor controlling r_3 in Eq. (3) is discussed. As the rate of formation of methyl acetate plus acetone is equal to $r_3 - r_5$, and r_5 is very small as discussed above, Eq. (9) is derived.

$$r_3 - r_5 = 2 \times \text{rate [methyl acetate (+ acetone) formation]} \cong r_3. \qquad (9)$$

Here, we define $R_s' \equiv r_3/r_1$, that is, the relative rate of methyl acetate plus acetone to that of acetic acid formation. Therefore, R_s' may be regarded to be a measure of k_3.

TABLE 3

Rate Constants of Several Steps of Acetaldehyde Oxidation Estimated

Catalysts	k_1[a]	k_2[b]	k_3[c]	k_4[d]
$H_3PMo_{12}O_{40}$	1.3×10^2	5.3×10^{-4}	2.2×10^{-3}	8.8×10^{-4}
$Na_2HPMo_{12}O_{40}$	7.5×10^1	5.3×10^{-4}	8.9×10^{-4}	4.2×10^{-4}
$Na_3PMo_{12}O_{40}$	3.0×10^1	4.0×10^{-4}	2.5×10^{-4}	8.4×10^{-4}
$Cs_{2.85}H_{0.15}PMo_{12}O_{40}$	1.4×10^1	3.2×10^{-3}	6.5×10^{-3}	5.5×10^{-3}
$Cs_3PMo_{12}O_{40}$	3.0×10^1	5.3×10^{-4}	9.1×10^{-4}	2.1×10^{-3}
$H_3PW_{12}O_{40}$	1.2×10^1	4.0×10^{-5}	$\sim 6.8 \times 10^{-3}$	~ 0

[a] Unit: $mol^{-0.5} \cdot min^{-1} \cdot g^{-1}$. Estimated by the results of acetaldehyde oxidation.
[b] Unit: $mol^{0.5} \cdot min^{-1} \cdot g^{-1}$. Estimated by the results of acetaldehyde oxidation.
[c] Unit: $mol^{0.4} \cdot min^{-1} \cdot g^{-1}$. Estimated by the results of acetic acid conversion.

By using R_s and $r_3 - r_5$ in place of r_1 (see Eq. (7)) and r_3 (see Eq. (9)), respectively, R_s' is estimated based on the results of acetaldehyde oxidation as shown in Table 1.

Figure 6a shows the correlation between the amount of Brønsted acid and R_s'. A fair correlation was observed. On the other hand, little correlation was observed between R_s' and the oxidizing ability of catalysts (Fig. 6b). If one assumes that $r_3 - r_5$ is equal to r_3 (Eq. (9)) and $r_3 = k_3 \cdot P_{CH_3COOH}^{0.6} P_{O_2}^{0}$, as was observed for PMo_{12} in the acetic acid conversion, k_3 can be estimated approximately based on the results of acetic acid conversion. k_3 thus estimated is shown in Table 3. A good correlation was found between k_3 (see Table 3 and ● in Fig. 6a) and the amount of acid sites. Therefore, the fair correlations in Fig. 6a (●, ○) indicate that the methyl acetate and acetone formation is an acid-catalyzed reaction.

The selectivity to methyl acetate in the oxidation of acetaldehyde over PW_{12} was higher than those of 12-molybdophosphates at the same conversion level. This may be

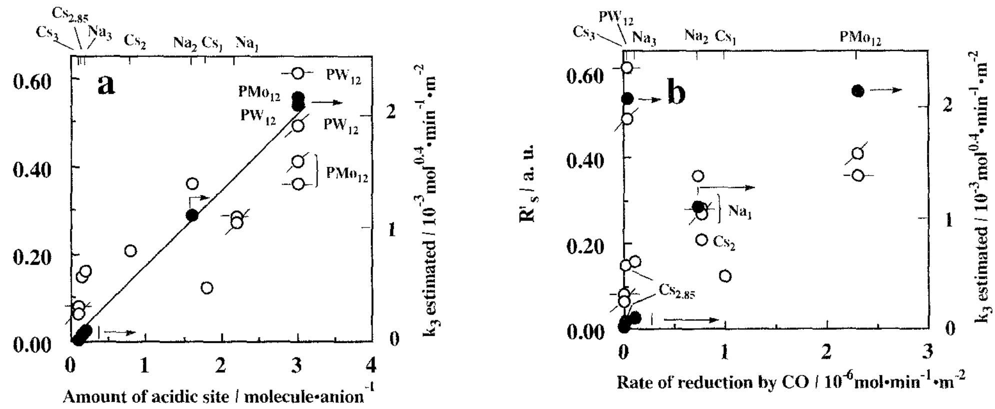


FIG. 6. Correlations between R_s' or sum of the rates of methyl acetate and acetone formation and (a) the reducibilities or (b) the acidities of heteropoly compounds. (○) R_s' (= r_3/r_1 (a.u.: arbitrary unit), see Table 1), and (●) sum of the rates of methyl acetate and acetone formation (see Table 2). Figure 6a shows the correlation between R_s' or sum of the rates of formation of methyl acetate plus acetone or k_3 and the amount of Brønsted acid sites. Figure 6b shows the correlation between R_s' or k_3 and the rate of reduction of catalyst by CO. Flags attached and abbreviations are the same as those in Fig. 5.

due to the stronger acid strength and low oxidizing ability of PW_{12}. Little formation of acetone over less acidic Na_3PMo_{12} and Cs_3PMo_{12} in acetic acid conversion is also reasonable.

The present results imply that the heteropoly compounds with high oxidizing abilities and the low amounts of Brønsted acidities would bring about a high yield to acetic acid.

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