

# Characteristics of Heteropoly Compounds as Catalysts for Selective Oxidation

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As catalysts for selective oxidation, heteropoly compounds such as 12-molybdophosphoric acid ( $H_3PMo_{12}O_{40}$ ) and its salts have been investigated, in relation to the acidic property, the contribution of bulk acid, the effect of steam in the feed gas, the thermal stability, the effect of countercations, and the oxidation activity and selectivity. It was found that, though the heteropoly compounds are different in several physical characteristics from ordinary mixed metal oxides, the catalytic actions can be understood, to a great extent, from the acid-base properties much as in the case of mixed-oxide catalysts.

## INTRODUCTION

Methyl methacrylate is in great demand as a raw material of so-called organic glass. It is manufactured by the acetone cyanohydrin process; no process based on the direct oxidation of methacrolein to methacrylic acid has yet achieved commercial success. However, increasing attention has been given to the improvement of the oxidation catalysts; more than 100 patents have appeared concerning the catalysts during the past decade. From a survey of the patent literature, Ohara and Niina (1) stated that the majority of catalysts recently proposed are heteropoly compounds containing both molybdenum and phosphorus as essential elements.

As for such heteropoly compounds as 12-molybdophosphoric acid ( $H_3PMo_{12}O_{40}$ ) and its salts, the structure and certain physical properties have been well determined in the fields of crystallography and inorganic chemistry (2-4). It should be noted that 12-molybdophosphoric acid is eminent as an oxidizing agent as well as an acid (4). On the other hand, the patent literature indicates that the heteropoly compounds are effective as catalysts for: (i) a variety of "acid-catalyzed reactions" and (ii) "acid-

formation-type" selective oxidations. Recently, several scientific studies have also reported on the catalytic action for the dehydration of 2-propanol (5), and the formation of methacrylic acid (5-11), and that of furan (12, 13).

It may be interesting to study the catalytic action of heteropoly compounds in connection with their well-defined structure, i.e., the Keggin structure (2). However, it should be more important to examine whether the catalytic action of heteropoly compounds can be differentiated from that of ordinary mixed-oxide catalysts.

We have studied selective oxidation on the basis of the idea that the catalytic action is governed by two functions: (i) the activation of a reactant, such as olefin and aldehyde, on the acidic sites and (ii) an intrinsic oxidation activity, which is connected with both the basic character and the metal-oxygen bonding strength (14).

The first purpose of this paper is to show several characteristics of the heteropoly compounds that are different from those of ordinary mixed metal oxides. The second purpose is to confirm if the catalytic action of the heteropoly compounds can be understood on the basis of the acid-base proper-

ties much as in the case of ordinary mixed-oxide catalysts.

## EXPERIMENTAL

### Catalysts

The supported heteropoly compounds were used as catalysts. Salts of 12-molybdophosphoric acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) were prepared according to the principle reported by Tsigidinos (3). That is,  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot \alpha\text{H}_2\text{O}$  (Kanto Chemical Company) was dissolved in water and the required quantities of second metallic components were added to the solution. As the compounds we used carbonates for Cs, Rb, K, Na, Li, Ba, and Ag; acetates for Al and Cr; and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $(\text{BiO})_2\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$ , and  $\text{NH}_3$ . Certain salts of 12-molybdophosphoric acid, such as Cs, Rb,  $(\text{NH}_4)$ , Ag, and Bi salts, are insoluble and the precipitates were observed. Thereafter, 10- to 20-mesh pumice originating from volcanic rock which consists of macropores (the density is about 0.35 g/ml and the surface area is less than 0.3  $\text{m}^2/\text{g}$ ) and is chemically inert, was mixed with the solution which, in some cases, contained the precipitate. The mixture was evaporated with vigorous stirring below 200°C. The amount of pumice was about 8 liters (2.8 kg) per mole of 12-molybdophosphoric acid and the catalyst was calcined in a stream of oxygen at 380°C for 4 to 5 hr, unless otherwise indicated.

### Acidity Measurements

The acidity (number of acidic sites) of the catalysts was measured by means of the adsorption of  $\text{NH}_3$  or pyridine from the gas phase, using either a static or a pulse method. The technique of the measurements has been described in earlier papers (15, 16).

### Reaction Procedures

The vapor-phase oxidation of 1-butene, 1,3-butadiene, furan, methyl ethyl ketone (MEK), methanol, propylene, ethylene,

benzene, acrolein, methacrolein, and acetaldehyde, the dehydration of 2-propanol, the isomerization of 1-butene, and the decomposition of formic acid were carried out in an ordinary continuous-flow system. The reactor and experimental procedures were the same as those employed in the earlier works (12-16).

## RESULTS

### Effect of the Amount of Supported Heteropoly Acid

A series of catalysts with different amounts of supported 12-molybdophosphoric acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) was prepared (all calcined at 380°C) and the acidity and the catalytic activity for several reactions were compared. First, 0.5 to 1.0 g of catalyst was titrated in water with 0.1 N NaOH. According to the titer at pH = 8, it was concluded that  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  in a calcined catalyst is neutralized as follows:

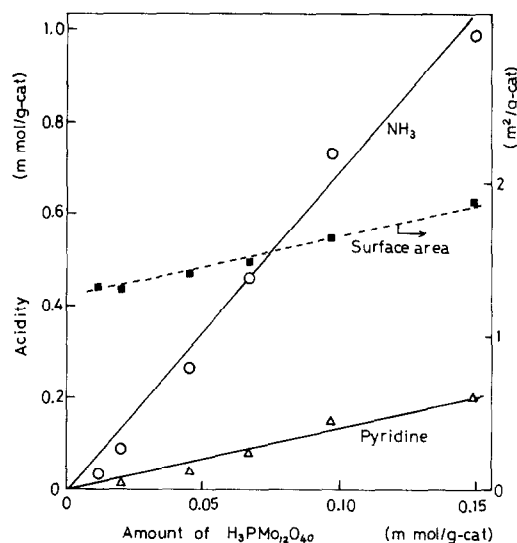
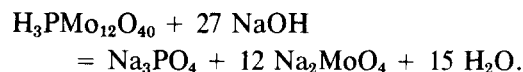


FIG. 1. Acidity and surface area as a function of the amount of supported  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . (○) Irreversible adsorption of  $\text{NH}_3$  at 200°C; (△) pyridine required to poison the isomerization activity for 1-butene at 200°C; (■) surface area.

As may be seen in Fig. 1, the surface area is markedly greater than that of pumice (less than  $0.3 \text{ m}^2/\text{g}$ ) and increases, to a small extent, with an increase in the amount of supported  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , whereas the acidities obtained from both the amount of  $\text{NH}_3$  irreversibly adsorbed at  $200^\circ\text{C}$  and the amount of pyridine required to poison the isomerization activity for 1-butene at  $200^\circ\text{C}$  increase proportionally to the amount of supported  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ .

It was also found that the amount of  $\text{NH}_3$  irreversibly adsorbed at  $200^\circ\text{C}$  is two times greater than the total number of protons of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , and that the amount of pyridine is equal to a half of the total number of protons; this value corresponds to the amount of pyridine required to form about 10 layers of pyridine on the surface. It is evident at least that basic molecules react not only with surface acid, but also with bulk acid.

The catalytic activities for several reactions are plotted as a function of the amount of supported  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  in Fig. 2. The

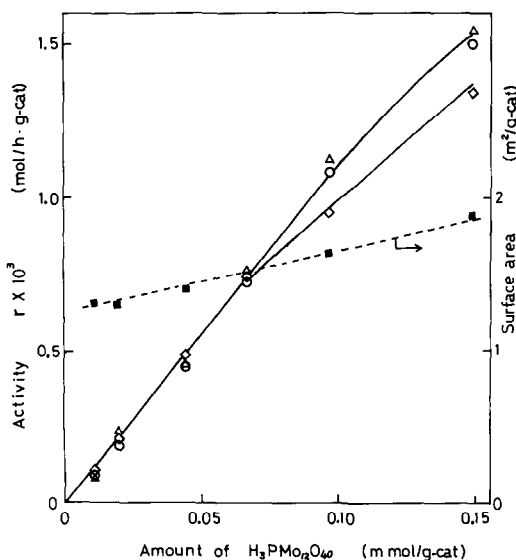


FIG. 2. Catalytic activity as a function of the amount of supported  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . (○) Oxidation of butadiene at  $344^\circ\text{C}$  and  $\text{C}_4\text{H}_6 = 1.0 \text{ mol}\%$  in air; (△) isomerization of 1-butene at  $190^\circ\text{C}$  and  $\text{C}_4\text{H}_8 = 1.0 \text{ mol}\%$  in air; (◇) dehydration of 2-propanol at  $130^\circ\text{C}$  and  $\text{C}_3\text{H}_7\text{O} = 1.65 \text{ mol}\%$  in air.

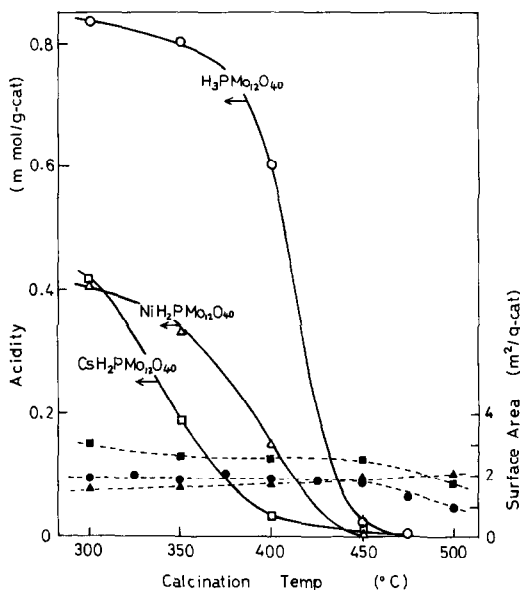


FIG. 3. Acidity and surface area as a function of the calcination temperature. (○, ●)  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ; (□, ■)  $\text{CsH}_2\text{PMo}_{12}\text{O}_{40}$ ; (△, ▲)  $\text{NiH}_2\text{PMo}_{12}\text{O}_{40}$  catalyst; (broken line) surface area. Acidity = amount of  $\text{NH}_3$  irreversibly adsorbed at  $200^\circ\text{C}$ .

catalytic activities increase proportionally to the amount of supported  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , indicating that the catalytic activities are correlated closely with the bulk acid rather than with the surface area. The results are in conformity with those reported by Otake and Onoda (5) for the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  system.

#### Effect of Calcination Temperature

It is known that heteropoly compounds are decomposed at around  $400^\circ\text{C}$  (4). It, therefore, seems necessary to ascertain the stability of catalytic activity. Three series of catalysts, such as  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{CsH}_2\text{PMo}_{12}\text{O}_{40}$ , and  $\text{NiH}_2\text{PMo}_{12}\text{O}_{40}$ , calcined at a temperature in the range of  $300$  to  $500^\circ\text{C}$ , were prepared, and the acidity and the catalytic activity for several reactions were compared.

First, the surface area and the acidity as measured by means of the  $\text{NH}_3$  adsorption are plotted in Fig. 3. The acidity decreases sharply with the calcination at  $350$  to  $450^\circ\text{C}$ , whereas the surface area remains almost constant in that temperature range.

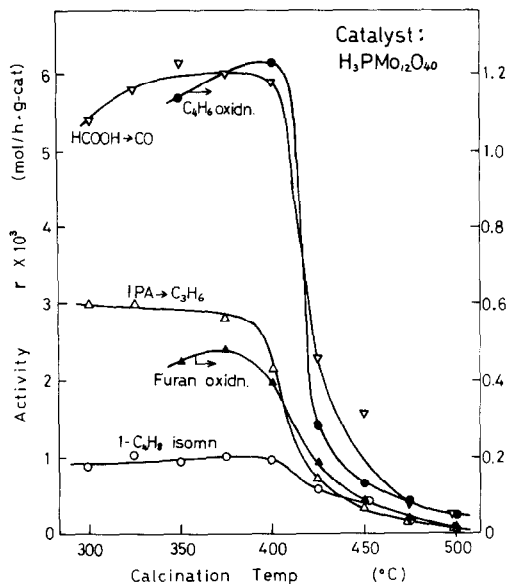


FIG. 4. Catalytic activities of the  $\text{H}_3\text{PMO}_{12}\text{O}_{40}$  catalysts as a function of the calcination temperature. (●) Oxidation of butadiene at  $335^\circ\text{C}$  and  $\text{C}_4\text{H}_6 = 1.0$  mol% in air; (▲) oxidation of furan at  $317^\circ\text{C}$  and  $\text{C}_4\text{H}_4\text{O} = 1.45$  mol% in air; (○) isomerization of 1-butene at  $250^\circ\text{C}$  and  $\text{C}_4\text{H}_8 = 1.0$  mol% in air; (Δ) dehydration of 2-propanol at  $160^\circ\text{C}$  and  $\text{C}_3\text{H}_8\text{O} = 1.65$  mol% in air; (▽) decomposition of formic acid at  $250^\circ\text{C}$  and  $\text{CH}_2\text{O}_2 = 2.3$  mol% in air.

The activity per gram of catalyst was compared for three acid-catalyzed reactions, such as the isomerization of 1-butene to 2-butenes, the dehydration of 2-propanol to propylene, and the decomposition of formic acid to CO, and for the oxidation of butadiene and furan. The results obtained from the  $\text{H}_3\text{PMO}_{12}\text{O}_{40}$  and  $\text{CsH}_2\text{PMO}_{12}\text{O}_{40}$  are shown in Figs. 4 and 5, respectively. The catalytic activity for all of the reactions tested declines sharply with the calcination at from  $400$  to  $430^\circ\text{C}$ .

#### Effect of Steam Addition to Feed Gas

In the patent literature, most contact oxidations using heteropoly compounds as catalysts were performed in the presence of 10 to 50 vol% of steam. Therefore, the effect of steam on the catalytic activity was examined for various reactions.

As may be seen in Fig. 6, the activity for

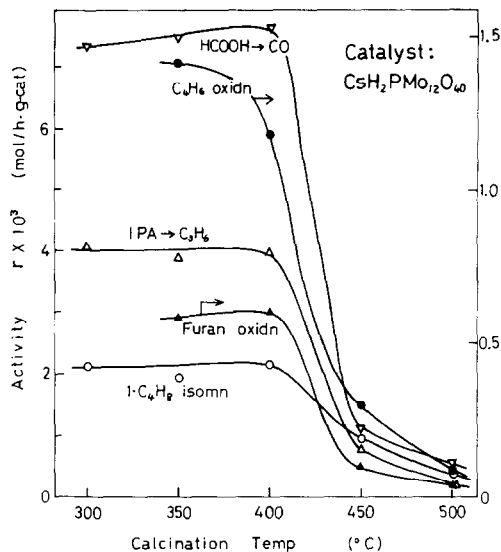


FIG. 5. Catalytic activities of the  $\text{CsH}_2\text{PMO}_{12}\text{O}_{40}$  catalyst as a function of the calcination temperature. Reaction conditions and symbols are the same as for Fig. 4.

such acid-catalyzed reactions as the isomerization of 1-butene, the dehydration of 2-propanol, the decomposition of formic acid to CO, and the oxidation of methanol to formaldehyde decreases gradually with an increase in the content of steam.

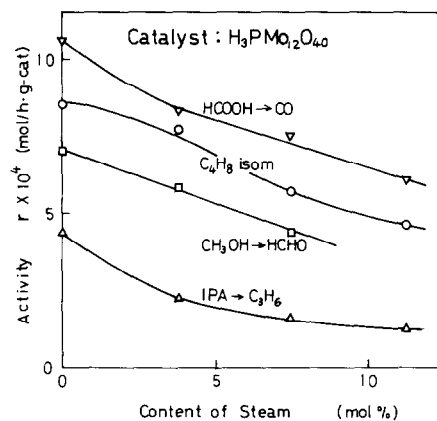


FIG. 6. Effect of steam addition to the feed gas on the catalytic activity. (○) Isomerization of 1-butene at  $190^\circ\text{C}$  and  $\text{C}_4\text{H}_8 = 1.0$  mol% in air; (Δ) dehydration of 2-propanol at  $130^\circ\text{C}$  and  $\text{C}_3\text{H}_8\text{O} = 1.65$  mol% in air; (▽) decomposition of formic acid at  $260^\circ\text{C}$  and  $\text{CH}_2\text{O}_2 = 2.3$  mol% in air; (□) oxidation of methanol at  $265^\circ\text{C}$  and  $\text{CH}_4\text{O} = 2.5$  mol% in air.

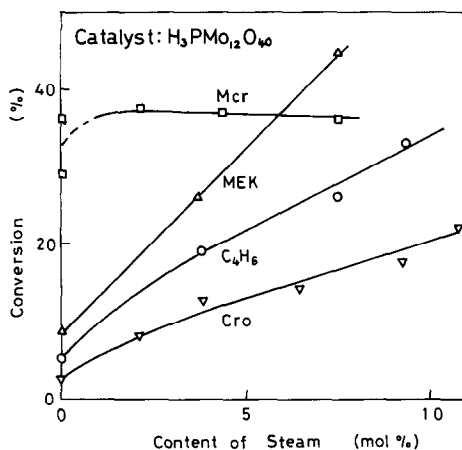


FIG. 7. Effect of steam addition to the feed gas on the catalytic activity. (○) Oxidation of butadiene to maleic anhydride at 322°C and  $C_4H_6 = 1.0$  mol% in air; (△) oxidation of MEK to acetic acid and acetaldehyde at 240°C and MEK = 1.5 mol% in air; (▽) oxidation of crotonaldehyde to furan at 278°C and  $C_4H_6O = 1.7$  mol% in air; (□) oxidation of methacrolein to methacrylic acid at 350°C and  $C_4H_6O = 1.6$  mol% in air.

On the other hand, the activity for such oxidations as that of butadiene to maleic anhydride, crotonaldehyde to furan, and MEK to acetic acid and acetaldehyde increases markedly with an increase in the steam content up to 10 mol% (Fig. 7). However, no clear effect of steam on the reaction rate can be observed in the case of the oxidation of methacrolein to methacrylic acid.

#### Characteristics of the $H_3PMo_{12}O_{40}$ Catalyst

In order to ascertain the characteristics of heteropoly compounds as oxidation catalysts, various kinds of organic compounds were passed through a bed of a  $H_3PMo_{12}O_{40}$  catalyst (20 g) under the following conditions: organic compounds = 1 to 2 mol% in air, steam = 7.5 mol%, total flow rate = 1.0 liter/min, reaction temperature = 200 to 400°C.

The results may be summarized as follows:

(i) Ethylene, propylene, and benzene are scarcely oxidized under these conditions.

Unlike the  $SnO_2-MoO_3$  (Sn/Mo = 2 atomic ratio) catalyst (17-19), propylene is not oxidized to acetone in the presence of steam.

(ii)  $C_4$ -olefins, such as 1- and 2-butenes, isobutylene, and 1,3-butadiene, can be oxidized under relatively severe conditions.

(iii) 1- and 2-butenes are oxidized mainly to maleic anhydride and  $CO_2$ , and the yield of butadiene is small (less than 3 mol%). MEK is not obtained, not even in the presence of steam (18, 20).

(iv) Butadiene is oxidized mainly to furan, maleic anhydride, and  $CO_2$ .

(v) Furan is oxidized to maleic anhydride and  $CO_2$ .

(vi) Acrolein and methacrolein are oxidized mainly to the corresponding unsaturated acids.

(vii) Crotonaldehyde is oxidized to furan, but not to crotonic acid (12, 21).

(viii) MEK is oxidized very easily to acetic acid and acetaldehyde.

(ix) Methanol is oxidized to formaldehyde.

(x) The other alcohols are dehydrated to the corresponding olefins, and they cannot be oxidized to ketones or aldehydes.

Table 1 shows the performances obtained from the  $H_3PMo_{12}O_{40}$  catalysts, together with those obtained from a  $V_2O_5-P_2O_5$  (P/V = 1.6 atomic ratio) mixed-oxide catalyst.

The kinetics for the oxidation of  $C_4$  compounds are summarized in Table 2. Except for the oxidation of crotonaldehyde, the reaction order in the oxygen concentration is high, 0.5 to 1.0, while that in the reactant concentration is small.

#### Effect of Countercations on Acidity

Salts of 12-molybdophosphoric acid,  $M_{x/n}^{n+}H_{3-x}PMo_{12}O_{40}$  (where  $x$  varies from 0 to 3), were prepared by adding various kinds of cations to  $H_3PMo_{12}O_{40}$ . The acidity was measured by means of the adsorption of  $NH_3$  (Figs. 8 and 9).

It was found that the acidity of salts,  $M_{x/n}^{n+}H_{3-x}PMo_{12}O_{40}$ , is strongly affected by

TABLE 1

 Selectivity of the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  (P/V = 1.6 Atomic Ratio) Catalysts<sup>a</sup>

No.	Oxidation Reactant → Product	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$		$\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$	
		Conversion (%)	Selectivity (mol%)	Conversion (%)	Selectivity (mol%)
1	Methacrolein → Methacrylic acid	60	60	50	54
2	Acrolein → Acrylic acid	40	61		
3	Furan → Maleic anhydride	98	61	98	50
4	Butadiene → Maleic anhydride	98	60	98	46
5	1-Butene → Maleic anhydride	90	50	90	42
6	MEK → $\text{CH}_3\text{COOH} + \text{CH}_3\text{CHO}$	92	82		
7	Methanol → HCHO	100	50		
8 <sup>b</sup>	Butadiene → Furan	70	23	70	9
9 <sup>b</sup>	Crotonaldehyde → Furan	95	45	95	19

<sup>a</sup> Reaction conditions:  $T = 250$  to  $400^\circ\text{C}$ , reactant-steam = 1 to 2-7.5 mol% in air, total flow rate = 1.0 liter/min, catalyst = 20 g.

<sup>b</sup>  $\text{O}_2/\text{reactant} = 4$  molar ratio.

the electronegativity (or acid-base property) of the cation as well as the amount of cation,  $x$ . The lower the electronegativity of the cation, the more markedly the acidity declines upon the substitution. It should also be noted that the acidity per gram of catalyst increases upon the substitution of an acidic cation, such as  $\text{Bi}^{3+}$  and  $\text{Fe}^{3+}$ .

The acidity of  $\text{M}_{x/n}^{n+}\text{PMo}_{12}\text{O}_{40}$  catalysts is plotted as a function of the electronegativity of metal ion,  $x_i$  (22), in Fig. 10. It was found that the acidity is closely related to the electronegativity, that is, the acid-base property, of counteranion.

TABLE 2

 Kinetics of Several Reactions on the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  Catalyst<sup>a</sup>

No.	Reactant of oxidation	Rate equation
1	Methacrolein	$r = k(R)^s \cdot (\text{O}_2)^{0.5} (\text{H}_2\text{O})^0$
2	Butadiene	$r = k(R)^s \cdot (\text{O}_2)^1 \cdot f(\text{H}_2\text{O})$
3	MEK	$r = k(R)^s \cdot (\text{O}_2)^1 \cdot f(\text{H}_2\text{O})$
4	Crotonaldehyde	$r = k(R)^0 \cdot (\text{O}_2)^0 \cdot f(\text{H}_2\text{O})$

<sup>a</sup>  $(R) = 0.05$  to 3 mol%,  $(\text{O}_2) = 2$  to 98 mol%,  $(\text{H}_2\text{O}) = 0$  to 8 mol%,  $s$ : less than 0.1,  $f(\text{H}_2\text{O})$ : rate increases with steam addition.

#### Effect of Counteranions on Catalytic Action for Butadiene Oxidation

The oxidation of butadiene to furan and maleic anhydride was chosen as a model reaction, and the effect of counteranions

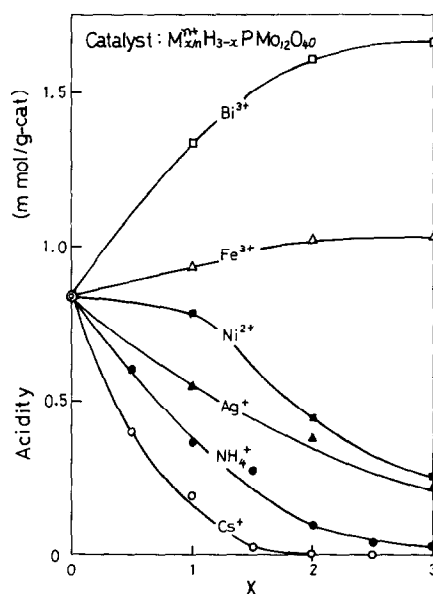


FIG. 8. Acidity of the salts of 12-molybdophosphoric acid as a function of the extent of proton replacement by a cation. Acidity = amount of  $\text{NH}_3$  irreversibly adsorbed at  $200^\circ\text{C}$ .

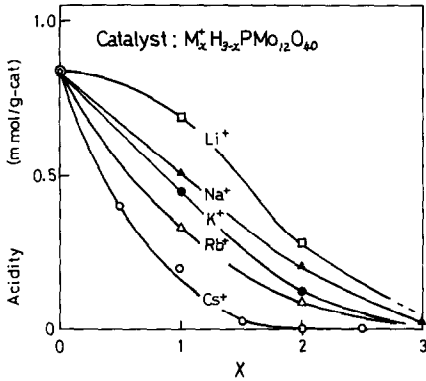


FIG. 9. Acidity of the salts of 12-molybdophosphoric acid as a function of the extent of proton replacement by a monovalent cation. Acidity = amount of  $\text{NH}_3$  irreversibly adsorbed at  $200^\circ\text{C}$ .

on the catalytic action for oxidation was studied. First, the activity of a series of  $\text{M}_{x/n}^{n+}\text{PMo}_{12}\text{O}_{40}$  catalysts is shown in Fig. 11 as a function of the electronegativity of counteranion,  $x_i$ . The range of activity variation is so wide that it is hard to express it by a reaction rate at a fixed temperature. Therefore, the value of  $10^3/T_{30}$  is used as a measure reflecting the activity, where  $T_{30}$  indicates the reaction temperature (in de-

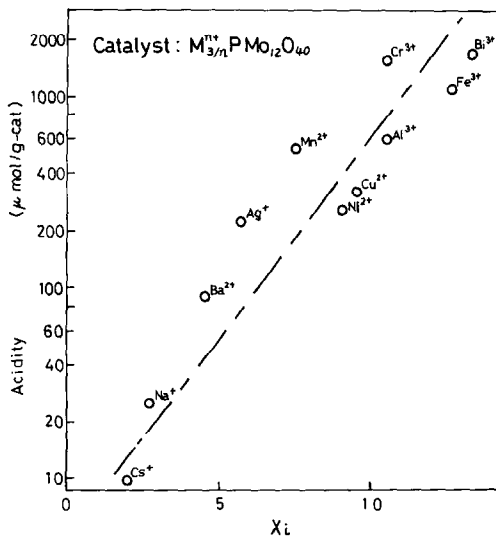


FIG. 10. Acidity of the neutral salt catalysts as a function of the electronegativity of the metal ion,  $x_i$ . Acidity = amount of  $\text{NH}_3$  irreversibly adsorbed at  $200^\circ\text{C}$ .

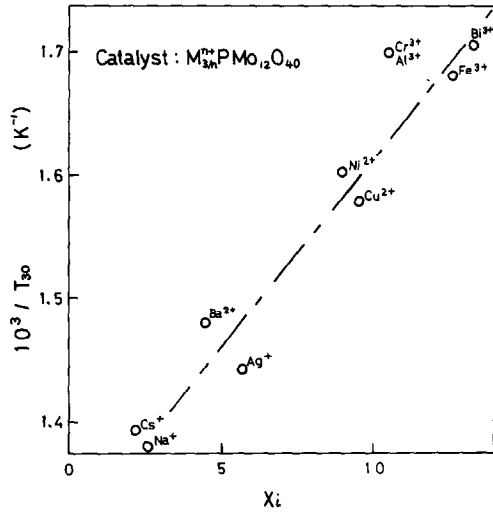


FIG. 11. Oxidation activity of the neutral salt catalysts as a function of the electronegativity of the metal ion,  $x_i$ .  $T_{30}$  is the reaction temperature corresponding to the butadiene conversion of 30% at catalyst = 10 g,  $\text{C}_4\text{H}_6 = 1.0$  mol% in air, total flow rate = 1.0 liter/min.

grees Kelvin) corresponding to the conversion of 30%. A clear correlation is obtained between the oxidation activity and the electronegativity of the cation. In light of the results shown in Fig. 10, it can be said that there is a rough correlation between the oxidation activity and the acidic property.

The effect of the amount of counteranion on the oxidation activity was also studied concerning several cations, such as  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$ , and  $\text{Bi}^{3+}$  (Fig. 12). The activity varies in different ways depending on the cations: the activity increases steadily with the  $(\text{NH}_4^+)$  substitution, it decreases steadily with the substitution of  $\text{Fe}^{3+}$  or  $\text{Ag}^+$ , and it passes through a maximum value in the case of the  $\text{Cs}^+$  substitution. It is, therefore, hard to relate the oxidation activity merely to the acidity shown in Fig. 8.

Figure 13 shows the maximum yield of furan, which is obtained at a butadiene conversion of about 70%, as a function of the amount of counteranion. It was found that: (i) in the cases of  $\text{Cs}^+$ ,  $\text{NH}_4^+$ , and  $\text{Na}^+$ , the maximum yield increases with an increase in the amount of counteranion ( $x$ ),

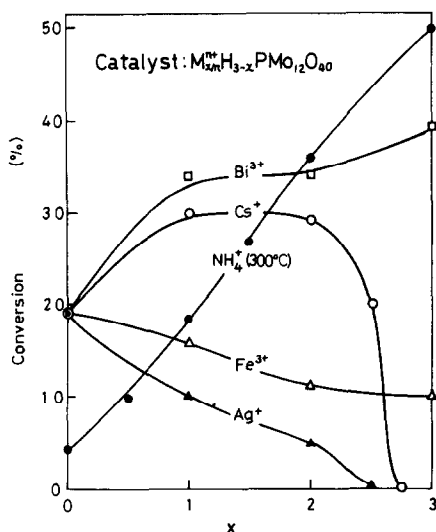


FIG. 12. Effect of the amount of the counteranion on the catalytic activity for butadiene oxidation. Reaction conditions:  $T = 320^\circ\text{C}$ , catalyst = 10 g,  $\text{C}_4\text{H}_6 = 1.0$  mol% in air, total flow rate = 1.0 liter/min.

goes through a maximum at  $x = 1.0$  to 1.5, and then sharply decreases upon further substitution, (ii) in the cases of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$ , the yield is little affected by a low substitution ( $x < 2$ ), but it declines with a high substitution ( $x > 2$ ), and (iii) the substitution of a more acidic cation, such as  $\text{Al}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , or  $\text{Ni}^{2+}$ , is almost entirely insensitive to the yield.

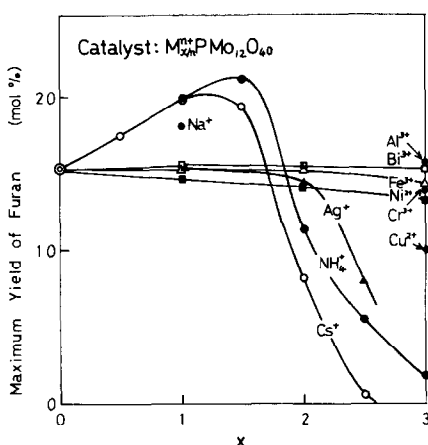


FIG. 13. Maximum yield of furan as a function of the amount of the counteranion. Reaction conditions:  $T = 300$  to  $400^\circ\text{C}$ , catalyst = 20 g,  $\text{C}_4\text{H}_6\text{-O}_2\text{-H}_2\text{O} = 1.0\text{-}4\text{-}7.5$  mol% in  $\text{N}_2$ , total flow rate = 1.0 liter/min.

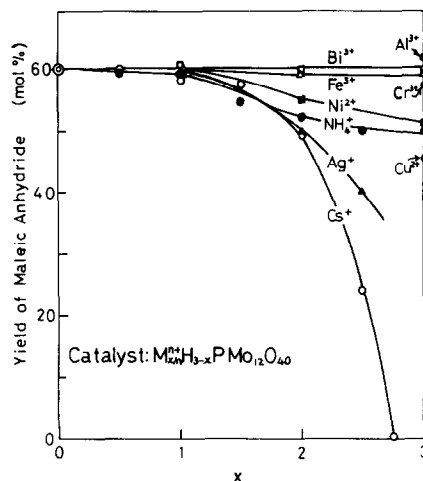


FIG. 14. Effect of the amount of counteranion on the yield of maleic anhydride at a butadiene conversion of 95 to 99%. Reaction conditions:  $T = 330$  to  $400^\circ\text{C}$ , catalyst = 20 g,  $\text{C}_4\text{H}_6\text{-H}_2\text{O} = 1.0\text{-}7.5$  mol% in air, total flow rate = 1.0 liter/min.

The effect of counteranion on the yield of maleic anhydride at a butadiene conversion of 95 to 99% is shown in Fig. 14. It was found that: (i) when the substitution amount is not high ( $x < 1.5$ ), the effect is small, regardless of the kind of cation, and (ii) when the substitution amount is high ( $x > 1.5$ ), the more basic the cation, the more markedly the yield decreases.

#### Oxidation Activity of $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ and $(\text{NH}_4)_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ Catalysts for MEK, Methacrolein, and Butadiene

It can be predicted that the effect of a counteranion on the oxidation activity will differ depending on the model reaction being dealt with. Accordingly, the oxidation activities for three reactants, such as MEK, methacrolein, and butadiene, were compared. The results obtained from two series of catalysts,  $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$  and  $(\text{NH}_4)_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ , are shown in Figs. 15 and 16. The activities for the three oxidations follow the same trend of variation, though the shapes of the activity curves are different, to some extent, depending on the reactant. It was found that:



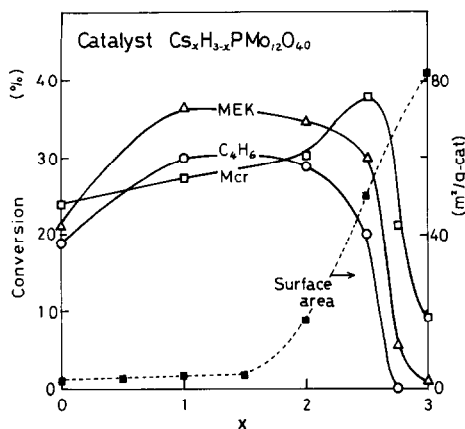


FIG. 15. Oxidation activity of the  $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$  catalysts as a function of the amount of cesium. Catalyst = 20 g; (○) oxidation of butadiene at  $T = 300^\circ\text{C}$ ,  $\text{C}_4\text{H}_6\text{-H}_2\text{O} = 1.0\text{-}7.5$  mol% in air, total flow rate = 1.0 liter/min; (△) oxidation of MEK at  $T = 240^\circ\text{C}$ ,  $\text{MEK-H}_2\text{O} = 1.5\text{-}7.5$  mol% in air, total flow rate = 1.0 liter/min; (□) oxidation of methacrolein at  $320^\circ\text{C}$ ,  $\text{C}_4\text{H}_8\text{O-H}_2\text{O} = 1.6\text{-}7.5$  mol% in air, total flow rate = 1.0 liter/min.

(i) when the amount of  $\text{Cs}^+$  is not high ( $x < 2$ ), the oxidation activity increases with the substitution, but when the amount is high ( $x > 2.5$ ), the activity for all reactants sharply declines, though the extent of this decline in activity is different depending on the reactant; the  $\text{Cs}_{2.75}\text{H}_{0.25}\text{PMo}_{12}\text{O}_{40}$  catalyst is really inactive for oxidation of butadiene, whereas it is active enough for the oxidation of methacrolein, and (ii) the activity increases steadily with an increase in the amount of  $\text{NH}_4^+$ .

#### DISCUSSION

Heteropoly compounds such as  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and certain salts are well soluble in water and other oxygen-containing organic compounds, unlike many metal oxides, suggesting that the bulk molecules as well as surface molecules can interact with foreign molecules. The two values of acidity obtained by the adsorption of two different basic molecules are well proportional to the amount of bulk  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , but not to the surface area. This means that the acidity obtained by the adsorption method indi-

cates the amount of bulk acid which can interact with the basic molecules under the operating conditions.

It is generally believed that active sites which are responsible for the catalytic action are located on the surface of the solid. However, in the case of the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  catalyst, the situation seems to be different; that is, the catalytic activities for both the acid-catalyzed reactions and oxidation reactions are proportional to the amount of bulk  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  or to the amount of bulk acid. This means that bulk  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  molecules are responsible for the catalytic action. The action of bulk molecules has also been studied from the results of  $^{18}\text{O}$  exchange between  $\text{H}_2^{18}\text{O}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  by Misono *et al.* (9).

However,  $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$  and  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  are insoluble in water; moreover, their surface areas are about 100 times greater than that of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . In the cases of these salt catalysts, the action of surface sites may become predominant compared with that of bulk molecules. This situation seems to be complex, depending on the counteraction.

As is shown in Figs. 4 and 5, the

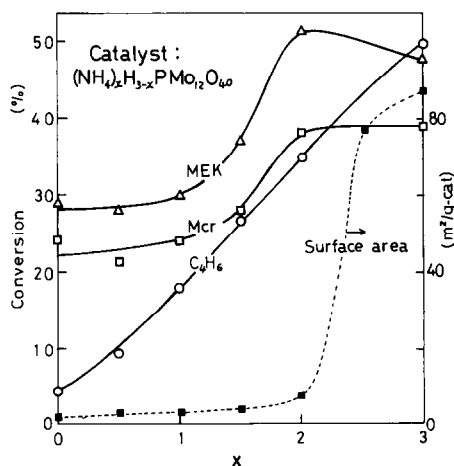


FIG. 16. Oxidation activity of the  $(\text{NH}_4)_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$  catalysts as a function of the amount of  $(\text{NH}_4)^+$ . Reaction conditions and symbols are the same as in Fig. 15, except the temperature of butadiene oxidation =  $283^\circ\text{C}$ .

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{CsH}_2\text{PMo}_{12}\text{O}_{40}$  catalysts lose their catalytic action at temperatures higher than  $400^\circ\text{C}$ , possibly by their thermal decomposition. The reactions must, then, be performed below  $400^\circ\text{C}$ . As is generally said (1), this is a disadvantage of the heteropoly compounds. It has been reported that the thermal stability can be improved by a replacement of the protons with monovalent cations, such as  $\text{Cs}^+$ ,  $\text{Tl}^+$ , and  $\text{HN}_4^+$  (1, 8). According to our results, however, the replacement with  $\text{Cs}^+$  had no clear effect on the thermal stability. Further detailed data are awaited.

The presence of steam in feed gas strongly increases the rate of oxidation for butadiene, MEK, and crotonaldehyde, but it depresses the rate for nonoxidation reactions, such as 2-propanol dehydration, butene isomerization, and decomposition of formic acid, though both the oxidation and nonoxidation reactions are catalyzed, to a certain extent, by the acidic character of the catalyst. This leads us to consider that the steam enhances the oxidation function of a catalyst rather than its acidic function.

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$  is strongly acidic, but it is poor in basic property. Therefore, it can be predicted that the catalyst is deficient in the reoxidation function (14). As is shown in Table 2, the rates of oxidation are 0.5 to 1.0 order with respect to oxygen concentration and nearly zero order with respect to the reactant. The results also suggest that the reactions are limited by the reoxidation step of a redox cycle, in contrast with the reaction over a basic catalyst such as  $\text{Bi}_2\text{O}_3\text{-MoO}_3$ .

Indeed, the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  catalyst is much more active in the oxidation of basic compounds than other  $\text{MoO}_3$ -based mixed-oxide catalysts. This high oxidation activity may be ascribed to the profound activation of reactant by strong acidic sites. On the other hand, the activity seems to be markedly affected by the reactivity of the reactant molecule itself. Possibly, the oxidizing power of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  is too weak to oxidize ethylene, propylene, and benzene.

Accordingly, it can be said that the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  catalyst is proper only for the oxidation of relatively reactive compounds, such as methacrolein, isobutylic acid, MEK, and  $\text{C}_4$ -olefins.

It is interesting to note that, in the oxidation of  $\text{C}_4$  compounds with the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  catalyst, methacrolein is oxidized to methacrylic acid by oxidation at the aldehyde group; butadiene and crotonaldehyde are oxidized to furan by oxidative cyclization; isobutyric acid is oxidized to methacrylic acid by oxidative dehydrogenation (7, 10); and MEK is oxidized to acetic acid and acetaldehyde by oxidative C-C fission. These results reveal that different types of reactions can be promoted by the same catalyst, depending on the difference in the reactant. This supports the view (14) that the selectivity of oxidation reaction is brought about by the difference in the mode or degree of reactant activation, not by the difference in the oxygen species.

As is shown in Figs. 8, 9, and 10, the acid-base character of counteranions is well reflected in the acidity of the salts of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . This may be caused by the homogeneity of bulk  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . The increase in the acidity by the addition of an acidic cation such as  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Cr}^{3+}$  may be ascribed, in part, to the increase in the surface area.

When the kind of counteranion is changed, the activity of  $\text{M}_{3/n}^{n+}\text{PMo}_{12}\text{O}_{40}$  catalysts for oxidation of butadiene varies widely and in a manner similar to the acidity, indicating that the reaction is catalyzed by acid (Figs. 10 and 11). On the other hand, when the kind of counteranion is fixed and the amount of counteranion is changed, the oxidation activity varies in a manner apparently different from the acidity, indicating that the activity is affected not only by the acid, but also by other functions (Figs. 8, 9, and 12).

It should be noted that the oxidation activity of salts of heteropoly acid,  $\text{M}_{x/n}^{n+}\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ , is not related to the oxidation activity of the metal oxide corre-

sponding to the counteraction,  $M_2O_n$ , but it is related to the electronegativity or the acid-base property of the counteraction. For example,  $Ag_2O$  and  $CuO$  are eminent in oxidation activity, but the addition of  $Ag^+$  and  $Cu^{2+}$  to  $H_3PMo_{12}O_{40}$  induces a remarkable decrease in the oxidation activity. The counteractions act merely as bases, not as oxidizing agents.

An increase in the maximum yield of furan is observed when about half of the protons are replaced by  $Cs^+$ ,  $Na^+$ , or  $NH_4^+$  (Fig. 13). It is assumed that the basic character (number and strength) proper to the reaction is obtained only by the  $Cs^+$ ,  $Na^+$ , and  $NH_4^+$  addition. Further detailed data are necessary to explain the results.

The effect of counteraction on the yield of maleic anhydride (Fig. 14) can be explained in terms of the acidic property of the catalyst (Fig. 8). That is, one of the conditions necessary to obtain an acidic product is the possession of a sufficient acidic property (14-16).

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