JOURNAL OF CATALYSIS 86, 173–186 (1984)

12-Heteropolymolybdates as Catalysts for Vapor-Phase Oxidative Dehydrogenation of Isobutyric Acid

2. Group Ib, IIb, IIIb, and VIII Metal Salts

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Received February 14, 1983; revised September 13, 1983

The effect of cations on the catalytic properties of 12-molybdophosphates, as oxidation catalysts, has been investigated in the vapor-phase oxidative dehydrogenation of isobutyric acid at 300°C. Both the reducibility by isobutyric acid and carbon monoxide and reoxidizability by gaseous oxygen of 12-molybdophosphates increased with increasing standard electrode potential (SEP) of cations (group Ib, IIb, IIIb, and VIII metal ions and Pb^{2+}, Mn^{2+}, Ce^{3+}, and La^{3+}). On the other hand, while the oxidizing activity (i.e., an affinity for electron) of Mo^{6+} in these 12-molybdophosphates paralleled the SEP of the cations, the electrons formed by reduction of these 12-molybdophosphates were preferentially captured by the cations when the cations had a high SEP. These results are discussed as the effect of cations on the electrochemical properties of the molybdenum atoms, and the catalytic results obtained are explained on the basis of the exclusive participation of the lattice oxygen, the delocalization of the electrons by the cations, and the acid–base properties of the catalyst. It is proposed that these cations play the role of an electron-reservoir: their electron-capturing nature and electron-donating nature, i.e., their redox properties decisively affect the reducibility and reoxidizability of 12-molybdophosphates. Mechanistic differences in the promotional effects of cations between the metal ions employed in this work and alkali metal and alkaline-earth metal ions are also shown.

INTRODUCTION

In recent years, considerable interests in the industrial application of 12-heteropoly acids and their salts as heterogeneous oxidation catalysts have been shown. For example, 12-molybdophosphoric acid, $H_3[PMo_{12}O_{40}]$ and its related compounds are now being investigated as catalysts for the vapor-phase oxidation of methacrylaldehyde and isobutyric acid to methacrylic acid (*1–3*). As often said, the most interesting feature of this investigation that it indicates is the possibility not only to substitute the protons with various cations but also to change the heteroatoms and the condensing metal atoms, thereby affecting the catalytic activity and selectivity in a drastic manner Thus, several mechanistic studies (*4–7*) have been published on the effects of the catalyst components (cations, heteroatoms, and condensing metal atoms) on the oxidation reactions concerned. In the mechanistic studies related with the catalytic activity of 12-molybdophosphates (*4, 5*), the effect of cations was in one case explained in terms of ionic potential (*4*) and it was in another case explained on the basis of the acid–base properties of the compounds (*5*), irrespective of the kind of cations employed. However, it is rather natural to expect mechanistic differences in the roles of metal ions as cations between transition metal ions and alkali metal and alkaline-earth metal ions because, unlike the latter two groups of metal ions, the cations of transition metals may cycle in oxidation state in the course of catalytic oxidations.

In our previous paper (*6*), the effects of cations (H^+, alkali metal and alkaline-earth

0021-9517/84 $3.00

metal ions) and heteroatoms (P^{5+}, As^{5+}, and Si^{4+}) on the catalytic activity of 12-heteropolymolybdates were investigated in the vapor-phase oxidative dehydrogenation of isobutyric acid The reducibility and reoxidizability of these 12-heteropolymolybdate-type catalysts and the trend in the yield ratio of acetone to methacrylic acid obtained with changing the cations and the heteroatoms were shown to be reasonably understood in terms of electronegativity via electrostatic effects (i e , with no change in oxidation state) produced by these catalyst components (cations and heteroatoms) on the strength of the molybdenum–oxygen bond and the acid–base properties of the catalyst (*6*)

In the present work, we have prepared group Ib(Cu^{2+} and Ag^{+}), IIb (Zn^{2+}, Cd^{2+}, and Hg^{2+}), IIIb (Al^{3+}, Ga^{3+}, In^{3+}, and Tl^{+}), and VIII metal (Co^{2+}, Ni^{2+}, and Pd^{2+}) and lead, manganese, cerium, and lanthanum 12-molybdophosphates and then determined their catalytic activity and selectivity for the oxidative dehydrogenation of isobutyric acid We have also investigated the behavior of electrons formed by reduction of these metal 12-molybdophosphates by means of X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR) and evaluated the oxidizing activity of the Mo^{6+} atoms contained in the catalysts as well as the reoxidizability of Mo^{5+} by gaseous oxygen These results are then discussed as effect of cations on the electrochemical and catalytic properties of 12-molybdophosphates and are compared with the already reported results (*6*) for alkali metal and alkaline-earth metal 12-molybdophosphates

METHODS

Vapor-phase catalytic oxidative dehydrogenation of isobutyric acid (IBA) was carried out at 300°C using a conventional flow fixed-bed reactor at atmospheric pressure The reactor system and the method of catalytic reaction employed in the present work were the same as those in our previous paper (*6*) Guaranteed reagent grade IBA (Wako Pure Chemical Industries, Ltd) was used The total feed rate was held constant at 150 (NTP) ml/min the standard feed composition was IBA 1 8 vol% and O_2 3 2 vol% Purchased nitrogen, helium, and hydrogen of greater than 99 99% purity were used without further purification All reaction products were analyzed by gas chromatography as described previously (*6*) The formation of acetone and propylene is always accompanied by an equimolar amount of CO or CO_2 (see Discussion) Hence, the combined yields of CO and CO_2, which are attributed to the destructive oxidation of IBA, shown in this paper were determined by deducting one-fourth of the yield of acetone + propylene from the experimentally determined yield of CO + CO_2

Guaranteed reagent grade 12-molybdophosphoric acid was purchased from Kanto Chemical Company, Inc Its cupric, silver, zinc, cadmium, mercuric, thallium, cobalt, nickel, lead, cerium, and lanthanum salts were prepared by adding their corresponding metal carbonates into the aqueous solution of 12-molybdophosphoric acid (20 g in 20 ml H_2O) at room temperature (*8*) Aluminum, gallium, indium, palladium, and manganese 12-molybdophosphates were prepared by the double decomposition of their corresponding metal sulfates with barium 12-molybdophosphate in an aqueous medium After the barium sulfate formed had been filtered, the aqueous solution of metal 12-molybdophosphate was evaporated to dryness over silica gel under vacuum at room temperature The solid metal 12-molybdophosphates obtained were then calcined at 300°C in air for 3 h and were stored over silica gel

XPS spectra were recorded with a Hewlet–Packard 5950A ESCA spectrometer (Al*Kα* radiation), the instrumental energy scale had been set up by the use of the Au $4f_{7/2}$ signal (83 8 eV) In the spectroscopic measurements charging effects were minimized by the use of a flood gun, and binding energies were referenced to the $C1s_{1/2}$ signal (285.0 eV). The ESR measurements were carried out at room temperature with a JEOL-PE spectrometer operating in the X band, adopting a 100-kHz modulation frequency. The g values of paramagnetic species were determined by the use of Mn^{2+} dissolved in magnesium oxide, and radical concentrations were estimated by a comparison with the standard solution of 2,2-diphenyl-1-picrylhydrazyl in benzene. The surface area was determined conventionally using the BET method after drying at 150°C for 1 h in flowing dried nitrogen. Thallium 12-molybdophosphate ($Tl_3[PMo_{12}O_{40}]$) had a relatively large surface area, i.e., 162 m^2/g, whereas the other metal 12-molybdophosphates employed in the present work had much smaller surface areas, 1–3 m^2/g. The result of differential thermal analysis revealed that these metal 12-molybdophosphates with the exception of the thallium salt began to decompose at 400–440°C in dry air. The thallium salt did not decompose even at 600°C.

RESULTS

Catalytic Results

Figure 1 shows the variation in the catalytic activity and selectivity of cupric 12-molybdophosphate ($Cu_3[PMo_{12}O_{40}]_2$) with elapsed time of reaction in the oxidative dehydrogenation of IBA at 300°C. Conversion of IBA was 74.7% at 30 min, but it decreased with time and leveled off at nearly a constant value of 46.4% after a preliminary period of 5 h. Similarly, the yield of methacrylic acid (MAA) decreased with time and it became nearly constant at 31.4% within 5 h, although the value of selectivity to MAA increased a little (3–4%) at the initial stages of the reaction and then it became nearly constant at 67.1%. The yields of acetone and propylene also showed a trend similar to that in the conversion of IBA. The selectivity to acetone and the yield ratio (acetone/MAA) were 23.0% and 0.33 at 30 min, but they decreased with time and they became nearly constant at 20.6% and 0.31 within 5 h. The yield of CO + CO_2 was 0.3–1.2% throughout the course of the reaction. These small variations in the values of selectivity to MAA and acetone are caused by some degree of reduction of the catalyst during the course of the oxidative dehydrogenation of IBA.

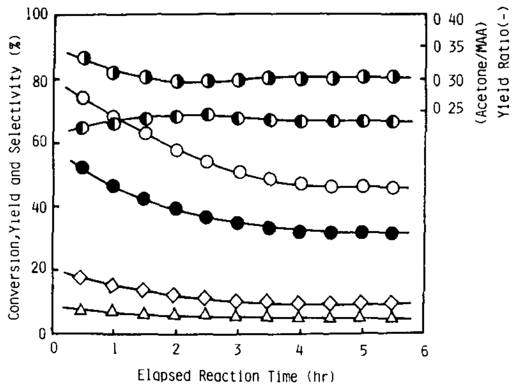


FIG. 1. Variation in the catalytic activity of cupric 12-molybdophosphate with time in the oxidative dehydrogenation of isobutyric acid. Reaction temperature 300°C. Feed: IBA 1.8 vol%, O_2 3.2 vol%, N_2, He-diluent. Contact time: 1.89 g-catalyst h/g-mol. (○) Conversion of IBA, (●) yield of MAA, (◇) yield of acetone, (△) yield of propylene, (◐) selectivity to MAA, (◑) (acetone/MAA) yield ratio. The yield of CO + CO_2 was 0.3–1.2%.

The steady-state catalytic activity and selectivity of the other divalent-metal salts were similarly determined at 300°C and the results obtained are summarized in Fig. 2. Conversion of IBA over the manganese salt ($Mn_3[PMo_{12}O_{40}]_2$) was as low as 13.7%, but it increased with increasing SEP of the cations and it was as high as 64.8% over the palladium salt ($Pd_3[PMo_{12}O_{40}]_2$). It is interesting to note that cupric, mercuric, and palladium 12-molybdophosphates showed relatively high catalytic activities for the oxidative dehydrogenation of IBA. The yields of acetone, MAA, propylene, and CO + CO_2 and the selectivity to MAA also increased with increasing SEP of the cations. MAA was formed with a selectivity of 48.8% over the manganese salt whereas MAA was formed with a selectivity of 59.7% over the palladium salt. The yield

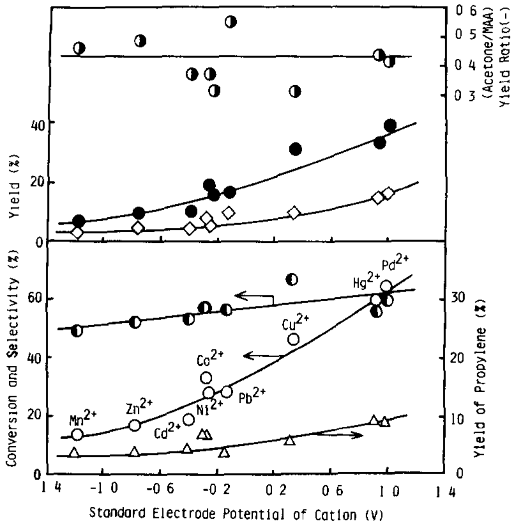


FIG 2 Correlation between the standard electrode potential of divalent-metal cations and the steady-state catalytic activity of their 12-molybdophosphates in the oxidative dehydrogenation of isobutyric acid Reaction conditions and symbols used are the same as those in Fig 1 The yield of CO + CO_2 was 0 1% (Mn^{2+})-1 4% (Pd^{2+})

ratio (acetone/MAA), however, had no special dependence on the SEP of the cations and it was nearly 0 43 (Fig 2)

Analogous effect of cations on the catalytic reaction of IBA was observed in the monovalent-metal salts (Table 1) That is, the conversion of IBA, the yields of MAA and acetone, and the selectivity to MAA followed the relation $Tl_3[PMo_{12}O_{40}] < Ag_3[PMo_{12}O_{40}]$

Kinetic Study

The catalytic oxidative dehydrogenation of IBA over some metal 12-molybdophosphates at 300°C was kinetically studied basing on a redox mechanism shown below

$$\mathrm{IBA} + \mathrm{O_s} \xrightarrow{k_1} \mathrm{Products} + \mathrm{O_v} \quad (1)$$

$$2\mathrm{O_v} + \mathrm{O_2} \xrightarrow{k_2} 2\mathrm{O_s} \quad (2)$$

where k is rate constant, and O_s and O_v are surface lattice oxygen and its vacancy, respectively IBA molecule is oxidized with rate constant k_1 while the reduced catalyst is reoxidized by gaseous oxygen with rate constant k_2 At a steady state,

$$2k_1[\mathrm{O_s}]P_{\mathrm{IBA}} = k_2[\mathrm{O_v}]^2P_{\mathrm{O_2}} \quad (3)$$

Here, $[O_s]$, $[O_v]$, and P are the surface concentration of O_s and O_v and the partial pressure of the reactant in the feed mixture, respectively Since $[O_s] + [O_v] = 1$, Eq (3) becomes

$$1 + [\mathrm{O_s}]^2 - \frac{2}{k_2P_{\mathrm{O_2}}}(k_2P_{\mathrm{O_2}} + k_1P_{\mathrm{IBA}})[\mathrm{O_s}] = 0 \quad (4)$$

Assuming that the catalyst is nearly completely oxidized during the oxidative dehydrogenation of IBA, i e $[O_s]^2 = 1$, it follows that

$$[\mathrm{O_s}] = \frac{k_2P_{\mathrm{O_2}}}{k_1P_{\mathrm{IBA}} + k_2P_{\mathrm{O_2}}} \quad (5)$$

Hence, the initial rate of the catalytic oxidation of IBA is

$$r = k_1[\mathrm{O_s}]P_{\mathrm{IBA}} = \frac{k_1k_2P_{\mathrm{IBA}}P_{\mathrm{O_2}}}{k_1P_{\mathrm{IBA}} + k_2P_{\mathrm{O_2}}} \quad (6)$$

TABLE 1

Summary of the Catalytic Activity of $Tl_3[PMo_{12}O_{40}]$ and $Ag_3[PMo_{12}O_{40}]$ in the Oxidative Dehydrogenation of Isobutyric Acid[a]

Time	Catalyst	SEP of cation (V)	Conversion of IBA (%)	Yield (%)				Selectivity to MAA (%)	Yield ratio Acetone/MAA (–)
				MAA	Acetone	Propylene	$CO + CO_2$		
30 min	$Tl_3[PMo_{12}O_{40}]$	−0 336	45 8	18 9	11 7	11 9	3 3	41 2	0 62
	$Ag_3[PMo_{12}O_{40}]$	0 779	54 8	26 6	17 8	9 4	1 3	48 5	0 66
Steady state	$Tl_3[PMo_{12}O_{40}]$	−0 336	32 0	13 3	9 0	7 4	2 3	41 7	0 67
	$Ag_3[PMo_{12}O_{40}]$	0 779	39 8	21 2	11 5	5 1	0 6	53 2	0 54

[a] Reaction conditions are the same as those in Fig 1

TABLE 2

Summary of the Kinetic Parameters for the Catalytic Oxidative Dehydrogenation of Isobutyric Acid over Metal 12-Molybdophosphates[a]

Catalyst	SEP of cation (V)	k_1[b]	k_2[b]	$[O_s]$ (−)[c]
$Cu_3[PMo_{12}O_{40}]_2$	0.337	0.063	1–5	0.965
$Hg_3[PMo_{12}O_{40}]_2$	0.920	0.234	1–5	0.884
$Pd_3[PMo_{12}O_{40}]_2$	0.987	0.287	1–5	0.861
$Tl_3[PMo_{12}O_{40}]$	−0.336	0.144	1–5	0.925
$Ag_3[PMo_{12}O_{40}]$	0.779	0.176	1–5	0.910

[a] Reaction temperature 300°C. Feed: IBA 1.4–2.0 vol%, O_2 2.5–3.6 vol%, N_2, He—diluent.

[b] In g-mol/g-catalyst · h · atm.

[c] At IBA 1.8 vol%, O_2 3.2 vol%, and k_2 = 1.0.

Thus

$$\frac{P_{IBA}P_{O_2}}{r} = \frac{P_{O_2}}{k_1} + \frac{P_{IBA}}{k_2} \qquad (7)$$

We could have obtained linear relationships based on Eq. (7) when P_{O_2} was changed with a constant value of P_{IBA}. The values of rate constants, k_1 and k_2, determined at 300°C for cupric, mercuric, palladium, thallium, and silver 12-molybdophosphates are summarized in Table 2. The value of intercept P_{IBA}/k_2 was an order of 0.01 for all of the metal 12-molybdophosphates studied. Hence, k_2 was estimated to be 1–5 although its exact values were not determined. Nevertheless, the values of rate constant for the reoxidation step (k_2) are always much greater than those of rate constant for the reduction step (k_1) and the values of $[O_s]$ calculated basing on Eq. (5) at IBA 1.8 vol%, O_2 3.2 vol%, and k_2 = 1.0 are approximately equal to unity for all of the catalysts studied (Table 2). These calculated values of $[O_s]$ indicate that these five metal 12-molybdophosphates were nearly completely oxidized during the catalytic oxidative dehydrogenation of IBA at 300°C. Furthermore, the observed relation of the value of k_1, which is in one case $Cu_3[PMo_{12}O_{40}]_2$ < $Hg_3[PMo_{12}O_{40}]_2$ < $Pd_3[PMo_{12}O_{40}]_2$ and is in another case $Tl_3[PMo_{12}O_{40}]$ < $Ag_3[PMo_{12}O_{40}]$, agrees with that of the conversion of IBA obtained with an integral reactor (Fig. 2, Tables 1 and 2). Therefore, it could be concluded that the reduction of catalyst by IBA is rate-controlling at 300°C.

Reduction by Carbon Monoxide

Reduction of the metal 12-molybdophosphates by carbon monoxide was carried out at 300°C using a pulse reactor (Fig. 3). In the case of the divalent-metal salts, yield of CO_2 over the manganese salt was as low as 0.24%, but it increased with increasing SEP of the cations and it was as high as 72.9% over the palladium salt. The increase in the yield of CO_2 with increasing SEP of cations was also seen in the case of the monovalent and trivalent-metal salts (Fig. 3). Additionally, the observed relation of the yield of CO_2 over cupric, mercuric, palladium, thallium, and silver 12-molybdophosphates, which is in one case $Cu_3[PMo_{12}O_{40}]_2$ < $Hg_3[PMo_{12}O_{40}]_2$ < $Pd_3[PMo_{12}O_{40}]_2$ and is in another case $Tl_3[PMo_{12}O_{40}]$ < $Ag_3[PMo_{12}O_{40}]$, agrees with that of the rate constant for the reduction of these metal 12-molybdophosphates by IBA at 300°C (k_1) (Fig. 3, Table 2). This supports the view that the reduction of catalyst is rate-con-

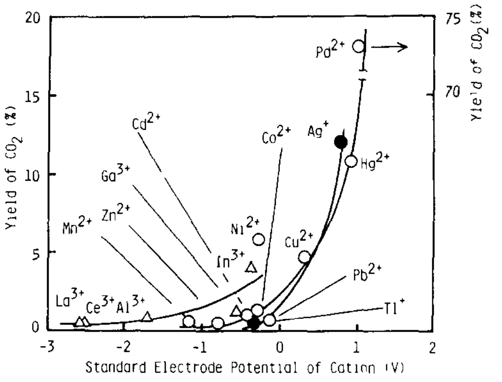


FIG. 3. Correlation between the standard electrode potential of cations and the yield of carbon dioxide in the reduction of metal 12-molybdophosphates by carbon monoxide (pulse method). Reaction temperature: 300°C. Catalyst: 0.50 g. Carrier gas: He 23 (NTP) ml/min. CO pulse: 1.0 (NTP) ml. (●) The monovalent-metal salts, (○) the divalent-metal salts, (△) the trivalent-metal salts.

trolling in the oxidative dehydrogenation of IBA at 300°C Thus, it is found that the reducibility of the mono-, di-, and trivalent metal 12-molybdophosphates by IBA and carbon monoxide employed in the present work increases with increasing SEP of the cations, although the reducibility is normalized to constant catalyst weight and is not to constant surface area The unusually great yield of CO_2 over the nickel salt (Fig 3) is presumably caused by the adsorption of carbon monoxide on the zerovalent nickel atoms formed (*9*)

The surface area of 12-heteropolymolybdates is markedly affected by degree of hydration as well as by the temperature they were exposed to (*10*) Hence, the surface area conventionally measured by the BET method cannot be used as the effective surface area during the catalytic oxidation of hydrocarbons, although there is a published paper (*4*) in which the effect of cations was discussed on the basis of the catalytic activity normalized to the unit BET surface area However, the regularity of the conversion of IBA and the yield of CO_2 in the reduction by carbon monoxide observed with changing cations (Figs 2 and 3, Tables 1 and 2) suggests that change in physicochemical properties of the catalyst was much more predominant than that in the effective surface area in determining the catalytic activity of the metal 12-molybdophosphates The observed greater values of the conversion of IBA and the yield of CO_2 in the reduction by carbon monoxide over the silver salt (2 m^2/g) than the thallium salt (162 m^2/g) (Table 1 and Fig 3) support this view Accordingly, we may consider that the correlation of SEP of the cations with the reducibility of the metal 12-molybdophosphates made in the present work is chemically meaningful

Reoxidation of Mo^{5+}

The catalyst (100 mg in a 3-mm-i d quartz tube) was reduced by hydrogen at 30 Torr pressure (1 Torr = 133 3 N/m^2) at 300°C for 1 h and then evacuated at the same temperature for 30 min After the value of *g* and radical concentration of Mo^{5+} formed had been determined, gaseous oxygen was introduced at 35 Torr pressure at room temperature and the catalyst was then heated step by step at 75, 100, 150, 200, 250, and 300°C for 30 min (Table 3) The ESR spectra of Mo^{5+} formed were relatively broad and anisotropic, whose g value ranged from 1 93 to 1 95 The reoxidation of Mo^{5+} atoms formed in zinc 12-molybdophosphate was initiated at ca 250°C, and only 13% of the Mo^{5+} atoms were reoxidized at 300°C However, Mo^{5+} atoms formed in the cadmium, cobalt, nickel, cupric, mercuric, and palladium salts with the exception of Mo^{5+} atoms formed in the lead salt could be reoxidized even at 100°C and they also showed relatively high reactivities to gaseous oxygen at 300°C (Table 3) In the case of the cupric salt, the ESR spectrum of Cu^{2+} which had originally been seen in the unpretreated cupric salt was fully recovered when the reduced salt was reoxidized at 250 and 300°C

The increase in the reoxidizability of Mo^{5+} with increasing SEP of cations is much more obvious in the case of the trivalent-metal salts That is, the temperature at which the reoxidation of Mo^{5+} was initiated lowered markedly with increasing SEP of the cations (Table 3) It appears that the activation energy for the reoxidation of Mo^{5+} atoms by gaseous oxygen lowers with increasing SEP of the cations, although no concrete difference in the reoxidizability of Mo^{5+} atoms was found in the case of the thallium and silver salts (Table 3) In this reoxidation study, formation of such negatively charged adsorbed oxygens as O_2^- and O^- was scarcely observed by means of ESR even at room temperature and at the temperatures at which the reoxidation took place This indicates that exclusive participation of lattice oxygen in the catalytic oxidation of IBA took place at 300°C

On the other hand, the values of concentration of Mo^{5+} atoms formed by the reduction with hydrogen (Table 3) indicate that

TABLE 3

Reoxidation of Mo^{5+} by Gaseous Oxygen Formed in Metal 12-Molybdophosphates[a]

Catalyst	SEP of cation (V)	Mo^{5+} concentration[b]	T_i^c (°C) (Mo^{5+} reoxidized (%))	Mo^{5+} reoxidized (%) at 300°C
$Zn_3[PMo_{12}O_{40}]_2$	−0.763	9.2	250(5)	13
$Cd_3[PMo_{12}O_{40}]_2$	−0.403	14.0	100(11)	49
$Co_3[PMo_{12}O_{40}]_2$	−0.277	15.0	100(35)	90
$Ni_3[PMo_{12}O_{40}]_2$	−0.246	11.7	100(80)	95
$Pb_3[PMo_{12}O_{40}]_2$	−0.126	11.4	250(15)	27
$Cu_3[PMo_{12}O_{40}]_2$	0.337	12.7[d]	100(46)	100
$Hg_3[PMo_{12}O_{40}]_2$	0.920	7.1[e]	100(55)	93
$Pd_3[PMo_{12}O_{40}]_2$	0.987	10.5[e]	100(19)	80
$Tl_3[PMo_{12}O_{40}]$	−0.336	0.9	20(93)	100
$Ag_3[PMo_{12}O_{40}]$	0.779	10.7[e]	20(50)	100
$La[PMo_{12}O_{40}]$	−2.52	3.9	250(32)	48
$Ce[PMo_{12}O_{40}]$	−2.483	9.6	200(5)	35
$Al[PMo_{12}O_{40}]$	−1.662	9.2[f]	100(17)	73
$Ga[PMo_{12}O_{40}]$	−0.529	5.0[f]	100(29)	89
$In[PMo_{12}O_{40}]$	−0.343	7.1[f]	100(27)	95

[a] Catalyst 0.10 g, previously reduced by 30 Torr hydrogen at 300°C for 1 h and then degassed at 300°C for 30 min Oxygen 35 Torr Reaction time 30 min

[b] A number of Mo^{5+} atoms formed per 100 Keggin anions ($[PMo_{12}O_{40}]^{3-}$)

[c] Temperature at which reoxidation of Mo^{5+} was initiated

[d] Reduced by 30 Torr hydrogen at 220°C for 20 min and then degassed at 220°C for 30 min

[e] Reduced by 30 Torr hydrogen at 150°C for 15 min, at 100°C for 3 min, and at 100°C for 4 min, respectively, and then degassed at 200°C for 30 min

[f] Reduced by 30 Torr hydrogen at 250°C for 15 min and then degassed at 250°C for 30 min

the reducibility by hydrogen also increases with increasing SEP of the cations for these three groups of metal 12-molybdophosphates The effect of cations on the reducibility of 12-molybdophosphates by hydrogen will be discussed in a following paper

Oxidizing Activity of Mo^{6+}

The oxidizing activity (i e , an affinity for electron) of Mo^{6+} atoms in the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates, which is strongly associated with the strength of the molybdenum–oxygen bond and the acid–base properties of the molybdenum atoms (see Discussion), was evaluated by adsorbing various aromatic hydrocarbons in dry *n*-hexane

The method of the experiment was the same as that employed in our previous paper (*6*) The results obtained are summarized in Table 4 The formation of aromatic cation radicals and Mo^{5+} is attributed to the electron transfer occurring via the overlapping of the aromatic π system with the outer-sphere molybdate framework "conduction bands" (*6*) The ESR spectra of the aromatic cation radicals formed were symmetrical and sharp, whose *g* value being 2.002–2.003 and whose peak-to-peak width ranging from 4.2 to 9.4 G, characteristic of aromatic cation radicals (*11*) The concentration of the aromatic cation radicals formed increased with decreasing ionization potential of the adsorbed molecules irrespective of the kind of catalyst employed (Table 4) Additionally, the Mo^{6+} atoms in the palladium salt are capable of oxidizing benzene molecules whereas those in the zinc, cadmium, cobalt, nickel, lead, and

TABLE 4

Formation of Aromatic Cation Radicals by Adsorption of Various Aromatic Hydrocarbons on Metal 12-Molybdophosphates[a]

Catalyst	Aromatic cation radicals (spins/g-catalyst) $\times 10^{-16}$				
	Benzene 9 52[b]	Toluene 9 23	Ethylbenzene 9 12	*o*-Xylene 8 56	Naphthalene 8 10
$Zn_3[PMo_{12}O_{40}]_2$	Neg[c]	0 7	0 9	1 2	13 1
$Cd_3[PMo_{12}O_{40}]_2$	Neg	0 5	2 0	2 0	37 7
$Co_3[PMo_{12}O_{40}]_2$	Neg	0 3	2 2	2 3	14 7
$Ni_3[PMo_{12}O_{40}]_2$	Neg	0 6	2 0	3 3	20 9
$Pb_3[PMo_{12}O_{40}]_2$	Neg	0 1	1 0	1 9	85 3
$Hg_3[PMo_{12}O_{40}]_2$	Neg	0 3	1 8	3 1	73 4
$Pd_3[PMo_{12}O_{40}]_2$	2 5	0 5	0 7	3 0	24 4
$Tl_3[PMo_{12}O_{40}]$	Neg	Neg	Neg	Neg	0 3
$Ag_3[PMo_{12}O_{40}]$	Neg	Neg	Neg	0 2	0 1

[a] Catalyst 0 10 g Adsorption time 20 h at room temperature Aromatic hydrocarbons 1/50–1/10 *M*

[b] Ionization potential (eV)

[c] Negligible

mercuric salts cannot oxidize benzene but they can oxidize toluene In the case of the monovalent-metal salts, the Mo^{6+} atoms in the silver salt cannot oxidize benzene, toluene, and ethylbenzene but they can oxidize *o*-xylene, whereas those in the thallium salt cannot oxidize even *o*-xylene but they can oxidize naphthalene (Table 4) Following Ref (*12*), these results are evidence of the view that the oxidizing activity of Mo^{6+} atoms in these metal 12-molybdophosphates parallels the SEP of the cations A similar parallelism had been observed in the case of alkali metal and alkaline-earth metal 12-molybdophosphates (*6*) On the other hand, the Mo^{6+} atoms in the trivalent-metal (lanthanum, cerium, aluminum, gallium, and indium) salts were capable of oxidizing benzene molecules (0 1 $\times$ 10^{16}–1 3 $\times$ 10^{16} spins/g-catalyst) Nevertheless, we may expect that a similar parallelism exists in the case of these trivalent-metal salts

XPS and ESR Studies on Reduction of Metal 12-Molybdophosphates

The behavior of electrons formed by reduction of palladium (Pd^{2+}, SEP = 0 987 V) and cupric (Cu^{2+}, SEP = 0 337 V) 12-molybdophosphates was investigated by means of XPS and ESR spectroscopy Figure 4 shows the XPS spectra of palladium in unpretreated and previously reduced palladium 12-molybdophosphates The spectrum in the Pd 3*d* region consists of a Pd $3d_{3/2}$ and Pd $3d_{5/2}$ doublet [Fig 4a] The values of binding energy of these two levels for the unpretreated palladium salt were 344 1 and 338 9 eV, respectively, in agreement with those reported for Pd^{2+} (*13*) In the reduced palladium salt (degree of reduction = 201 electrons per 100 Keggin anions) each signal was shifted to lower binding energy and was split into the two signals [Fig 4b], although the reason for this shift in binding energy for the Pd 3*d* region was unknown Curve resolution revealed that the spectrum in the Pd 3*d* region for the reduced palladium salt consisted of two doublets, Pd^{2+} $3d_{3/2}$ (343 1 eV) and Pd^{2+} $3d_{5/2}$ (338 1 eV), and Pd^0 $3d_{3/2}$ (341 5 eV) and Pd^0 $3d_{5/2}$ (336 4 eV) (*14*), with a Pd^0/Pd^{2+} ratio of 0 65/0 35 The result of ESR analysis revealed that the concentration of Mo^{5+} formed by the reduction was 2 0 $\times$ 10^{19}

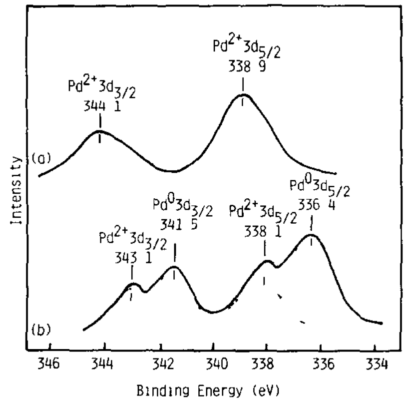


FIG 4 XPS spectra of palladium in palladium 12-molybdophosphate (a) Unpretreated (b) Previously reduced by 30 Torr hydrogen at 100°C for 3 min and then degassed at 100°C for 30 min (degree of reduction = 201 electrons per 100 Keggin anions)

spins/g-catalyst (Mo^{5+} 6 7 atoms per 100 Keggin anions) On the other hand, the binding energy of P $2p_{1/2,3/2}$ was ca 135 3 eV for both the unpretreated and reduced palladium salts This indicates that the valence state of P^{5+} was preserved during the reduction According to Pope and co-workers (*15*), all electrons introduced into a 12-heteropolyanion are trapped by the particular condensing metal atoms Additionally, there have been published results (*16, 17*) indicating that the electrons introduced into solid 12-heteropoly compounds are delocalized uniformly in the bulk Thus, it is found that 97% of the electrons formed by the reduction were captured by Pd^{2+} as cations ($\rightarrow$Pd^{0}) whereas the rest (3%) were captured by Mo^{6+} in the 12-molybdophosphate anions ($\rightarrow$Mo^{5+})

The reduction of cupric 12-molybdophosphate by hydrogen was investigated by means of ESR spectroscopy The unpretreated cupric salt gave a broad anisotropic ESR spectrum, with $g_{\perp}$ value of 2 054 (Fig 5a) characteristic of Cu^{2+} (*18*) Upon reduction, the spectrum of Cu^{2+} decreased markedly in intensity with a formation of Mo^{5+} (g = 1 93) and nearly disappeared when the cupric salt had been reduced by hydrogen at 30 Torr pressure at 230°C for 30 min (Figs 5b and c) The Cu^{2+} spin concentrations were 2 5 × 10^{20} spins/g-catalyst and 6 9 × 10^{19} spins/g-catalyst for the unpretreated cupric salt and the cupric salt reduced by hydrogen at 30 Torr pressure at 205°C for 30 min (degree of reduction = 132 electrons per 100 Keggin anions), respectively Here the concentration of Mo^{5+} formed by the reduction (205°C, 30 min) was 2 5 × 10^{19} spins/g-catalyst Thus, 88% of the electrons formed by the reduction (205°C, 30 min) were captured by Cu^{2+} as cations ($\rightarrow$Cu^{+}) whereas the rest (12%) were captured by Mo^{6+} atoms in the 12-molybdophosphate anions ($\rightarrow$ Mo^{5+})

Analogous experiments had already been carried out for zinc (Zn^{2+}, SEP = −0 763 V), silver (Ag^{+}, SEP = 0 779 V), and potassium (K^{+}, SEP = −2 923 V) 12-molybdophosphates (*17, 19*) For the zinc salt previously reduced by hydrogen at 300°C (degree of reduction = 8 5 electrons per 100 Keggin anions), the electrons formed were

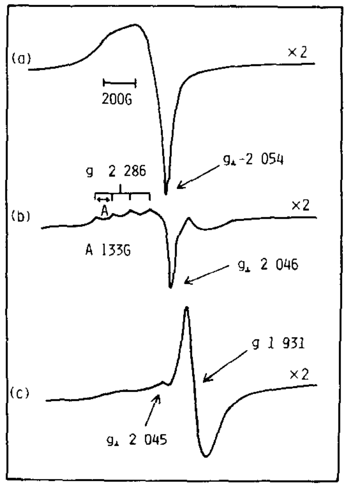


FIG 5 Variation in the ESR spectrum of cupric 12-molybdophosphate with increasing degree of reduction Catalyst 0 10 g, reduced by 30 Torr hydrogen for 30 min and then degassed for 30 min at the same temperature as employed in the reduction (a) Unpretreated (b) Reduced at 205°C (degree of reduction = 132 electrons per 100 Keggin anions) (c) Reduced at 230°C (213 electrons per 100 Keggin anions)

scarcely captured by Zn^{2+} as cations and nearly 100% of the electrons were captured by Mo^{6+} atoms in the 12-molybdophosphate anions (*19*) Similarly, 97% of the electrons formed by reduction were captured by Ag^+ as cations ($\rightarrow Ag^0$) for silver 12-molybdophosphate ($Ag_3[PMo_{12}O_{40}]$) whereas nearly 100% of the electrons formed by reduction were rather captured by Mo^{6+} atoms in the 12-molybdophosphate anions for potassium 12-molybdophosphate ($K_3[PMo_{12}O_{40}]$) (*17, 19*) Thus, it is interesting to note that the percentages of electrons captured by the cations are in the order $Zn^{2+} \ll Cu^{2+} < Pd^{2+}$ although the degree of reduction for the salts of these cations increases in the same direction This relation undoubtedly follows the order of increase in the SEP of the cations A similar relation is seen in the case of the silver and potassium salts It appears that the reducibility of the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates by IBA and carbon monoxide employed in the present work is associated with the ability of the cations to capture the electrons formed by reduction

DISCUSSION

Generally the prime factor affecting the reducibility of metal oxides as heterogeneous oxidation catalysts is the strength of the metal–oxygen bond It has been shown that the bond strength in MoO_3, V_2O_5, and Bi_2O_3 catalysts promoted by alkali metal and alkaline-earth metal oxides decreases with decreasing the oxidizing activity of the host metal atoms (*20–22*) It has also been shown that the reoxidizability of metal oxides by gaseous oxygen as heterogeneous oxidation catalysts increases with increasing the electron-donating nature of metal atoms at reduced state (*23*) On the other hand, the acid–base properties of the catalysts are important factors, in addition to the types and strength of the metal–oxygen bonds, affecting the selectivity of the heterogeneous catalytic oxidations (*23–25*) In our previous study on the catalytic properties of alkali metal and alkaline-earth metal 12-molybdophosphates as heterogeneous oxidation catalysts (*6*), the oxidizing activity of the Mo^{6+} atoms was found to correlate the electronegativity of the cations and both the reducibility of these metal salts by IBA and the reoxidizability of Mo^{5+} atoms by gaseous oxygen formed in these metal salts increased, as had been expected from the results for usual metal oxide catalysts reported (*20–23*), with decreasing electronegativity of the cations The trends in these redox properties of the metal 12-molybdophosphates as catalysts obtained with changing the cations were thus shown to be well understood as an electrostatic effect produced by the cations (alkali metal and alkaline-earth metal ions) on the strength of the molybdenum–oxygen bond and the acid–base properties of the catalyst (*6*)

In the present work, however, both the reducibility of metal 12-molybdophosphates by IBA and carbon monoxide and the reoxidizability of the Mo^{5+} atoms by gaseous oxygen rather increased with increasing SEP of the cations (group IB, IIb, IIIb and VIII metal ions and Pb^{2+}, Mn^{2+}, Ce^{3+}, and La^{3+}) although a regular correlation between the oxidizing activity of the Mo^{6+} atoms and the value of SEP of the cations was observed (Figs 2 and 3, Tables 1–4) Since the SEP of a metal ion is strongly associated with its electron affinity (hence electronegativity), the findings made in the present work suggest that the mechanism of the action of metal ions as cations is different between alkali metal and alkaline-earth metal ions (SEP = (−2 71)–(−3 05)V) and the metal ions employed in the present work (SEP = (+0 987)–(−2 52)V) The difference in the mechanism of the action of metal ions as cations suggested above is caused by the different redox properties of these metal ions as shown below

That is, based on the observed regular correlation of the oxidizing activity of the Mo^{6+} atoms with the SEP of the cations (Table 4) and the trend in the reducibility of alkali metal and alkaline-earth metal 12-molybdophosphates reported (*6*), the strength of the molybdenum-oxygen bond in the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates employed in the present work is expected to increase with increasing SEP of the cations However, the reducibility of the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates by IBA and carbon monoxide rather increased with increasing SEP of the cations irrespective of the valence state of the cations employed (Figs 2 and 3, Tables 1 and 2) This suggests that unlike the case of alkali metal and alkaline-earth metal 12-molybdophosphates a factor other than the strength of the molybdenum–oxygen bond decisively affected the reducibility of the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates We believe that this factor is the ability of the cations to capture the electrons formed by reduction The preferential capture of the electrons by the cations of a high SEP, found in the present work (Figs 4 and 5), supports this view Thus, when one electron transfer between Mo^{5+} and the cations takes place, reduction of the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates by IBA can be written as

$$\begin{tikzcd}
2Mo^{6+} + O^{2-} + 2Me^{n+} \arrow[dr] & 2Mo^{5+} + 2Me^{n+} \rightleftarrows 2Mo^{6+} + 2Me^{(n-1)+} \\
IBA \arrow[ur] & MAA + H_2O
\end{tikzcd} \qquad (8)$$

where Me^{n+} is a cation It is reasonable to consider that such cations having a high electron affinity as Pd^{2+}, Hg^{2+}, and Cu^{2+} strongly shift the above reaction to the right side through capture of the electrons formed by the reduction, because this delocalization of electrons by the cations causes an increase in the free energy change of the reduction and hence causes an decrease in the activation energy for this reduction step (Horiuchi–Polanyi rule) This kind of effect of cations can hardly be expected in the case of alkali metal and alkaline-earth metal ions (SEP = (−2 71)–(−3 05)V)

Ai (*5*) found that both the acidity of various metal 12-molybdophosphates and their catalytic activity for the vapor-phase oxidation of butadiene increased with increasing electronegativity of cations Based on this finding, he pointed out that the catalytic actions of 12-heteropoly compounds as heterogeneous oxidation catalysts can be understood from the acid–base properties of the reaction system (*5*) As shown elsewhere in the present work, however, the reducibility of the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates increased with increasing SEP of the cations irrespective of the acid–base properties of the reducing agents employed (IBA and carbon monoxide) (Figs 2 and 3, Tables 1 and 2) Therefore, we would like to believe that the observed trend in the reducibility of the metal 12-molybdophosphates by IBA and carbon monoxide (Figs 2 and 3, Tables 1 and 2) is intrinsic to these 12-molybdophosphates and is not influenced by the acid–base properties of reducing agents Ai (*26*) also reported a similar view in his following paper

As a result, we propose that cations have two kinds of roles as affecting the reducibility of 12-molybdophosphates That is, the one is the effect on the strength of the molybdenum–oxygen bond through changing the electrochemical properties of the molybdenum atoms whereas the other is the effect on the cleavage of the molybdenum–oxygen bond through delocalization of the electrons formed by reduction The former role predominates in the case of alkali metal and alkaline-earth metal ions as cations whereas the latter role predominates in the case of the group Ib, IIb, IIIb, and VIII metal ions and Pb^{2+}, Mn^{2+}, Ce^{3+}, and La^{3+} employed as cations in the present work

We now discuss the effect of cations on the reoxidizability of 12-molybdophosphates As described elsewhere in this paper, the reoxidizability of Mo^{5+} atoms by gaseous oxygen formed in alkali metal and alkaline-earth metal 12-molybdophosphates was already found to be decisively affected by the electron-donating nature of the Mo^{5+} atoms (*6*) This finding was shown to be consistent with the negligible observation of such adsorbed oxygen species as O_2^- and O^- in the course of the reoxidation of these metal salts (*6*) The negligible observation of these adsorbed oxygen species in the course of the reoxidation of the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates found in the present work (see Results) suggests that the prime factor affecting the reoxidizability of Mo^{5+} atoms formed in these 12-molybdophosphates is similar to that in the case of alkali metal and alkaline-earth metal 12-molybdophosphates That is, it seems that the reoxidizability of Mo^{5+} atoms by gaseous oxygen formed in the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates is also affected by the electron-donating nature of the Mo^{5+} atoms Unlike the case of alkali metal and alkaline-earth metal 12-molybdophosphates, however, the electrons formed by reduction for the group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates are captured not only by the Mo^{6+} atoms but also they are captured by the cations (Figs 4 and 5) Accordingly, the electrons requisite for the reoxidation step must be supplied from the Mo^{5+} atoms and the reduced cations as written below

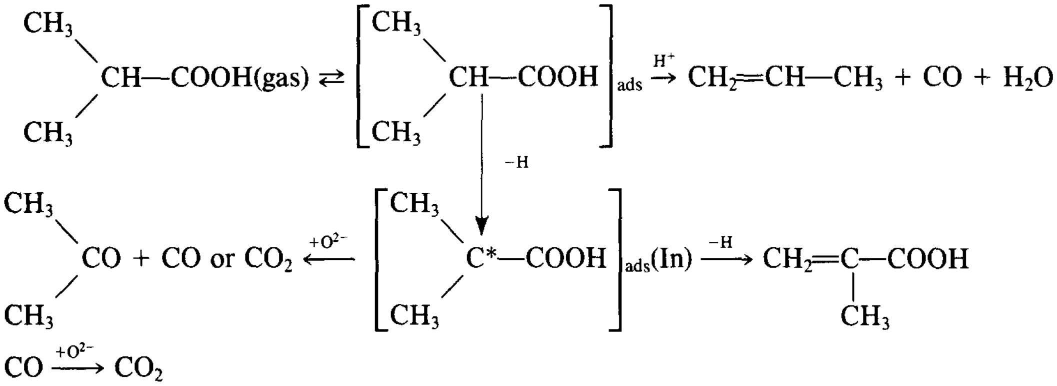
$$\begin{tikzcd} 2Mo^{6+} + 2Me^{(n-1)+} \rightleftarrows 2Mo^{5+} + 2Me^{n+} \arrow[dr] & 2Mo^{6+} + 2Me^{n+} \\ \tfrac{1}{2}O_2 \arrow[ur] & O^{2-} \end{tikzcd} \qquad (9)$$

In the case of alkali metal and alkaline-earth metal 12-molybdophosphates, all electrons requisite for the reoxidation step are supplied from the Mo^{5+} atoms (*6*) At any rate, when the cations have a high SEP, the electrons requisite in the reoxidation step are supplied mainly from the reduced cations However, the observed increase in the reoxidizability of the Mo^{5+} atoms with increasing SEP of the cations (Table 3) appears to be in contradiction with the view that the reoxidizability is decisively affected by the electron-donating nature of the catalyst Ai (*26*) also found a similar trend in the reoxidizability of transition metal 12-molybdophosphates, and he considered that this trend resulted from the change in diffusion coefficient of the lattice oxygen (*26*) However, we would like to consider that such cations having a high SEP as Pd^{2+}, Hg^{2+}, Cu^{2+}, and Ag^+, once reduced, have a relatively high electron-donating nature when compared with cations having a low SEP This view could be supported by a well-known fact that these four metal ions are readily reduced and reoxidized The unusually high reoxidizability of Mo^{5+} atoms formed in the silver and thallium salts is understandable, to some extent, by the relatively low oxidizing activity of these metal salts (Tables 3 and 4), as already found for potassium, rubidium, and cesium 12-molybdophosphates (*6*) At any rate, the remarkable increase in both the reducibility and reoxidizability of 12-molybdophosphate anions caused by Pd^{2+} as a cation, which was found in the present work (Figs 2 and 3, Tables 2 and 3), is in agreement with the already reported result (*27*) that the redox properties of V_2O_5 catalyst was greatly enhanced by the addition of a small amount of PdO

Thus it is found that the group Ib, IIb, IIIb, and VIII metal ions and Pb^{2+}, Mn^{2+},

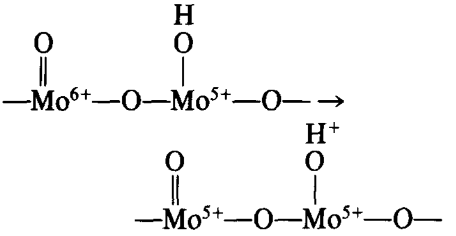
Ce^{3+}, and La^{3+} as cations capture the electrons formed in the reduction step in proportion to the value of SEP of the metal ions and supply these electrons to oxygen in the reoxidation step Hence one might say that these metal ions as cations play the role of an electron-reservoir their electron-capturing nature and electron-donating nature, i e , their redox properties decisively affect the reducibility and reoxidizability of 12-molybdophosphates as heterogeneous oxidation catalysts

Trends in the yield ratio (acetone/MAA) and the yield of propylene are discussed in relation to the reaction mechanism We already proposed the following reaction scheme for the oxidative dehydrogenation of IBA in which the oxidative dehydrogenation proceeds via a homolytic mechanism (*6*)



That is, the adsorbed IBA molecule forms an intermediate (In) when it is dehydrogenated by the lattice oxygen Further dehydrogenation of the In gives MAA whereas acetone is formed when the surface lattice oxygen adds onto the carbon atom C* According to Otake and his co-workers (*28*), the adsorbed IBA molecule is decomposed to propylene, carbon monoxide, and water when it interacts with a Brønsted acid Here, the carbon atom C* in the In acquires a positive charge by donating its electrons to the catalyst and the neighboring COOH group By analogy with allylic oxidation (*24, 25*), the nucleophilic addition of the surface lattice oxygen onto the carbon atom proceeds readily when it has a high positive charge The yield ratio (acetone/MAA) observed did not increase with increasing SEP of the cations and it had no dependence on the SEP of the cations although a regular correlation of the oxidizing activity (hence acidic property) of the metal 12-molybdophosphates with the SEP of the cations was observed (Fig 2, Table 4) For the metal 12-molybdophosphate-type catalysts employed in the present work, the effect of the acidic property of the catalyst on the formation of acetone seems to be weak

On the other hand, as Brønsted acids, that participate in the formation of propylene, such acids as those formed by adsorption of water on the cations (*29*) are probable Also the Brønsted acids formed by partial hydrolytic decomposition (*8*) which might have occurred during the preparation of the salts and catalytic oxidation are likely However, the amount of Brønsted acids formed by the hydrolytic decomposition must be small as compared with that of Brønsted acids formed by the adsorption of water during the catalytic oxidative dehydrogenation of IBA It has been reported that Brønsted acids are formed by the oxidation of hydrogen atoms at the surface of cupric and silver 12-tungstophosphates (*30*) This report suggests that some portion of the hydrogen atoms abstracted from IBA molecule is oxidized to form Brønsted acids during the catalytic oxidative dehydrogenation of IBA



$$-\overset{\overset{\displaystyle O}{\|}}{Mo^{6+}}-O-\overset{\overset{\displaystyle H}{\overset{\displaystyle O}{|}}}{Mo^{5+}}-O-\rightarrow -\overset{\overset{\displaystyle O}{\|}}{Mo^{5+}}-O-\overset{\overset{\displaystyle H^{+}}{\overset{\displaystyle O}{|}}}{Mo^{5+}}-O- \qquad (10)$$

The amount of Brønsted acids formed by the oxidation of hydrogen atoms [Eq (10)] must also be small because the surface hydroxyls formed are readily dehydrated during the catalytic oxidative dehydrogenation of IBA at 300°C Thus, we believe that the Brønsted acids formed by adsorption of water on the cations played the important role of propylene formation during the catalytic oxidative dehydrogenation of IBA over the metal 12-molybdophosphates at 300°C The increase in the yield of propylene with increasing SEP of the cations (Fig 2) supports this view The route for the complete oxidation of IBA to carbon oxides and water remains unknown

ACKNOWLEDGMENTS

We thank Professor Iwao Yasumori and Dr Yasunobu Inoue of the Department of Chemistry, Tokyo Institute of Technology for obtaining the XPS spectra and helpful discussions of the spectroscopic results

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