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

I. Alkali and Alkaline-Earth Metal Salts

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The effects of cations and heteroatoms on the catalytic activity and selectivity of 12-heteropolymolybdates, as catalysts, have been investigated in the vapor-phase oxidative dehydrogenation of isobutyric acid. The conversion of isobutyric acid at 300°C increased with decreasing electronegativity of the cations (H^+, alkali, and alkaline-earth metal ions) and the heteroatoms (P^{5+}, As^{5+}, and Si^{4+}), whereas it decreased with the change in the nature of the cations at 250°C. The yield ratio (acetone/methacrylic acid) at 300°C showed a behavior similar to the conversion, but the ratio was maximum over lithium and strontium salts. On the other hand, the electron affinity of Mo^{6+} in these 12-heteropolymolybdate-type catalysts paralleled the electronegativity of the cations and the heteroatoms, and the reactivity of Mo^{5+} to gaseous oxygen increased with decreasing electronegativity of these catalyst components (cations and heteroatoms). These results are discussed as the effects of these catalyst components on the electrochemical properties of the molybdenum atom, and the catalytic results obtained are explained on the basis of the exclusive participation of the lattice oxygen, the strength of molybdenum–oxygen bond, and the acid–base properties of the catalyst. It is shown that the molybdenum–oxygen bond is weakened as the catalyst components become less electronegative.

INTRODUCTION

Heteropoly acids and their salts forming a unique group of compounds produced by condensation of molybdates, tungstates, or other heavy-metal oxyanions together with a "heteroion" have long been investigated from the viewpoint of their structure and electronic properties, and the results are summarized in a number of reviews published (*1–3*). While all the species having the ratio of the condensing metal atoms to the "heteroatoms" from 12:1 to 1:1 have been reported, the one having the ratio of 12:1, which has the Keggin structure, has been reported most frequently (*1–3*). In recent years, considerable interests in the industrial applications of 12-heteropoly compounds 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 methacrolein and isobutyric acid to methacrylic acid (*4–7*). The most interesting feature of this investigation that it indicates is the possibility not only to substitute the protones 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. Nevertheless, only a few mechanistic studies (*8*) have been published on the effect of the catalyst components, including the condensing metals, on the oxidation reactions concerned.

In our previous paper (*9*), 12-heteropolymolybdates were shown to be active and selective catalysts for the oxidative dehydrogenation of isobutyric acid, and the mechanism of the surface reaction was discussed. In this work, we have first determined the catalytic activity and selectivity of 12-heteropolymolybdates containing various kinds of cations and heteroatoms for the oxidative dehydrogenation of isobutyric

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acid and then evaluated the oxidizing activity of the Mo^{6+} contained in the compounds and also the reactivity of Mo^{5+} to gaseous oxygen. These results are then discussed as effects of cations and heteroatoms on the electrochemical and catalytic properties of 12-heteropolymolybdates.

METHODS

Vapor-phase oxidation of isobutyric acid (IBA) was carried out at 250 and 300°C, using a conventional flow fixed-bed reactor at atmospheric pressure. The reactor system comprised a 12-mm-i.d. Pyrex tube, 580 mm long, and a concentric thermowell. The reactor was heated with a cylindrical electric furnace. The catalyst (yellow powder) was mixed with quartz sand (30–50 mesh), and Raschig rings (2 × 2 mm) were added above and below the catalyst bed. Both the quartz and Raschig rings were treated with an aqueous solution of nitric acid and then calcined at 1000°C.

Guaranteed reagent grade IBA (Wako Pure Chemical Industries, Ltd.) was used. It was fed into the reactor by bubbling nitrogen through the saturator held at the controlled temperature. Air was purified as shown previously (*10*). Helium was used as a diluent. The total feed rate was held constant at 150 NTPml/min: the standard feed composition was IBA 2.1 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. Gaseous products, i.e., propylene, CO_2, and CO were analyzed by injecting a portion of the gaseous effluent directly into the chromatographic columns. However, such liquid products as IBA, methacrylic acid (MAA), and acetone were collected in the trap cooled with a liquified nitrogen bath in 25-min intervals, and then they were washed out with 1.0 *M* solution of acetic acid in isopropyl alcohol. The solution was then analyzed and the result was considered as the representative reaction performance at the middle point of the respective trapping intervals. Three columns in series, 5.0 m of propylene carbonate (40 wt% on C-22), 2.0 m of ethylene glycol–$AgNO_3$ (60 wt% on Chromosorb P), and 2.0 m of molecular sieve 13X, and hydrogen as the carrier gas were used at room temperature for the analysis of the gaseous products. Acetone by means of 3.0 m of PEG 6000 (10 wt% on Celite 545, 80°C) using hydrogen as the carrier gas, and the other liquid products were analyzed with 3.0 m of SP-1200 (5 wt% on Uniport S, 135°C) using helium. The formation of acetone and propylene is always accompanied by an equimolar amount of CO or CO_2 (See Discussion). Therefore, 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 (H_3P) was purchased from Kanto Chemical Co., Inc. Its alkali metal, and alkaline-earth metal salts were prepared using their corresponding metal carbonates by the method reported (*11*). 12-Molybdosilicic acid, $H_4[SiMo_{12}O_{40}]$, (H_4Si), was prepared from MoO_3 and Na_2SiO_3 (*12*). These 12-heteropolymolybdates were then calcined at 300°C in air for 3 hr. Ammonium 12-molybdophosphate (NH_4P) and 12-molybdoarsenate (NH_4As) were prepared from ammonium paramolybdate and phosphoric or arsenic acid, respectively, using the evaporation–calcination method (*9*). These heteropoly compounds with the exception of the alkaline-earth metal salts were relatively highly crystallized.

The ESR measurements were carried out with a JEOL JES-PE spectrometer operating in the *X* band, adopting 100 kHz modulation frequency. The *g* values of paramagnetic species were determined by use of 2,2-diphenyl-1-picrylhydrazyl, and radical concentrations were estimated by comparing 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 hr in flowing dried nitrogen. Several 12-heteropolymolybdates had relatively large surface areas, i.e., 112 m^2/g (K_3P), 164 m^2/g (Rb_3P), 130 m^2/g (Cs_3P), 35 m^2/g (NH_4P), and 24 m^2/g (NH_4As), whereas the other 12-heteropolymolybdates had much smaller surface areas, 2–5 m^2/g (H_4Si, H_3P, NaH_2P, Na_2HP, Li_3P, and Na_3P), and 1–2 m^2/g (alkaline-earth metal salts). The result of differential thermal analysis revealed that most of these 12-heteropolymolybdates began to decompose at 400–440°C in dry air. However, Li_3P and H_4Si decomposed at 345°C, whereas K_3P, Rb_3P, and Cs_3P did not even at 600°C. Thus, we could use these 12-heteropolymolybdates in the catalytic oxidation of IBA at 300°C.

RESULTS

Effect of Cations

The catalytic oxidation of IBA over H_3P, alkali metal, and alkaline-earth metal salts was first investigated. Figure 1 shows the variation in the catalytic activity and selectivity of H_3P with elapsed time of reaction in the oxidative dehydrogenation of IBA at 300°C. Conversion of IBA was 55.2% at 22.5 min, but it decreased with time and leveled off at nearly a constant value of 32.0% after a preliminary period of about 5 hr. Similarly, the values of yield and selectivity to MAA became nearly constant at 16.3 and 50.9% within 5 hr, although they varied a little with time at initial stages of the reaction. The yields of acetone and propylene showed a trend similar to that in the conversion of IBA, but the selectivity to these two products remained almost constant at 28.6–29.7% and at 20.2–20.6% throughout the course of the reaction. The yield of CO + CO_2 was 0.1–0.2% throughout the course of the reaction. The selectivity to MAA + acetone was 79.7–81.2% with the exception of the initial value observed. These constant values of selectivity indicate no special change in the surface properties during the course of the reaction.

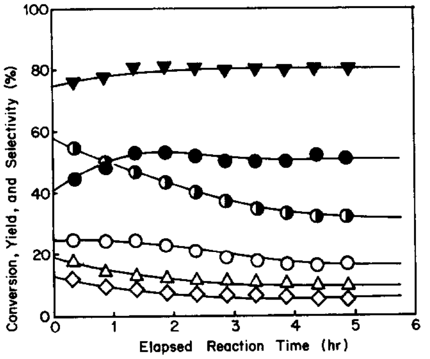


FIG. 1. Variation in the catalytic activity of 12-molybdophosphoric acid with time in the oxidative dehydrogenation of isobutyric acid. Reaction temp.: 300°C. Feed: IBA 2.1 vol%, O_2 3.2 vol%, N_2,He—diluent. Contact time: 1.88 g-catalyst · hr/g-mole. ◑: Conversion of IBA, ○: yield of MAA, △: yield of acetone, ◇: yield of propylene, ●: selectivity to MAA, ▼: selectivity to MAA + acetone. The yield of CO + CO_2 was 0.1–0.2%.

The steady-state catalytic activity and selectivity of the other alkali metal, and alkaline-earth metal salts were similarly determined at 300°C (Table 1). MAA was formed with a selectivity of 44.0–66.0%. It is seen that conversion of IBA and yields of MAA, propylene, and CO + CO_2 increased gradually when H^+ of H_3P was substituted step by step by less electronegative Na^+. The increases in conversion and yields with decreasing electronegativity (E.N.) of cations were also observed in the case of trialkali metal salts, and they followed the order: $Li_3P < Na_3P < K_3P < Rb_3P < Cs_3P$. The selectivity to propylene over H_3P, NaH_2P, and Na_2HP was relatively high, 17.8–20.3%, whereas it was as low as 5.5–11.0% over the trialkali metal salts. It is noteworthy that the yield ratio (acetone/MAA) increased with decreasing E.N. of the cations, and the maximum yield ratio was realized over Li_3P; then the ratio decreased with further decrease in E.N. of the cations. The relatively high yield ratios over Rb_3P and Cs_3P are probably caused by consecutive oxidation of MAA formed.

TABLE 1

Summary of the Steady-State Catalytic Activity of Alkali Metal and Alkaline-Earth Metal 12-Molybdophosphates in the Oxidative Dehydrogenation of Isobutyric Acid[a]

Catalyst	E.N. of cation[b]	Conversion of IBA (%)	Yield (%) of				Selectivity (%) to		Yield ratio (−)
			MAA	Acetone	Propylene	CO + CO_2	MAA	Propylene	Acetone/MAA
H_3P^c	2.1	32.0	16.3	9.0	6.5	0.2	50.9	20.3	0.56
NaH_2P^c	1.7[d]	67.8	34.5	20.6	12.2	0.5	50.9	18.0	0.59
Na_2HP^c	1.3[d]	77.4	38.4	25.2	13.8	0.6	49.7	17.8	0.66
Li_3P	1.0	50.5	25.5	22.3	2.8	0.2	50.5	5.5	0.88
Na_3P	0.9	54.6	30.5	19.4	3.5	0.8	55.9	6.4	0.64
K_3P	0.8	75.8	50.1	17.4	7.3	1.1	66.0	9.6	0.35
Rb_3P	0.8	92.0	56.0	22.5	8.8	4.6	60.9	9.5	0.40
Cs_3P	0.7	95.7	55.5	24.4	10.5	5.4	58.0	11.0	0.44
$Ca_{1.5}P$	1.0	17.2	8.4	5.7	3.0	0.1	49.0	17.7	0.67
$Mg_{1.5}P$	1.2	24.3	11.2	7.9	4.8	0.1	46.1	19.8	0.70
$Sr_{1.5}P$	1.0	43.2	19.0	16.2	7.8	0.2	44.0	18.1	0.85
$Ba_{1.5}P$	0.9	68.5	38.3	20.7	11.7	0.2	55.9	17.1	0.54

[a] Reaction temp.: 300°C. Feed: IBA 2.1 vol%, O_2 3.2 vol%, N_2,He—diluent. Contact time: 0.757 g-catalyst · hr/g-mole.

[b] Pauling's electronegativity.

[c] Contact time: 1.88 g-catalyst · hr/g-mole. This is also the case with the alkaline-earth metal salts.

[d] Average value.

Analogous effect of cations on the surface reaction was observed with the alkaline-earth metal salts (Table 1). The conversion of IBA over $Ca_{1.5}P$ was lower than that over $Mg_{1.5}P$ although Pauling's E.N. was Ca < Mg. However, the observed values of conversion over calcium, and magnesium salts seem reasonable because, for example, Ca^{2+} is more electronegative than Mg^{2+} in their oxides for the standard heat of formation of CaO is 151.7 kcal/g-mole and that of MgO is 143.8 kcal/g-mole (*13*). $Sr_{1.5}P$ showed the maximum yield ratio (acetone/MAA) among these four alkaline-earth metal salts. It is interesting to note that the selectivity to propylene over these neutral salts is relatively high, 17.1–19.8%, as compared with that of the trialkali metal salts, 5.5–11.0%.

The conversion of IBA over the trialkali metal salts increased in the reverse direction when the feed composition was made richer in IBA than O_2 and at the same time, the reaction temperature was lowered to 250°C (Table 2). Although the conversion of IBA determined after a preliminary period of 15 min increased in a similar manner as at 300°C; i.e., $H_3P < NaH_2P < Na_2HP$, and $Li_3P < Na_3P < K_3P < Rb_3P < Cs_3P$, it rapidly decreased with time, and at steady state, it decreased with decreasing E.N. of the cations, and it was as low as 1.0–2.0% over K_3P, Rb_3P, and Cs_3P. The selectivity to propylene remained 3.0–9.1% throughout the course of the reaction. These three salts were blue after use in the catalytic oxidation of IBA, indicating their intensive degree of reduction during the reaction. Thus, the steady-state catalytic activity at 250°C is a case in which the reoxidation of catalyst is the rate-controlling step, and the rate of reoxidation seems high when the cations are more electronegative. Hence, it could be concluded that the reduction of catalyst is rate-controlling at 300°C.

TABLE 2

Summary of the Catalytic Activity of Alkali Metal 12-Molybdophosphates in the Oxidative Dehydrogenation of Isobutyric Acid at 250°C[a]

Catalyst	Conversion of IBA (%)	
	at 15 min	at steady state
H_3P	47.3	22.1
NaH_2P	58.4	18.8
Na_2HP	75.4	17.8
Li_3P	18.7	7.6
Na_3P	37.8	15.4
K_3P	57.3	1.1
Rb_3P	62.7	1.0
Cs_3P	63.9	2.0

[a] Reaction temp.: 250°C. Feed: IBA 3.1 vol%, O_2 2.1 vol%, N_2,He—diluent. Contact time: 7.42 g-catalyst · hr/g-mole.

Effect of Heteroatoms

The results of catalytic reaction at 300°C over 12-heteropolymolybdates containing P^{5+}, As^{5+}, and Si^{4+} as heteroatoms are summarized in Table 3. All data were taken similarly when the steady-state catalytic activity was attained. The conversion of IBA, the yields of various products, and the yield ratio (acetone/MAA) over the acid-type catalysts as well as over the ammonium-salt-type catalysts increased markedly with decreasing E.N. of the heteroatoms. Since such observation agrees with that observed in the stepwise substitution of H^+ in H_3P by Na^+ (Table 1), the reduction of catalyst could also be rate-controlling for these two groups of catalysts. The selectivity to propylene over NH_4P and NH_4As was nearly the same (7.3 and 7.6%) but it was somewhat high (20.3 and 27.2%) over H_3P and H_4Si. The H_4Si previously used in the catalytic oxidation of IBA dissolved completely in water, indicating its negligible degree of decomposition during the oxidation of IBA (*11*).

Oxidizing Activity of Mo^{6+}

The most important factor affecting the catalytic activity of metal oxides in oxidation reactions is the strength of the metal–oxygen bond. The bond strength in MoO_3, V_2O_5, and Bi_2O_3 catalysts has been shown to be strongly influenced by the E.N. of the

TABLE 3

Comparison of the Steady-State Catalytic Activity of Various 12-Heteropolymolybdates at 300°C[a]

Catalyst	E.N. of heteroatom[b]	Conversion of IBA (%)	Yield (%) of				Selectivity (%) to		Yield ratio (−)
			MAA	Acetone	Propylene	CO + CO_2	MAA	Propylene	Acetone/MAA
H_3P	2.1	32.0	16.3	9.0	6.5	0.2	50.9	20.3	0.56
H_4Si	1.8	100	35.7	26.1	27.2	11.0	35.7	27.2	0.73
NH_4P	2.1	61.8	43.0	13.8	4.7	0.3	69.6	7.6	0.32
NH_4As	2.0	71.7	46.0	19.3	5.2	1.2	64.2	7.3	0.42

[a] Reaction conditions are the same as those of case (c) in Table 1.

[b] Pauling's electronegativity.

metal atoms (*14–16*). On the other hand, the acid–base properties of the catalysts are very important factors, in addition to the types and strengths of the metal–oxygen bonds, affecting the selectivity of the surface reactions (*17–19*). The oxidizing activity of Mo^{6+} atoms in these 12-heteropolymolybdates, which is strongly associated with electron affinity, E.N., and acid–base properties of the metal atoms, was evaluated by adsorbing various aromatic hydrocarbons in dry *n*-hexane.

The catalyst sample (100 mg in a 3-mm-i.d. quartz tube) was dried in flowing dry air at 250°C for 3 hr, and approximately 800 μl of the appropriate aromatic solution ($\frac{1}{10}$–$\frac{1}{50}$ *M*) was injected at room temperature. After purging with nitrogen, the tube was sealed with a glass cap and kept at room temperature for 20 hr. Concentrations of Mo^{5+} and aromatic radical cations formed were then determined by means of ESR at room temperature (Table 4). Although the dried-catalyst sample remained yellow in color, a small amount of Mo^{5+}, up to 0.08×10^{16} spins/100 mg catalyst, was found in the catalyst suspended in *n*-hexane. Thus, the Mo^{5+} concentrations listed in Table 4 are the corrected values. The Mo^{5+} formed in H_3P had the *g* value of 1.952–1.955 and its concentration increased from 0.1×10^{16} (benzene) to 8.2×10^{16} spins/100 mg catalyst (pyrene) with decreasing ionization potential of the adsorbed molecules. Here, 8.2×10^{16} spins/100 mg H_3P corresponds to the formation of one Mo^{5+} per 400 Keggin anions ($[PMo_{12}O_{40}]$). A similar trend in the Mo^{5+} concentration is roughly seen with the alkali metal salts. Furthermore, it seemed that the concentration decreased with decreasing E.N. of the cations. The Mo^{6+} atoms in H_3P, NaH_2P, Na_2HP, and Li_3P are capable of oxidizing benzene molecules whereas those in Na_3P cannot oxidize benzene but they can oxidize *o*-xylene. Similarly, the Mo^{6+} in K_3P, Rb_3P, and Cs_3P cannot oxidize benzene and *o*-xylene molecules, but they are able to oxidize naphthalene. Similar results were

TABLE 4

Formation of Mo^{5+} and Aromatic Cation Radicals by Adsorption of Various Aromatic Hydrocarbons on 12-Molybdophosphates[a]

Catalyst	Mo^{5+} (spins/100 mg catalyst) × 10^{-16}				
	Benzene 9.43–9.52[b]	*o*-Xylene 8.56	Naphthalene 8.10	Anthracene 7.58	Pyrene 7.55
H_3P	0.1	1.5	3.9	7.0	8.2
NaH_2P	0.03	0.9	2.7	3.9	3.7
Na_2HP	0.3	1.1	0.9	2.3	2.5
Li_3P	1.0	0.04	1.3	11.5	16.1
Na_3P	Neg[c]	0.02	0.8	1.5	2.4
K_3P	Neg	Neg	0.08	3.5	1.7
Rb_3P	Neg	Neg	0.08	6.0	2.5
Cs_3P	Neg	Neg	0.04	3.8	2.3
$Ca_{1.5}P$	0.1(0.02)[d]	0.4(0.01)	0.4(0.5)	0.7(0.2)	1.0(0.5)
$Mg_{1.5}P$	Neg(Neg)	0.2(0.07)	0.7(0.7)	0.4(0.6)	0.5(1.1)
$Sr_{1.5}P$	Neg(Neg)	0.3(0.02)	0.1(0.06)	0.5(0.6)	0.7(0.6)
$Ba_{1.5}P$	Neg(Neg)	0.9(0.03)	1.8(0.7)	2.8(0.6)	3.9(1.4)

[a] Catalyst: 100 mg. Adsorption time: 20 hr at room temperature.

[b] Ionization potential (eV). Ref. (*39*).

[c] Negligible.

[d] Aromatic cation radicals (spins/100 mg catalyst × 10^{-16}).

observed with the alkaline-earth metal salts (Table 4). In accordance with Ref. (*20*), these results are good evidence of the existence of parallelism that the oxidizing activity of Mo^{6+} increases with increasing E.N. of the cations. The relatively low Mo^{5+} concentrations in the case of pyrene–K_3P, Rb_3P, and Cs_3P are attributable to size effect (*20*).

The formation of Mo^{5+} was always accompanied by that of positive aromatic hydrocarbon radical ions, whose ESR spectra being symmetrical and sharp, whose *g* value ranging from 2.002 to 2.003, and whose peak to peak width ranging from 4.2 to 9.4 G, characteristic of aromatic radical cations (*21*). Furthermore, the radical concentrations agreed fairly well with those of Mo^{5+}, especially at relatively high concentrations, as illustrated in the case of the alkaline-earth metal salts (Table 4).

Reoxidation of Mo^{5+}

The catalyst (100 mg in a 3-mm-i.d. quartz tube) was reduced at 30 Torr hydrogen (1 Torr = 133.3 N/m^2) at 300°C for 1 hr and then evacuated at the same temperature for 30 min. After the value of *g* and radical concentration of Mo^{5+} formed (denoted as C_0, number of Mo^{5+} formed per 100 Keggin anions) were determined, gaseous oxygen was introduced at 25 Torr at room temperature and the catalyst was then heated at various temperatures for 30 min. The ESR spectra of Mo^{5+} formed were relatively broad and anisotropic. The *g* values increased with decreasing E.N. of the cations as well as of the heteroatoms in the five groups of catalysts (Table 5). The reoxidation of Mo^{5+} atoms formed in H_3P was initiated at about 250°C, and 20.3% of Mo^{5+} atoms were oxidized at 300°C (Fig. 2). Although the initial Mo^{5+} concentration decreased by stepwise substitution of H^+ in H_3P by Na^+ (C_0 = 4.0 and 2.2 for NaH_2P and Na_2HP, respectively; C_0 for H_3P and Na_3P, see Fig. 2), the reoxidizability of Mo^{5+} increased: the reoxidation was initiated at about 75°C, and 53.5, 57.8, and 97.1% of the initial Mo^{5+} in NaH_2P, Na_2HP,

TABLE 5

Summary of the g Values of Mo^{5+} Formed in Various 12-Heteropolymolybdates[a]

Catalyst	g
H_3P	1.931
NaH_2P	1.949
Na_2HP	1.951
Li_3P	1.941
Na_3P	1.945
K_3P	1.952
Rb_3P	1.956
Cs_3P	1.956
$Ca_{1.5}P$	1.921
$Mg_{1.5}P$	1.933
$Sr_{1.5}P$	1.924
$Ba_{1.5}P$	1.939
H_3P	1.931
H_4Si	1.937
NH_4P	1.939
NH_4As	1.949

[a] Catalyst: 100 mg, reduced with 30 Torr H_2 at 300°C for 1 hr.

and Na_3P, respectively, were oxidized at 300°C. In the case of the trialkali metal salts, the temperature at which reoxidation was initiated, decreased in a drastic manner with decreasing E.N. of the cations though the initial concentration of Mo^{5+} did not vary widely (Fig. 2).

The above findings were also evident with the alkaline-earth metal salts. However, the Mo^{5+} atoms were not so easily oxidized as those on the trialkali metal salts though the initial concentration of Mo^{5+} was nearly the same as that of the trialkali metal salts ($C_0 = 1.6$, 2.6, 0.88, and 0.74 for Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+} salts, respectively). The reaction became observable at 200°C, but at 300°C 69.2, 57.8, 49.1, and 42.5% of the initial Mo^{5+} in $Ca_{1.5}P$, $Mg_{1.5}P$, $Sr_{1.5}P$, and $Ba_{1.5}P$, respectively, remained unoxidized.

In the case of H_4Si ($C_0 = 2.9$), reoxidation proceeded even at 100°C; 6.7, 16.1, and 36.6% of the initial Mo^{5+} were oxidized at 100, 130, and 200°C, respectively. This is in contrast to the result in the case of H_3P (Fig. 2). Similarly, the Mo^{5+} atoms in NH_4As ($C_0 = 0.76$) were more easily oxidized than those in NH_4P ($C_0 = 3.0$). That is, 26.4 and 44.5% of the initial Mo^{5+} in NH_4As were oxidized at 75 and 100°C, respectively, whereas Mo^{5+} in NH_4P was scarcely oxidized at 75°C, but 32.0% disappeared at 100°C. As a result, the reoxidizability of Mo^{5+} increased significantly with decreasing E.N. of the cations and heteroatoms. It appears that the activation energy for the reoxidation of Mo^{5+} is small when these catalyst components (cations and heteroatoms) are less electronegative. In this experiment, no formation of negatively charged oxygen species such as O_2^- and O^- was observed by means of ESR even at 77°K and at temperature at which reoxidation took place. This indicated that exclusive participation of lattice oxygen in the catalytic oxidation took place.

DISCUSSION

The effects of cations and heteroatoms on the electrochemical properties of molybdenum atoms are discussed in relation to the reoxidizability of Mo^{5+}. The formation of Mo^{5+} and aromatic radical cations by

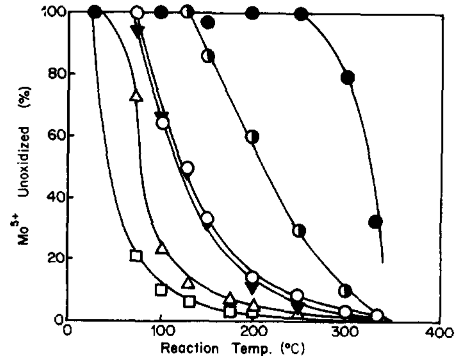


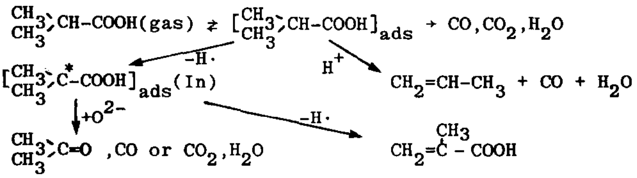
FIG. 2. Reaction of Mo^{5+} with gaseous oxygen formed in 12-molybdophosphoric acid and its trialkali metal salts. Catalyst: 100 mg, previously reduced with 30 Torr H_2 at 300°C for 1 hr. Reaction time: 30 min. Oxygen: 25 Torr. ●: H_3P ($C_0 = 9.5$), ◑: Li_3P (0.17), ○: Na_3P (1.2), ▼: K_3P (1.5), △: Rb_3P (1.2), □: Cs_3P (1.6).

adsorption of aromatic hydrocarbons (Table 4) is attributed to the electron transfer occurring via the overlapping of the aromatic π system with the outer-sphere molybdate framework "conduction bands" as proposed previously (*22–24*). The increase in the oxidizing activity of Mo^{6+} with increasing E.N. of the cations (Table 4) indicates that Keggin anions electrically interact with these cations. Through this interaction, the reoxidizability of Mo^{5+} formed in the Keggin anions is affected. In the case of the usual MoO_3 and V_2O_5 catalysts, the reoxidation of Mo^{5+} and V^{4+} by gaseous oxygen proceeds through the accompanying formation of the adsorbed oxygen species, O_2^- and O^-, and is completed with the formation of lattice oxygen O^{2-}; i.e., O_2(gas) $\rightarrow O_2^- \rightarrow O^- \rightarrow O^{2-}$(lattice) with rising temperature (*10, 25, 26*). No observation of such adsorbed oxygen species on the surface of 12-heteropolymolybdates (See Results) suggests that these oxygen species, once formed, are rapidly converted to lattice oxygen. That is, in the course of the reoxidation, the energy barrier is the highest for the step in which the electrons transfer from Mo^{5+} to physically adsorbed diatomic oxygen molecules. This peculiar behavior may be caused by the ionic character of 12-heteropolymolybdate crystals, in which the electrons formed by reduction are strongly trapped by particular molybdenum atoms (*27*). At any rate, this energy barrier is lowered as the electron-donating nature of Mo^{5+} rises. Thus, the increase in the reoxidizability of Mo^{5+} with decreasing E.N. of the cations (Fig. 2, etc.) is reasonable because the relatively high electron-donating nature of Mo^{5+} can be expected when the oxidizing activity of Mo^{6+} is low.

The following relations, $H_3P < H_4Si$ and $NH_4P < NH_4As$, associated with the reoxidizability of Mo^{5+} (see Results) suggest that the electron-donating nature of Mo^{5+} is also affected by the E.N. of the heteroatoms. Accordingly, the relation of the oxidizing activity of Mo^{6+} in terms of heteroatoms in one case is $Si^{4+} < P^{5+}$ and in another, it is $As^{5+} < P^{5+}$. These relations evidently follow the increasing order of the E.N. of the heteroatoms. The first of the two relations agrees with the order of the half-wave potential of the 12-heteropolytungstic and 12-heteropolymolybdic acids reported (*1, 22, 28*). Thus, the electrochemical properties of molybdenum atoms in 12-heteropolymolybdates with which the acid–base properties of the atoms and the strengths of the metal–oxygen bonds are strongly associated are found to be affected decisively by the E.N. of the cations and heteroatoms. The increase in the *g* value of Mo^{5+} with decreasing E.N. of the catalyst components (Table 5) is a result of this effect. The observations made in the present study are supported by previously reported results, i.e., the reduction of Co^{3+} to Co^{2+} by adsorption of toluene on $K_5[Co(III)W_{12}O_{40}]$ (*24*) and the coordination of cations on the lattice oxygen at the outer-sphere molybdate framework (*29, 30*). Analogous promotional effects of alkali metal and alkaline-earth metal oxides as well as of group Va element oxides have already been reported in the case of the usual MoO_3, V_2O_5, Bi_2O_3, and TiO_2 catalysts (*14–16, 31*).

The mechanism of redox cycles of 12-molybdophosphates has been studied by many Japanese workers (*7, 32, 33*), and although all of them recognized the important roles of the lattice oxygen, the terminal (Mo=O) and/or the bridged one (Mo—O—Mo), involved in the mechanism, their conclusions are of variance. However, the exclusive participation of the lattice oxygen in the catalytic oxidation of IBA cannot be denied as shown elsewhere in this paper. Eguchi and co-workers (*8*) reported the following order of catalytic activity per unit BET surface area in the oxidation of methacrolein at 320°C: $Cs_3P < K_3P < Na_3P$. This order is similar to our trend of activity (Table 1) when the conversion of IBA is normalized to the unit BET surface area. However, the surface area of 12-heteropolymolybdates is markedly affected by degree of hydration as well as by the temperature they are exposed to (*34*). Hence, the surface area conventionally measured by the BET method cannot be used as the effective area during the catalytic oxidation of hydrocarbons. However, regularity of the conversion of IBA and the yield of various products with changing cations and heteroatoms (Tables 1, 2, and 3) strongly suggests nonappearance of large difference in the effective surface area during the catalytic oxidation of IBA. Assuming this suggestion, trends observed in the catalytic results are readily understandable based on the conventional viewpoint. Thus, the conclusion that the reduction of catalyst is the rate-controlling step at 300°C (Tables 1 and 3) is not unreasonable because the metal–oxygen bond in the usual MoO_3, V_2O_5, and Bi_2O_3 catalysts was weak when the E.N. of promoters such as alkali metal and alkaline-earth metal oxides as well as group Va element oxides was low (*14–16*). On the other hand, the increase in the rate of reoxidation of a catalyst with increasing E.N. of the cations (Table 2) appears to be in contradiction with the observed effect of the cations on the reoxidizability of Mo^{5+} (Fig. 2, etc.). This is caused by the large difference in the activation energy of the reoxidation of Mo^{5+}, as pointed out in the Mo^{5+} reoxidizability study. That is, the rate of reoxidation of Mo^{5+} having a high activation energy is likely to be greater than that of Mo^{5+} having a low activation energy at higher temperature. The same trend in the rate of reoxidation of the catalyst as derived from the oxidation of IBA (Table 2), i.e., the increase in the rate with increasing strength of the metal–oxygen bond was also observed in the case of the usual metal oxide catalysts for the oxidation of propylene (*35*). This supports our viewpoint.

Trends in the yield ratio (acetone/MAA) and the selectivity to propylene are discussed in relation to the reaction mechanism. M. Otake and co-workers (*4, 7*) proposed a heterolytic mechanism for the oxidative dehydrogenation of IBA, but we propose the following reaction scheme in which the oxidative dehydrogenation proceeds via a homolytic mechanism (*9*) as in the case of allylic oxidation (*36*).



The adsorbed IBA molecule is decomposed to propylene, CO, and water when it interacts with a Brønsted acid (*37*). On the other hand, 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*. This carbon atom acquires a positive charge by donating its electrons to the catalyst as in the case of aromatic hydrocarbons (Table 4) and to the neighboring COOH group. By analogy with allylic oxidation (*17, 18*), the nucleophilic addition of the surface lattice oxygen to the carbon atom proceeds readily when it has a high positive charge and when the bond between molybdenum and lattice oxygen is weak. Thus, the observation of the maximum yield ratios over Li_3P and $Sr_{1.5}P$ (Table 1) is a result of the effect of E.N. of the cations on the acidic properties of the molybdenum atoms and on the reactivity of the lattice oxygen in reverse direction. The increase in the yield ratio with decreasing E.N. of the heteroatoms (Table 3) can be understood similarly. The above reaction scheme shows that 78.6–94.7% of the IBA reacted was via the passway through In (Table 1, Fig. 1).

The oxidation of IBA and the formation of propylene compete with each other. As Brønsted acids, that participate in the formation of propylene, such acids as cations and those formed by partial hydrolytic decomposition (*11*) which might have occurred during the preparation of the salts and catalytic oxidation are probable. Also the Brønsted acids formed by adsorption of water on the alkaline-earth metal cations and the molybdenum atoms, as in the case of metal sulfates (*38*), are likely. Although it remains unknown which of the acids play the significant role in the formation of propylene, the relatively high selectivity to propylene over the acidic 12-heteropolymolybdates (H_4Si, H_3P, NaH_2P, and Na_2HP) and the alkaline-earth metal salts as compared with that over the trialkali metal salts and the ammonium salts (Tables 1, 2, and 3) is an expected result. However, the increase in the yield of propylene with decreasing E.N. of the cations (Table 1) remains unclarified.

As described above, the effects of cations and heteroatoms on the catalytic oxidation of IBA over various 12-heteropolymolybdates can be well understood in terms of E.N., as in the case of the usual metal oxide catalysts (*14–16, 31*). This viewpoint does not agree with the one (*8*) in which the effect of cations was explained in terms of ionic potential.

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