

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

3. Molybdotungstophosphoric and Molybdovanadophosphoric Acids

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The effect of condensing metal atoms (tungsten and vanadium) on the catalytic properties of 12-heteropolyphosphoric acids, as heterogeneous oxidation catalysts, has been investigated. While both the reducibility by isobutyric acid and carbon monoxide and reoxidizability by gaseous oxygen of molybdovanadophosphoric acids ($H_{3+n}[PMo_{12-n}V_nO_{40}]$, $n = 0, 1, 2$, and 3) paralleled their highest oxidation-reduction potential and showed the maximum at $H_4[PMo_{11}V_1O_{40}]$, the reoxidizability of molybdotungstophosphoric acids ($H_3[PMo_{12-n}W_nO_{40}]$, $n = 0, 1, 2, \dots, 6$, and 12) increased with lowering their highest oxidation-reduction potential and their reducibility decreased markedly with increasing the content of tungsten atom irrespective of the change in their highest oxidation-reduction potential. The preferential formation of V^{4+} in the reduced molybdovanadophosphoric acids and that of Mo^{5+} in the reduced molybdotungstophosphoric acids, which were revealed by ESR, also suggested different mechanistic roles of condensing metal atoms between tungsten and vanadium atoms. These results are discussed as the effect of condensing metal atoms on the reducibility and reoxidizability of 12-heteropolyphosphoric acids, and it is shown that unlike the tungsten atoms as a Mo-O bond strength modifier the vanadium atoms play the role of an electron reservoir: their redox properties decisively affect the reducibility and reoxidizability of molybdovanadophosphoric acids. It is also shown that potassium, rubidium, and cesium salts of $H_4[PMo_{11}V_1O_{40}]$ are fairly selective catalysts for the oxidative dehydrogenation of isobutyric acid to methacrylic acid.

INTRODUCTION

Heteropoly acids and their salts are a unique group of compounds produced by condensation of molybdates, tungstates, or other heavy metal oxyanions together with a heteroion (1, 2). Since 12-molybdophosphoric acid, $H_3[PMo_{12}O_{40}]$ and its related compounds have recently been reported to be superior catalysts for the vapor-phase oxidation of methacrylaldehyde and isobutyric acid (IBA) to methacrylic acid (MAA) (3-6), the effects of the catalyst components (cations, heteroatoms, and condensing metal atoms) on the catalytic properties of 12-heteropoly compounds as heterogeneous oxidation catalysts have extensively been investigated (7-13). However, only a few mechanistic studies (3) have been pub-

lished on the effect of condensing metal atoms. Otake and Onoda (3) determined the catalytic activity and selectivity of molybdotungstophosphoric acids and molybdovanadophosphoric acids for the oxidative dehydrogenation of IBA and then correlated the highest oxidation-reduction potential of molybdovanadophosphoric acids with their catalytic activity and selectivity to MAA, although the physical meaning of the proposed correlation was not shown.

In our previous papers (9, 13), the effects of cations (H^+ , alkali metal and alkaline-earth metal ions, and group Ib, IIb, IIIb, and VIII metal ions) and heteroatoms (P^{5+} , As^{5+} , and Si^{4+}) on the reducibility and reoxidizability of 12-heteropolymolybdates as heterogeneous oxidation catalysts were mechanistically investigated in the vapor

phase oxidative dehydrogenation of IBA. In the present work, we have prepared molybdotungstophosphoric acids and molybdovanadophosphoric acids and then determined their catalytic activity and selectivity for the oxidative dehydrogenation of IBA. We have also investigated the behavior of the electrons formed by reduction of these 12-heteropolyphosphoric acid-type catalysts by means of electron spin resonance (ESR) and evaluated the oxidizing activity (i.e., an affinity for electron) of the catalysts by means of cyclic voltammetry as well as the reoxidizability by gaseous oxygen by means of ESR. These results are then discussed as the effect of condensing metal atoms on the physicochemical and catalytic properties (reducibility and reoxidizability) of the 12-heteropolyphosphoric acids and are compared with the results (9, 13) reported for metal 12-molybdophosphates. The catalytic activity and selectivity of various metal salts of 11-molybdo-1-vanadophosphoric acid ($H_4[PMo_{11}V_1O_{40}]$) for the oxidative dehydrogenation of IBA are also determined.

METHODS

Vapor phase catalytic oxidative dehydrogenation of IBA was carried out at 300°C with 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 papers (9, 13). Guaranteed reagent grade IBA (Wako Pure Chemical Industries, Ltd.) was used. The total feed rate was held constant at 150 NTPml/min: the standard feed composition was IBA 1.8 vol% and O_2 3.1 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 reported previously (9). 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 shown in this paper,

which are attributed to the destructive oxidation of IBA, 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 and 12-tungstophosphoric acid ($H_3[PW_{12}O_{40}]$) were purchased from Kanto Chemical Co., Inc. Molybdotungstophosphoric acids and molybdovanadophosphoric acids were prepared following the procedures of Tsigdinos and Hallada (14). These 12-heteropolyphosphoric acids obtained (powder) were then calcined at 300°C in air for 3 hr and were then stored over silica gel. Metal salts of $H_4[PMo_{11}V_1O_{40}]$ were similarly prepared as in the case of 12-molybdophosphates (9, 13).

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 by the BET method after drying at 150°C for 1 hr in flowing dried nitrogen. Both molybdotungstophosphoric acids and molybdovanadophosphoric acids prepared as solid catalysts had small surface areas, 1–3 m^2/g . The result of differential thermal analysis revealed that those 12-heteropolyphosphoric acids began to decompose above 400°C in dry air. The highest oxidation–reduction potential of these 12-heteropolyphosphoric acids was determined at 20°C by means of cyclic voltammetry: a conventional H-cell (volume = ca. 20 ml) equipped with platinum wire electrodes was used.

RESULTS

Catalytic Results

Figure 1 shows the variation in the catalytic activity and selectivity of 10-molybdo-

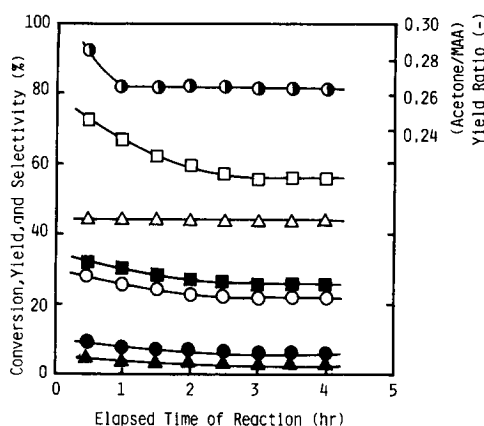


Fig. 1. Variation in the catalytic activity of 10-molybdo-2-tungstophosphoric acid with time in the oxidative dehydrogenation of isobutyric acid. Reaction temperature: 300°C. Feed: IBA 1.8 vol%, O₂ 3.1 vol%, N₂, He—diluent. Contact time: 3.14 g-catalyst · hr/g-mol. □, Conversion of IBA; ■, yield of MAA; ○, yield of propylene; ●, yield of acetone; ▲, yield of CO + CO₂; △, selectivity to MAA, ●, (acetone/MAA) yield ratio.

2-tungstophosphoric acid (H₃[PMo₁₀W₂O₄₀]) with elapsed time of reaction in the oxidative dehydrogenation of IBA at 300°C. Conversion of IBA was as high as 72.3% at 30 min, but it decreased with time and leveled off at nearly a constant value of 54.4% after a preliminary period of 4 hr. Similarly, the yields of MAA, propylene, and acetone decreased with time and they became nearly constant at 23.9, 21.7, and 6.3%, respectively, within 4 hr. Although the selectivities to MAA and propylene remained nearly constant at 43.6–44.0% and 39.2–40.0%, respectively, throughout the course of the reaction, the selectivity to acetone decreased a little at the initial stages of the reaction (12.2% at 30 min → 11.2% at 1 hr) and then became nearly constant at 11.2–11.6% after a preliminary period of 1 hr. The relatively great values of the selectivity to acetone and the (acetone/MAA) yield ratio at 30 min (Fig. 1) are caused by the relatively high degree of the oxidation states of the catalyst at the initial stages of the reaction. At any rate, the observation of nearly constant values of the selectivity to MAA,

propylene, and acetone throughout the course of the reaction indicates that the surface properties of the catalyst did not change much during the course of the oxidative dehydrogenation of IBA at 300°C. The combined yield of CO and CO₂ due to the destructive oxidation of IBA was as low as 2.5–3.7% throughout the course of the reaction (Fig. 1).

The steady-state catalytic activity and selectivity of the other molybdotungstophosphoric acids were similarly determined at 300°C and the results obtained are summarized in Table 1. Conversion of IBA over H₃[PMo₁₂O₄₀] was as high as 80.6%, but it decreased as the molybdenum atoms in H₃[PMo₁₂O₄₀] were replaced by tungsten atoms and the conversion was as low as 9.0% over H₃[PW₁₂O₄₀]. The yields of MAA and acetone and the selectivity to MAA showed a trend similar to the conversion of IBA: the selectivity was the highest, 60.5%, over H₃[PMo₁₂O₄₀] whereas that was the lowest, 1.5%, over H₃[PW₁₂O₄₀] (Table 1). However, the yield and selectivity to propylene showed different trends. That is, the yield of propylene rather increased as the molybdenum atoms in H₃[PMo₁₂O₄₀] were replaced step by step with tungsten atoms and it reached the maximum value (21.7–22.8%) over H₃[PMo₁₀W₂O₄₀] and H₃[PMo₉W₃O₄₀]. It should be noted that the observed trend in the yield of propylene agreed with the trend in the highest oxidation–reduction potential of molybdotungstophosphoric acids (Table 1). In contrast to the selectivity to MAA, the selectivity to propylene increased markedly with increasing the content of tungsten atom and it was as high as 91.5% over H₃[PW₁₂O₄₀]. Thus, H₃[PW₁₂O₄₀] promoted predominantly the acid–base catalytic reaction of IBA (i.e., propylene formation, see Discussion) and had a negligible activity as an oxidation catalyst. The (acetone/MAA) yield ratio showed the minimum value (0.26) over H₃[PMo₁₀W₂O₄₀] (Table 1). Similar trends in the conversion of IBA, yields, and selectivity to the products were ob-

TABLE 1

Summary of the Steady-State Catalytic Activity of Molybdotungstophosphoric Acids in the Oxidative Dehydrogenation of Isobutyric Acid^a

Catalyst	Highest oxidation-reduction potential (V vs SCE) ^b	Conversion of IBA (%)	Yield (%) of			Selectivity (%) to		Yield ratio (-) of acetone/MAA	
			MAA	Acetone	Propylene	CO + CO ₂	MAA		Propylene
H ₃ [PMo ₁₂ O ₄₀]	0.318	80.6	48.8	20.3	10.0	1.5	60.5	12.5	0.42
H ₃ [PMo ₁₁ W ₁ O ₄₀]	0.326	70.0	40.5	12.7	14.8	2.0	57.8	21.1	0.32
H ₃ [PMo ₁₀ W ₂ O ₄₀]	0.330	54.4	23.9	6.3	21.7	2.5	43.7	40.0	0.26
H ₃ [PMo ₉ W ₃ O ₄₀]	0.328	44.0	14.1	3.8	22.8	4.3	32.5	51.9	0.27
H ₃ [PMo ₈ W ₄ O ₄₀]	0.320	28.1	5.5	1.8	18.4	2.5	19.5	65.4	0.32
H ₃ [PMo ₇ W ₅ O ₄₀]	0.306	23.8	4.0	1.8	15.1	2.9	16.7	63.6	0.45
H ₃ [PMo ₆ W ₆ O ₄₀]	0.299	22.3	2.3	1.2	17.2	1.6	10.5	77.2	0.50
H ₃ [PW ₁₂ O ₄₀]	< -0.25	9.0	0.1	<0.1	8.2	0.6	1.5	91.5	—

^a Reaction temperature: 300°C. Feed: IBA 1.8 vol%, O₂ 3.1 vol%, N₂, He—diluent. Contact time: 3.14 g-catalyst · hr/g-mol.^b At 20°C. Anode: Pt wire and 1 N H₂SO₄ (dioxane/water = 1/1). Cathode: Pt wire and 0.01 M molybdotungstophosphoric acids in 1 N H₂SO₄ (dioxane/water = 1/1).

TABLE 2

Summary of the Steady-State Catalytic Activity of Molybdovanadophosphoric Acids in the Oxidative Dehydrogenation of Isobutyric Acid^a

Catalyst	Highest oxidation-reduction potential (V vs SCE) ^b	Conversion of IBA (%)	Yield (%) of			Selectivity (%) to		Yield ratio (-) of acetone/MAA	
			MAA	Acetone	Propylene	CO + CO ₂	MAA		Propylene
H ₃ [PMo ₁₂ O ₄₀]	0.318	48.0	27.4	15.1	5.5	0.1	57.1	11.4	0.55
H ₄ [PMo ₁₁ V ₁ O ₄₀]	0.501	75.0	51.6	11.9	10.4	1.0	68.8	13.9	0.23
H ₅ [PMo ₁₀ V ₂ O ₄₀]	0.482	52.3	37.6	7.9	6.7	0.1	71.9	12.8	0.21
H ₆ [PMo ₉ V ₃ O ₄₀]	0.470	33.2	23.8	4.7	4.7	0.1	71.6	14.2	0.20

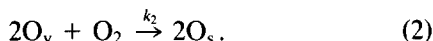
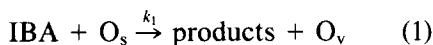
^a Reaction temperature: 300°C. Feed: IBA 1.8 vol%, O₂ 3.1 vol%, N₂, He—diluent. Contact time: 1.50 g-catalyst · hr/g-mol.^b At 20°C. Determined similarly as in the case of molybdotungstophosphoric acids (Table 1).

served at the initial stage (at 30 min) of the oxidative dehydrogenation of IBA.

The steady-state catalytic activity and selectivity of molybdovanadophosphoric acids for the oxidative dehydrogenation of IBA were similarly determined at 300°C (Table 2). Unlike molybdotungstophosphoric acids, both the conversion of IBA and the yield of MAA paralleled the value of the highest oxidation–reduction potential of molybdovanadophosphoric acids: the conversion and the yield were the greatest over $H_4[PMo_{11}V_1O_{40}]$. The yield of propylene also paralleled the value of the highest oxidation–reduction potential of the acids as in the case of molybdotungstophosphoric acids. The selectivity to MAA increased as the molybdenum atoms in $H_3[PMo_{12}O_{40}]$ were replaced step by step with vanadium atoms and the selectivity was as high as ca. 72% over $H_5[PMo_{10}V_2O_{40}]$ and $H_6[PMo_9V_3O_{40}]$. The (acetone/MAA) yield ratio decreased from 0.55 to 0.20–0.23 with replacement of the molybdenum atoms by vanadium atoms (Table 2). The observed trends in the catalytic activity and selectivity of 12-heteropoly phosphoric acids in the oxidative dehydrogenation of IBA (Tables 1 and 2) are similar to those reported by Otake and Onoda (3).

Kinetic Study

The catalytic oxidative dehydrogenation of IBA over some molybdotungstophosphoric acids and molybdovanadophosphoric acids at 300°C was kinetically studied on the basis of the redox mechanism shown below.



Where k is rate constant, and O_s and O_v are surface lattice oxygen and its vacancy, respectively. Assuming that the catalyst is nearly completely oxidized during the oxidative dehydrogenation of IBA, the following two equations had been derived for the surface concentration of O_s and the initial

TABLE 3

Summary of the Kinetic Parameters for the Catalytic Oxidative Dehydrogenation of Isobutyric Acid over Molybdotungstophosphoric Acids and Molybdovanadophosphoric Acids^a

Catalyst	k_1^b	k_2^c	$[O_s] (-)^d$
$H_3[PMo_{12}O_{40}]$	0.180	1–2	0.906
$H_3[PMo_{10}W_2O_{40}]$	0.172	1–2	0.909
$H_3[PMo_8W_4O_{40}]$	0.096	1–2	0.947
$H_3[PMo_6W_6O_{40}]$	0.030	1–2	0.983
$H_4[PMo_{11}V_1O_{40}]$	0.329	1–2	0.847
$H_5[PMo_{10}V_2O_{40}]$	0.201	1–2	0.960

^a Reaction temperature: 300°C. Feed: IBA 1.3–2.2 vol%, O_2 2.5–3.6 vol%, N_2 , He—diluent.

^{b,c} g-mol/g-catalyst · hr · atm.

^d At IBA 1.8 vol%, O_2 3.1 vol%, and $k_2 = 1.0$.

rate of the catalytic oxidative dehydrogenation of IBA(13).

$$[O_s] = \frac{k_2 P_{O_2}}{k_1 P_{IBA} + k_2 P_{O_2}} \quad (3)$$

$$r = \frac{k_1 k_2 P_{IBA} P_{O_2}}{k_1 P_{IBA} + k_2 P_{O_2}} \quad (4)$$

Here P is the partial pressure of reactant in the feed mixture. Thus,

$$\frac{P_{IBA} P_{O_2}}{r} = \frac{P_{O_2}}{k_1} + \frac{P_{IBA}}{k_2} \quad (5)$$

The linear relationship between $P_{IBA} P_{O_2}/r$ and P_{O_2} was really observed when P_{O_2} was changed with a constant value of P_{IBA} , and the values of rate constant, k_1 and k_2 , determined at 300°C for several 12-heteropoly phosphoric acids are summarized in Table 3. The value of intercept P_{IBA}/k_2 was always an order of 0.01 for all of the catalysts studied. Thus, k_2 was estimated to be 1–2 although its exact values were not determined. The values of rate constant for the reoxidation step (k_2) are undoubtedly much greater than those of rate constant for the reduction step (k_1) and the values of $[O_s]$ calculated using Eq. (3) at IBA 1.8 vol%, O_2 3.1 vol%, and $k_2 = 1.0$ are approximately equal to unity for all of the 12-heteropoly phosphoric acid-type catalysts studied (Ta-

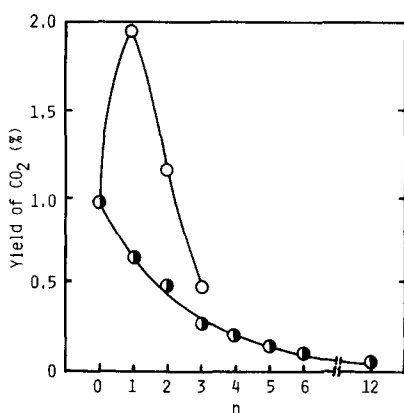


FIG. 2. Reduction of molybdotungstophosphoric acids and molybdovanadophosphoric acids by carbon monoxide at 300°C. Catalyst: 0.50 g. Pulse reactor: CO pulse 1.0 NTPml, carrier gas—He 24 NTPml/min. ●, H₃[PMo_{12-n}W_nO₄₀] (n = 0, 1, . . . 6, and 12); ○, H_{3-n}[PMo_{12-n}V_nO₄₀] (n = 0, 1, 2, and 3).

ble 3). This indicates that these six 12-heteropolyphosphoric acid-type catalysts were nearly completely oxidized during the catalytic oxidative dehydrogenation of IBA at 300°C. Additionally, the observed relation of the value of k_1 , which is in one case $H_3[PMo_6W_6O_{40}] < H_3[PMo_8W_4O_{40}] < H_3[PMo_{10}W_2O_{40}] < H_3[PMo_{12}O_{40}]$ and is in another case $H_3[PMo_{12}O_{40}] < H_5[PMo_{10}V_2O_{40}] < H_4[PMo_{11}VO_{40}]$, agrees with that of the conversion of IBA obtained with an integral reactor (Tables 1, 2, and 3). Therefore, we conclude that the reduction of catalyst by IBA is rate controlling at 300°C.

Reduction by Carbon Monoxide

Reduction of 12-heteropolyphosphoric acid-type catalysts by carbon monoxide was carried out at 300°C using a pulse reactor (Fig. 2). In the case of molybdotungstophosphoric acids, the yield of CO₂ over H₃[PMo₁₂O₄₀] was 0.97%, but it decreased monotonously with increasing the content of tungsten atom and it was as low as 0.05% over H₃[PW₁₂O₄₀] (Fig. 2). In contrast, the yield of CO₂ increased from 0.97 to 1.95% when one molybdenum atom in H₃[PMo₁₂O₄₀] was replaced by one vanadium atom,

and the yield of CO₂ then decreased with further increase in the content of vanadium atom (Fig. 2). Thus, the observed relations of the yield of CO₂ in the reduction of molybdotungstophosphoric acids and molybdovanadophosphoric acids by CO agreed with those of the rate constant for the reduction of these 12-heteropolyphosphoric acids by IBA at 300°C (k_1) (Fig. 2, Table 3). This supports the view that the reduction of catalyst is rate controlling in the oxidative dehydrogenation of IBA at 300°C. Thus, it is found that the reducibility of molybdotungstophosphoric acids by IBA and CO decreases with increasing the content of tungsten atom irrespective of the change in their highest oxidation–reduction potential whereas that of molybdovanadophosphoric acids parallels their highest oxidation–reduction potential, although the reducibility is normalized to constant catalyst weight and is not to constant catalyst surface area.

The surface area of 12-heteropoly compounds is markedly affected by degree of hydration (15). Hence, the conventionally determined BET surface area cannot be used as the effective surface area during the oxidative dehydrogenation of IBA at 300°C. In our previous papers (9, 13), however, the catalytic activity of 12-heteropoly-molybdates for the reaction of IBA could well be understood on the basis of the catalytic activity normalized to constant catalyst weight. In the present work, the BET surface areas of molybdotungstophosphoric acids and molybdovanadophosphoric acids employed as catalysts are small and are close to each other, 1–3 m²/g (see Methods). Additionally, the parallel relations of the value of the highest oxidation–reduction potential of the catalyst with the yield of propylene and the reducibility of molybdovanadophosphoric acids by IBA and CO are obtained (Tables 1 and 2, Fig. 2). Hence, we may compare the catalytic activity and reducibility of these 12-heteropolyphosphoric acids on the basis of the conversion of IBA and the yield of the

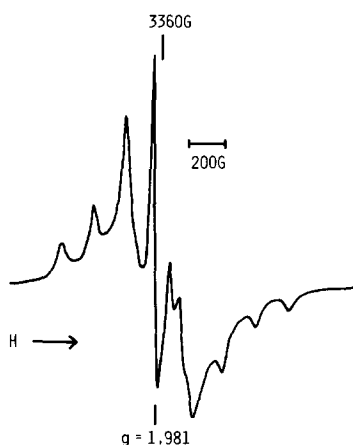


FIG. 3. The ESR spectrum of reduced 11-molybdo-1-vanadophosphoric acid. Catalyst: 0.10 g, reduced by hydrogen at 50 Torr pressure at 300°C for 30 min and then degassed at 300°C for 30 min.

products normalized to constant catalyst weight.

Reoxidation Study

The catalyst (0.10 g in a 3-mm-i.d. quartz tube) was reduced by hydrogen at 50 Torr pressure (1 Torr = 133.3 N/m²) at 300°C for 30 min and was evacuated at 300°C for 30 min (degree of reduction = 70–80 electrons/100 KU, KU = Kegggin unit, e.g., [PMo₁₂O₄₀]). After the value of *g* and spin concentration of paramagnetic species formed had been determined, gaseous oxygen was introduced at 50 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.

The ESR spectra of paramagnetic species formed in the reduction of molybdotungstophosphoric acids (H₃[PMo_{12-n}W_nO₄₀], *n* = 0, 1, 2 . . . 6) were relatively broad and anisotropic, whose *g* value ranged from 1.93 to 1.94. The paramagnetic species formed in these reduced molybdotungstophosphoric acids are Mo⁵⁺, because the *g* value of W⁵⁺ formed in reduced 12-tungstophosphoric acid is as low as 1.827 (16). In contrast, the preferential formation of V⁴⁺ in reduced 12-heteropolyphosphoric acids was seen in the case of molybdo-

phosphoric acids. That is, the ESR spectrum of paramagnetic species formed in the reduced H₄[PMo₁₁V₁O₄₀] had hyperfine splitting caused by the nuclear magnetic moment of vanadium I = ½ (Fig. 3), as reported by Otake and co-workers (17). Analogous ESR spectra were observed in the reduced H₅[PMo₁₀V₂O₄₀] and H₆[PMo₉V₃O₄₀]. As reported previously (17), this spectroscopic result indicates the preferential formation of V⁴⁺ than Mo⁵⁺ in the reduced molybdovanadophosphoric acids.

The reoxidation of Mo⁵⁺ formed in the reduced H₃[PMo₁₂O₄₀] was initiated at ca. 250°C, but the Mo⁵⁺ atoms formed in the reduced H₃[PMo₁₁W₁O₄₀], H₃[PMo₁₀W₂O₄₀], and H₃[PMo₉W₃O₄₀] could be reoxidized even at 100°C. In the case of H₃[PMo₈W₄O₄₀], H₃[PMo₇W₅O₄₀], and H₃[PMo₆W₆O₄₀], the reoxidation took place at much lower temperatures, 75, 25, and 25°C, respectively (Fig. 4). With the exception of H₃[PMo₁₂O₄₀], the temperature at which the reoxidation was initiated thus lowered markedly with lowering the highest oxidation–reduction potential of molybdotungstophosphoric acids. Additionally,

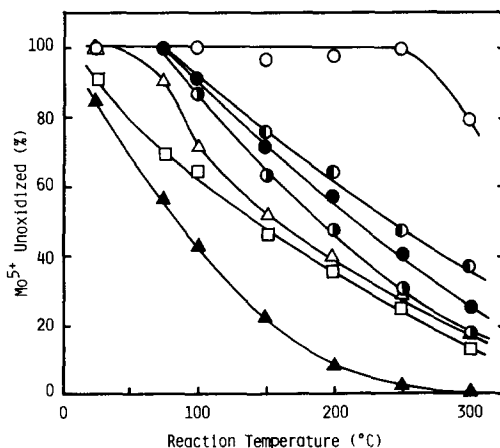


FIG. 4. Reoxidation of molybdotungstophosphoric acids by gaseous oxygen. Catalyst: 0.10 g, reduced by hydrogen at 50 Torr pressure at 300°C for 30 min and then degassed at 300°C for 30 min. Oxygen: 50 Torr. Reaction time: 30 min. ○, H₃[PMo₁₂O₄₀]; ●, H₃[PMo₁₁W₁O₄₀]; ●, H₃[PMo₁₀W₂O₄₀]; ●, H₃[PMo₉W₃O₄₀]; △, H₃[PMo₈W₄O₄₀]; □, H₃[PMo₇W₅O₄₀]; ▲, H₃[PMo₆W₆O₄₀].

TABLE 4

Summary of the Steady-State Catalytic Activity of Metal 11-Molybdo-1-vanadophosphates in the Oxidative Dehydrogenation of Isobutyric Acid^a

Catalyst	BET surface area (m ² /g)	Conversion of IBA (%)	Yield (%) of				Selectivity to MAA (%)
			MAA	Acetone	Propylene	CO + CO ₂	
Li ₃ H[PMo ₁₁ V ₁ O ₄₀]	4.3	29.5	19.7	9.1	0.7	0.1	66.8
Na ₃ H[PMo ₁₁ V ₁ O ₄₀]	4.1	7.5	5.2	1.9	0.5	0.1	69.3
K ₃ H[PMo ₁₁ V ₁ O ₄₀]	113	46.5	36.0	10.4	0.3	0.1	77.4
Rb ₃ H[PMo ₁₁ V ₁ O ₄₀]	122	44.9	33.7	7.0	1.7	2.6	75.0
Cs ₃ H[PMo ₁₁ V ₁ O ₄₀]	126	26.0	19.3	3.4	1.0	2.3	74.2
Pb ₃ H ₂ [PMo ₁₁ V ₁ O ₄₀] ₂	4.0	18.1	11.3	2.9	4.0	0.1	62.4
Cu ₃ H ₂ [PMo ₁₁ V ₁ O ₄₀] ₂	2.7	26.3	18.7	5.3	2.1	0.1	71.1
Hg ₃ H ₂ [PMo ₁₁ V ₁ O ₄₀] ₂	4.9	37.7	26.3	10.4	1.0	0.1	69.8

^a Reaction temperature: 300°C. Feed: IBA 1.5 vol%, O₂ 3.1 vol%, N₂, He—diluent. Contact time: 1.51 g-catalyst · hr/g-mol.

the percentages of Mo⁵⁺ reoxidized at 300°C were 63, 75, 81, 83, 87, and 99% for H₃[PMo₁₀W₂O₄₀], H₃[PMo₉W₃O₄₀], H₃[PMo₁₁W₁O₄₀], H₃[PMo₈W₄O₄₀], H₃[PMo₇W₅O₄₀], and H₃[PMo₆W₆O₄₀], respectively (Fig. 4). Thus, the reoxidizability of molybdotungstophosphoric acids by gaseous oxygen increased with lowering the highest oxidation–reduction potential of the acids. Although H₃[PW₁₂O₄₀] could hardly be reduced by hydrogen at 300°C, the W⁵⁺ atoms formed in an electrolytically reduced 12-tungstophosphate anions were readily reoxidized by gaseous oxygen even at room temperature (25°C).

On the other hand, the reoxidizability of molybdovanadophosphoric acids rather decreased with lowering of their highest oxidation–reduction potential, and the temperature at which the reoxidation by gaseous oxygen was initiated increased when the molybdenum atoms in H₃[PMo₁₂O₄₀] were replaced by vanadium atoms. That is, the reoxidation of V⁴⁺ atoms formed in the reduced H₄[PMo₁₁V₁O₄₀], H₅[PMo₁₀V₂O₄₀], and H₆[PMo₉V₃O₄₀] was initiated at ca. 300°C, and 16, 5, and 2% of the V⁴⁺ atoms, respectively, were reoxidized at 300°C. In this reoxidation study, formation of such negatively charged adsorbed oxygen species as O₂⁻ and O⁻ was scarcely observed by means of ESR even at room temperature and at the temperatures at which the reox-

idation took place. This indicates that exclusive participation of the lattice oxygen in the catalyst took place in the catalytic oxidative dehydrogenation of IBA at 300°C.

Catalytic Activity of Metal

11-Molybdo-1-vanadophosphates

Since H₄[PMo₁₁V₁O₄₀] was the most active and at the same time fairly selective for the catalytic oxidative dehydrogenation of IBA to MAA (Table 2), alkali metal, lead, copper, and mercury 11-molybdo-1-vanadophosphates were prepared and their catalytic activity and selectivity for the oxidative dehydrogenation of IBA were determined at 300°C (Table 4). The potassium, rubidium, and cesium salts showed relatively great catalytic activities and could have produced MAA with a fairly high selectivity of 74–77%. Although the BET surface areas of these metal salts presented in Table 4 are not always effective ones during the catalytic oxidative dehydrogenation of IBA at 300°C, the relation of the conversion of IBA over the alkali metal salts, which is in one case Na₃H[PMo₁₁V₁O₄₀] < Li₃H[PMo₁₁V₁O₄₀] and is in another case Cs₃H[PMo₁₁V₁O₄₀] < Rb₃H[PMo₁₁V₁O₄₀] < K₃H[PMo₁₁V₁O₄₀] (Table 4), indicates that the catalytic activity of the alkali metal salts as oxidation catalysts increases with increasing electronegativity of alkali metal ions as cations. On the other hand, the relation of

the conversion of IBA over the transition metal salts, $\text{Pb}_3\text{H}_2[\text{PMo}_{11}\text{V}_1\text{O}_{40}]_2 < \text{Cu}_3\text{H}_2[\text{PMo}_{11}\text{V}_1\text{O}_{40}]_2 < \text{Hg}_3\text{H}_2[\text{PMo}_{11}\text{V}_1\text{O}_{40}]_2$ (Table 4), agrees with the relation of standard electrode potential of the cations as already found for group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates (13).

DISCUSSION

In our previous papers (9, 13), the effects of cations and heteroatoms on the reducibility and reoxidizability of 12-heteropolymolybdates as catalysts for the oxidative dehydrogenation of IBA were investigated. The results obtained are summarized as follows. That is, the oxidizing activity of the Mo^{6+} atoms as condensing metal atoms paralleled such affinity for electron of cations and heteroatoms as electronegativity and standard electrode potential, and the catalyst components (cations, heteroatoms, and condensing metal atoms) were thus found to interact electrically with each other through the chemical bonds (9, 13). On the other hand, since the reducibility of alkali metal and alkaline-earth metal 12-molybdophosphates by IBA increased with lowering of the electronegativity of these metal ions as cations, we considered that the Mo–O bond in 12-molybdophosphate anions is weak when the oxidizing activity of the Mo^{6+} atoms is low, and we then explained the roles of alkali metal and alkaline-earth metal ions as cations as affecting the Mo–O bond strength via electrostatic effects produced by these cations (9). In contrast, the reducibility of group Ib, IIb, IIIb, and VIII metal 12-molybdophosphates rather increased with increase of the standard electrode potential of these metal ions as cations (13). Since these four groups of metal ions as cations captured the electrons formed in the reduction step in proportion to the value of the standard electrode potential, we proposed that the Mo–O bond in 12-molybdophosphate anions breaks off readily also when the delocalization of the electrons by these metal cations formed in the reduction step takes place extensively

(13). In addition to these findings, it was shown that the reoxidizability of these two series of metal 12-molybdophosphates by gaseous oxygen increases with increase of the electron-donating nature of reduced metal 12-molybdophosphates, and the effect of heteroatoms (P^{5+} , As^{5+} , and Si^{4+}) on these reduction and reoxidation properties of 12-heteropolymolybdates was similarly understood as in the case of alkali metal and alkaline-earth metal ions as cations (9). We also pointed out that these observed effects of cations and heteroatoms on the reduction and reoxidation properties of 12-heteropolymolybdates as heterogeneous oxidation catalysts are similar to those in usual metal oxide catalysts and are not inherent to 12-heteropoly compound-type catalysts (9, 13). Here, we would like to show that the effects of tungsten and vanadium atoms as condensing metal atoms on the reducibility and reoxidizability of 12-heteropolyphosphoric acids can similarly be understood as in the case of cations, although the observed trends in the catalytic properties of molybdotungstophosphoric acids and molybdovanadophosphoric acids (Tables 1 and 2, Figs. 2, 3, and 4) suggest different mechanistic roles of these two condensing metal atoms.

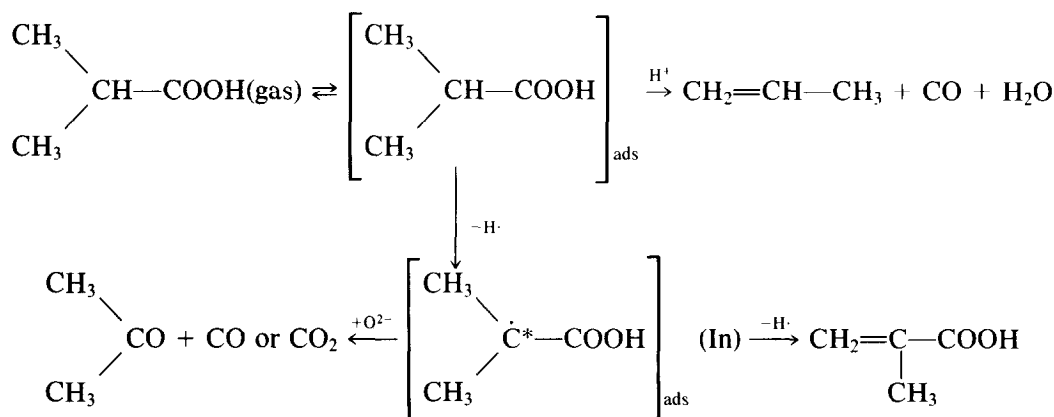
That is, the reduction-controlling catalytic oxidative dehydrogenation of IBA and the nearly constant values of selectivity throughout the course of the catalytic reaction of IBA (Table 3, Fig. 1) indicate that the catalytic activity and selectivity of the 12-heteropolyphosphoric acids can be related to the physicochemical properties of these acids determined at completely oxidized state. Additionally, both the negligible activity of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ as an oxidation catalyst and the negligible yield of CO_2 in the reduction of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ with CO (Table 1, Fig. 2) indicate that the W–O bond in molybdotungstophosphoric acids is hard to break off and that such lattice oxygen as $\text{Mo}^{6+}=\text{O}$ or $\text{Mo}^{6+}-\text{O}-\text{Mo}^{6+}$ is active for the catalytic oxidative dehydrogenation of IBA. The concentration of the active lattice

oxygen in molybdotungstophosphoric acids undoubtedly decreases with increase of the content of tungsten atom. Additionally, the formation of Mo^{5+} in the reduced molybdotungstophosphoric acids (see Results), which is in agreement with the previously reported results for $\text{H}_3[\text{PMo}_{11}\text{W}_1\text{O}_{40}]$ (16), supports that the oxidation state of W^{6+} atoms in molybdotungstophosphoric acids is preserved in the course of the catalytic oxidative dehydrogenation of IBA. Since the value of the highest oxidation-reduction potential of molybdotungstophosphoric acids varied with the composition of condensing metal atoms (Table 1), we could say that the role of the tungsten atoms is, additionally, to vary the concentration of the active lattice oxygen, to modify the redox and acid-base properties of molybdotungstophosphoric acids via electrostatic effects.

The preferential formation of Mo^{5+} upon reduction (see Results) also indicates that the highest oxidation-reduction potential of molybdotungstophosphoric acids is associated with the oxidizing activity of Mo^{6+} atoms in these acids at solid state and hence their acidic properties. No theoretical correlation has been reported between the strength of the metal-oxygen bond in metal oxides and the oxidizing activity of the metal atoms. Analogous to the correlation of the Mo-O bond strength with the oxidizing activity of Mo^{6+} atoms in alkali metal and alkaline-earth metal 12-molybdophosphates reported (9), however, the observed

trend in the value of the highest oxidation-reduction potential of molybdotungstophosphoric acids (Table 1) suggests that the Mo-O bond strength in the acids increases by replacing the molybdenum atoms in $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ with tungsten atoms to reach the maximum at $\text{H}_3[\text{PMo}_{10}\text{W}_2\text{O}_{40}]$ and then decreases with further increase in the content of tungsten atom. Nevertheless, both the conversion of IBA in the catalytic oxidative dehydrogenation and the yield of CO_2 in the reduction by CO at 300°C decreased monotonically with increase of the content of tungsten atom (Table 1, Fig. 2). It appears that both the values of the conversion of IBA and the yield of CO_2 at 300°C were predominantly affected by the concentration of the active lattice oxygen ($\text{Mo}^{6+}=\text{O}$ or $\text{Mo}^{6+}-\text{O}-\text{Mo}^{6+}$) in molybdotungstophosphoric acids, although the reducibility of the acids, when it is normalized to one Mo-O bond, must be affected by the strength of the Mo-O bond.

The product distribution of the catalytic oxidative dehydrogenation of IBA is readily understandable by assuming the suggested changes in the Mo-O bond strength and the acidic properties of molybdotungstophosphoric acids with the composition of condensing metal atoms. We already proposed the following reaction scheme for the catalytic oxidative dehydrogenation of IBA in which the dehydrogenation of IBA proceeds via a homolytic mechanism (9).



That is, the adsorbed IBA molecule forms an intermediate (In) when the hydrogen atom bonded to the tertiary carbon atom of IBA is dehydrogenated by the surface lattice oxygen. Further dehydrogenation of one hydrogen atom by the lattice oxygen from the methyl group of In gives MAA whereas acetone is formed when the surface lattice oxygen adds onto the central carbon atom C* of In. Here, this carbon atom acquires a positive charge by donating its 2P electrons to the catalyst and also to the neighboring COOH group. Hence the addition of the surface lattice oxygen onto the carbon atom proceeds through a nucleophilic mechanism. By analogy with allylic oxidation (18, 19), this nucleophilic addition proceeds readily when the carbon atom has a high positive charge and when the Mo–O bond breaks off readily. This view was really supported by the results of the oxidative dehydrogenation of IBA over alkali metal and alkaline-earth metal 12-molybdophosphates reported (9). Thus, the observation of the minimum (acetone/MAA) yield ratio over the most acidic catalyst ($H_3[PMo_{10}W_2O_{40}]$) (Table 1) is evidence of the view that the Mo–O bond in $H_3[PMo_{10}W_2O_{40}]$ is the strongest in a series of molybdotungstophosphoric acids studied. On the other hand, the adsorbed IBA molecule is decomposed to propylene, carbon monoxide, and water when the IBA molecule interacts with a Brønsted acid (20). Hence, the observed parallel relation of the yield of propylene with the value of the highest oxidation–reduction potential of molybdotungstophosphoric acids (Table 1) is an expected result because the strength of cations (H^+) as a Brønsted acid increases with increasing the highest oxidation–reduction potential of the acids.

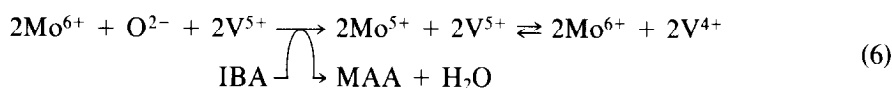
We now discuss the effect of tungsten atoms on the reoxidizability of molybdotungstophosphoric acids. As shown in Fig. 4, the reoxidizability of the Mo^{5+} atoms by gaseous oxygen increased markedly with lowering of the highest oxidation–reduction potential of molybdotungstophos-

phoric acids. Since the electron-donating nature of Mo^{5+} atoms formed in the reduced molybdotungstophosphoric acids increases with lowering of the highest oxidation–reduction potential of the acids, the observed results concerning the reoxidizability of the Mo^{5+} atoms (Fig. 4) is an expected result and is in harmony with the already reported results (9) for alkali metal and alkaline-earth metal 12-molybdophosphates. Thus, the effect of tungsten atoms on the catalytic properties (reducibility and reoxidizability) of molybdotungstophosphoric acids as heterogeneous oxidation catalysts is reasonably understood as affecting not only the oxidizing activity of the Mo^{6+} atoms (hence the Mo–O bond strength) through an electrostatic mechanism but also the concentration of the active lattice oxygen ($Mo^{6+}=O$ or $Mo^{6+}-O-Mo^{6+}$). The role of tungsten atoms as a Mo–O bond strength modifier agrees with that of alkali metal and alkaline-earth metal ions as cations for 12-molybdophosphates reported (9).

In contrast to tungsten atoms, the effect of vanadium atoms as condensing metal atoms on the reducibility and reoxidizability of molybdovanadophosphoric acids is understandable as playing the role of an electron reservoir. That is, the observed decrease in the reducibility of $H_{3+n}[PMo_{12-n}V_nO_{40}]$ ($n = 1, 2, \text{ and } 3$) with increase of the content of vanadium atom in spite of the decrease in the highest oxidation–reduction potential of the acids (Table 2, Fig. 2) does not support the view that the lattice oxygen bonded to the vanadium atom or the vanadium atoms ($V=O$ or $V-O-V$) is reduced by IBA and CO. We believe that the active lattice oxygen which is reducible by IBA and CO is the lattice oxygen bonded to the molybdenum atom or the molybdenum atoms ($Mo^{6+}=O$ or $Mo^{6+}-O-Mo^{6+}$) as in the case of molybdotungstophosphoric acids. The concentration of the active lattice oxygen in molybdovanadophosphoric acids again decreases with increase of the content of the vanadium atom. Further-

more, judging from the trend in the value of the highest oxidation–reduction potential of molybdovanadophosphoric acids (Table 2), the Mo–O bond strength is expected to increase with replacement of one molybdenum atom in $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ by one vanadium atom and then decrease with further replacement of the molybdenum atoms by vanadium atoms. These two trends in the concentration of the active lattice oxygen and the Mo–O bond strength are similar to those of molybdotungstophosphoric acids. Nevertheless, the reducibility of molyb-

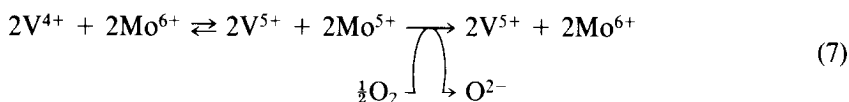
dovanadophosphoric acids by IBA and CO showed the maximum at $\text{H}_4[\text{PMo}_{11}\text{V}_1\text{O}_{40}]$ (Table 2, Fig. 2). We believe that this unexpected result is caused by the role of the V^{5+} atoms as an electron reservoir. Both the formation of V^{4+} in the reduced molybdovanadophosphoric acids and the increase in the reducibility of the acids with increase of the value of their highest oxidation–reduction potential (Table 2, Figs. 2 and 3) support this view. Thus, the reduction of molybdovanadophosphoric acids by IBA can be written as follows:



It is reasonable to consider that the V^{5+} atoms strongly shift the above reaction to the right side through capture of the electrons formed by the reduction in proportion to the value of the highest oxidation–reduction potential of molybdovanadophosphoric acids. An analogous role was already found for group Ib, IIb, IIIb, and VIII metal ions as cations for 12-molybdophosphates (13). The observed increase in the catalytic activity of alkali metal 11-molybdo-1-vanadophosphates for the oxidative dehydrogenation of IBA with increasing electronegativity of alkali metal ions

(Table 4) can be understood on the basis of the view that the electron-capturing nature of the V^{5+} atoms increased with the change in the nature of alkali metal ions as cations. The parallel relation of the yield of propylene with the value of the highest oxidation–reduction potential of molybdovanadophosphoric acids (Table 2) is understood similarly as in the case of molybdotungstophosphoric acids.

On the other hand, the electrons captured by the V^{5+} atoms in the reduction step must be supplied to oxygen in the reoxidation step.



The temperature at which the reoxidation by gaseous oxygen was initiated increased from 250 to 300°C with replacement of the molybdenum atoms in $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ by vanadium atoms (see Results). We believe that this increase in reaction temperature was caused by the relatively larger electron affinity of the V^{5+} than Mo^{6+} atoms. The observed increase in the reoxidizability

of the V^{4+} with increase of the highest oxidation–reduction potential of molybdovanadophosphoric acids (see Results) does not agree with the results for molybdotungstophosphoric acids (Fig. 4) and alkali metal and alkaline-earth metal 12-molybdophosphates reported (9). However, a similar result was already obtained in the effect of group Ib, IIb, IIIb, and VIII

metal ions as cations on the reoxidizability of 12-molybdophosphates (13). It seems that the electrons, once captured by the V^{5+} atoms having a great reducibility, are mobile also in the reoxidation step. At any rate, it is evident that the redox properties of molybdovanadophosphoric acids are decisively affected by those of V^{5+} in the acids. The remarkable decrease in the (acetone/MAA) yield ratio caused by the replacement of the molybdenum atoms with vanadium atoms (Table 2) remains unknown.

In conclusion, we feel that while few studies have been published with which our model presented herein should be compared, it is based on the different redox properties of tungsten and vanadium atoms and explains well our findings in respect to the catalytic properties of molybdotungstophosphoric acids and molybdovanadophosphoric acids and offers a reasonable explanation for the parallel relation of the catalytic activity of the latter acids with their highest oxidation-reduction potential found by Otake and Onoda (3).

REFERENCES

1. Tsigdinos, G. A., "Molybdenum Chemicals Bulletin," cdb-12a (revised), 1969, and cdb-15, 1971. Climax Molybdenum Co.
2. Sasaki, Y., and Matsumoto, K., *Kagaku no Ryoiki* **29**, 853 (1975).
3. Otake, M., and Onoda, T., *Shokubai (Catalyst)* **18**, 169 (1976).
4. Ohara, T., *Shokubai (Catalyst)* **19**, 157 (1977).
5. Nakamura, S., and Ichihashi, M., "Proceedings of 7th Intern. Congr. Catal., Tokyo (1980)," part B, p. 755. Kodansha Ltd.
6. Otake, M., and Onoda, T., "Proceedings of 7th Intern. Congr. Catal., Tokyo (1980)," part B, p. 780. Kodansha Ltd.
7. Eguchi, K., Aso, I., Yamazoe, N., and Saiyama, T., *Chem. Lett. (Tokyo)* 1345 (1979).
8. Ai, M., *J. Catal.* **71**, 88 (1981).
9. Akimoto, M., Tsuchida, Y., Sato, K., and Echigoya, E., *J. Catal.* **72**, 83 (1981).
10. Misono, M., Koyama, T., Sekiguchi, H., and Yoneda, Y., *Chem. Lett. (Tokyo)* 53 (1982).
11. Ai, M., *Appl. Catal.* **4**, 245 (1982).
12. Yoshida, S., Niiyama, H., and Echigoya, E., *J. Phys. Chem.* **86**, 3150 (1982).
13. Akimoto, M., Shima, K., Ikeda, H., and Echigoya, E., *J. Catal.* **86**, 173 (1984).
14. Tsigdinos, G. A., and Hallada, C. J., *Inorg. Chem.* **7**, 437 (1968).
15. Misono, M., Konishi, Y., Furuta, M., and Yoneda, Y., *Chem. Lett. (Tokyo)* 709 (1978).
16. Prados, R. A., and Pope, M. T., *Inorg. Chem.* **15**, 2547 (1976).
17. Otake, M., Komiyama, Y., and Otaki, T., *J. Phys. Chem.* **77**, 2896 (1973).
18. Seiyama, T., Egashira, M., Sakamoto, T., and Aso, I., *J. Catal.* **24**, 76 (1972).
19. Akimoto, M., and Echigoya, E., *J. Chem. Soc., Faraday Trans. I* **75**, 1757 (1979).
20. Otake, M., and Onoda, T., *J. Catal.* **38**, 494 (1975).