

Oxidation of Isobutane Catalyzed by $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ -Based Heteropoly Compounds

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The oxidation of isobutane has been found to be catalyzed by 12-molybdophosphates. Among the alkali metals, the substitution of Cs^+ for H^+ in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ resulted in the greatest enhancement of the yield of methacrylic acid and the yield reached a maximum around the Cs^+ content of 2.5. The rate per specific surface areas of $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ ($x = 0\text{--}3$) decreased monotonously with x . It was suggested that isobutane oxidation is a surface-type reaction and the catalytic activity is controlled by the oxidizing ability of the catalyst surface. The catalytic properties of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ were changed by the substitution of metal ions: Ni^{2+} , Mn^{2+} , or Fe^{3+} substitution greatly increased the sum of yields of methacrylic acid and methacrolein, while the Co^{2+} , Cu^{2+} , Hg^{2+} , Pt^{2+} , or Pd^{2+} substitution decreased the sum of the yields. Among the transition and precious metals, the highest activity and total yield of methacrylic acid and methacrolein were observed for Ni. The preferred content of Ni was 0.08. © 1996 Academic Press, Inc.

INTRODUCTION

Methacrylic acid has been used for the synthesis of methyl methacrylate, an important monomer of resin. Industrial production of methacrylic acid has traditionally been achieved by the reaction of acetone with hydrogen cyanide (1–3). However, the process uses the dangerous hydrogen cyanide and overproduces solid ammonium bisulfate. Recently, alternative methods, the methylation of propionaldehyde and the oxidation of isobutene, have been developed (1–3). These processes still have problems using high-price feedstocks and consist of two-step reactions (1–4). Therefore, it would be much more desirable to use cheaper feedstock and isobutane and to produce methacrylic acid directly from isobutane and molecular oxygen (1, 2).

Selective oxidation of lower alkanes by molecular oxygen is of great interest and growing importance (1, 2, 4).

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Recently, the processes for the oxidation of propane and *n*-butane have been industrialized (5, 6). The oxidation of propane and isobutane with heteropoly catalysts was first reported by Harold and Samuel in 1979 (7). Ai (8) and Centi *et al.* and Cavani *et al.* (9, 10) reported that heteropoly compounds catalyze the oxidation of lower alkanes, especially propane, isobutane, and pentane (8–10).

Solid heteropoly compounds are suitable oxidation catalysts for various reactions such as dehydrogenation of isobutyric acid as well as oxidation of aldehydes. To understand oxidation catalysis by solid heteropoly compounds, the contrast between surface and bulk-type II catalysis and acid-redox bifunctionality of heteropoly catalysts must be properly taken into account, along with relationships between the oxidizing properties of catalysts and their catalytic activities (11–16). Heterogeneous catalytic reactions on heteropoly compounds are classified into three different types, surface, bulk-type I (pseudoliquid phase), and bulk-type II. The surface reactions are typical of ordinary heterogeneous catalysis, and therefore the surface acidity and oxidizing ability are important. The following are typical reactions that have already been found to be described by either of the two types of catalysis by $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and its alkali salts:

Surface-type: oxidation of CO, acetaldehyde, and methacrolein.

Bulk-type II: oxidation of H_2 , oxidative dehydrogenation of cyclohexene, isobutyric acid.

We have expanded our fundamental knowledge regarding metal-catalyzed O_2 -based liquid-phase oxidation of alkenes (17) and alkanes (18) by using heteropoly compounds. In addition, we have preliminarily reported that heteropoly compounds can well catalyze heterogeneous oxidation of isobutane and propane (19).

Here we report in more detail how catalytic activity of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ for the oxidation of isobutane is changed by alkali, transition, and precious metal substitution and attempt to clarify the factors controlling the catalytic activity. Further attempts are made to investigate the reaction mechanism and whether the isobutane oxidation belongs to a surface-type or bulk-type II reaction.

EXPERIMENTAL

Catalysts. 12-Molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) was commercially obtained from Nippon Inorganic Colour and Chemical Co., Ltd. The other reagents were analytical grade and used without further purification.

The catalysts were prepared as follows: 3.6 cm^3 of aqueous solution of metal nitrate ($0.08 \text{ mol} \cdot \text{dm}^{-3}$) was added dropwise to 60.0 cm^3 of aqueous solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 28\text{H}_2\text{O}$ ($0.06 \text{ mol} \cdot \text{dm}^{-3}$), followed by the addition of 22.5 – 56.3 cm^3 of aqueous solution of cesium carbonates ($0.08 \text{ mol} \cdot \text{dm}^{-3}$) at 50°C . The resulting suspension or solution was evaporated to dryness at 50°C and the powder samples were carefully collected. The actual composition may be $\text{Cs}_q\text{A}^{n+}_x\text{H}_y\text{PMo}_{12}\text{O}_z$ ($A = \text{Ni}, \text{Fe}, \text{etc.}$), but in this article they are designated as $\text{Cs}_q\text{A}^{n+}_x\text{H}_{3-q-nx}\text{PMo}_{12}\text{O}_{40}$. The other metal salts were prepared in a similar way.

BET surface areas were measured by means of N_2 adsorption using Coulter Omnisorp 100MP after use in reaction. The powder X-ray diffraction patterns were recorded on a powder X-ray diffractometer (Materials Analysis and Characterization, MXP³) by using $\text{CuK}\alpha$ radiation. The infrared spectra of KBr pellets were recorded on a Perkin-Elmer paragon 1000PC spectrometer. The ^{31}P MASNMR spectra were measured using a Bruker AC300P spectrometer. Aqueous H_3PO_4 , 85%, was used as a standard reference of ^{31}P NMR spectra. All measurements were carried out at room temperature.

Reaction. The reaction was performed in a flow reactor (Pyrex tube, 12 mm internal diameter) at the applied temperature of 270 – 360°C under an atmospheric pressure. The feed gas consisted of 17 vol% of isobutane, 33 vol% of O_2 , and N_2 balance unless otherwise stated. Total flow rates were ca. $30 \text{ cm}^3 \cdot \text{min}^{-1}$. It was confirmed for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ that the conversion and selectivity was little changed by the mixing with SiC (1.5 g) to prevent an undesirable temperature rise. Prior to the reaction, 1 g of each catalyst was treated in an O_2 stream ($60 \text{ cm}^3 \cdot \text{min}^{-1}$) for 1 h at 300°C . The gases at the outlet of the reactor were taken out intermittently with the aid of a sampler directly connected to the system and analyzed by FID and TCD gas chromatograph with FFAP, Porapack Q, and molecular sieve 5A columns. The conversion and the selectivity were collected after 2–5 h of reaction, when nearly steady-state conversion and selectivity were obtained for each catalyst. Selectivity was calculated on the C_4 (isobutane) basis. The carbon balance was in the range 90–100%.

RESULTS AND DISCUSSION

Oxidation of isobutane. Figure 1 shows the time course of the oxidation of isobutane at 340°C . The conversion and selectivity reached almost constant after 4 h; e.g., the conversions were 27, 21, 19, 17, 15, and 16% at 0.5, 1, 2, 3,

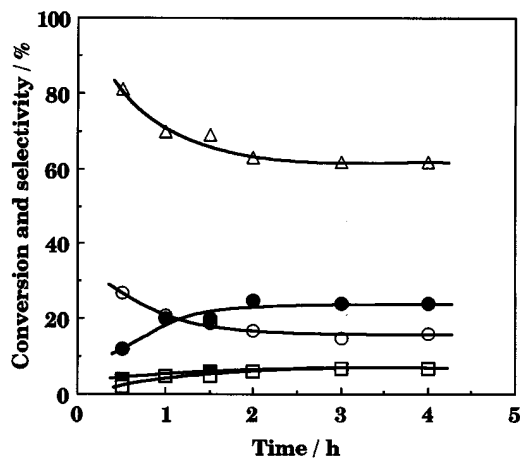


FIG. 1. Time course of the oxidation of isobutane catalyzed by $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ at 340°C . \circ , \bullet , \blacksquare , \square , and \triangle represent conversion of isobutane and selectivities to MAA, MAL, AcOH, and CO_x , respectively.

4, and 5 h, respectively. The products were methacrylic acid (MAA), methacrolein (MAL), acetic acid, and CO_x ($\text{CO} + \text{CO}_2$). Similar products were observed for the other heteropoly catalysts used. The color of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ after having been used as catalyst was yellow green, suggesting that the oxidation state is rather high under reaction conditions.

The kinetic measurements showed that the pressure dependencies were expressed by $-d[i\text{-C}_4\text{H}_{10}]/dt = k \cdot P_{i\text{-C}_4\text{H}_{10}}^1 \cdot P_{\text{O}_2}^0$ at 340°C for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$, in the range of partial pressures of isobutane 0.17–0.25 atm and oxygen 0.27–0.33 atm. A $P_{i\text{-C}_4\text{H}_{10}}^0$ dependence, that is, saturation kinetics, was reached by a partial pressure of isobutane of 0.5 atm while a $P_{\text{O}_2}^1$ dependence was observed by lowering a partial pressure of oxygen of 0.2 atm. Conversion was kept below 12% for the determination of the pressure dependency. It was confirmed that conversions linearly increased up to ca. 20% with W (weight of catalyst)/ F (flow rate).

Figure 2 shows the temperature dependency of the conversion and selectivity upon $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$. The conversion of isobutane monotonously increased with increase in the reaction temperature and was 47% at 360°C . The selectivity to MAL monotonously decreased with increase in the reaction temperature and that to MAA reached the maximum at 320 – 340°C . It follows that the yield of MAA reached maximum at 360°C and the value was 8.5%.

Figure 3a shows the selectivity vs conversion relationships for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$. The selectivities to MAL and CO_x extrapolated to 0% conversion were ca. 75 and 25%, respectively, showing that there are two paths in the first steps: One is the selective oxidation, $i\text{-C}_4\text{H}_{10} \rightarrow i\text{-C}_4\text{H}_8 \rightarrow \text{MAL}$, and the other is complete oxidation, $i\text{-C}_4\text{H}_{10} \rightarrow \text{CO}_x$. The selectivity to MAL monotonously

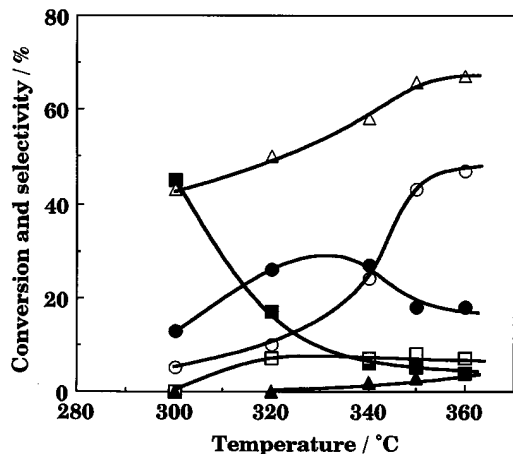


FIG. 2. Temperature dependency of conversion and selectivity. Catalyst, $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$. \circ , \bullet , \blacksquare , \square , and \triangle are defined in Fig. 1 legend. \blacktriangle , selectivity to acetone.

decreased with increase in the conversion and that to MAA showed the maximum at ca. 10% conversion. The decrease of selectivities to MAA and MAL above 10% conversion is mainly due to the successive oxidation of MAA and MAL because the amount of CO_x increased in parallel. No acetic acid was observed at low conversion. It has been reported that no acetic acid was observed for the oxidation of MAL when the conversion was low (20). These facts suggest that acetic acid was formed by the oxidation of MAA. In addition, the formation of isobutene was observed under oxygen-poor conditions (21) and it was reported that MAL was produced in the oxidation of isobutene (22).

A similar variation was observed for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ as shown in Fig. 3b. The selectivities to MAL and CO_x extrapolated to 0% conversion were close to those obtained for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$, suggesting that the ratio of rates of the first two steps did not change with V^{5+} substitution. On the other hand, the V^{5+} substitution resulted in the increase in the selectivity to MAA as shown in Figs. 3a and 3b, suggesting that the complete oxidations of MAL and MAA are suppressed and that the step of $\text{MAL} \rightarrow \text{MAA}$ is accelerated by the V^{5+} substitution.

The formation of acetone started to increase when the conversion exceeded 20% in Fig. 3a. We reported the acetone formation in the oxidation of acetic acid catalyzed by $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ ($x=0, 2.85$) (23). On the other hand, it is possible that acetone is formed by the protonation of MAA followed by the oxidation according to Ref. (24). Therefore, acetone would be formed by the oxidation of AcOH and/or MAA.

On the basis of above discussion, the reaction scheme 1 is proposed at present although further detailed mechanistic study such as oxidation of isobutene, MAL, and MAA should be necessary: Isobutane is oxidatively dehydrogenated into isobutene, and then isobutene is successively oxidized to form MAL followed by the oxidation into

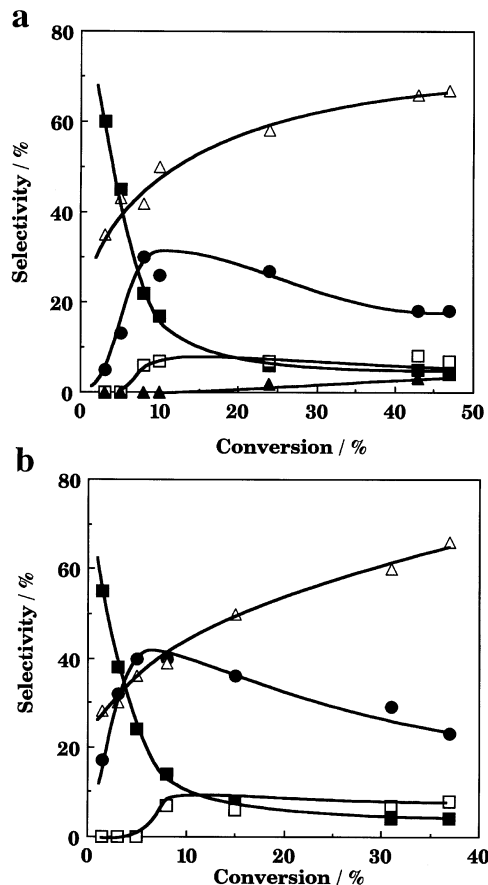
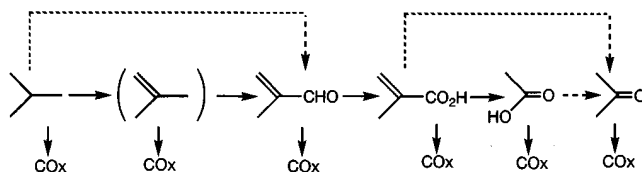


FIG. 3. Conversion dependency of selectivity. (a) Catalyst, $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$. (b) Catalyst, $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$. The data were obtained by changing W/F or reaction temperatures in the range 270–360°C. Symbols defined in Fig. 2 legend.

MAA. MAA is then oxidized to AcOH. However, there may be a direct oxidation path from isobutane into MAL shown by the dotted line in Scheme 1.

When the oxidation of isobutane, propane, and ethane were catalyzed by $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$, the conversion decreased in the order of $i\text{-C}_4\text{H}_{10} > \text{C}_3\text{H}_8 > \text{C}_2\text{H}_6$ (25). The order is the same as that of the C–H bond strength. This agreement suggests that the rate-determining step for the oxidation of lower alkanes involves C–H dissociation such as $i\text{-C}_4\text{H}_{10} \rightarrow i\text{-C}_4\text{H}_8$ MAL and/or $i\text{-C}_4\text{H}_{10} \rightarrow \text{CO}_x$ in Scheme 1. The first-order dependency of the rate on the partial pressure of isobutane supports the idea.



SCHEME 1

In addition, MAL and MAA were formed by the stoichiometric reaction of isobutane with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (26), suggesting that the catalytic oxidation of isobutane proceeds by the redox mechanism. The color of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalyst suggests that the oxidation state is rather high under reaction conditions. Therefore, it is likely that the reduction of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ by isobutane is rate determining.

Effect of Cs salt formation. The results on $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ catalysts are shown in Table 1. The conversions were 7, 6, 11, 16, 17, and 8% for $x=0, 1, 2, 2.5, 2.85,$ and 3, respectively, and the highest conversion was observed around $x=2.5-2.85$. The yields of MAA on $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ were 0.3, 1.4, 3.7, 3.9, 0.8, and 0% for $x=0, 1, 2, 2.5, 2.85,$ and 3, respectively. It follows that the substitution of Cs^+ for H^+ in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ resulted in the great enhancement of the MAA production and the yield reached the maximum around $x=2.5$. The sum of the yields of MAA and MAL on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ reached 5.1% and was the highest among $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ catalysts. It has been reported that $(\text{VO})_2\text{P}_2\text{O}_7$ shows high catalytic activity for the oxidation *n*-butane and *n*-pentane (5) and that $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is more active than $(\text{VO})_2\text{P}_2\text{O}_7$ for the oxidation of isobutane (26). Similarly the substitution of Cs^+ for H^+ in $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ resulted in the great enhancement of the MAA production and the yield reached the maximum around $x=2.5$ for $\text{Cs}_x\text{Ni}_{0.08}\text{H}_{3.84-x}\text{PVMo}_{11}\text{O}_{40}$ catalysts (19b).

We previously reported that there are two different groups of reactions as classified by the dependency of the rate of noncatalytic reduction of 12-molybdophosphates on the specific surface area. One is the oxidative dehydrogenation reaction, for which the rate per unit weight of catalyst does not depend on the specific surface area. H_2 , isobutyric acid, and cyclohexene are typical reactants.

The other is the oxygen-addition reaction, for which the rate is proportional to the surface area. We also reported that the catalyst oxidizing ability as assayed with CO (a

surface-type reductant) represents in the oxidizing ability of catalyst surface and is correlated with such surface-type catalysis as oxidations of acetaldehyde and CO (14, 23). Here, we extend this classification to the catalytic oxidation of isobutane. The main products of the oxidation of isobutane catalyzed by $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ were methacrylic acid, methacrolein, acetic acid, CO, and CO_2 . Since they all are oxygenated products, the reaction would belong to the surface type.

Figure 4a shows a correlation between the rates of oxidation of isobutane and noncatalytic reduction of catalysts by CO. A good correlation exists between the catalytic activity and the rate of catalyst reduction by CO. The correlation noted in Fig. 4a indicates that the catalytic activity is controlled by the oxidizing ability of catalysts. In addition, these results are very similar to those observed for other surface-type reactions, suggesting that oxidation of isobutane is a surface-type reaction. A good correlation was also observed between the rates of oxidation of isobutane and acetaldehyde shown in Fig. 4b. This good correlation supports the idea. Further study is necessary to clarify the reason why the oxidation of isobutane belongs to a surface-type reaction taking the reaction mechanism into account.

The surface areas of $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ ($x=0, 1, 2, 2.5, 2.85, 3$) catalysts were 1.1, 2.1, 5.9, 9.5, 46.0, and 46.0 $\text{m}^2 \cdot \text{g}^{-1}$, respectively, and increased with x while the oxidizing ability of catalysts per surface area decreased with x . The surface oxidizing ability was estimated by multiplying the rates of catalytic reaction of acetaldehyde per surface area by the quantity of polyanions present on the surface. The surface oxidizing ability thus obtained reached the maximum at $x=2.5$. A similar trend was observed when the rates of reduction of catalysts by CO were used for the estimation instead of rates of catalytic reaction of acetaldehyde. Therefore, the high activity of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ probably results from the higher surface oxidizing ability.

Effect of metals added. Table 2 shows the effect of alkali metals. The catalytic activity increased in the order of

TABLE 1
Oxidation of Isobutane over $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ at 340°C^a

| x | Surface area ($\text{m}^2 \cdot \text{g}^{-1}$) | Conv. (%) | Rate ($10^{-5} \text{ mol} \cdot \text{min}^{-1} \cdot \text{m}^{-2}$) | Selectivity ^b (%) | | | | | Sum of yields of MAA + MAL (%) |
|----------------|---|-----------|--|------------------------------|-----|------|----|---------------|--------------------------------|
| | | | | MAA | MAL | AcOH | CO | CO_2 | |
| 0 | 1.1 | 7 | 1.34 | 4 | 18 | 8 | 44 | 26 | 1.5 |
| 1 | 2.1 | 6 | 0.60 | 23 | 17 | 10 | 32 | 18 | 2.4 |
| 2 | 5.9 | 11 | 0.39 | 34 | 10 | 7 | 29 | 21 | 4.8 |
| 2.5 | 9.5 | 16 | 0.36 | 24 | 7 | 7 | 41 | 21 | 5.1 |
| 2.85 | 46.0 | 17 | 0.08 | 5 | 10 | 5 | 44 | 37 | 2.4 |
| 3 ^c | 46.0 | 8 | 0.04 | 0 | 10 | 6 | 32 | 35 | 0.8 |

^a Isobutane, 17 vol%; O_2 , 33 vol%; N_2 , balance; catalyst, 1.0 g; total flow rate, ca. 30 $\text{cm}^3 \cdot \text{min}^{-1}$.

^b Calculated on the C_4 (isobutane) basis.

^c The selectivity to acetone was 17%.

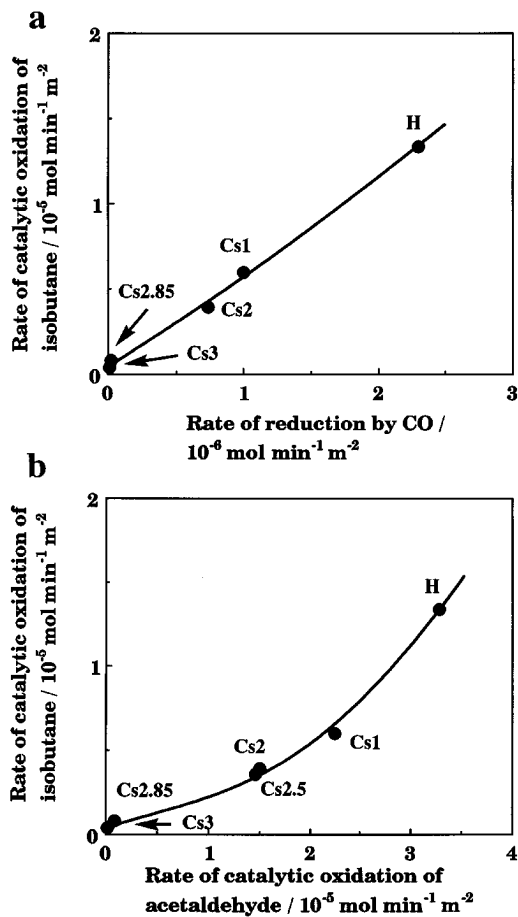


FIG. 4. Correlation between rates of oxidation of isobutane and those of noncatalytic reduction of catalysts by CO (14) or catalytic oxidation of acetaldehyde (23). Cs x and H show Cs $_x$ H $_{3-x}$ PMo $_{12}$ O $_{40}$ and H $_3$ PMo $_{12}$ O $_{40}$, respectively.

H < Li < Na < K < Cs and the selectivity to MAA also increased in the same order. Therefore, the highest yield of MAA was obtained for Cs $_{2.5}$ Ni $_{0.08}$ H $_{0.34}$ PMo $_{12}$ O $_{40}$.

A similar order of catalytic activities for the oxidation of isobutyric acid at 300°C was reported (24). The authors supposed that oxygen atoms bonded to Mo become more reactive as the electronegativity of the counteranion decreases although the surface areas of catalysts were 2–130 m $^2 \cdot \text{g}^{-1}$ and quite different from each other.

The catalytic properties of Cs $_{2.5}$ H $_{0.5}$ PMo $_{12}$ O $_{40}$ were changed by the addition of transition metal ions. Table 3 shows the effect of additives. The addition of Ni, Mn, or Fe increased the yields of MAA, and MAL and Ni most efficiently increased the yields of MAA and MAL up to 6.5 and 1.5%, respectively. The 6.5% yield of MAA was comparable to or higher than 6.2%, the maximum value reported at the likely steady state in patent literatures (27). In contrast, Co, Cu, Hg, Pt, and Pd decreased the yields. Similarly the conversion and yields of MAA and MAL were increased by the addition of Ni to Cs $_2$ HPMo $_{12}$ O $_{40}$.

Table 4 shows the results of the oxidation of isobutane catalyzed by Cs $_{2.5}$ Ni $_x$ H $_{0.5-2x}$ PMo $_{12}$ O $_{40}$. The conversion gradually increased with x , reached the maximum at $x=0.08$, and then decreased. The selectivity to MAA also slightly increased with x , reached maximum at $x=0.04$ – 0.08 , and decreased above 0.8. It follows that the sum of the yields of MAA and MAL reached the maximum around $x=0.08$. It is clear that the preferred content of Ni is 0.08. The increase in catalytic activity in the range of $x=0$ – 0.08 is probably due to the promotion of the first step in Scheme 1 by Ni.

Figure 5 shows the change of rates per specific surface areas of Cs $_{2.5}$ Ni $_x$ H $_{0.5-2x}$ PMo $_{12}$ O $_{40}$ catalysts. The rates showed a trend similar to that observed for the conversion and became very small at $x=0.16$. The formal number of protons in Cs $_{2.5}$ Ni $_x$ H $_{0.5-2x}$ PMo $_{12}$ O $_{40}$ decreases with x and disappears at $x=0.25$. The parallel decrease of the catalytic activity with the formal number of protons above $x=0.08$ and the appropriate agreement of Ni contents, where the catalytic activity and protonic acidity almost disappeared, suggest that not only oxidizing ability but also protonic acidity is a controlling factor of the catalytic activity. It was reported that the catalytic oxidation of MAL is catalyzed by the oxidizing ability and protonic acidity of catalysts (28).

Stability of Cs $_{2.5}$ Ni $_{0.08}$ H $_{0.34}$ PMo $_{12}$ O $_{40}$ catalyst. To confirm the structure of Cs $_{2.5}$ Ni $_{0.08}$ H $_{0.34}$ PMo $_{12}$ O $_{40}$ during the reaction, the infrared, XRD, and ^{31}P NMR spectra were measured before and after the reaction. The results are shown in Fig. 6. In the range 700–1100 cm $^{-1}$, the sample showed the intense 1063 cm $^{-1}$, 966 cm $^{-1}$ (with a shoulder at 970 cm $^{-1}$), and 866 cm $^{-1}$ bands and the very broad 800 cm $^{-1}$ band, which are assigned to $\nu(\text{P-O})$, $\nu(\text{Mo=O})$, corner-sharing

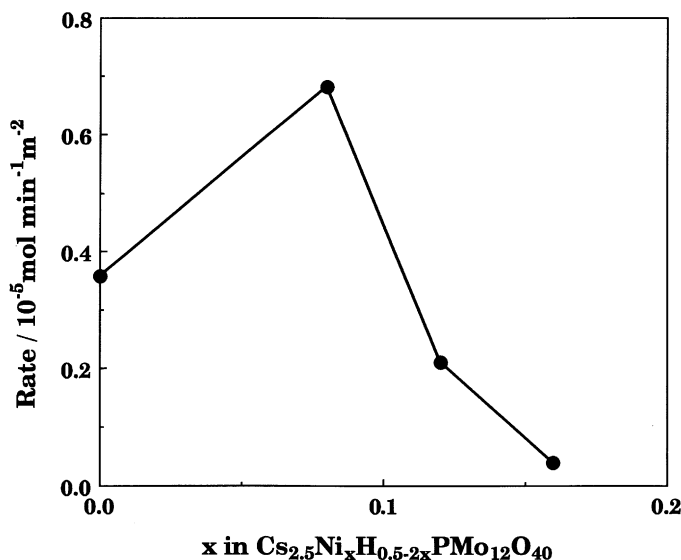


FIG. 5. Effect of Ni $^{2+}$ substitution for H $^{+}$ in Cs $_{2.5}$ H $_{0.5}$ PMo $_{12}$ O $_{40}$ on catalytic activity at 340°C.

TABLE 2

Effect of Alkali Metal Ion (A^+) Substitution for H^+ in $H_{2.84}Ni_{0.08}PMo_{12}O_{40}$ on Oxidation of Isobutane at $340^\circ C^a$ (Catalyst, $A_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$)

| A^+ | Surface area ($m^2 \cdot g^{-1}$) | Conv. (%) | Rate ($10^{-5} \text{ mol} \cdot \text{min}^{-1} \cdot m^{-2}$) | Selectivity ^b (%) | | | | | Sum of yields of MAA + MAL (%) |
|-----------|-------------------------------------|-----------|---|------------------------------|-----|------|----|-----------------|--------------------------------|
| | | | | MAA | MAL | AcOH | CO | CO ₂ | |
| H^+ | 2.0 | 6 | 0.63 | 8 | 18 | 8 | 40 | 26 | 1.6 |
| Li^+ | 3.3 | 14 | 0.89 | 8 | 16 | 3 | 35 | 38 | 3.4 |
| Na^{+c} | 1.7 | 19 | 2.36 | 12 | 21 | 5 | 31 | 27 | 6.3 |
| K^{+d} | 2.4 | 20 | 1.76 | 23 | 16 | 7 | 32 | 20 | 7.8 |
| Cs^{+e} | 7.4 | 24 | 0.68 | 27 | 6 | 7 | 36 | 23 | 8.0 |

^a See Table 1, footnote a.

^b See Table 1, footnote b.

^c The selectivity to isobutyric acid was 4%.

^d The selectivity to acetone was 2%.

^e The selectivity to acetone was 2%.

TABLE 3

Effect of Transition Metal Ion (M^{n+}) Substitution for H^+ in $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on Oxidation of Isobutane at $340^\circ C^a$ (Catalyst, $M_{0.08}^{n+}Cs_{2.5}H_{0.5-0.08n}PMo_{12}O_{40}$)

| M^{n+} | Surface area ($m^2 \cdot g^{-1}$) | Conv. (%) | Rate ($10^{-5} \text{ mol} \cdot \text{min}^{-1} \cdot m^{-2}$) | Selectivity ^b (%) | | | | | Sum of yields of MAA + MAL (%) |
|------------|-------------------------------------|-----------|---|------------------------------|-----|------|----|-----------------|--------------------------------|
| | | | | MAA | MAL | AcOH | CO | CO ₂ | |
| H^+ | 9.5 | 16 | 0.36 | 24 | 7 | 7 | 41 | 21 | 5.1 |
| Ni^{2+c} | 7.4 | 24 | 0.68 | 27 | 6 | 7 | 36 | 23 | 8.0 |
| Mn^{2+} | 5.0 | 21 | 0.88 | 20 | 11 | 9 | 44 | 16 | 6.5 |
| Fe^{3+} | 7.0 | 14 | 0.42 | 35 | 11 | 7 | 27 | 26 | 6.3 |
| Cu^{2+} | 3.3 | 12 | 0.76 | 12 | 10 | 7 | 37 | 34 | 2.6 |
| Co^{2+} | 4.5 | 7 | 0.33 | 11 | 15 | 6 | 48 | 20 | 1.9 |
| Hg^{2+} | 9.3 | 15 | 0.34 | 10 | 10 | 6 | 43 | 30 | 2.4 |
| Pd^{2+d} | 6.5 | 8 | 0.26 | 0 | 1 | 0 | 4 | 94 | 0.1 |
| Pt^{2+e} | 14.9 | 34 | 0.48 | 0 | 0 | 0 | 0 | 100 | 0 |

^a See Table 1, footnote a.

^b See Table 1, footnote b.

^c The selectivity to acetone was 2%.

^d The selectivity to acetone was 1%.

^e Reaction temperature, $300^\circ C$.

TABLE 4

Oxidation of Isobutane Catalyzed by $Cs_{2.5}Ni_xH_{0.5-2x}PMo_{12}O_{40}$ at $340^\circ C^a$

| x | Surface area ($m^2 \cdot g^{-1}$) | Conv. (%) | Rate ($10^{-5} \text{ mol} \cdot \text{min}^{-1} \cdot m^{-2}$) | Selectivity ^b (%) | | | | | Sum of yields of MAA + MAL (%) |
|-------------------|-------------------------------------|-----------|---|------------------------------|-----|------|----|-----------------|--------------------------------|
| | | | | MAA | MAL | AcOH | CO | CO ₂ | |
| 0 | 9.5 | 16 | 0.36 | 24 | 7 | 7 | 41 | 21 | 5.0 |
| 0.04 | | 21 | | 26 | 10 | 6 | 39 | 20 | 7.6 |
| 0.08 ^c | 7.4 | 24 | 0.68 | 27 | 6 | 7 | 36 | 23 | 8.0 |
| 0.12 | 17.4 | 17 | 0.21 | 22 | 14 | 5 | 35 | 24 | 6.1 |
| 0.16 | 37.5 | 7 | 0.04 | 24 | 17 | 5 | 28 | 26 | 2.9 |

^a See Table 1, footnote a.

^b See Table 1, footnote b.

^c The selectivity to acetone was 2%.

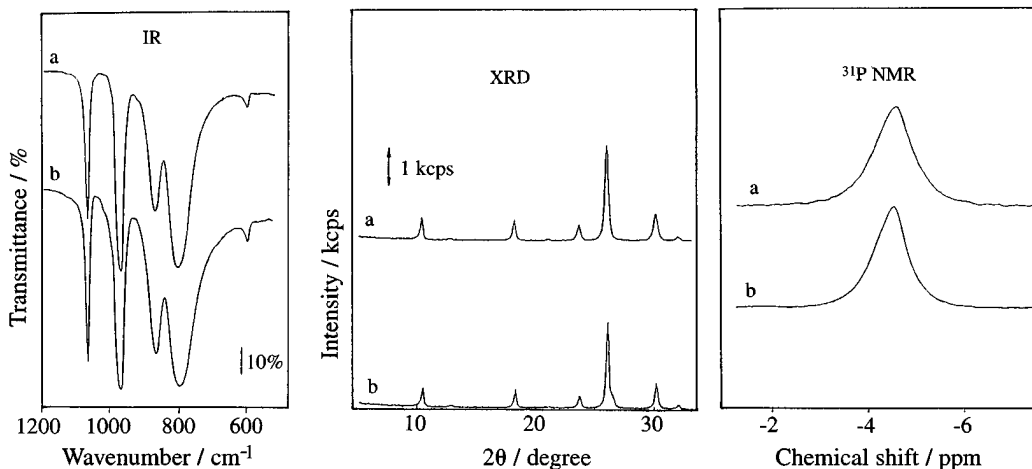


FIG. 6. Infrared, XRD, and ^{31}P NMR spectra of pretreated and spent $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ (KBr pellet). (a) Pretreated in O_2 at 300°C for 1 h; (b) after reaction at 360°C .

$\nu(\text{Mo}-\text{O}-\text{Mo})$, and edge-sharing $\nu(\text{Mo}-\text{O}-\text{Mo})$ of the Keggin structure, respectively, by analogy with the assignment for $\text{PMo}_{12}\text{O}_{40}^{3-}$ Keggin anion (29). The infrared spectrum did not change after the reaction except for the only slight decrease in the intensity of 866 cm^{-1} and 800 cm^{-1} bands. The decrease in the intensity is probably due to the reduction of Mo^{6+} to Mo^{5+} in Keggin anion (30). The slight reduction is consistent with the change of the catalyst color to yellow green during the catalytic test.

In addition, in the 2θ range $5\text{--}35^\circ$, the XRD pattern of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ showed the signals at 10.5 , 18.3 , 23.8 , 26.1 , 30.2 , and 32.1° , which are assigned to cubic system ($a = 11.8\text{ \AA}$), and little changed after the reaction. No signals due to NiO and MoO_3 were observed. In addition, no formation of NiO was observed by XRD for $\text{Ni}_{1.5}\text{PMo}_{12}\text{O}_{40}$, of which the Ni content was $4.6\text{ wt}\%$ and ca. 20 times higher than that of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$. It was also reported that $\text{Ni}_{1.5}\text{PMo}_{12}\text{O}_{40}$ was stable below 400°C (31, 32). The facts support the idea that NiO is not formed. ^{31}P NMR spectrum of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ showed one signal at -4.5 ppm and little changed during the reaction. TG-DTA data showed that $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ underwent two-step dehydration below 300°C , being decomposed at 482°C . Therefore, these data suggest the maintenance of the Keggin structure during the reaction in the range $300\text{--}400^\circ\text{C}$. Such high thermal stability of Keggin anion by the Cs salt formation has been reported (32). Experiments are in progress to investigate the stability in more detail.

To summarize, the above results demonstrate that: (1) the example of catalytic oxidation of isobutane by molecular oxygen on Cs^+ - and Ni^{2+} -substituted $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ species; (2) the preferred catalyst is $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$; (3) the yield of MAA reaches maximum at 360°C and the value was 8.5% .

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