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Effects of additives on catalytic performance of heteropoly compounds for selective oxidation of light alkanes

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Abstract

Effects of the addition of various transition metals to heteropoly compounds on the catalytic performance for oxidation of light alkanes were reviewed. The catalytic selective oxidation of isobutane, propane, and ethane proceeded and the performance was variously changed by the additives. The addition of iron effectively enhanced the catalytic performance under both oxygen-rich and -poor conditions, while copper was found to most enhance the catalytic performance under oxygen-poor conditions. It is suggested that the enhancement by the iron addition under oxygen-rich conditions is due to the promotion of reduction of catalyst and that the enhancement by the copper and iron addition under oxygen-poor conditions is due to the promotion of the reoxidation of the catalyst.

Keywords: Selective oxidation; Lower alkanes; Role of additives; Iron; Copper

1. Introduction

Among hydrocarbons, lower alkanes is of great interest due to the cheapness, abundance, and low reactivities as feedstocks [1–3]. The utilization of molecular oxygen for the oxidation of hydrocarbons is a rewarding goal because molecular oxygen has the highest content of active oxygen and forms no by-products. Therefore, the reaction of lower alkanes with molecular oxygen is very interesting. The catalytic function of heteropoly compounds in the solid state has attracted much attention because their redox and acidic properties can be controlled at atomic/molecular levels [4–9]. The addition of transition metals to heteropoly compounds is important to control the redox properties [10–13], as these additives are utilized as industrial catalysts for the oxidation of methacrolein [9]. However, the relations to oxidation catalysis remain unclarified [4,5,9].

There have been several attempts to oxidize lower alkanes by using heteropoly catalysts. It has been reported that the hydrogen form of $H_3PMo_{12}O_{40}$ catalyzed the oxidation of lower alkanes and that the substitution of V^{5+} for Mo^{6+} modified the catalytic activity and selectivity [14–19]. The catalytic performance is much enhanced by the addition of transition metals [18–24,45]. Iron and copper have been most widely used additives for enhancing catalytic activity of heteropoly compounds in the patent literature [25–30]. However, the effects to the catalytic performance are still ambiguous because iron and copper were added with many kinds of metals under various reaction conditions. Therefore, the clarification of the effect of iron and copper on the catalytic performance of heteropoly compounds is interesting.

Here, our work on the effectiveness of transition metals addition to heteropoly compounds for the oxidation of lower alkanes are reviewed.

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2. Experimental

$H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ heteropolyacids were commercially obtained from Nippon Inorganic Color and Chemical and used after purification with ether abstraction and recrystallization. It was confirmed for $H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ that atomic ratios of P:Mo:V were 1.0:12.0:0.0 and 1.0:11.0:1.0, respectively. The purity of $H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ confirmed by ^{31}P NMR were $\geq$99 and 95%, respectively. The cesium- and transition-metal-containing catalysts were prepared according to the previous report [18,45]. The actual composition may be $Cs_{2.5}M_{0.08}H_xPVMo_{11}O_z$ (M = Cu, Fe, Ni, etc.), but in this paper they will be designated as $Cs_{2.5}M_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$. The other reagents used were analytical grade and used without further purification.

After catalytic tests of the heteropoly compounds, they (ca. 30 mg) were transferred into ESR tubes. The ESR spectra were recorded on a JEOL JES-RE1X spectrometer at room temperature. For quantitative measurements, the signal was doubly integrated and compared with that of $CuSO_4{\cdot}5H_2O$ powder.

The reaction was performed in a flow reactor (Pyrex tube, 12 mm internal diameter) at an applied temperature under atmospheric pressure. Prior to the reaction, 1 g each of as-prepared catalyst was mixed with SiC (1.5 g) to prevent an undesirable temperature rise and treated in an O_2 stream (60 $cm^3\,min^{-1}$) for 1 h at 300–350°C. The gases at the outlet of the reactor were sampled intermittently with the aid of a sampler directly connected to the system and analyzed by FID and TCD gas chromatography with FFAP, Porapak Q, and Molecular Sieve 5A columns. Selectivities were fractions of the sum of the products and calculated on the C_{2-4}(ethane, propane, isobutane)-basis. The carbon and oxygen balances were more than 90%. Acrolein, acrylic acid, methacrolein, and methacrylic acid were abbreviated by ACR, AA, MAL, and MAA, respectively.

3. Results and discussion

3.1. Effects of transition metal additives on oxidation of isobutane

By optimizing the quantity and type of constituent elements of polyanions and counter cations, fairly good yields were obtained for the oxidation of isobutane. Table 1 shows results for the oxidation of isobutane catalyzed by $Cs_xH_{3-x}PMo_{12}O_{40}$ under oxygen-rich conditions. The conversions were 7, 6, 11, 16, 17, and 8% for $x = 0$, 1, 2, 2.5, 2.85, and 3, respectively, and the sum of yields of MAA and MAL reached a maximum at $x = 2.5$.

Fig. 1 shows a good correlation between the rates of oxidation of isobutane and non-catalytic reduction of catalysts by CO. The correlation noted in Fig. 1 indicates that the catalytic activity is controlled by the oxidizing ability of catalysts. The protonic acidity is also a factor controlling the catalytic activity [18,45].

The catalytic properties of $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ were changed by the addition of transition metal additives. Table 2 shows the effect of transition metal additives on oxidation of isobutane. The addition of Ni, Mn, or Fe increased the yields of MAA and

Table 1
Oxidation of isobutane over $Cs_xH_{3-x}PMo_{12}O_{40}$ at 340°C under oxygen-rich conditions[a]

x	Conversion (%)	Selectivity[b] (%)					Sum of yields of MAA + MAL (%)
		MAA	MAL	AcOH	CO	CO_2	
0	7	4	18	8	44	26	1.5
1	6	23	17	10	32	18	2.4
2	11	34	10	7	29	21	4.8
2.5	16	24	7	7	41	21	5.1
2.85	17	5	10	5	44	37	2.4
3[c]	8	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, 30 $cm^3\,min^{-1}$.
[b] Calculated on the C_4(isobutane)-basis.
[c] The selectivity to acetone was 17%.

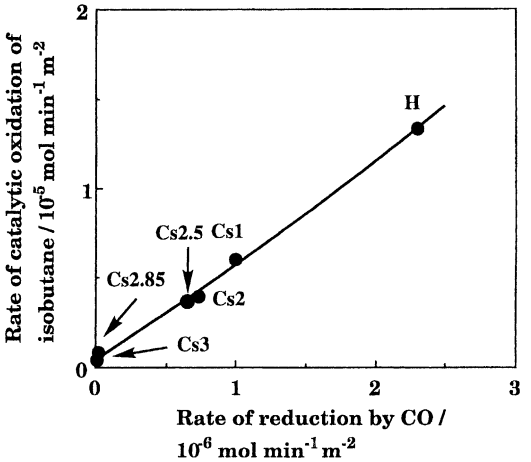

Fig. 1. Correlation between rates of oxidation of isobutane and those of non-catalytic reduction of catalysts by CO at 350°C cited from Ref. [18]. Cs_x and H show $Cs_xH_{3-x}PMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, respectively.

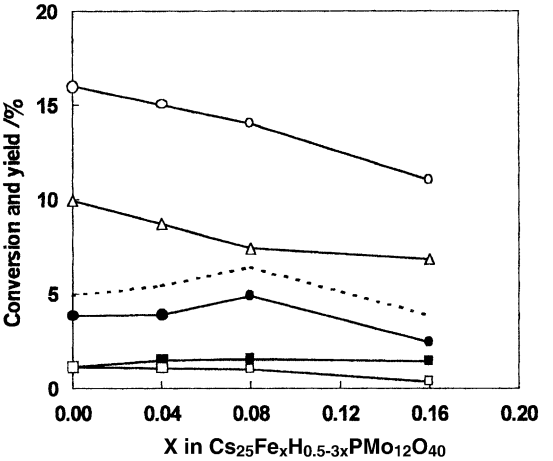

Fig. 2. Oxidation of isobutane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ at 340°C. (○), (●), (■), (□), and (△) represent conversion of isobutane and yields of methacrylic acid, methacrolein, acetic acid, and CO_x, respectively. Broken line indicates the sum of yields of methacrylic acid and methacrolein (isobutane:O_2:N_2 = 17:33:50; catalyst weight, 1.0 g; total flow rate, 30 $cm^3\,mol^{-1}$).

MAL. In contrast, Co and Cu decreased the yields. Hereafter, we focused on the effects of iron and copper addition because iron and copper have been most widely used additives for enhancing catalytic activity of heteropoly compounds in the patent literature as described in Section 1.

3.2. Effects of iron addition

Fig. 2 shows results for the oxidation of isobutane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ at 340°C under oxygen-rich conditions. The products were methacrylic acid, methacrolein, acetic acid, CO, and CO_2. The yields of methacrylic acid and methacrolein increased from $x = 0$ to 0.08 while the conversion decreased little. It follows that the sum of yields of methacrylic acid and methacrolein reached a maximum at $x = 0.08$ and then decreased. Similar changes in conversions and selectivities were observed for the oxidation of isobutane catalyzed by Ni added $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, and the decrease in activity above $x = 0.08$ is explained by the decrease in Brønsted acidity [18,45].

Table 3 shows the results of the oxidation of isobutane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$

Table 2
Effects of transition metal ions (M^{n+}) on oxidation of isobutane over $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ at 340°C under oxygen-rich conditions[a] (catalyst, $Cs_{2.5}M^{n+}_{0.08}H_{0.5-0.08n}PMo_{12}O_{40}$)

M^{n+}	Conversion (%)	Selectivity (%)					Sum of yields of MAA + MAL (%)
		MAA	MAL	AcOH	CO	CO_2	
H^+	16	24	7	7	41	21	5.1
Ni^{2+}	24	27	6	7	36	23	8.0
Mn^{2+}	21	20	11	9	44	16	6.5
Fe^{3+}	14	35	11	7	27	26	6.3
Cu^{2+}	12	12	10	7	37	34	2.6
Co^{2+}	7	11	15	6	48	20	1.9

[a] Reaction conditions, see Table 1.

Table 3
Effect of addition of Fe^{3+} to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on oxidation of isobutane at 340°C under oxygen-poor conditions[a] (catalyst, $Cs_{2.5}M_x^{n+}H_{0.5-nx}PMo_{12}O_{40}$)

M^{n+} (x)	Conversion (%)	Yield[b] (%)					
		MAL	Isobutene	Acetone	AcOH	CO	CO_2
H^+ (0.08)	10	1.5	1.2	3.0	0.1	3.0	1.2
Fe^{3+} (0.08)	15	4.5	0.3	3.8	0.3	4.2	1.8
Fe^{3+} (0.16)	13	0.9	0.0	2.0	0.5	7.0	2.6

[a] Isobutane, 33 vol.%; O_2, 13 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3\,min^{-1}$.
[b] Calculated on the C_4(isobutane)-basis.

Table 4
Effect of addition of Fe^{3+} to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of propane at 360°C[a] (catalyst, $Cs_{2.5}M_{0.08}^{n+}H_{1.5-0.08n}PVMo_{11}O_{40}$)

M^{n+}	Conversion (%)	Yield[b] (%)						Sum of yields of AA + ACR (%)
		AA	ACR	Propene	AcOH	CO	CO_2	
H^+	12	1.0	0.1	0.7	1.0	7.4	1.8	1.1
Fe^{3+}	13	2.3	0.3	1.2	1.4	6.5	1.3	2.6

[a] Propane, 30 vol.%; O_2, 40 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, ca. 30 $cm^3\,min^{-1}$.
[b] Calculated on the C_3(propane)-basis.

under oxygen-poor conditions. The products were methacrolein, isobutene, acetic acid, CO, and CO_2. Methacrylic acid was not observed under oxygen-poor conditions. The conversion and selectivity to methacrolein were increased by the addition of iron ($x = 0.08$). Further addition of iron much decreased the selectivity to methacrolein in a similar way to Fig. 2.

Table 4 shows the results of the oxidation of propane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ at 360°C under oxygen-rich conditions. The content of iron was kept 0.08, where the highest sum of yields of methacrylic acid and methacrolein was obtained for the oxidation of isobutane in Fig. 2. The addition of iron to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ resulted in an increase in selectivities to acrylic acid and acrolein, while the conversion changed little.

Tables 5 and 6 show effects of addition of iron to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on the selective oxidation of ethane at 425°C under oxygen-rich and -poor conditions, respectively. The products were ethene, CO, and CO_2 under both conditions. Selectively oxygenated products of acetic acid and acetaldehyde were not observed under the conditions. Under oxygen-rich conditions, the addition of iron increased the selectivity to ethene from 35 to 39%, while the conversion did not

Table 5
Effect of addition of Fe^{3+} to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of ethane at 425°C under oxygen-rich conditions[a] (catalyst, $Cs_{2.5}M_{0.08}^{n+}H_{1.5-0.08n}PVMo_{11}O_{40}$)

M^{n+}	Conversion (%)	Yield[b] (%)		
		C_2H_4	CO	CO_2
H^+	9.7	3.4	5.2	1.1
Fe^{3+}	10.0	3.9	4.2	1.8

[a] Ethane, 33 vol.%; O_2, 33 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3\,min^{-1}$.
[b] Calculated on the C_2(ethane)-basis.

Table 6
Effect of addition of Fe^{3+} to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of ethane at 425°C under oxygen-poor conditions[a] (catalyst, $Cs_{2.5}M_{0.08}^{n+}H_{1.5-0.08n}PVMo_{11}O_{40}$)

M^{n+}	Conversion (%)	Yield[b] (%)		
		C_2H_4	CO	CO_2
H^+	4.0	2.4	0.8	0.7
Fe^{3+}	6.4	3.7	1.7	1.0

[a] Ethane, 57 vol.%; O_2, 9 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3\,min^{-1}$.
[b] Calculated on the C_2(ethane)-basis.

change. On the other hand, under oxygen-poor conditions, the addition of iron increased the conversion from 4 to 6% without much change in the selectivity.

3.3. Effects of copper addition

The conversion and selectivity for the oxidation of ethane catalyzed by $Cs_{2.5}Cu_{0.08}H_{1.34}PVMo_{11}O_{40}$ became nearly almost constant after 2 h under oxygen-poor conditions; e.g., the conversions were 9.2, 8.8, 8.6, 8.7, 8.6, and 8.6% at 0.25, 0.5, 0.75, 1, 2, and 3 h, respectively. Similarly, nearly steady state conversion and selectivity were observed after 2–5 h for each catalyst and oxidation.

The results for $Cs_{2.5}M_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts are compared. The products were ethene, CO, and CO_2. No acetic acid and acetaldehyde were observed under these conditions. The conversions were 8.6, 6.4, 5.8, 5.7, 4.0, and 3.4% for M = Cu, Fe, Mn, Co, H, and Ni, respectively, and the highest conversion was observed for Cu. The oxygen conversions among Co-, Mn-, and Fe-added compounds did not change much and were lower than Cu-added one. The same order was obtained for conversions at 350°C. These facts show that the activity order in Table 5 reflects that of true activities. The selectivities to ethene on $Cs_{2.5}M_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ were 52, 58, 59, 30, 61, and 58% for M = Cu, Fe, Mn, Co, H, and Ni, respectively. The yields of ethene on $Cs_{2.5}M_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ were 4.5, 3.7, 3.4, 1.7, 2.4, and 2.0% for M = Cu, Fe, Mn, Co, H, and Ni, respectively. It follows that the addition of Cu^{2+} to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ resulted in the greatest enhancement of the ethene production.

The space time yield of ethene was 1.6×10^{-5} mol min^{-1} g^{-1}, of which the value is higher than those for Mo–V–P–Sb–O, BaF_2–LaOF, supported Pt or Ag catalysts, Al_2O_3–B_2O, and Ga–MFI zeolite catalysts [31–36] and lower than those of Mo–V–Nb–O [37–40] and supported V–Sb–O [41] catalysts. The active temperature is lower than those of Mo–V–P–Sb–O, BaF_2–LaOF, supported Pt or Ag catalysts, Al_2O_3–B_2O, and Ga–MFI zeolite catalysts, [27–32] but not lower than examples on Mo–V–Nb–O catalysts [37–40] as is consistent with the results of the comparison of the space time yields described above.

Similar enhancements of the catalytic performance by the copper addition were observed for the oxidation of propane and isobutane as shown in Tables 7 and 8, respectively. The conversion and sum of the yields of selective oxidation products (propene, acrolein, and acrylic acid) increased by the addition of copper for the oxidation of propane. In the oxidation of isobutane, the sum of the yields of methacrolein and isobutene increased from 2.7 to 5.2% with an increase in the conversion.

In contrast, under oxygen-rich conditions, the addition of copper to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ decreased the conversion of ethane from 9.7 to 6.6% and the selectivity to ethene was also decreased from 35 to 31% [23]. Similar decreases were observed for the oxidation of propane and isobutane [18,19,45]. Thus, the present results demonstrated that the addition of copper enhanced the catalytic performance of heteropoly compounds for oxidation of lower alkanes under oxygen-poor conditions.

3.4. Role of iron and copper under oxygen-rich and -poor conditions

It was clearly demonstrated that iron is an effective additive for the selective oxidation of light alkanes both under oxygen-rich and -poor conditions in contrast with the fact that copper is an effective

Table 7
Effect of addition of Cu^{2+} to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of propane at 380°C under oxygen-poor conditions[a] (catalyst, $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$)

M^{n+}	Conversion (%)	Yield[b] (%)							Sum of yields of AA + ACR + propene (%)
		AA	ACR	Propene	Ethene	AcOH	CO	CO_2	
H^+	15.1	0.5	0.7	3.4	0.5	1.6	1.4	7.0	4.6
Cu^{2+}	17.9	0.6	0.9	4.1	1.0	1.9	1.7	7.7	5.6

[a] Propane, 33 vol.%; O_2, 17 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 30 cm^3 min^{-1}.
[b] Calculated on the C_3(propane)-basis.

Table 8
Effect of addition of Cu^{2+} to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on oxidation of isobutane at 340°C under oxygen-poor conditions[a] (catalyst, $Cs_{2.5}M^{n+}_{0.08}H_{0.5-0.08n}PMo_{12}O_{40}$)

M^{n+}	Conversion (%)	Yield[b] (%)						Sum of yields of MAL + isobutene (%)
		MAL	Isobutene	Acetone	AcOH	CO	CO_2	
H^+	10.0	1.5	1.2	3.0	0.1	3.0	1.2	2.7
Cu^{2+}	14.0	4.9	0.3	3.4	0.3	3.7	1.4	5.2

[a] Isobutane, 33 vol.%; O_2, 13 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3\,min^{-1}$.
[b] Calculated on the C_4(isobutane)-basis.

additive only under oxygen-poor conditions. Under oxygen-rich conditions, the addition of iron increased selectivities without an increase in conversions. Iron may suppress the complete oxidation of alkenes (propene, ethene), aldehydes (methacrolein, acrolein), and carboxylic acids (methacrylic acid, acrylic acid). Under oxygen-poor conditions, conversions were increased by the addition of iron. A similar increase in conversion was observed for the addition of copper and the role is the acceleration of the reoxidation of catalysts [24]. Iron would also promote the reoxidation of catalyst.

ESR signals of $Cs_{2.5}M_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts tested for the oxidation of ethene showed broad signals ($g = 2$) ranging from 200 to 500 mT. Fig. 3 shows the correlation between the activity of $Cs_{2.5}M_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts for the oxidation of ethane and the doubly integrated ESR signal intensity. The catalytic activity decreased with the increase in the signal intensity. No XRD signals assigned to the metals were observed for each sample, suggesting that transition metals added are present as ions. The ESR signal intensities of Cu^{2+}, Ni^{2+}, and Fe^{3+} for even as-prepared samples were less

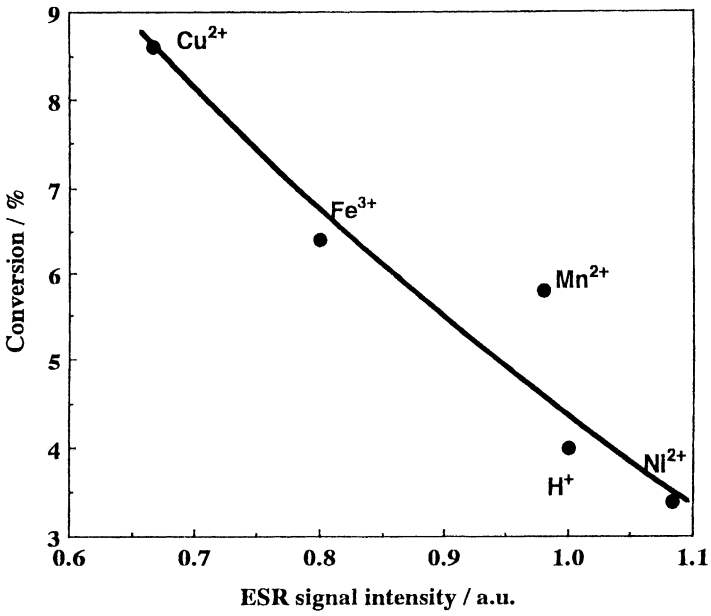

Fig. 3. Correlation between the catalytic activity for the oxidation of ethane and doubly integrated ESR signal intensity of catalyst tested for the reaction. $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts were abbreviated by M^{n+}. The ESR signals of $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts tested for the oxidation of ethane showed broad signals around $g = 2$ ranging from 200 to 500 mT. The signal intensity of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ was taken as unity. The signal intensity of 1.4 mg of $CuSO_4{\cdot}5H_2O$ was 0.67.

than one-fifth of those of tested samples. Therefore, the signal intensities would reflect the numbers of Mo^{5+} and V^{4+}, i.e., degree of reduction of polyanion, and the polyanion of copper-containing catalyst would be the most oxidized. It was also observed for V-free $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ that copper-containing $Cs_{2.5}Cu_{0.08}H_{0.34}PMo_{12}O_{40}$ was more oxidized than $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ after tested for the oxidations of propane and isobutane under oxygen-poor conditions. These facts suggest that copper promotes the catalyst reoxidation. It was also suggested for the oxidative dehydrogenation of isobutyric acid that copper promotes the reoxidation of heteropoly catalyst [44]. In accord with this idea, about first order dependency of the rate on the partial pressure of oxygen was observed for the oxidations of isobutane, propane, and ethane under oxygen-poor conditions. For example, when the oxidation of propane was carried out at 380°C and $P_{C_3H_8}$ of 0.33 atm using $Cs_{2.5}Cu_{0.08}H_{1.34}PVMo_{11}O_{40}$ catalyst, the conversions were 18, 27, and 36% at P_{O_2} of 0.17, 0.25, and 0.33 atm, respectively, and linearly increased with P_{O_2}.

The contrast of effects of copper addition is important from the standpoints of the catalyst design based on heteropoly compounds because heteropoly compounds show high catalytic activity for the oxidation of isobutane, propane, and methacrolein under oxygen-rich [4,5,18,19,27,42,45] and -poor [25,26,43] conditions. The contrasts of effects of copper may be due to the change of the rate-determining step. The catalyst reoxidation step is the rate-determining step under oxygen-poor conditions, while catalyst reduction under oxygen-rich conditions.

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