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RESEARCH NOTE

Selective Oxidation of Ethane, Propane, and Isobutane Catalyzed by Copper-Containing $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ under Oxygen-Poor Conditions

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Effects of the addition of various transition metal additives to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on the catalytic performance for oxidation of ethane were compared under oxygen-poor conditions and copper was found to most enhance the catalytic performance. Similar enhancements by the addition of copper were observed for the oxidation of propane and isobutane under oxygen-poor conditions. It is suggested that the enhancement by the copper addition is due to the promotion of the reoxidation of the catalyst. © 1998 Academic Press

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 (1–6). The addition of transition metals to heteropoly compounds is important to control the redox properties (7–10), as these additives are utilized as industrial catalysts for the oxidation of methacrolein (6). However, the relation to oxidation catalysis remains unclarified (1, 2, 6).

Selective oxidation of lower alkanes with molecular oxygen is of great interest because of the low costs and chemically low reactivities as feedstocks (11–13). 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). Under these *oxygen-rich* conditions, the addition of nickel, iron, or manganese increased the yields of selective products for the oxidation of lower alkanes (17–20) and the addition of copper could not enhance the catalytic performance (18–20). On the other hand, in the patent literature copper is usually added for alkane oxidation (21–27). Therefore, the effect of copper is not clear and demonstrating how copper enhances the catalytic performance of heteropoly compounds is interesting.

In this paper, we attempted to demonstrate the effectiveness of copper addition to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ heteropoly compound for the oxidation of ethane, propane, and isobutane under *oxygen-poor* conditions and to investigate the role of copper.

$H_4PVMo_{11}O_{40}$ heteropolyacid was commercially obtained from Nippon Inorganic Colour and Chemical Co., Ltd. and used after purification with ether abstraction and recrystallization. It was confirmed for $H_4PMo_{11}VO_{40}$ that atomic ratios of P : Mo : V was 1.0 : 11.0 : 1.0. The purity of $H_4PMo_{11}VO_{40}$ confirmed by ^{31}P NMR was 95%. The cesium- and transition-metal-containing catalysts were prepared according to the previous report (18). The actual composition may be $Cs_{2.5}M^{n+}_{0.08}H_xPVMo_{11}O_z$ (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. The spectra were recorded 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 ID) 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 ($60\ cm^3 \cdot min^{-1}$) 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

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TABLE 1

Effect of Addition of Transition Metal Ion (M^{n+}) to $Cs_{2.5}H_{1.5}$-$PVMo_{11}O_{40}$ on Oxidation of Ethane at 425°C under Oxygen-Poor Conditions[a]

M^{n+}[b]	Conv.[c]/%	Selectivity[d]/%			Yield of ethene/%
		C_2H_4	CO	CO_2	
Cu^{2+}	8.6	52	33	15	4.5
Fe^{3+}	6.4	58	26	16	3.7
Mn^{2+}	5.8	59	20	21	3.4
Co^{2+}	5.7	30	35	35	1.7
H^{+}	4.0	61	21	18	2.4
Ni^{2+}	3.4	58	23	19	2.0

[a] Ethane, 57 vol%; O_2, 9 vol%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3 \cdot min^{-1}$.

[b] $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts were abbreviated by M^{n+}.

[c] The oxygen conversions calculated for Cu^{2+}-, Fe^{3+}-, Mn^{2+}-, Co^{2+}-, H^{+}-, and Ni^{2+}-added catalysts were 100, 72, 67, 87, 44, and 39%, respectively.

[d] Calculated on the C_2 (ethane)-basis.

C_{2-4} (ethane, propane, isobutane)-basis. The carbon balance was more than 90%.

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 $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts are compared in Table 1. 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 much change and were lower than Cu-added one (see note in Table 1). The same order was obtained for conversions at 350°C. These facts show that the activity order in Table 1 reflects that of true activities. The selectivities to ethene on $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ were 52, 58, 59, 30, 61, and 58% for M = Cu, Fe, Mn, Co, H, and Ni, respectively. The yields of ethene on $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ 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} $mol \cdot min^{-1} \cdot g^{-1}$, 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 (28–33) and lower than those of Mo-V-Nb-O (34–37) and supported V-Sb-O (38) 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 (24–29), but not lower than examples on Mo-V-Nb-O catalysts (34–37) 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 2 and 3, 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% (20). Similar decreases were observed for the oxidation of propane and isobutane (18, 19). The contrast of effects of copper addition is important from the standpoint 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 (1, 2, 18, 19, 23, 39) and -poor (21, 22, 40) conditions. The contrast of effects of copper may be due to the change of the rate-determining step from catalyst reoxidation under

TABLE 2

Effect of Addition of Copper Ion to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on Oxidation of Propane at 380°C under Oxygen-Poor Conditions[a]

M^{n+}[b]	Conv./%	Yield[c]/%						
		Propene	Acrolein	Acrylic acid	Ethene	AcOH	CO	CO_2
Cu^{2+}	17.9	4.1	0.9	0.6	1.0	1.9	1.7	7.7
H^{+}	15.1	3.4	0.7	0.5	0.5	1.6	1.4	7.0

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

[b] See Table 1.

[c] Calculated on the C_3 (propane)-basis.

TABLE 3

Effect of Addition of Copper Ion to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on Oxidation of Isobutane at 340°C under Oxygen-Poor Conditions[a]

M^{n+}[b]	Conv./%	Yield[c]/%					
		Methacrolein	Isobutene	Acetone	AcOH	CO	CO_2
Cu^{2+}	14.0	4.9	0.3	3.4	0.3	3.7	1.4
H^+	10.0	1.5	1.2	3.0	0.1	3.0	1.2

[a] Isobutane, 33 vol%; O_2, 13 vol%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3 \cdot min^{-1}$.

[b] See Table 1.

[c] Calculated on the C_4 (isobutane)-basis.

oxygen-poor conditions to catalyst reduction under oxygen-rich conditions.

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 ethene showed broad signals ($g = 2$) ranging from 200–500 mT. Figure 1 shows the correlation between the activity of $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts for the oxidation of ethene 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 than one-fifth 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 promoted the reoxidation of heteropoly catalyst (41). 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}.

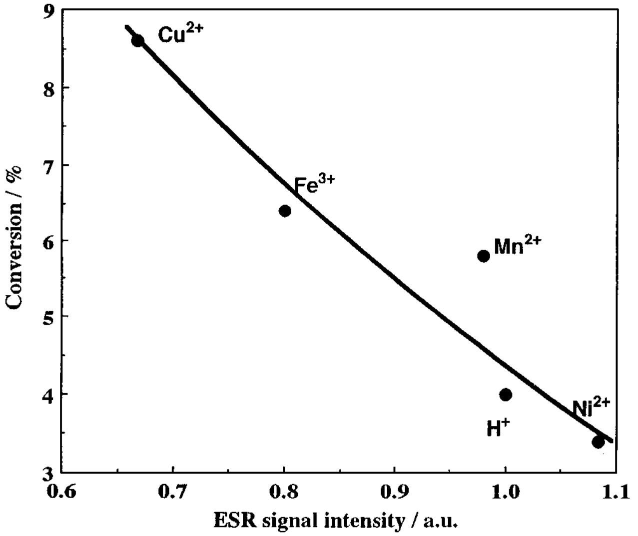

FIG. 1. Correlation between the catalytic activity for the oxidation of ethene (a) and doubly integrated ESR signal intensity (b) of catalyst tested for the reaction. (a) See Table 1. Abbreviation of catalysts, see Table 1. (b) The signal intensity of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ was taken as unity. The signal intensity of 1.4 mg of $CuSO_4 \cdot 5H_2O$ was 0.67.

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 due to the promotion of the reoxidation of the catalyst.

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