

Copper as an Effective Additive for Enhancement of Catalytic Activity of $\text{Cs}_{2.5}\text{H}_{1.5}\text{PVMo}_{11}\text{O}_{40}$ for Selective Oxidation of Lower Alkanes

Noritaka Mizuno,* Wonchull Han,† and Tetsuichi Kudo†

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Hongo, Tokyo 113-8656

† Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8558

(Received February 17, 1998; CL-980112)

Copper was found to be an effective additive to increase the yield of the selective oxidation products likely due to the promotion of the reoxidation of the catalyst.

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.¹⁻⁵ The addition of transition metals to heteropoly compounds is important to control the redox properties⁶⁻⁹ and several kinds of metals were added in the case of industrial heteropoly catalysts for the oxidation of methacrolein.⁵ However, the relation to oxidation catalysis and roles remain unclarified.^{1,2,5}

Selective oxidation of lower alkanes with molecular oxygen is of great interest because of the low costs and chemically low reactivities as feedstocks.¹⁰⁻¹² Heteropoly compounds can also catalyze the oxidation of lower alkanes.¹³⁻¹⁸ The substitution of V^{5+} for Mo^{6+} modified the catalytic activity and selectivity.^{16,17} In addition, various kinds of transition metals have been added and copper is one of the common additives in the patent literature.²¹⁻²⁷ However, the effect of copper is inconsistent because copper was added with the other transition metals¹⁹⁻²⁵ and the catalytic performance was sometimes suppressed by the addition.^{16-18,22,23,27} Therefore, the effect of copper is not clear and demonstrating how copper enhances the catalytic performance of heteropoly compounds is interesting.

Here, we demonstrate that the addition of copper enhances the catalytic activity and attempt to clarify the roles.

$\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ heteropolyacid was commercially obtained from Nippon Inorganic Colour and Chemical Co., Ltd. The cesium- and transition-metal-containing catalysts were prepared according to the previous report.¹⁶ The actual composition may be $\text{Cs}_{2.5}\text{M}^{\text{n}+}\text{H}_{0.08}\text{PVMo}_{11}\text{O}_{40}$ ($\text{M} = \text{Cu, Fe, Ni, etc.}$), but in this paper they will be designated as $\text{Cs}_{2.5}\text{M}^{\text{n}+}\text{H}_{1.5-0.08}\text{PVMo}_{11}\text{O}_{40}$. 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 of each as-prepared catalyst was mixed with SiC (1.5 g) to prevent an undesirable temperature rise and treated in an O_2 stream ($60 \text{ cm}^3 \cdot \text{min}^{-1}$) 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. The conversion and the selectivity were determined after 2 - 5 h of reaction. Selectivities were fractions of the sum of the products and calculated on the $\text{C}_2\text{-4}$ (ethane, propane, isobutane)-basis. The carbon balance was more than 90%.

The conversion and selectivity for the oxidation of ethane catalyzed by $\text{Cs}_{2.5}\text{Cu}_0.08\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ became nearly almost constant after 2 h under the conditions used; 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 $\text{Cs}_{2.5}\text{M}^{\text{n}+}0.08\text{H}_{1.5-0.08}\text{PVMo}_{11}\text{O}_{40}$ catalysts are compared in Fig. 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 $\text{M} = \text{Cu, Fe, Mn, Co, H, and Ni}$, respectively, and the highest conversion was observed for Cu. The selectivities to ethene on $\text{Cs}_{2.5}\text{M}^{\text{n}+}0.08\text{H}_{1.5-0.08}\text{PVMo}_{11}\text{O}_{40}$ were 52, 58, 59, 30, 61, and 58% for $\text{M} = \text{Cu, Fe, Mn, Co, H, and Ni}$, respectively. The yields of ethene on $\text{Cs}_{2.5}\text{M}^{\text{n}+}0.08\text{H}_{1.5-0.08}\text{PVMo}_{11}\text{O}_{40}$ were 4.5, 3.7, 3.4, 1.7, 2.4, and 2.0% for $\text{M} = \text{Cu, Fe, Mn, Co, H, and Ni}$, respectively. It follows that the addition of Cu^{2+} to $\text{Cs}_{2.5}\text{H}_{1.5}\text{PVMo}_{11}\text{O}_{40}$ resulted in the greatest enhancement of the ethene production.

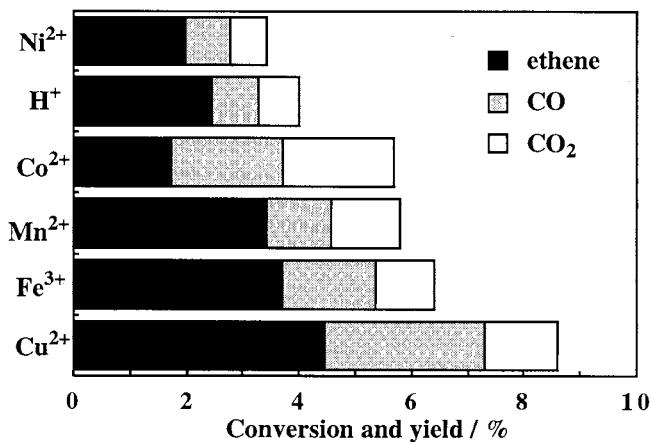


Figure 1. Effect of addition of transition metal ion ($\text{M}^{\text{n}+}$) on oxidation of ethane at 425 °C.^a

^a Ethane, 57 vol%; O_2 , 9 vol%; N_2 , balance; catalyst, $\text{Cs}_{2.5}\text{M}^{\text{n}+}0.08\text{H}_{1.5-0.08}\text{PVMo}_{11}\text{O}_{40}$, 1.0 g; total flow rate, $15 \text{ cm}^3 \cdot \text{min}^{-1}$. $\text{Cs}_{2.5}\text{M}^{\text{n}+}0.08\text{H}_{1.5-0.08}\text{PVMo}_{11}\text{O}_{40}$ catalysts were abbreviated as $\text{M}^{\text{n}+}$.

A similar enhancement of the catalytic performance by the copper addition was observed for the oxidation of isobutane (isobutane, 33 vol%; O₂, 13 vol%; N₂, balance): The sum of the yields of methacrolein and isobutene increased from 2.7 to 5.2% with a slight increase in the conversion.

In contrast, under more oxidizing conditions (ethane, 33 vol%; O₂, 33 vol%; N₂, balance), the addition of copper to Cs_{2.5}H_{1.5}P₂Mo₁₁O₄₀ decreased the conversion from 9.7 to 6.6% and the selectivity to ethene was also decreased from 35 to 31%.¹⁸ Similar decreases were observed for the oxidation of propane and isobutane.^{16,17} 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 various conditions.^{1,2,16-27}

Figure 2 shows the correlation between the catalytic activity for the oxidation of ethene and the doubly integrated ESR signal intensity of catalyst tested for the reaction. 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 Cu²⁺, Ni²⁺, and Fe³⁺ for even as-prepared samples were less than one fifth of those of tested samples. Therefore, the signal intensities would reflect the numbers of Mo⁵⁺ and V⁴⁺, i.e., degree of reduction of polyanion, and the polyanion of copper-containing catalyst would be the most oxidized. During the oxidation of isobutane

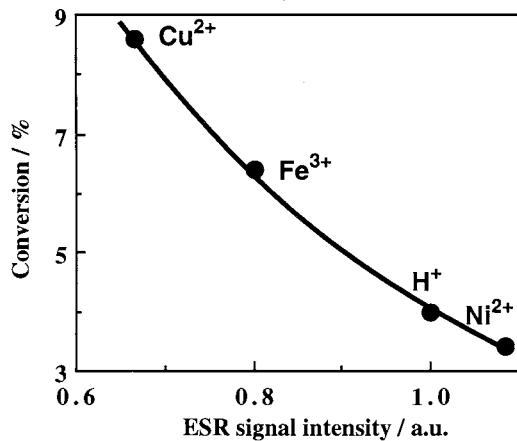


Figure 2. Correlation between the catalytic activity for the oxidation of ethene^a and doubly integrated ESR signal intensity^b of catalyst tested for the reaction.

^a See Fig. 1. Abbreviation of catalysts, see Fig. 1. ^b The signal intensity of Cs_{2.5}H_{1.5}P₂Mo₁₁O₄₀ was taken as unity. The signal intensity of 1.4 mg of CuSO₄·5H₂O was 0.67.

under similar conditions, Cs_{2.5}Cu_{0.08}H_{0.34}PMo₁₂O₄₀ was also less reduced than Cs_{2.5}H_{0.5}PMo₁₂O₄₀. Therefore, copper would promote the catalyst reoxidation. In consistent with this idea, about first order dependency of the rate on the partial pressure of oxygen was observed for the oxidations of isobutane and ethane.

Thus, the present results demonstrated that the addition of

copper enhanced the catalytic performance of heteropoly compounds for oxidation of lower alkanes likely due to the promotion of the reoxidation of the catalyst.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

- 1 N. Mizuno and M. Misono, *Chem. Rev.*, **98**, 199 (1998).
- 2 T. Okuhara, N. Mizuno, and M. Misono, *Adv. Catal.*, **41**, 113 (1996).
- 3 Y. Ono, "Perspectives in Catalysis", ed by J. M. Thomas and K. I. Zamaraev, Blackwell, London, 1992, p. 341.
- 4 Y. Izumi, K. Urabe, and A. Onaka, "Zeolite, Clay, and Heteropolyacids in Organic Reactions", Kodansha, Tokyo-VCH, Weinheim (1992).
- 5 M. Misono, *Catal. Rev.-Sci. Eng.*, **29**, 269 (1987).
- 6 M. Ai, *Appl. Catal.*, **4**, 245 (1982).
- 7 M. Akimoto, Y. Tsuchida, K. Sato, and E. Echigoya, *J. Catal.*, **72**, 83 (1981).
- 8 K. Eguchi, I. Aso, N. Yamazoe, and T. Seiyama, *Chem. Lett.*, **1979**, 1345.
- 9 H. Niiyama, H. Tsuneki, and E. Echigoya, *Nippon Kagaku Kaishi*, **1979**, 996.
- 10 Y. Takita, *Shokubai (Catalysts and Catalysis)*, **38**, 34 (1996).
- 11 J. B. Moffat, *Appl. Catal.*, **146**, 65 (1996).
- 12 H. H. Kung, *Adv. Catal.*, **40**, 1 (1994).
- 13 M. Ai, Proc. 8th Intern. Congr. Catal., Berlin, 1984, Verlag Chemie, Weinheim, 1985, vol. 5, p. 475.
- 14 G. Centi, J. P. Nieto, C. Ipalucci, K. Briukman, and E. M. Serwicka, *Appl. Catal.*, **46**, 197 (1989).
- 15 G. Centi, V. Lena, F. Trifiro, D. Ghoussoob, C. F. Aïssi, M. Guelton, and J. P. Bonnelle, *J. Chem. Soc., Faraday Trans.*, **86**, 2775 (1990).
- 16 N. Mizuno and H. Yahiro, *J. Phys. Chem. B*, **102**, 437 (1998); N. Mizuno, M. Tateishi, and M. Iwamoto, *J. Catal.*, **163**, 87 (1996).
- 17 N. Mizuno, W. Han, and T. Kudo, *J. Mol. Catal. A: Chemical*, **114**, 309 (1996).
- 18 N. Mizuno, W. Han, and T. Kudo, *Chem. Lett.*, **1996**, 1121.
- 19 S. Yamamoto and T. Yamaguchi, JP No. 42033 (1990) assigned to Asahi Chemical Industry Co., Ltd.
- 20 K. Nagai, Y. Nagaoka, H. Sato, and M. Ohsu, EP No. 418657 (1990) assigned to Sumitomo Chemical Co., Ltd.
- 21 T. Kuroda and M. Ohkita JP No. 128247 (1992) assigned to Mitsubishi Rayon Co., Ltd.
- 22 H. Imai, T. Yamaguchi, and M. Sugiyama, JP No. 145249 (1988) assigned to Asahi Chemical Industry Co., Ltd.
- 23 K. Nagai, Y. Nagaoka, H. Sato, and M. Ohsu, JP No. 106839 (1991) assigned to Sumitomo Chemical Co., Ltd.
- 24 T. Kuroda, and M. Ohkita, JP No. 59739 (1992) assigned to Mitsubishi Rayon Co., Ltd.
- 25 K. Okusako, T. Ui, and K. Nagai, JP No. 20700 (1997) assigned to Sumitomo Chemical Co., Ltd.
- 26 S. Yamamoto and T. Yamaguchi, JP No. 42034 (1990) assigned to Asahi Chemical Industry Co., Ltd.
- 27 I. Matsuura and Y. Aoki, JP No. 331085 (1993) assigned to Nippon Shokubai Co., Ltd.
- 28 W. Lee and W. Ueda, *Catal. Lett.*, **46**, 261 (1997).
- 29 W. Ueda, Y. Suzuki, W. Lee, and S. Imaoka, *Stud. Surf. Sci. Catal.*, **101**, 1065 (1996).