Selective Oxidative Dehydrogenation of Ethane Catalyzed by $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ Catalyst Precursor

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Cs^{+}-, V^{5+}-, and Mn^{2+}-addition to $H_3PMo_{12}O_{40}$ efficiently increased the catalytic activity and selectivity to ethene for the title reaction. The yield of ethene for $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ catalyst was 2.0% at 350 °C and reached 4.3% at 425 °C.

Selective oxidative dehydrogenation of lower alkanes with molecular oxygen is of great interest because of the low costs and chemically low reactivities as feedstocks.[1-4] To date, vanadium-containing oxide catalysts such as Mo-V-O,[5] supported V-Sb-O,[6] Mo-V-Nb-O,[5,7-9] and Mo-V-P-Sb-O[10] have been reported to be effective for the title reaction. BaF_2-LaOF,[11] supported Pt[12] or Ag catalysts,[13] Al_2O_3-B_2O,[14] and Ga-MFI zeolite[15] are other examples. However, the activity appears usually above 390 °C and is still low.[2,5-16]

Here, we wish to report the effective catalytic performance of $Cs_{2.5}Mn_{0.08}H_{0.34}PVMo_{11}O_{40}$ catalyst for the oxidative dehydrogenation of ethane under the conditions used.

$H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ heteropolyacids were commercially obtained from Nippon Inorganic Colour and Chemical Co., Ltd. The catalysts were prepared as follows: An aqueous solution of metal nitrate (0.08 mol·dm^{-3}) was added dropwise to an aqueous solution of $H_4PVMo_{11}O_{40}$ (0.06 mol·dm^{-3}), followed by the addition of an aqueous solution of Cs_2CO_3 (0.08 mol·dm^{-3}) at 50 °C. The resulting suspension or solution was evaporated to dryness at 50 °C. The actual composition may be $Cs_{2.5}M^{n+}_{0.08}H_xPV_yMo_{12-y}O_z$ (M = Cu, Fe, Ni, etc.), but in this paper they will be designated as $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$.

The reaction was performed in a flow reactor. 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 cm^3·min^{-1}) for 1 h at 350 °C. The reactions were performed in a flow reactor at an applied temperature of 350 - 425 °C under atmospheric pressure. The feed gas typically consisted of 33 vol% of ethane, 33 vol% of O_2 and N_2 balance, and total flow rates was 15 cm^3·min^{-1}. The gases at the outlet of the reactor were taken out intermittently and analyzed by FID and TCD gas chromatograph with FFAP, Porapack Q, and Molecular Sieve 5A columns. Selectivities were fractions in the sum of the products and calculated on the C_2(ethane)-basis. The carbon balance was more than 96%.

Figure 1 shows the time course of the oxidative dehydrogenation of ethane at 425 °C. The conversion and selectivity for the oxidation of ethane catalyzed by $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ reached almost constant after 4 h; e.g., the conversions were 16, 14, 12, 11, 10, and 10% at 0.5, 1, 2, 3, 4, and 5 h, respectively. Similarly, nearly steady state conversion and selectivity were observed after 3 - 6 h for each catalyst. The products were ethene, CO, and CO_2. The selectivity to ethene was 43% and the yield reached 4.3%.

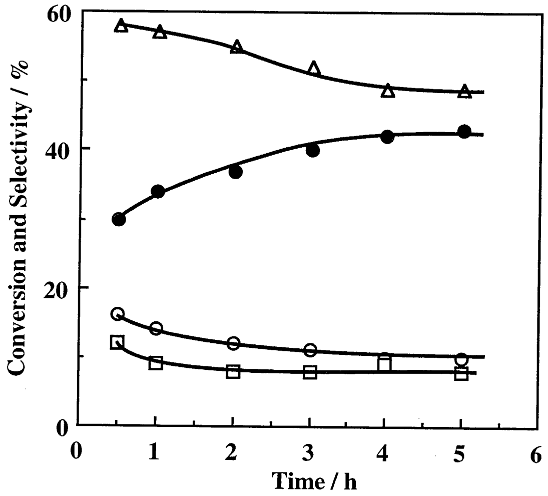

Figure 1. Time course of the oxidative dehydrogenation of ethane catalyzed by $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ at 425 °C.
○, ●, □, and △ are conversion of ethane and selectivities to ethene, CO, and CO_2, respectively.

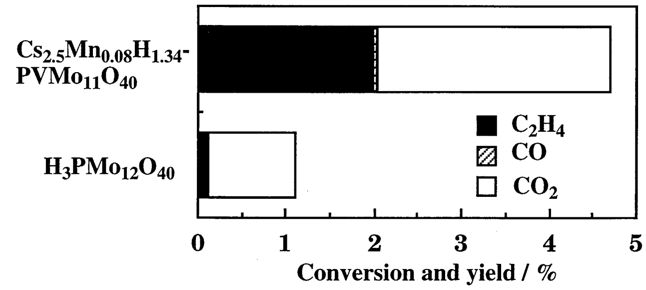

Figure 2. Conversion and yield for $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ and $H_3PMo_{12}O_{40}$ catalysts at 350 °C.

Figure 2 compares the catalytic performance of $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ with that of $H_3PMo_{12}O_{40}$ at 350 °C. Even at 350 °C, the $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ catalyst still showed the activity and the conversion and selectivity to ethene were 4.7% and 42%, respectively. The active temperature is lower than those of supported V-Sb-O,[6] Mo-V-P-Sb-O,[10] BaF_2-LaOF,[11] supported Pt[12] or Ag catalysts,[13] Al_2O_3-B_2O,[14] and Ga-MFI zeolite,[15] and approximately the same as those of Mo-V-O and Mo-V-Nb-O catalysts.[5,7,8,16] These facts show the effectiveness of $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ catalyst.

The space time yield of ethene at 350 °C for

Table 1. Effect of transition metal ion (M^{n+})-substitution for H^+ in $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of ethane at 425 °C

M^{n+}	Conv. / %	Selectivity / %			Yields of ethene / %
		C_2H_4	CO	CO_2	
Mn^{2+}	10	43	8	49	4.3
Fe^{3+}	10	39	42	18	3.9
H^+	9.7	35	54	11	3.4
Co^{2+}	9.5	44	17	39	4.2
Ni^{2+}	7.5	49	13	38	3.7
Cu^{2+}	6.6	31	38	31	2.0

$Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ was 0.4 x 10^{-5} $mol \cdot min^{-1} \cdot g^{-1}$. The value is in the range of 0.3 - 7 x 10^{-5} $mol \cdot min^{-1} \cdot g^{-1}$ reported for the active Mo-V-O and Mo-V-Nb-O catalysts for the oxidative dehydrogenation of ethane.[5-7]

On the other hand, the conversion and selectivity to ethene at 350 °C were 1.1% and 1.0%, respectively, for $H_3PMo_{12}O_{40}$, and much lower than those for $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ and $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ catalysts, showing that Cs^+-, V^{5+}-, and Mn^{2+}-addition enhanced the catalytic performance.

The results on $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ catalysts are shown in Table 1. The conversions decreased in the order of M = Mn ≈ Fe ≥ H ≥ Co ≥ Ni > Cu and the highest conversion was observed for Mn and Fe. The selectivities to ethene on $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ decreased in the order of M = Ni > Co ≈ Mn > Fe ≥ H > Cu. It follows that the yields of ethene on $Cs_{2.5}M^{n+}_{0.08}H_{1.5-0.08n}PVMo_{11}O_{40}$ were 4.3, 4.0, 3.4, 4.2, 3.7, and 2.0% for M = Mn, Fe, H, Co, Ni, and Cu, respectively. Thus, the addition of Mn^{2+}, Co^{2+}, Fe^{3+} or Ni^{2+} to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ resulted in the enhancement of the ethene production and that the maximum yield was observed for M^{n+} = Mn^{2+}.

In summary, the present results demonstrate the oxidative dehydrogenation of ethane by molecular oxygen catalyzed by molybdovanadophosphate species and that among them $Cs_{2.5}Mn_{0.08}H_{1.34}PVMo_{11}O_{40}$ gives the highest yield of ethene.

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References

1 E. A. Mamedov and V. C. Corberan, *Appl. Catal., A: General*, **127**, 1 (1995).
2 H. H. Kung, *Adv. Catal.*, **40**, 1 (1994).
3 M. V. Landau, M. L. Kaliya, M. Herskowitz, P. F. Oosterkamp, and P. S. G. Bocque, *CHEMTECH*, Feb., 24 (1996).
4 Y. Takita, *Shokubai (Catalysts & Catalysis)*, **38**, 34 (1996).
5 R. Burch and R. Swarnakar, *Appl. Catal.*, **70**, 129 (1991).
6 R. J. López, N. S. Godjayeva, V. C. Corberan, J. L. G. Fierro, and E. A. Mamedov, *Appl. Catal. A: General*, **124**, 281 (1995).
7 O. Desponds, R. L. Keiski, and G. A. Somorjai, *Catal. Lett.*, **19**, 17 (1993).
8 A. S.-Moghaddam, A. A. Adesina, and D. L. Trimm, *Science and Technology in Catalysis 1994*, Kodansha (1995), p. 197.
9 E. M. Thorsteinson, T. P. Wilson, F. G. Young, and P. H. Kasai, *J. Catal.*, **52**, 116 (1978).
10 S. Albonetti, F. Cavani, F. Trifiro, and M. Koutyrev, *Catal. Lett.*, **30**, 253 (1995).
11 X. P. Zhou, Z. S. Chao, J. Z. Luo, H. L. Wan, and K. R. Tsai, *Appl. Catal. A: General*, **133**, 263 (1995).
12 S. S. Bharadwaj and L. D. Schmidt, *J. Catal.*, **155**, 403 (1995).
13 S. S. Bharadwaj, C. Yokoyama, and L. D. Schmidt, *Appl. Catal. A: General*, **140**, 73 (1996).
14 G. Colorio, J. C. Vedrine, A. Auroux, and B. Bonnetot, *Appl. Catal. A: General*, **137**, 55 (1996).
15 K. M. Dooley, T. F. Guidry, and G. L. Price, *J. Catal.*, **157**, 66 (1995).
16 Thorsteinson et al.[9] reported that Mo-V-Nb-O was active at ca. 200 °C. However, later studies[5,7,8] have shown that the actual active temperature was at and above 350 °C.