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Catalytic performance of $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ for direct oxidation of lower alkanes

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Abstract

Keggin-type 12-molybdophosphates have been found to catalyze the selective oxidation of isobutane, propane, and ethane into methacrylic acid, acrylic acid, and ethene, respectively, with molecular oxygen. Cs^+ , Fe^{3+} , or Ni^{2+} -substitution for H^+ and V^{5+} -substitution for Mo^{6+} in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ enhanced the catalytic activity for the oxidation of propane. Among the catalysts tested $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ gave the highest yield of acrylic acid: 13%. It was suggested by IR, XRD, TG-DTA data that the Keggin structure was maintained during the oxidation.

Keywords: Lower alkanes; Oxidation; Heteropoly compounds; Iron

1. Introduction

Selective oxidation of lower alkanes by molecular oxygen is of great interest and growing importance [1–3]. Recently, the processes for the oxidation of propane and *n*-butane have been industrialized [3–5]. The oxidizing properties or strong acidity of heteropoly compounds induce a lot of studies on their heterogeneous and homogeneous catalysis [6]. The additional attractive and important aspects are oxidative stability and introduction of various components into heteropolyanions and the counteranions. The oxidation of propane and isobutane with heteropoly catalysts was first reported by Harold and Samuel in 1979 [7]. Ai [8], Centi et al.

[9,10], Asahi Chemical Industry [11], Sumitomo Chemical [12] (the highest yields of MAA and MAL reported at the likely stationary state were 6.2 and 1.2%, respectively), Mizuno et al. [13] Cavani et al. [14], and Ueda et al. [15] reported that heteropoly compounds catalyze the oxidation of lower alkanes, especially propane, isobutane, and pentane [8–15]. It is interesting that the reduced heteropoly compounds showed higher selectivity to methacrylic acid for the oxidation of isobutane [11]. After that, we also reported the oxidation of isobutane proceeded under oxygen-poor conditions [13], followed by Ueda's paper [15].

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 [2,16,17]. However, the process uses the dangerous hydrogen cyanide and overproduces solid

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ammonium bisulfate. Recently, alternative methods, the methylation of propionaldehyde and the oxidation of isobutene, have been developed [2,16,17]. These processes still have problems in using high-price feedstocks and consist of two-step reactions [2,16,17]. Therefore, it would be much more desirable to use cheaper feedstock, isobutane and to produce methacrylic acid directly from isobutane and molecular oxygen [2,16].

As for propane functionalization, the oxidative dehydrogenation [174], ammoxidation [18], and oxygenation [19,20] of propane have recently been reported. The oxidation of propane into acrylic acid in the presence of heteropoly catalysts prepared from $H_3PMo_{12}O_{40}$ and antimony pentachloride gave rather low conversion and selectivity (10 and 19%, respectively) [7]. Recently, a yield of ca. 9% was obtained with $H_5PV_2Mo_{10}O_{40}$ [21]. The addition of Cr ion also enhanced the catalytic performance [22].

Mizuno and Misono previously reported that $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ showed high catalytic activity for the oxidation of acetaldehyde due to the high surface oxidizing ability [23]. On the other hand, the acidity plays an important role in the activation of hydrocarbons such as *n*-butane [3] and methacrolein [1,24]. Heteropoly compounds have both properties. Therefore, we applied them to the heterogeneous oxidation catalysis of lower alkanes and have very recently reported the direct oxidation of isobutane into methacrylic acid with molecular oxygen catalyzed by $Cs_{2.5}Ni_{0.08}$ -substituted $H_3PMo_{12}O_{40}$ [13,25] and the enhancement of catalytic activity of $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ by the V^{5+} -substitution for Mo^{6+} [26,27]. In addition, we have also expanded our fundamental knowledge regarding metal-catalyzed O_2 -based liquid-phase oxidation of cyclohexane and other alkanes by using heteropoly compounds [28]. The efforts continued to focus on the selective oxidation of propane to yield acrylic acid and it was preliminarily reported that $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ was an active catalyst [29].

Here we wish to report in more detail how

catalytic activity of $H_3PMo_{12}O_{40}$ for the oxidation of isobutane and propane is changed by Cs, Fe, and V-substitution and apply the system to the oxidation of ethane and methane.

2. Experimental

2.1. Catalysts

$H_{3+x}PMo_{12-x}V_xO_{40}$ heteropolyacids were commercially obtained from Nippon Inorganic Colour and Chemical. The other reagents used were analytical grade and used without further purification.

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 $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 0-4$; 0.06 mol dm^{-3}), followed by the addition of an aqueous solution of cesium carbonates (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 $Cs_pA_q^{n+}H_xPV_yMo_{12-y}O_z$ ($A = \text{Fe, Ni, etc.}$), but in this paper it will be designated as $Cs_pA_q^{n+}H_{3+y-p-nq}PV_yMo_{12-y}O_{40}$.

The powder X-ray diffraction patterns were recorded on a powder X-ray diffractometer (Materials Analysis and Characterization, MXP³) by using Cu K α radiation. The infrared spectra of KBr pellets were recorded on a Perkin Elmer Paragon 1000PC spectrometer.

2.2. Reaction

The reaction was performed in a flow reactor (Pyrex tube, 12 mm internal diameter) at the applied temperature of $300-400^\circ\text{C}$ under an atmospheric pressure. The conditions of oxidation of isobutane, propane, ethane, and methane were as follows: Catalyst weight: 1.0 g. Oxidation of isobutane: isobutane, 17 vol%; O_2 , 33 vol%; N_2 , balance; total flow rate ca. $30 \text{ cm}^3 \text{ min}^{-1}$. Oxidation of propane: propane, ca. 30 vol%; O_2 , ca. 40–50 vol%; N_2 , balance; total

flow rate ca. 15 or 30 cm³ min⁻¹. Oxidation of ethane: ethane, 33 vol%; O₂, 33 vol%; N₂, balance; total flow rate ca. 30 cm³ min⁻¹. Oxidation of methane: methane, 33 vol%; O₂, 33 vol%; N₂, balance; total flow rate ca. 30 cm³ min⁻¹.

Prior to each 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 O₂ stream (60 cm³ 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, Porapak Q, and Molecular Sieve 5A columns. The conversion and the selectivity data 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_n-basis (*n* in C_nH_{2n+2}). The carbon balance was in the range of 90–100%.

3. Results and discussion

3.1. Oxidation of isobutane

Fig. 1 shows the results of the oxidation of isobutane catalyzed by Cs_{2.5}Fe_{0.08}H_{1.26}PVMO₁₁O₄₀ at 340°C (isobutane/oxygen/nitrogen = 5/10/15 cm³ min⁻¹). The conversion and selectivity became almost constant after 3 h. The products were methacrylic acid (MAA), methacrolein (MAL), acetic acid, and CO_x (CO and CO₂). The steady-state conversion and selectivity to MAA, MAL, AcOH, and CO_x were 21, 25, 4, 19 and 53%, respectively.

It has already been reported that the effectiveness of the additives and the extent of methacrylic acid formation depended significantly on the reaction conditions [13]. Therefore, the results were compared with those carried out under oxygen-poor condition (isobutane/oxygen/nitrogen = 5/2/8 cm³ min⁻¹). The conversion and selectivity to MAA, MAL, AcOH, and CO_x at 340°C were 7, 27, 6,

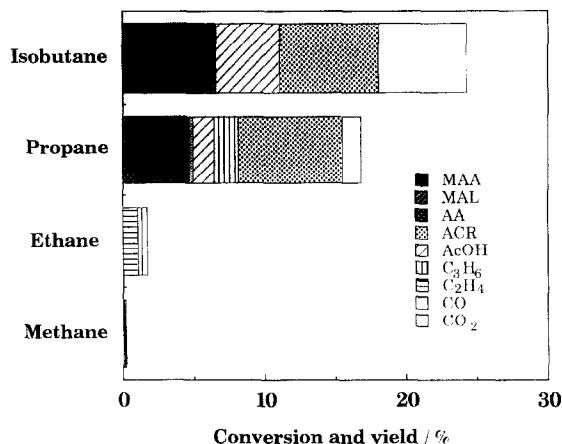


Fig. 1. Oxidation of isobutane, propane, ethane, and methane catalyzed by Cs_{2.5}Fe_{0.08}H_{1.26}PVMO₁₁O₄₀. Catalyst: 1.0 g. Oxidation of isobutane: isobutane, 17 vol%; O₂, 33 vol%; N₂, balance; total flow rate ca. 30 cm³ min⁻¹; reaction temperature, 360°C. Oxidation of ethane: ethane, 33 vol%; O₂, 33 vol%; N₂, balance; total flow rate ca. 30 cm³ min⁻¹; reaction temperature, 340°C. Oxidation of methane: methane, 33 vol%; N₂, balance; total flow rate ca. 30 cm³ min⁻¹; reaction temperature, 360°C.

11 and 55%, respectively, and the conversion was one third of that obtained under oxygen-rich conditions while the selectivity to MAA and MAL changed little. Therefore, the following oxidation of isobutane was carried out under oxygen-rich conditions.

We have previously reported that the substitution of Cs⁺ for H⁺ in H₃PMO₁₂O₄₀ and H_{3.84}Ni_{0.08}PVMO₁₁O₄₀ resulted in great enhancement of the methacrylic acid production in the oxidation of isobutane and the yield reached the maximum around *x* = 2.5 [13,25–27]. It was shown that the increase in the surface area by the Cs⁺-substitution results in high catalytic activity and that the surface oxidizing ability and protonic acidity are controlling factors [13,25].

Table 1 shows the results of the oxidation of isobutane catalyzed by Cs_{2.5}Fe_{*x*}H_{0.5–3*x*}PMO₁₂O₄₀. The conversion changed little from *x* = 0 to 2 and decreased a little from *x* = 2 to 3. The selectivity to MAA reached its maximum at *x* = 0.08 and decreased above 0.08. It follows that the preferred content of Fe is 0.08 and the sum of the yields of MAA and MAL was 6.3%,

Table 1
Oxidation of isobutane catalyzed by $\text{Cs}_{2.5}\text{Fe}_x\text{H}_{0.5-3x}\text{PMo}_{12}\text{O}_{40}$ at 340°C ^a

x	Conversion (%)	Selectivity ^b (%)					Sum of yields of MAA + MAL (%)
		MAA	MAL	AcOH	CO	CO ₂	
0	16	24	7	7	41	21	5.1
0.04	15	26	10	7	36	22	5.4
0.08	14	35	11	7	27	26	6.3
0.16	11	22	13	3	31	31	3.9

^a Isobutane, 17 vol%; O₂, 33 vol%; N₂, balance; catalyst, 1.0 g; total flow rate ca. 30 cm³ min⁻¹.

^b Calculated on the C₄ (isobutane)-basis.

which value is a little lower than 7.4%, the maximum value reported at the likely steady-state in the literature, including patents [11–13]. In the oxidation of isobutane, $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ gave the highest yield of methacrylic acid, 9.0% at 340°C [26,27].

The variation of conversion and selectivity caused by the Fe addition is in contrast with that by Ni: the conversion greatly increased with Ni but the selectivity to MAA increased a little for the oxidation of isobutane catalyzed by $\text{Cs}_{2.5}\text{Ni}_x\text{H}_{0.5-2x}\text{PMo}_{12}\text{O}_{40}$ ($x = 0-0.08$) [25]. The difference may be due to Ni mainly accelerating the rate-determining step isobutane → MAA (and MAL) while Fe mainly suppresses the complete oxidation of MAA (and MAL) produced and accelerates the reaction MAL → MAA. However, further mechanistic studies such as oxidations of MAA and MAL are necessary.

3.2. Oxidation of propane

3.2.1. Optimum condition

Fig. 2 shows the time course of the oxidation of propane catalyzed by $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ at 360°C . The conversion and selectivity became almost constant after 3 h; e.g., the conversions were 16, 17, 17, and 17% at 0.5, 1, 2, and 3 h, respectively. Similarly, nearly steady state conversion and selectivity were obtained for each catalyst. The products were acrylic acid (AA), acrolein (ACR), propene, acetic acid, and CO_x. The same products were observed for the other heteropoly catalysts used.

The formation of isobutene was hardly observed in the oxidation of isobutane under oxygen-rich conditions [13]. The observation of propene is probably because of the smaller reactivity than that of isobutene.

The color of $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ after having been used as catalyst was green, suggesting reduction of the catalyst. Spectroscopic characterization of the oxidation states of Fe, V, and Mo is important and in progress. When the reaction temperature was raised to 400°C and then lowered, little hysteresis was observed for the conversion and selectivity. These data suggest the absence of irreversible deactivation of $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$.

Fig. 3a shows the temperature dependency of the conversion and selectivity upon $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$. The conversions

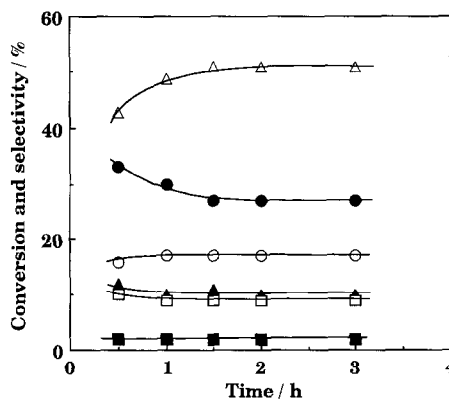


Fig. 2. Time course of the oxidation of propane catalyzed by $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ at 360°C . \circ , \bullet , \blacksquare , \blacktriangle , \square , and \triangle represent conversion of propane and selectivities to AA, ACR, propene, AcOH, and CO_x, respectively. Propane, 30 vol%; O₂, 40 vol%; N₂, balance; total flow rate 30 cm³ min⁻¹.

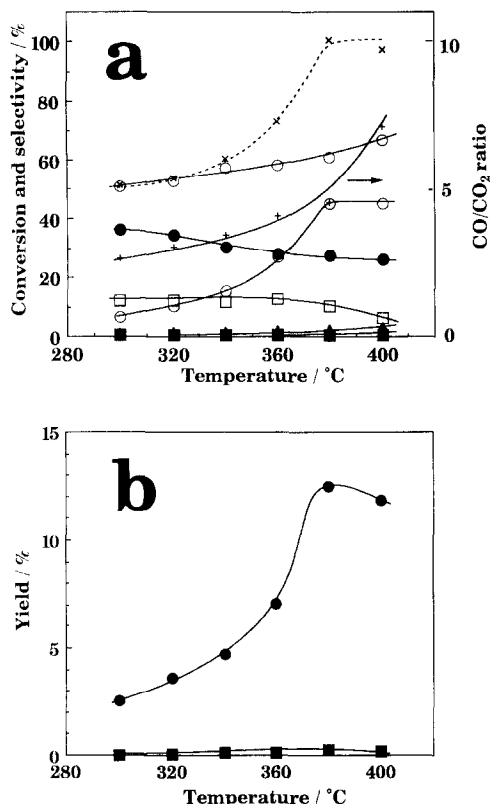


Fig. 3. Temperature dependency of conversion, selectivity, and yield for the oxidation of propane. Catalyst, $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$. Propane, 30 vol%; O_2 , 50 vol%; N_2 , balance; total flow rate $15 \text{ cm}^3 \text{ min}^{-1}$. (a) Temperature dependency of conversion and selectivity. Broken line: conversion of dioxygen calculated on the basis of the following reactions: $\text{C}_3\text{H}_8 + 1.5\text{O}_2 \rightarrow \text{ACR} + 2\text{H}_2\text{O}$, $\text{C}_3\text{H}_8 + 2\text{O}_2 \rightarrow \text{AA} + 2\text{H}_2\text{O}$, $\text{C}_3\text{H}_8 + 2\text{O}_2 \rightarrow 1.5\text{AcOH} + \text{H}_2\text{O}$, $\text{C}_3\text{H}_8 + 3.5\text{O}_2 \rightarrow 3\text{CO} + 4\text{H}_2\text{O}$, $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$. (b) Temperature dependency of yields of AA and ACR. \circ , \bullet , \blacksquare , \blacktriangle , \square , and \triangle : see Fig. 2; +: CO/CO_2 ratio.

were 8, 12, 17, 29, 47, and 48% at 300, 320, 340, 360, 380, and 400°C, respectively, and increased with reaction temperature. The leveling-off of the conversion at and above 380°C is probably due to the consumption of molecular oxygen in the gas phase. In fact, the oxygen conversion observed was ca. 100% at 380°C and the same as that calculated, shown by the broken line in Fig. 3a. The selectivity to AA gradually decreased with reaction temperature and that to AcOH decreased above 360°C. The decrease of selectivity to AA and AcOH above 360°C is mainly due to the successive oxidation because the amount of CO_x increased in parallel.

The temperature dependency of the yields of AA and ACR for $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ is shown in Fig. 3b. The yields of AA at 300, 320, 340, 360, 380 and 400°C were 2.6, 3.6, 4.7, 7.0, 13 and 12%, respectively, and the maximum yield was obtained around 380°C. A similar trend was observed for the yield of ACR. It is noteworthy that the 13% yield of AA is higher than 10.5%, of which the value is the highest among the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5\text{-TeO}_2$ catalyst [20] and heteropoly compounds [15,22].

3.2.2. Effect of substitution of countercation

The effects of substitution of Cs^+ and transition metal ions for H^+ and V^{5+} for Mo^{6+} were investigated. For the kinetic comparison of the

Table 2

Oxidation of propane over $\text{M}_{0.08}^{n+}\text{Cs}_{2.5}\text{H}_{0.5-0.08n}\text{PMo}_{12}\text{O}_{40}$ at 360°C^a

M^{n+}	Conversion (%)	Selectivity ^b (%)					Yield of AA (%)	
		AA	ACR	propene	AcOH	CO	CO ₂	
Rh^{3+}	17	8	1	6	7	28	50	1.4
Fe^{3+}	13	18	2	9	11	50	10	2.4
Ni^{2+}	12	17	2	8	10	54	10	2.0
H^+	12	8	1	6	8	62	15	1.0
Co^{2+}	8	16	3	13	11	49	10	1.3
Cu^{2+}	8	9	3	10	4	55	19	0.7
Mn^{2+}	6	19	3	15	10	46	7	1.1

^a Catalyst. 1.0 g; total flow rate $30 \text{ cm}^3 \text{ min}^{-1}$. Propane, 30 vol%; O_2 , 40 vol%; N_2 , balance.

^b Calculated on the C_3 (propane)-basis.

activity, the total flow rate was increased from 15 to 30 cm³ min⁻¹ and the reaction temperature was lowered from 380 to 340 or 360°C to keep the conversions less than 15%, where the linear correlation between W (weight of catalyst)/ F (flow rate) was observed for Cs_{2.5}Fe_{0.08}H_{1.26}PVMo₁₁O₄₀.

The catalytic activity of H₃PMo₁₂O₄₀ was increased by the substitution of Cs⁺ for H⁺: the conversions of propane at 340°C and a total flow rate of 30 cm³ min⁻¹ are ca. 0 and 5% for H₃PMo₁₂O₄₀ and Cs_{2.5}H_{0.5}PMo₁₂O₄₀, respectively.

The catalytic properties of Cs_{2.5}H_{0.5}PMo₁₂O₄₀ were also changed by the addition of transition metal ions. Table 2 shows the effect of additives. The content of transition metals was kept at 0.08, because the preferable content of Fe in the oxidation of isobutane was 0.08 (Table 1). The conversions were 17, 13, 12, 12, 8, 8, and 6% for M = Rh, Fe, Ni, H, Co, Cu, and Mn, respectively, and the highest conversion was observed for Rh. The selectivities to AA on M_{0.08}ⁿ⁺Cs_{2.5}H_{0.5-0.08n}PMo₁₂O₄₀ were 8, 18, 17, 8, 16, 9, and 19 for M = Rh, Fe, Ni, H, Co, Cu, and Mn, respectively. It follows that the yields of AA on M_{0.08}ⁿ⁺Cs_{2.5}H_{0.5-0.08n}PMo₁₂O₄₀ were 1.4, 2.4, 2.0, 1.0, 1.3, 0.7, and 1.1% for M = Rh, Fe, Ni, H, Co, Cu, and Mn, respectively. Therefore, the substitution of Fe³⁺ or Ni²⁺ for H⁺ in Cs_{2.5}H_{0.5}PMo₁₂O₄₀ resulted in the enhancement of the AA production and the maximum yield was observed for Mⁿ⁺ = Fe³⁺. A similar increase in the yield of methacrylic acid by the

substitution of Fe³⁺ for H⁺ was observed for the oxidation of isobutane.

With the addition of Fe the selectivity to AA increased while the conversion changed little. This fact is similar to that observed for the oxidation of isobutane as described in the former section and may be due to the suppression of complete oxidation of AA (and ACR) and the acceleration of the reaction ACR → AA although further mechanistic studies such as oxidations of AA and ACR are necessary. The stoichiometric oxidation of ACR into AA by 12-molybdophosphoric acid was reported [30].

3.2.3. Effect of V⁵⁺-substitution

The data of the propane oxidation catalyzed by Cs_{2.5}Fe_{0.08}H_{0.26+x}PV_xMo_{12-x}O₄₀ are shown in Table 3. The conversions were 13, 17, 10, and 11% for $x = 0, 1, 2,$ and $3,$ respectively, and the highest conversion was observed at $x = 1$. The selectivities to AA on Cs_{2.5}Fe_{0.08}H_{0.26+x}PV_xMo_{12-x}O₄₀ catalysts were 18, 27, 16 and 8% for $x = 0, 1, 2$ and $3,$ respectively, and the highest selectivity to AA was also observed at $x = 1$. It follows that the substitution of V⁵⁺ for Mo⁶⁺ in Cs_{2.5}Fe_{0.08}H_{0.26}PMo₁₂O₄₀ resulted in great enhancement of the AA production and the yield reached the maximum at $x = 1$. The catalytic activity of Cs_{2.5}Ni_{0.08}H_{0.34}PMo₁₂O₄₀ was also increased by the substitution of V⁵⁺ for Mo⁶⁺ (Fig. 4). A similar enhancement of the catalytic activity of H₃PMo₁₂O₄₀ by the V⁵⁺-substitution for the oxidation of n -pentane, n -butane, and isobutane has been reported [7–9].

Table 3
Effect of V⁵⁺-substitution for Mo⁶⁺ in Cs_{2.5}Fe_{0.08}H_{0.26}PMo₁₂O₄₀ on oxidation of propane at 360°C^a

x	Conversion ^b (%)	Selectivity ^{b,c} (%)					Yield of AA (%)	
		AA	ACR	propene	AcOH	CO		CO ₂
0	13	18	2	9	11	50	10	2.4
1	17	27	2	10	9	43	8	4.5
2	10	16	1	23	10	38	12	1.6
3	11	8	1	56	5	22	8	0.9

^a Catalyst, 1.0 g; total flow rate 30 cm³ min⁻¹. Propane, 30 vol%; O₂, 40 vol%; N₂, balance.

^{b,c} See Table 2.

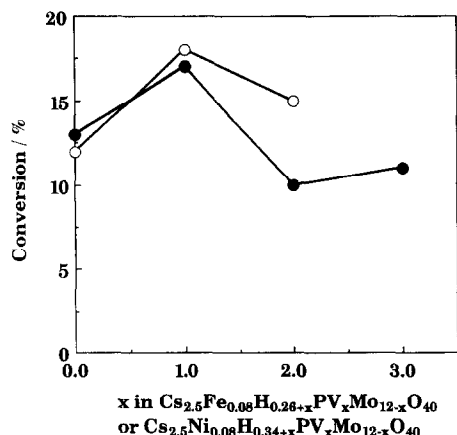


Fig. 4. Effect of V^{5+} -substitution for Mo^{6+} in $Cs_{2.5}Fe_{0.08}H_{0.26}PMo_{12}O_{40}$ and $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ on the catalytic activity for the oxidation of propane at $360^{\circ}C$. ●: $Cs_{2.5}Fe_{0.08}H_{x+0.26}PV_xMo_{12-x}O_{40}$; ○: $Cs_{2.5}Ni_{0.08}H_{x+0.34}PV_xMo_{12-x}O_{40}$. Propane, 30 vol%; O_2 , 40 vol%; N_2 , balance; total flow rate $30\text{ cm}^3\text{ min}^{-1}$.

Similarly, the substitution of V^{5+} for Mo^{6+} in $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ resulted in the enhancement of the MAA production for the oxidation of isobutane [26,27]. The conversions were 10, 15, 13, 12, and 10% for $x = 0, 1, 2, 3,$ and 4 , respectively, and the highest conversion was observed around $x = 1$. The selectivities to MAA on $Cs_{2.5}Ni_{0.08}H_{0.34+x}PV_xMo_{12-x}O_{40}$ catalysts were 27, 36, 28, 10, and 4% for $x = 0, 1, 2, 3,$ and 4 , respectively, and the highest selectivity to MAA was also observed at $x = 1$. On the basis of conversion versus selectivity data, we have previously reported for the oxidation of isobutane catalyzed by $Cs_{2.5}Ni_{0.08}H_{0.34+x}PV_xMo_{12-x}O_{40}$ ($x = 0, 1$) that V^{5+} -substitution resulted in the increase in the selectivity to MAA and that the increase is due to suppression of the complete oxidations of MAA and MAL and acceleration of the step $MAL \rightarrow MAA$ [25]. By analogy with the isobutane oxidation, the increase in the selectivity to AA by the substitution of V^{5+} for the oxidation of propane is probably due to the suppression of the complete oxidation of AA and acceleration of the step $ACR \rightarrow AA$.

3.3. Oxidation of ethane and methane

$Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ also catalyzed the selective oxidation of ethane. The conversion was 1.7% and the selectivities to ethene, CO, and CO_2 were 65, 14, and 21%, respectively, at $360^{\circ}C$. Neither corresponding aldehyde nor acid was observed for the oxidation of ethane and only oxidative dehydrogenation and complete oxidation proceeded. This may be due to the smaller reactivity of ethene formed than that of propene and isobutene. The increase in the reaction temperature up to $400^{\circ}C$ resulted in the conversion and yield of ethene of 4.0 and 2.9%, respectively, of which the values were lower than those reported for V–P and Mo–V-based catalysts [1].

The conversion of methane was 0.2% and it was less reactive than ethane. The products were only carbon oxides. Hydrogen was added into the gas stream, but no methanol formation was observed for $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ catalyst. It was reported that $FePO_4$ catalyzed the oxidation of methane into methanol in a gas mixture of hydrogen and oxygen [31].

The results of oxidation of isobutane, propane, ethane, and methane catalyzed by $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ are compared in Fig. 1. The conversion level decreased with reactants in the order of $i-C_4H_{10} > C_3H_8 > C_2H_6 > CH_4$. 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.

Further studies in more detail to clarify factors controlling the activity and selectivity on the basis of data of the characterization of acidic and redox properties and reaction mechanisms are in progress.

3.4. Thermal stability of $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$

In order to confirm the structure of $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ during the reaction,

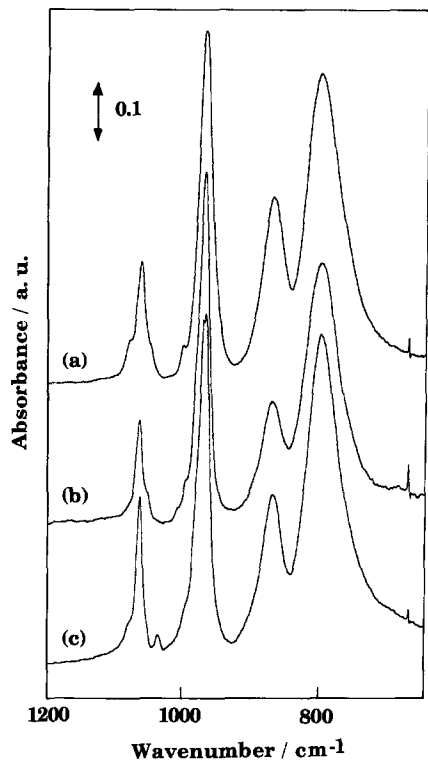


Fig. 5. Infrared spectra of as-prepared, pretreated, and spent $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ (KBr pellet). (a) As-prepared sample; (b) the sample after reaction at 400°C ; (c) sample heated in air up to 500°C at a rate of $5^\circ\text{C}/\text{min}$.

the infrared spectra were measured before and after the reaction. The spectra are shown in Fig. 5. In the range $700\text{--}1100\text{ cm}^{-1}$, the as-prepared sample showed the intense 1060 cm^{-1} (with a shoulder at ca. 1077 cm^{-1}) 965 cm^{-1} , 866 cm^{-1} , and 797 cm^{-1} bands (Fig. 5a). The bands at 1060 cm^{-1} , 965 cm^{-1} , 866 cm^{-1} , and 797 cm^{-1} are characteristic of a Keggin structure [32]. The infrared spectrum changed little after the reaction except for the decrease in the intensity of the 1077 cm^{-1} shoulder and 1060 cm^{-1} , 866 cm^{-1} , and 797 cm^{-1} bands (Fig. 5b). The decrease is mainly due to the reduction of the Keggin anion [33]. It was reported that a 1077 cm^{-1} shoulder is due to the lowering of the symmetry of a Keggin anion by the substitution of V^{5+} for Mo^{6+} in $\text{PMo}_{12}\text{O}_{40}^{3-}$ [34,35]. Therefore, the decrease in the intensity of the 1077 cm^{-1} shoulder may suggest that the elimi-

nation of V^{5+} from a Keggin anion in part takes place. The elimination of vanadium during the oxidation of isobutyric acid was reported [34]. Further experiments are in progress to clarify the situation of the vanadium ion, taking into account the possibility of extraframework vanadium species.

After $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ catalyst was heated in air up to 500°C , a new band appeared at 1035 cm^{-1} (Fig. 5c). It was reported that a crystalline V_2O_5 showed the $\nu(\text{V}=\text{O})$ band at ca. 1020 cm^{-1} [35,36] and that the band frequency was shifted by the presence of the other oxides [36]. Therefore, the band at 1035 cm^{-1} is probably assigned to the $\nu(\text{V}=\text{O})$ band of V_2O_5 , showing the elimination of V^{5+} from the $\text{PVMo}_{11}\text{O}_{40}^{4-}$ Keggin anion after the treatment at 500°C . The shift to higher frequency is probably due to the coexistence of a heteropolyanion.

In the 2θ range $5\text{--}35^\circ$, the XRD patterns of used $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$ showed signals at 10.7 , 18.4 , 23.8 , 26.2 , 30.3 , and 32.1° (cubic system) and changed little after the reaction. No signals due to MoO_3 and V_2O_5 were observed. This result was consistent with the IR observation that no $\nu(\text{V}=\text{O})$ bands of crystalline V_2O_5 were detected for spent $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{1.26}\text{PVMo}_{11}\text{O}_{40}$. TG-DTA data showed $\text{Cs}_{2.5}\text{Fe}_{0.08}\text{H}_{0.26}\text{PVMo}_{11}\text{O}_{40}$ underwent two-step dehydration below ca. 360°C , being decomposed above 540°C . Therefore, these data suggest the maintenance of the Keggin structure during the reaction in the range $300\text{--}400^\circ\text{C}$. Such a high thermal stability of the Keggin anion by the Cs salt formation has been reported [37].

Thus, IR and XRD data suggest the maintenance of the Keggin structure during the reaction in the range $300\text{--}400^\circ\text{C}$.

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