

Oxidation of Isobutane Catalyzed by Partially Salified Cesium Molybdovanadophosphoric Acids

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The catalytic activity for the oxidation of isobutane catalyzed by 12-molybdophosphoric acid was much changed by the V^{5+} - and Cs^+ -substitution for Mo^{6+} and H^+ , respectively. The best yield of methacrylic acid was 9.0% and was obtained for the heteropoly catalyst with V and Cs contents of 1 and 2.5, respectively. The high catalytic activity obtained for $Cs_{2.5}Ni_{0.08}H_{1.34}PVMo_{11}O_{40}$ is presumably due to the high surface area. The activities of 12-molybdovanadophosphoric acids as well as those of 12-molybdophosphoric acid partially salified with Cs^+ were controlled by the oxidizing ability of catalysts. The conversion vs selectivity relationships, the simulation of the data, and kinetic results for $Cs_{2.5}Ni_{0.08}H_{1.34}PVMo_{11}O_{40}$ and $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ catalysts show that the first steps, i.e., selective and complete oxidation reactions of isobutane, are rate-determining and mainly catalyzed by molybdenum ion and that vanadium ion efficiently accelerates the selective oxidation of methacrolein to methacrylic acid. Cs^+ -substitution for H^+ in $H_{3.84}Ni_{0.08}PVMo_{11}O_{40}$ greatly change the selectivity up to a Cs content of 2.5 and suppressed the elimination of the vanadium ion from the Keggin anion.

Introduction

Selective oxidation of lower alkanes by molecular oxygen is of great interest because of their low costs and chemically low reactivities as feedstocks.^{1–14} For example, the production of methacrylic acid directly from isobutane and molecular oxygen has been desired because the process can use cheap feedstock of isobutane and air.^{1,2}

The oxidizing properties or the strong acidity of heteropoly compounds induces a lot of studies on heterogeneous and homogeneous catalysis.^{15–22} The additional attractive and important aspects are their stability under reaction conditions and the flexibility of introduction of various components into heteropolyanions and the counteranions. Acid forms of heteropoly compounds have usually been used as catalysts in earlier work on the heterogeneous oxidation of propane and isobutane.^{23–26}

We have reported that heteropoly compounds partially salified with cesium can well catalyze the heterogeneous oxidation of isobutane,²⁷ propane,²⁸ ethane,²⁹ and methane³⁰ with molecular oxygen and that the oxidizing ability is a controlling factor of catalytic activity of $Cs_xH_{3-x}PMo_{12}O_{40}$ catalysts for the oxidation of isobutane.²⁷ Trifiro et al. have also reported that 12-molybdophosphates catalyzed the oxidation reactions of isobutane^{31,32} and ethane.³³

On the other hand, it has been reported that the substitution of V^{5+} for Mo^{6+} in $H_3PMo_{12}O_{40}$ modified the catalytic activity and selectivity for the various heterogeneous alkane oxidation

reactions.^{15,17–19,22} The present author also preliminarily reported that V^{5+} -substitution for Mo^{6+} in $Cs_{2.5}Ni_{0.08}H_{1.34}PMo_{12}O_{40}$ increased the yield of methacrylic acid and methacrolein and that the maximum yields were obtained for the mono- V^{5+} -substituted heteropoly compound, $Cs_{2.5}Ni_{0.08}H_{1.34}PVMo_{11}O_{40}$.^{27b} Recently, the state of vanadium in the acid forms of 12-molybdovanadophosphates such as $H_4PVMo_{11}O_{40}$ has been investigated, and it was clarified that vanadium in the Keggin anion in part comes out from the anion.^{34,35} A similar elimination of vanadium ion from $H_4PVMo_{11}O_{40}$ in the liquid phase has been reported.³⁶ However, little is known of the factors controlling the catalytic activity of solid Cs^+ and V^{5+} -substituted heteropoly compounds and their roles.^{15,17–19,22–26,27b,34,35,37}

Here we report how catalytic activity and selectivity for the oxidation of isobutane catalyzed by $Cs_xH_{3+y-x}PV_yMo_{12-y}O_{40}$ are changed by the contents of Cs^+ (x) and V^{5+} (y) and attempt to clarify the factors controlling them.

Experimental Section

Catalyst Preparation. $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 0–3$) heteropolyacids were commercially obtained from Nippon Inorganic Colour and Chemical Co., Ltd. and used after purification with ether abstraction and recrystallization. It was confirmed for $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$ that atomic ratios of P:Mo and P:Mo:V were 1.0:12.0 and 1.0:11.0:1.0, respectively. The purities of $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$, confirmed by ³¹P NMR, were 100 and 95%, respectively, and high, but $H_5PMo_{10}V_2O_{40}$ and $H_6PMo_9V_3O_{40}$ were mixtures of polyanions and the purities were much lower as has been reported.^{38,39} The

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other reagents used were analytical grade and used without further purification.

The catalysts were prepared as follows: An aqueous solution of nickel nitrate (0.08 mol dm^{-3}) was added dropwise to an aqueous solution of $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ ($x = 0-4$; 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 $\text{Cs}_q\text{Ni}_{0.08}\text{H}_{3.84+x-q}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$, but in this paper it will be designated as $\text{Cs}_q\text{Ni}_{0.08}\text{H}_{2.84+x-q}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$.

The reduction of $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ catalysts by CO was carried out in a circulation system at 350°C , and the rates of reduction were measured by the initial pressure decrease as described previously.²⁸

Reaction. The reaction was performed in a flow reactor (Pyrex tube, 12 mm internal diameter) at the applied temperature of $270-360^\circ\text{C}$ under atmospheric pressure. The feed gas consisted of 17 vol % of isobutane, 33 vol % of O_2 , and N_2 balance, unless otherwise stated. Total flow rates were ca. $30 \text{ cm}^3 \text{ min}^{-1}$. Prior to the reaction, 1 g of each catalyst was mixed with SiC (1.5 g) to prevent an undesirable temperature rise and treated in an O_2 stream ($60 \text{ cm}^3 \text{ min}^{-1}$) 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 a flame ionization detector (FID) and thermal conductivity detector (TCD) gas chromatograph with FFAP, Porapak Q, and Molecular Sieve 5A columns. Selectivity was calculated on the C_4 (isobutane)-basis. The carbon balance was in the range of 90–100%.

Brunauer–Emmett–Teller (BET) surface areas were measured by means of N_2 adsorption using Coulter Omnisorp 100MP. After use for the oxidation reaction, the catalyst was evacuated at room temperature, and then the surface area was measured again. Just before and after the catalytic reaction, the change of the surface area was within $\pm 10\%$. The infrared spectra of KBr pellets were recorded on a Perkin-Elmer Paragon 1000PC spectrometer.

^{31}P and ^{51}V Magic-Angle Spinning (MAS) NMR Measurements. After catalytic tests, the heteropoly compounds were transferred into a spinner in dry N_2 . The MAS NMR spectra were measured using a Bruker AC 300 spectrometer at a spinning rate of 10–15 kHz. Aqueous 85% H_3PO_4 and VOCl_3 were used as standard references of ^{31}P and ^{51}V MAS NMR spectra, respectively. All measurements were carried out at room temperature.

Electron Spin Resonance (ESR) Measurements. After catalytic tests, the heteropoly compounds (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 or -95°C . For quantitative measurements, the signal was doubly integrated and compared with that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powder.

Results

Oxidation of Isobutane. *Oxidation Catalyzed by $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$.* The conversion and the selectivity were determined after 3–5 h of reaction, when nearly steady-state conversion and selectivity were obtained for each catalyst; e.g., the conversions for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ at 320°C were 21, 18, 17, 15, and 15% at 1, 2, 3, 4, and 5 h, respectively. The products were methacrylic acid (MAA), methacrolein (MAL), acetic acid (AcOH), and CO_x ($\text{CO} + \text{CO}_2$). Similar products were observed for the other heteropoly catalysts used.

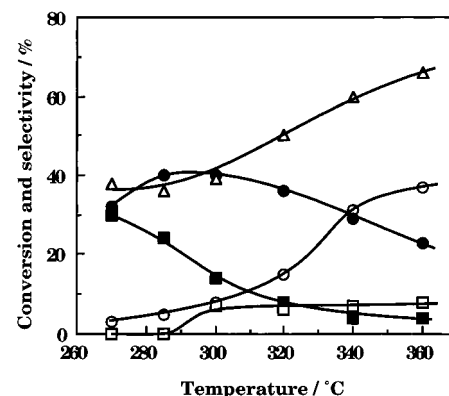


Figure 1. Dependencies of the conversion and selectivity on reaction temperature for $\text{Cs}_{2.5}\text{H}_{1.34}\text{Ni}_{0.08}\text{PVMo}_{11}\text{O}_{40}$ catalyst. \circ , \bullet , \blacksquare , \square , and \triangle are conversion of isobutane and selectivities to MAA, MAL, AcOH, and CO_x , respectively.

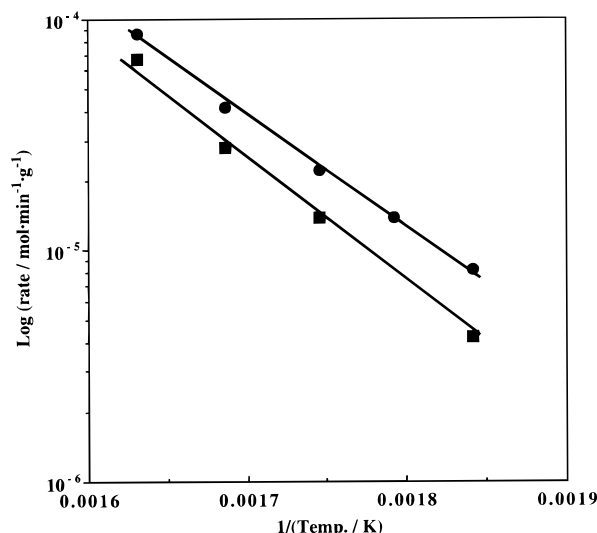


Figure 2. Arrhenius plots of $\text{Cs}_{2.5}\text{H}_{1.34}\text{Ni}_{0.08}\text{PVMo}_{11}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{H}_{0.34}\text{Ni}_{0.08}\text{PMo}_{12}\text{O}_{40}$ catalysts. \bullet , $\text{Cs}_{2.5}\text{H}_{1.34}\text{Ni}_{0.08}\text{PVMo}_{11}\text{O}_{40}$; \blacksquare , $\text{Cs}_{2.5}\text{H}_{0.34}\text{Ni}_{0.08}\text{PMo}_{12}\text{O}_{40}$.

Figure 1 shows the dependence of the conversion and selectivity on reaction temperature for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst. The conversion of isobutane monotonically increased with an increase in the reaction temperature and was 37% at 360°C . The selectivity to MAL monotonically decreased with increases in reaction temperatures and that to MAA reached the maximum of 40% at $285-300^\circ\text{C}$. The yield of MAA reached maximum at 340°C and was 9.0%. The value is higher than 8.5%, the maximum value reported at the likely steady state in the literature.^{23,27,31,40}

Figure 2 shows the Arrhenius plots for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalysts. For the determination of the rates, the conversions were kept below 10%, where the rates were proportional to W/F as shown in Figure 3. A fairly good linear correlation was observed. The apparent activation energy was 110 and 120 kJ mol^{-1} for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalysts, respectively, and the values were close to each other.

Figure 3 shows the dependencies of the conversion on W/F , where W is the weight of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{x+0.34}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ ($x = 0, 1$) catalysts and F is the flow rate of isobutane. While the conversion linearly increased up to 10% as W/F increased, the slope of the curve became smaller at higher values of W/F .

Figure 4a shows the dependencies of the selectivities to MAL, MAA, AcOH, and CO_x on percent conversion of isobutane. The

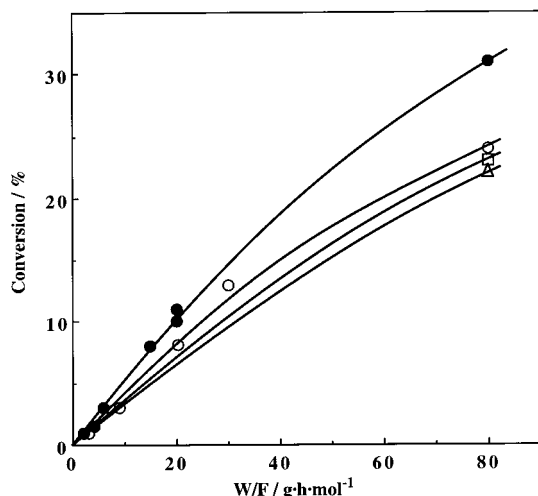


Figure 3. Dependences of conversion on W/F for $\text{Cs}_{2.5}\text{H}_{x+0.34}\text{Ni}_{0.08}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ ($x = 0-3$) catalysts at $340\text{ }^\circ\text{C}$. \circ , $\text{Cs}_{2.5}\text{H}_{0.34}\text{Ni}_{0.08}\text{PMo}_{12}\text{O}_{40}$; \bullet , $\text{Cs}_{2.5}\text{H}_{1.34}\text{Ni}_{0.08}\text{PVMo}_{11}\text{O}_{40}$; \square , $\text{Cs}_{2.5}\text{H}_{2.34}\text{Ni}_{0.08}\text{PV}_2\text{Mo}_{10}\text{O}_{40}$; \triangle , $\text{Cs}_{2.5}\text{H}_{3.34}\text{Ni}_{0.08}\text{PV}_3\text{Mo}_9\text{O}_{40}$.

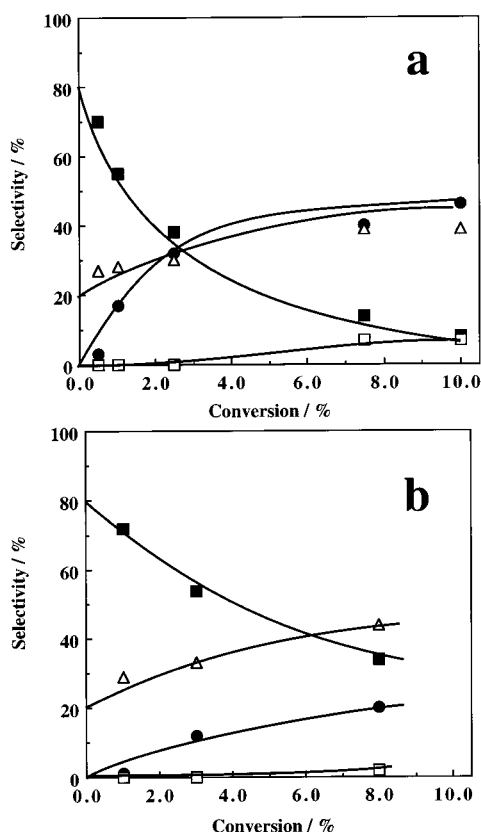


Figure 4. Dependences of the selectivities to MAA, MAL, AcOH, and CO_x on percent conversion of isobutane. \bullet , \blacksquare , \square , and \triangle , see Figure 1. The solid lines were obtained by the simulation (see text). (a) $\text{Cs}_{2.5}\text{H}_{1.34}\text{Ni}_{0.08}\text{PVMo}_{11}\text{O}_{40}$. (b) $\text{Cs}_{2.5}\text{H}_{0.34}\text{Ni}_{0.08}\text{PMo}_{12}\text{O}_{40}$.

selectivities to MAL and CO_x extrapolated to 0% conversion were ca. 80% and 20%, respectively. The selectivity to MAL monotonically decreased with an increase in conversion. On the other hand, the selectivities to MAA and CO_x increased sharply and gradually, respectively. The selectivity to AcOH increased with an induction period.

A similar variation was observed for that $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalyst as shown in Figure 4b. The selectivities to MAL and CO_x extrapolated to 0% conversion were ca. 80% and 20%, respectively, and almost agreed with those obtained

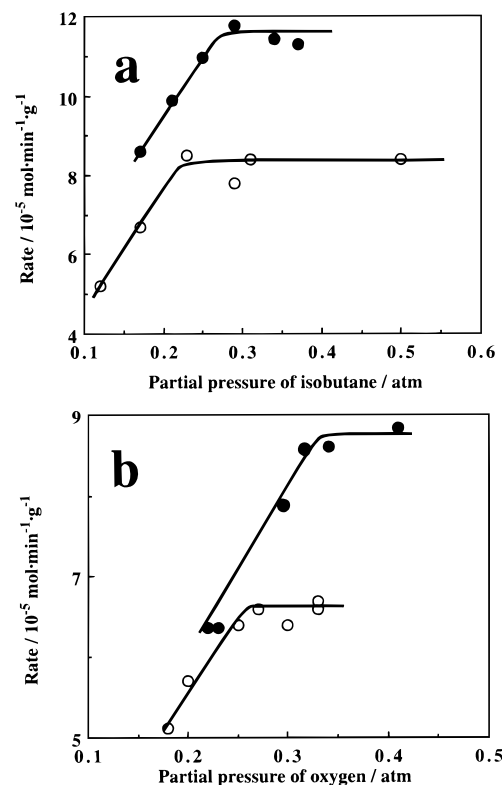


Figure 5. Dependences of rates on partial pressure of isobutane and oxygen. \bullet , $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$; \circ , $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$. The oxidation was carried out at $340\text{ }^\circ\text{C}$. (a) Dependency on partial pressure of isobutane. (b) Dependency on partial pressure of oxygen.

TABLE 1: Oxidation of Isobutane Catalyzed by $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ at $320\text{ }^\circ\text{C}$

x	surface area/ $\text{m}^2\text{ g}^{-1}$	conv/ %	rate/ $10^{-5}\text{ mol min}^{-1}\text{ g}^{-1}$	selectivity/%				
				MAA	MAL	AcOH	CO	CO_2
0	7.4	10	2.1	27	12	5	30	26
1	40.8	15	3.2	36	9	6	25	24
2	17.1	13	2.7	28	8	6	25	33
3	11.5	12	2.5	10	8	9	35	38

for the $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst. The selectivities to MAL and MAA more slowly decreased and increased than the $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst.

The dependences of rates on the partial pressures of isobutane and oxygen are shown in parts a and b of Figure 5, respectively. For the determination, the conversions were kept below 10%, where the rates were proportional to W/F as shown in Figure 3. The rate for the $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst increased with an increase in $P_{i-\text{C}_4\text{H}_{10}}$ from 0.17 to 0.30 atm and reached an approximately constant value. Similarly the rate increased with P_{O_2} from 0.22 to 0.33 atm, and a $P_{i-\text{C}_4\text{H}_{10}}^0$ dependence, that is, saturation kinetics, was reached by a partial pressure of isobutane of 0.41 atm. Under the reaction conditions (i.e., $P_{i-\text{C}_4\text{H}_{10}} = 0.17\text{ atm}$; $P_{\text{O}_2} = 0.33\text{ atm}$), the pressure dependencies were expressed by $-d[i-\text{C}_4\text{H}_{10}]/dt = kP_{i-\text{C}_4\text{H}_{10}}^{0.70}P_{\text{O}_2}^{0.7-0}$. Similar dependencies of the rates on $P_{i-\text{C}_4\text{H}_{10}}$ and P_{O_2} , $-d[i-\text{C}_4\text{H}_{10}]/dt = kP_{i-\text{C}_4\text{H}_{10}}^{0.70}P_{\text{O}_2}^0$, were observed for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ except that the kinetic saturation was reached at lower pressures.

Effect of V^{5+} -Substitution. The results of the oxidation of isobutane catalyzed by $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ ($x = 0-3$) catalysts are shown in Table 1. The conversion increased from $x = 0$ to 1 and then decreased a little. The selectivity to MAA also increased from $x = 0$ to 1 and then decreased, while the selectivity to MAL decreased a little from $x = 0$ to 1 and

TABLE 2: Oxidation of Isobutane Catalyzed by $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ at 340 °C

x	surface area/ $\text{m}^2 \text{g}^{-1}$	conv/ %	rate/ $10^{-5} \text{mol min}^{-1} \text{g}^{-1}$	selectivity/%				
				MAA	MAL	AcOH	CO	CO_2
0	1.1	7	1.2	4	18	8	44	26
1	2.6	5	1.0	30	36	trace	17	17
2	1.5	5	1.0	34	28	2	18	18
3	2.0	10	2.0	14	14	12	35	25

TABLE 3: Oxidation of Isobutane Catalyzed by $\text{Cs}_x\text{H}_{3.84-x}\text{Ni}_{0.08}\text{PVMo}_{11}\text{O}_{40}$ at 340 °C

x	surface area/ $\text{m}^2 \text{g}^{-1}$	conv/ %	rate/ $10^{-5} \text{mol min}^{-1} \text{g}^{-1}$	selectivity/%				
				MAA	MAL	AcOH	CO	CO_2
0	4.5	6	1.2	30	23	5	29	13
1	4.7	4	0.8	30	30	0	27	13
2	15.8	12	2.4	47	11	5	20	17
2.5	40.8	31	6.2	29	4	7	32	28
3	83.4	8	1.6	11	9	5	33	43

was almost constant above $x = 1$. Similar changes in conversion (Figure 3) and selectivity with x were observed at the reaction temperature of 340 °C.

The results for $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ catalysts are shown in Table 2. The selectivities to MAA and MAL were much increased by the mono- or di- V^{5+} -substitution, while the conversion slightly changed with x .

Effect of Cs^+ -Substitution. The results for $\text{Cs}_x\text{Ni}_{0.08}\text{H}_{3.84-x}\text{PVMo}_{11}\text{O}_{40}$ catalysts are shown in Table 3. The conversion decreased a little from $x = 0$ to 1, monotonically increased from $x = 1$ to 2.5, and then decreased.

Characterization of Catalysts. ESR and NMR spectroscopies have been reported to be effective in investigating the state of vanadium.^{25,26,34,41–44} However, since the compounds with vanadium content of >1 cannot be obtained in the pure state but a mixture of polyanions as described in the Experimental Section and literature,^{34c,39,42} it is difficult to understand clearly the role of elements and the origin of signals. Therefore, ESR and NMR spectroscopies were applied to investigate the catalysts with vanadium contents of 0 and 1 after use for the reactions.

Parts a and b of Figure 6 show ESR spectra of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PVMo}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$, respectively, measured at room temperature after use for the oxidation of isobutane. The extents of reduction calculated were 3.7×10^{-2} and 1.4×10^{-2} electron/anion for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PVMo}_{12}\text{O}_{40}$ catalysts, respectively, and very small. The respective colors of catalysts were green and yellow green and were consistent with the slight extents of reduction.

The spectrum in Figure 6a can be simulated with one type of spin, $g_{\parallel} = 1.877$, $g_{\perp} = 1.983$, $A_{\parallel} = 96$ (G), and $A_{\perp} = 42$ (G). The Δg value ($g_{\perp} - g_{\parallel} = 0.106$) suggests a relatively large distortion of MoO_6 octahedra, while the Keggin structure is not irreversibly destroyed as reported in ref 42.

Figure 6b shows the ESR spectrum of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$. By lowering the sample temperature to -95 °C, the best fit was obtained with two signals as shown in Figure 7: One is assigned to V^{4+} in VO_2^{2+} , which is present as a counteranion (out of Keggin anion) and simulated with $g_{\parallel} = 1.976$, $g_{\perp} = 1.932$, $A_{\parallel} = 196$ (G), and $A_{\perp} = 75$ (G). The other is a signal with $g_{\text{iso}} = 1.976$, $\Delta H_{\text{pp}} = 350$ (G), and is due to numerous paramagnetic centers in the dipole–dipole interaction as reported previously.^{34c,42,45} The result of the simulation with the listed parameters was shown by the dotted line. The simulation line well reproduced the observed spectrum.

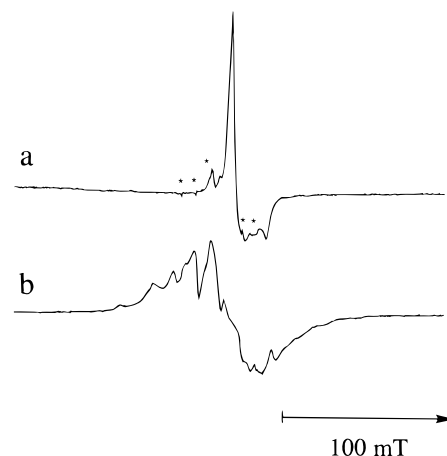


Figure 6. ESR spectra of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PVMo}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalysts after use for the oxidation of isobutane at 340 °C. Spectra were measured at room temperature (9.217 GHz). (a) $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PVMo}_{12}\text{O}_{40}$. (b) $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$. Five asterisks are assigned to the signals of the Mn marker and the other one is overlapped with a signal of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$.

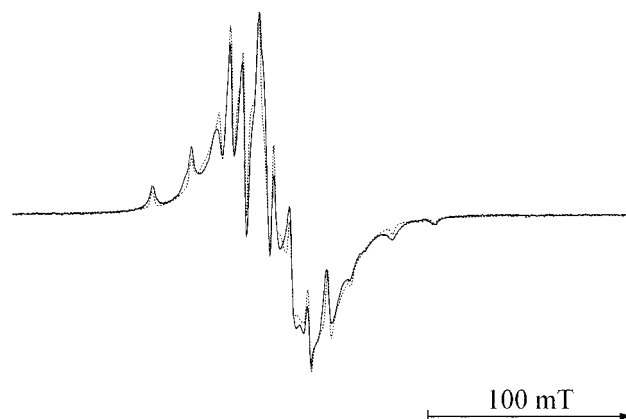


Figure 7. ESR spectrum of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst at -95 °C (9.218 GHz) after use for the oxidation of isobutane at 340 °C. The dotted line is obtained by the simulation (see text).

The changes of infrared spectra were consistent with the ESR data: Only a slight decrease in the intensity of 866-cm^{-1} and 797-cm^{-1} bands, which are assigned to corner-sharing $\nu(\text{Mo}-\text{O}-\text{M})$ ($\text{M} = \text{Mo}, \text{V}$), and edge-sharing $\nu(\text{Mo}-\text{O}-\text{M})$ ($\text{M} = \text{Mo}, \text{V}$) of the Keggin structure, respectively, was observed for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PVMo}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalysts. The slight decrease in the intensity is due to the low extents of reduction of Mo^{6+} or V^{5+} of Keggin anion.⁴⁶

Figure 8a shows the ^{51}V NMR spectrum of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst after use for the oxidation of isobutane. It was confirmed that the signal positions were not changed by the spinning rates. Two intense signals were observed at -538 and -558 ppm with shoulders at ca. -570 and -530 ppm. The -538 ppm signal is probably due to V^{5+} in $\text{PVMo}_{11}\text{O}_{40}^{4-}$ Keggin anion because as-prepared $\text{Cs}_3\text{PVMo}_{11}\text{O}_{40}$ or $\text{Cs}_3\text{-HPVMo}_{11}\text{O}_{40}$ samples showed the most intense signal at -538 ppm. The -558 ppm signal has been assigned to V^{5+} in VO_2^{+} ^{35,47} or in a perfect tetrahedral environment.^{34b} It was confirmed that $\text{H}_4\text{PVMo}_{11}\text{O}_{40} \cdot 7-8\text{H}_2\text{O}$ and $\text{H}_4\text{PVMo}_{11}\text{O}_{40} \cdot 30\text{H}_2\text{O}$ gave signals at -566 and -530 ppm, respectively. Therefore, the shoulder signals at -570 and -530 ppm are likely assigned to V^{5+} in the $\text{PVMo}_{11}\text{O}_{40}^{4-}$ Keggin anion of hydrogen form with different amounts of water of crystallization. The intensity ratio of signals at -530 , -538 , -558 , and -570 ppm

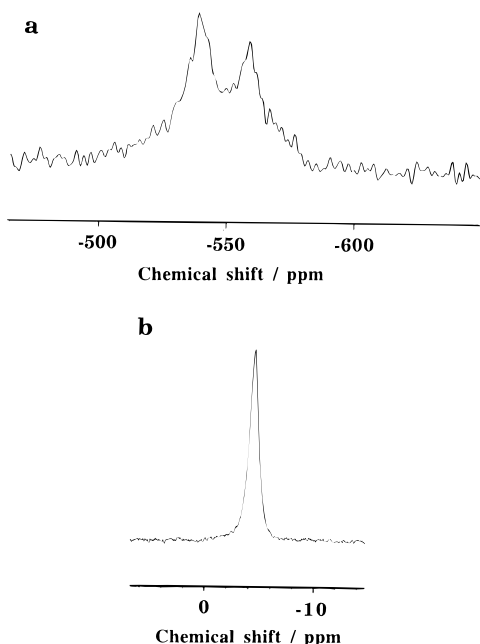


Figure 8. ^{51}V and ^{31}P NMR spectra of spent $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$. Spinning rate, 10 kHz. (a) ^{51}V NMR spectrum, ca. 4000 transients. (b) ^{31}P NMR spectrum, ca. 100 transients. The oxidation of isobutane was carried out at 340 °C.

is 0.07:0.54:0.21:0.18, showing that about 80% of all V^{5+} exist in Keggin anions.

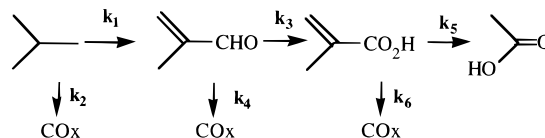
Figure 8b shows the ^{31}P NMR spectrum of $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst after use for the oxidation of isobutane. One broad signal was observed at -4.51 ppm with a half-width of 1.5 ppm. The ^{31}P NMR spectra of $\text{Cs}_4\text{PVMo}_{11}\text{O}_{40}$ and $\text{H}_4\text{PVMo}_{11}\text{O}_{40} \cdot 7-8\text{H}_2\text{O}$, which are suggested to give ^{51}V NMR signals in Figure 8a, showed sharp signals at -4.69 and -3.69 ppm, respectively. It was reported that $\text{PMo}_{12}\text{O}_{40}^{3-}$ was formed by the thermal treatment of $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$.^{34b} The fact suggests in the present case the formation of partially salified cesium 12-molybdophosphoric acid such as $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$, which gave ^{31}P signals at -4.17 and -4.50 ppm after the treatment in air at 300 °C. These signals can also be included in -4.51 ppm signal shown in Figure 8b. Therefore, those signals can be included in a broad -4.51 -ppm signal.

The amounts of vanadium in and out of the Keggin anion calculated on the basis of NMR and ESR data, on the assumption that a signal with $g_{\text{iso}} = 1.976$ and $\Delta\text{Hpp} = 350$ in Figure 6b comes from V^{4+} as well, were 0.76 and 0.24 atom anion $^{-1}$, respectively, and agreed with those (0.7 and 0.3 atom anion $^{-1}$, respectively,) obtained with the change in intensity of the $\nu(\text{V}-\text{O}-\text{P})$ IR band.

Discussion

Reaction Scheme. As shown in Figure 4a, the selectivities to MAL and CO_x extrapolated to 0% conversion were ca. 80% and 20%, respectively, showing that there are two paths in the first steps: One is the selective oxidation, $i\text{-C}_4\text{H}_{10} \rightarrow \text{MAL}$, and the other is complete oxidation, $i\text{-C}_4\text{H}_{10} \rightarrow \text{CO}_x$. The selectivities to MAA and CO_x increased when that to MAL decreased, suggesting the successive oxidation of MAL to MAA and CO_x . Therefore, MAA is produced by the oxidation of MAL. It is well known that molybdovanadophosphoric acids well catalyzed the oxidation of MAL to MAA,^{15-19,22,48-52} supporting the idea. No acetic acid was observed at low conversion. It has been reported that no acetic acid was

SCHEME 1: Reaction Mechanism of the Oxidation of Isobutane



observed for the oxidation of MAL when the conversion was low.⁴⁸ These facts suggest that acetic acid was formed by the oxidation of MAA. A similar variation was observed for the $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalyst as shown in Figure 4b, and the activation energies were close to each other, showing the lack of change of the reaction scheme with the V^{5+} -substitution.

It has been reported for $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ ($x = 0-3$) catalysts that the first-order rate constants for the oxidation of MAL at 340 °C were in the range of $2-8 \times 10^{-4} \text{ dm}^3 \text{ s}^{-1} \text{ g}^{-1}$.^{48-50,52} The values were about 10 times larger than $3-8 \times 10^{-5} \text{ dm}^3 \text{ s}^{-1} \text{ g}^{-1}$ reported for oxidation of isobutane.^{27d} In addition, the activation energy for the oxidation of isobutane was 110–120 kJ mol $^{-1}$ and much higher than 43 kJ mol $^{-1}$ reported for the oxidation of MAL catalyzed by mono- V^{5+} -substituted 12-molybdophosphate.⁵⁰ These facts show that the rate-determining step is the first two steps, $i\text{-C}_4\text{H}_{10} \rightarrow \text{MAL}$ and $i\text{-C}_4\text{H}_{10} \rightarrow \text{CO}_x$. The simulation of results shown in Figures 4a,b supports the idea as described in the following section.

When the rates of catalytic oxidation of isobutane was plotted against those of CO oxidation to CO_2 in the absence of oxygen (i.e., noncatalytic reduction of $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ by CO), a good correlation exists between them. We have previously reported a similar good correlation between them for $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ catalysts.^{27d} Both sets of data can be fitted with one solid line. Therefore, the good correlation shows that not only for $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ catalysts but also for $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ catalysts the oxidizing ability is a controlling factor of the catalytic activities for the oxidation of isobutane. Taking into account that the first two steps are rate-determining and that the oxidizing ability is a controlling factor of the catalytic activities, the reduction of catalyst with isobutane is the slowest. The reaction order, which was high in $P_{i\text{-C}_4\text{H}_{10}}$ and low in P_{O_2} (0.7th and 0th, respectively) under the present reaction conditions, is consistent with the idea.

States and Roles of Vanadium and Molybdenum. *States of Vanadium and Molybdenum.* After use for the oxidation of isobutane at 340 °C, $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalysts were only slightly reduced: Both of the oxidation states of molybdenum were almost 6.00 and the oxidation state of vanadium for the latter sample was more than 4.96. It was confirmed for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalyst that the Keggin structure was not irreversibly destroyed. The idea is consistent with the ^{31}P NMR, IR, and X-ray diffraction data previously reported.^{27d}

As for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{1.34}\text{PVMo}_{11}\text{O}_{40}$ catalyst, ca. 20% of all vanadium ions exist out of the Keggin anion. Taking into account the report that VO^{2+} and $\text{PMo}_{12}\text{O}_{40}^{4.09-}$ were formed by the reaction of fully oxidized $\text{PVMo}_{11}\text{O}_{40}^{4-}$ with isobutyric acid,⁵³ VO^{2+} and Mo^{5+} are probably formed by the reaction of $\text{PVMo}_{11}\text{O}_{40}^{4-}$ with isobutane. VO_2^+ obtained in this work would be formed by the reoxidation of VO^{2+} by O_2 .

Roles of Vanadium and Molybdenum. As shown in Figure 4b, the extrapolated selectivities to MAL and CO_x to 0% conversion for $\text{Cs}_{2.5}\text{Ni}_{0.08}\text{H}_{0.34}\text{PMo}_{12}\text{O}_{40}$ catalyst were ca. 80 and 20%, respectively, and did not change with the introduction of vanadium. After use of catalysts for the oxidation of isobutane

TABLE 4: Rate Constants of Oxidation of Isobutane^a

catalyst	k_1	k_2	k_3	k_4	k_5	k_6
Cs _{2.5} Ni _{0.08} H _{1.34} PVMO ₁₁ O ₄₀	1.7×10^{-4}	4.1×10^{-5}	1.4×10^{-2}	4.4×10^{-3}	3.0×10^{-4}	6.0×10^{-4}
Cs _{2.5} Ni _{0.08} H _{0.34} PMO ₁₂ O ₄₀	1.3×10^{-4}	3.2×10^{-5}	2.0×10^{-3}	2.0×10^{-3}	2.7×10^{-4}	5.0×10^{-4}

^a k_i , dm³ s⁻¹ g⁻¹; see Scheme 1.

at 340 °C, the oxidation state of molybdenum in Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ was almost 6.0 and almost the same as that in Cs_{2.5}Ni_{0.08}H_{0.34}PMO₁₂O₄₀. In addition, the activation energies for the oxidation of isobutane was close to each other. These facts show that the first steps are mainly catalyzed by molybdenum. In addition, the catalytic activity was well correlated with the oxidizing ability of catalyst and the molybdenum was almost in the fully oxidized state. These facts suggest that the reduction of Mo⁶⁺ is rate-determining. The report that MAL and MAA were formed by the stoichiometric reaction of isobutane with H₃PMO₁₂O₄₀⁵⁴ supports the idea.

Next the selectivity change is investigated. As shown in Figure 4a,b, Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ and Cs_{2.5}Ni_{0.08}H_{0.34}PMO₁₂O₄₀ catalysts exhibited different selectivity–conversion correlations. The quantitative explanation of the selectivity changes were attempted based on the reaction Scheme 1. Approximately first-order dependencies on the partial pressures of MAL and MAA have also been reported for oxidation reactions of MAL and MAA, respectively.^{48,51} On the basis of these reports and the results in Figure 5a,b, to the first approximation, reaction orders of the oxidation reactions of isobutane, MAL, and MAA are assumed to be unity. k_i 's in Scheme 1 are the first-order rate constants. The selectivity extrapolated to 0% conversion is equivalent to $100k_1/(k_1 + k_2)$ (= 0.8 in this case). The values of k_1 and k_2 thus determined for Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ and Cs_{2.5}Ni_{0.08}H_{0.34}PMO₁₂O₄₀ catalysts are listed in Table 4. The best fit results are shown as the solid line in Figure 4a,b. The values of $k_3 - k_6$ obtained by the simulation are also listed in Table 4. This simulation reproduced well the experimental results. The value of $k_1 + k_2$ is the smallest in Table 4 among $k_1 + k_2$, $k_3 + k_4$, and $k_5 + k_6$, supporting the idea that the first two steps are rate-determining.

It is noted in Table 4 that k_i/k_1 ratios did not change much between Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ and Cs_{2.5}Ni_{0.08}H_{0.34}PMO₁₂O₄₀ catalysts except for k_3/k_1 : k_3 was much increased by the introduction of a vanadium ion. This result is consistent with the observations that the selectivities to MAL and MAA for Cs_{2.5}Ni_{0.08}H_{0.34}PMO₁₂O₄₀ catalyst more slowly decreased and increased than those for Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ catalyst and that the selectivity to CO_x increased in a similar way. Therefore, the introduction of vanadium efficiently enhances the oxidation of MAL to MAA. As described at the beginning of this section, the state of molybdenum did not change much between Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ and Cs_{2.5}Ni_{0.08}H_{0.34}PMO₁₂O₄₀ catalysts. Therefore, the large change in selectivity with the introduction of vanadium is caused by the vanadium. This is the reason Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ shows the highest selectivity to MAA while the conversion is also the highest in Table 1.

A large increase in the selectivity to MAA by mono-V⁵⁺-substitution observed for the acid forms as shown in Table 2 probably results from the acceleration of oxidation of MAL to MAA by a vanadium ion as well. Taking into account that a large part (ca. 80%) of the vanadium ions were released by the thermal treatment of H₄PVMO₁₁O₄₀ at 340 °C, the released vanadium ion, which exists as VO₂⁺ and/or VO²⁺, may be active for the oxidation as well. The report that VO²⁺ works catalytically for the oxidative dehydrogenation of isobutyric acid⁵³ supports the idea. The decrease in selectivity to MAA

at a vanadium content of 3 in Tables 1 and 2 would be related to the formation of VO₂, which has been postulated.^{53,55}

Role of Cesium. The effect of Cs⁺-substitution for H⁺ in H_{3.84}Ni_{0.08}PVMO₁₁O₄₀ was investigated. The results for Cs_xNi_{0.08}H_{3.84-x}PVMO₁₁O₄₀ catalysts are shown in Table 3. The conversion changed little from $x = 0$ to 1, monotonically increased from $x = 1$ to 2.5, and then decreased. The change in the specific surface area in the range of $x = 0$ –2.5 was similar to that in the conversion. Therefore, the highest conversion at $x = 2.5$ is mainly due to the high surface area of Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ catalyst. Similarly the conversion much decreased while the specific surface increased from $x = 2.5$ to 3.0 for Cs_xH_{3-x}PMO₁₂O₄₀ catalysts.^{27d} The decrease in the conversion is due to a decrease in the oxidizing ability of catalyst, as reported.^{27d,56,57} Therefore, the decrease in conversion from $x = 2.5$ to 3 for Cs_xH_{3.84-x}Ni_{0.08}PVMO₁₁O₄₀ in Table 3 is likely due to the decrease in the oxidizing ability.

Next the selectivity change with Cs⁺-substitution is investigated. In this case, the selectivity should be compared at the same conversion level. Therefore, the selectivities for Cs_x-H_{3.84-x}Ni_{0.08}PVMO₁₁O₄₀ ($x = 0, 1, 2, 3$) catalysts were compared with those of Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ catalyst in Figure 4a. The data of catalysts with $x = 0, 1$, and 2 are approximately fitted with the line obtained for Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ catalyst. This shows that the selectivity does not change much among $x = 0$ –2.5 and that the selectivities to MAA and MAL decreased at $x = 3.0$. The decrease in the selectivity is due to a decrease in the protonic acidity, which facilitates the desorption of products, prevents the complete oxidation, and takes part in the activation of hydrocarbons.

66% of the whole vanadium ions are present in Keggin anions for Cs_{2.5}Ni_{0.08}H_{1.34}PVMO₁₁O₄₀ catalyst. In contrast, about 80% of the vanadium ions were released by the thermal treatment of H₄PVMO₁₁O₄₀ at 340 °C. In addition, a –559 ppm signal, which was assigned to extra-Keggin vanadium ion,^{34b} was observed for the ⁵¹V NMR spectrum and ca. 70% of V⁵⁺ exist as VO₂⁺ (out of Keggin anion). Téze et al. have also reported that 60–70% of the vanadium ions were released by the thermal treatment of H₄PVMO₁₁O₄₀ at 320 °C.^{34b} These facts show that Cs⁺-substitution for H⁺ in H₄PVMO₁₁O₄₀ suppresses the elimination of the vanadium ion from the anion.

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