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Catalytic oxidation of methacrolein to methacrylic acid over silica-supported
11-molybdo-1-vanadophosphoric acid with different heteropolyacid loadings

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Abstract

Catalytic oxidation of methacrolein (MAL) to methacrylic acid (MAA) over SiO₂-supported H₄PMo₁₁VO₄₀ with different H₄PMo₁₁VO₄₀ loadings was investigated. H₄PMo₁₁VO₄₀/SiO₂ showed high activity in comparison with unsupported H₄PMo₁₁VO₄₀, and 3.3 mol% H₄PMo₁₁VO₄₀/SiO₂ (50 wt% H₄PMo₁₁VO₄₀) had the highest activity, which was five-times larger than that of unsupported H₄PMo₁₁VO₄₀ due to high dispersion of H₄PMo₁₁VO₄₀ on SiO₂, as determined by temperature-programmed desorption of benzonitrile. On the other hand, the supported catalysts were less selective towards the formation of MAA. From X-ray diffraction and Raman spectroscopy, it was determined that H₄PMo₁₁VO₄₀ decomposed to form MoO₃ on SiO₂ during the catalytic reaction. Since SiO₂-supported MoO₃ and unsupported MoO₃ had only very low selectivity towards the formation of MAA in the oxidation of MAL, it was concluded that the formation of MoO₃ caused the decrease in the catalytic performance of the supported catalysts.

Keywords: Supported heteropolyacids; Methacrolein oxidation; Methacrylic acid; Temperature-programmed desorption
1. Introduction

Methacrylic acid (MAA) is an important intermediate in the production of methyl methacrylate and other derivatives, including polymers. Selective oxidation to produce MAA via methacrolein (MAL) is a two-stage process involving the oxidation of isobutene to MAL, followed by MAL to MAA. The first step of the reaction is conducted in the presence of a Mo-Bi-oxide catalyst, and the second step involves Keggin-type heteropoly compounds containing Mo, V, and P as catalysts [1-2]. The oxidation of MAL to MAA has some issues, and in order to improve the yield of MAA, a highly active and selective catalyst is needed.

Selective oxidation of MAL over heteropoly compounds composed of P and Mo has been studied extensively [3-14]. It has been shown that substituting some Mo atoms with V atoms improves the catalytic activity and selectivity for the formation of MAA [13]. In addition, substituting H\(^+\) with Cs\(^+\) retards the oxidation of MAA to CO and CO\(_2\) [13,14].

Solid heteropolyacids, that is to say, unsupported heteropolyacids, can be used as heterogeneous catalysts. However, they have low surface area and consequently have only a small number of active sites available. Thus, solid heteropolyacids frequently show only low catalytic activity. Increasing the surface
area of heteropolyacids by supporting them on a carrier with a high surface area could afford highly active catalysts. Supporting H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ on SiO₂, TiO₂, and active carbon shows a great success in solid acid catalysts [15-20].

As for oxidation catalysts, supported H₃⁺ₓPMo₁₂⁻ₓVₓO₄₀ (x = 0 – 2) have been investigated for gas-phase oxidations of methanol [21-24], ethanol [25,26], ethene [27], propene [28], ethane [29], isobutane [30], ammoxidation of 2-methyl pyrazine [31], and liquid-phase oxidations of tetrahydrothiophene [32,33], cycloalkenes [34], toluene [35], benzyl alcohol [36] and styrene [37,38]. Nowińska et al. have demonstrated that SiO₂-supported H₅PMo₁₀V₂O₄₀ is higher active than unsupported one for the oxidation of ethane [27]. Liu and Iglesia have reported that supporting H₃₊ₙPMo₁₂₋ₙVₙO₄₀ on SiO₂ enhances the catalytic activity and decreases the COₓ selectivity in a one-step synthesis of dimethoxymethane via the oxidation of dimethyl ether or methanol [21]. Kim et al. have reported that H₃PMo₁₁O₄₀ supported on a mesostructured cellular SiO₂ foam, in which the support has been modified with 3-aminopropyl triethoxysilane, shows high activity for the oxidation of ethanol to acetaldehyde at 503 K [25]. However, there are only a few reports on supported heteropolyacid catalysts being used in the selective oxidation of MAL. Kim et al. [39,40] have demonstrated that H₅PMo₁₀V₂O₄₀ supported on nitrogen-containing
mesoporous carbon and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ supported on polystyrene have higher activity for the oxidation of MAL and selectivity towards the formation of MAA compared with the corresponding unsupported catalysts.

In this study, we investigated the catalytic performance of SiO$_2$-supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ for the selective oxidation of MAL to MAA and compared its catalytic performance with unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. The effects of the loading amount of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ on the activity and selectivity were investigated. Changes in the catalytic performance, especially selectivity against the loading amounts, are discussed in conjunction with the chemical and physical properties of the catalysts before and after the catalytic reaction.

2. Experimental

2.1. Preparation of catalysts

MoO$_3$, V$_2$O$_5$, and 85% H$_3$PO$_4$, which were used to prepare $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, were purchased from Wako Pure Chemical Co., Ltd. MoO$_3$ (31.7 g), V$_2$O$_5$ (1.82 g), and water (1.5 dm$^3$) were added to a roundbottom flask. After the addition of 85%
H₃PO₄ (2.3 g) into the resulting suspension, it was heated and vigorously stirred at 358 K for 3 h. After the solution was cooled to room temperature, the insoluble matter was filtered off to obtain a clear orange solution. Then the solvent was evaporated to obtain H₄PMo₁₁VO₄₀, which was dried in air at 333 K overnight.

SiO₂-supported H₄PMo₁₁VO₄₀ with different H₄PMo₁₁VO₄₀ loadings were prepared by using an incipient-wetness method with an aqueous solution of H₄PMo₁₁VO₄₀ (0.08 mol dm⁻³) and SiO₂ (Aerosil 300: 295 m² g⁻¹, Nippon Aerosil Co., Ltd.). H₄PMo₁₁VO₄₀/SiO₂ with 0.37, 1.4, and 3.3 mol% loadings, which correspond to 10, 30, and 50 wt%, respectively, were prepared by changing the amount of the aqueous H₄PMo₁₁VO₄₀ solution added. The resulting wet solid was dried in air at 333 K overnight and was then calcined in air at 523 K for 4 h. Since each Keggin cluster (KU) occupies about 1.44 nm² [41], a theoretical monolayer of KU with 0.69 KU nm⁻² formed. Thus, the catalysts with loadings of 0.37, 1.4, and 3.3 mol% correspond to monolayer coverages of 0.18, 0.71, and 1.65, respectively, if Keggin clusters are ideally dispersed on SiO₂.

As a reference, 3.96 mol% MoO₃/SiO₂ (9.0 wt% MoO₃) was prepared by using an impregnation method involving SiO₂ and an aqueous solution of MoO₃, which was prepared by adding aqueous ammonia (25%, Wako Pure Chemical Co.,
Ltd.) to an aqueous suspension of MoO$_3$.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku Mini Flex) with Cu Kα radiation ($\lambda = 0.154$ nm). Raman spectroscopy was performed using a laser Raman spectrometer (JASCO, RMP 200) with a 100 mW laser with a wavelength of 532 nm and a CCD detector. Temperature-programmed desorption of benzonitrile (BN-TPD) was carried out using a custom-built TPD system equipped with a mass spectrometer (ANELVA, M-QA100S) as a detector. After the catalyst was pretreated in a N$_2$ flow at 523 K for 1 h, it was exposed to 0.122 $\mu$mol h$^{-1}$ of BN in a He flow at 373 K for 2 h. The weakly adsorbed or physisorbed BN was removed in a He flow at 373 K for 2 h and then at 393 K. The temperature was then increased at a rate of 10 K min$^{-1}$ to 873 K under a He flow while monitoring the mass signals ($m/e = 18, 28, 44, \text{ and } 103$ for H$_2$O, CO, CO$_2$, and BN, respectively) in the exit gas.

2.3. Catalytic reaction
Catalytic oxidation of MAL was performed in a continuous flow reactor at 573 K and atmospheric pressure. Before the reaction, the catalyst was pretreated under a flow of a gas mixture consisting of O\(_2\) (10.7 vol %), H\(_2\)O (17.9 vol %), and N\(_2\) (balance) at a total flow rate of 28 cm\(^3\) min\(^{-1}\) and a temperature of 593 K for 1 h. After the temperature was decreased to 573 K, a reactant gas mixture of MAL (3 vol %), O\(_2\) (6 vol %), H\(_2\)O (15 vol %), and N\(_2\) (balance) was fed into the reactor to start the catalytic reaction. The amount of the catalyst and total flow rate were adjusted to control the conversion. The reaction products were analyzed by using on-line gas chromatographs (GCs) connected at the outlet of the reactor. For acetic acid (AcOH), MAL, and MAA, a GC (Shimadzu GC-14B) equipped with a flame ionization detector and a capillary column (TC-FFAP, 0.25 mm × 50 m) was utilized. For CO and CO\(_2\), a GC (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and two packed columns (Molecular Sieve 5A, 2.85 mm × 3 m and Activated Carbon, 2.85 mm × 2 m) was used. In order to prevent interference from organic compounds, prior to the GC-TCD analysis, the gas was passed through a dry-ice trap to remove them. As an internal standard for GC analysis, CH\(_4\) (31%) diluted with He was mixed at the outlet of the reactor.
3. Results and discussion

3.1. Catalytic oxidation of MAL over unsupported and SiO$_2$-supported H$_4$PMo$_{11}$VO$_{40}$

Fig. 1 shows time courses of the catalytic oxidation of MAL over unsupported H$_4$PMo$_{11}$VO$_{40}$ and 1.4 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$, in which $WF^{-1}$ were 101 and 17 g-cat h mol-MAL$^{-1}$, respectively, where $W$ is the weight of the catalyst (g) and $F$ is the flow rate of MAL (mol h$^{-1}$). In the initial stage of the reaction, selectivity of unsupported H$_4$PMo$_{11}$VO$_{40}$ towards the formation of MAA slightly increased and then reached nearly constant values after 50 min. On the other hand, the conversion of MAL and the selectivity toward AcOH and CO$_x$ decreased with time in the initial stage of the reaction and reached nearly constant values after 50 min. For 1.4 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$, although the selectivity changed in the initial stage of the reaction, constant selectivities were obtained within 300 min. Conversion of MAL was basically constant during the reaction. Since 0.37 and 3.3 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$ also showed constant conversions and selectivities within 300 min, the activity and selectivities were estimated from data obtained after 300 min.
In Fig. 2, the catalytic activity and selectivity are plotted as a function of the loading amount of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ on SiO$_2$, where catalytic activity means the rate of MAL consumed per total weight of the catalyst. Catalytic activities and selectivities were determined from data obtained at $\sim$10% conversion. Unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ had a catalytic activity of $13 \: \mu$mol g$^{-1}$ min$^{-1}$ at 573 K, whereas 3.3 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$/SiO$_2$ had a catalytic activity of $74 \: \mu$mol g$^{-1}$ min$^{-1}$, which is 5 times higher than that of unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. However, the catalytic activity decreased with a decrease in the loading amount, and 0.37 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$/SiO$_2$ showed activity similar to that of unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. However, if we consider the amount of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ contained in 0.37 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$/SiO$_2$, the catalytic activity per unit weight of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ is 10 times higher for 0.37 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$/SiO$_2$ than it is for the unsupported catalyst. This improvement in the catalytic activity is due to the increase in the number of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ exposed on the outermost surface by supporting it on SiO$_2$. This effect will be discussed in detail in Section 3.2.

In contrast to the catalytic activity, selectivities toward the formation of MAA of SiO$_2$-supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ were slightly lower than that of unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. Unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ showed 75% selectivity for the
formation of MAA. The selectivities of 3.3 and 1.4 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$ were 66% and 63%, respectively. However, 0.37 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$ was much less selective.

3.2. Kinetic study on the oxidation of MAL over unsupported and SiO$_2$-supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$

In order to investigate the effect of supporting $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ on SiO$_2$ on the oxidation of MAL, we used 1.4 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$ as a typical supported catalyst and compared its catalytic properties with unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ via a kinetic study. Fig. 3 shows selectivity dependences on the conversion of MAL for unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and 1.4 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$. At low conversion, the selectivity for MAA formation was relatively high for both catalysts, and the selectivities for AcOH and CO$_x$ were low. However, the selectivity for MAA decreased as the conversion increased for both catalysts, indicating that MAA was successively oxidized to AcOH and CO$_x$. When the selectivity was extrapolated to 0% conversion, the selectivities of unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ for MAA, AcOH and CO$_x$ were 84%, 7%, and 9%, respectively, and those of 1.4 mol%
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$ were 65%, 15%, and 15%, respectively. It should be emphasized that the selectivities for AcOH and CO$_x$ were not 0% even at 0% conversion for both catalysts, indicating that AcOH and CO$_x$ directly form from MAL. Based on these findings, we propose the reaction pathway shown in Scheme 1.

We assumed that the reaction to consume MAL was a first-order reaction, where the first-order reaction rate constant ($k_{\text{total}}$) corresponds to the sum of each rate constant ($k_1$, $k_2$, and $k_3$ in Scheme 1). By optimizing $k_{\text{total}}$, the behavior of the $WF^{-1}$ dependencies on the conversion of MAL could be fitted for both catalysts, and values of $k_{\text{total}}$ were estimated to be $0.94 \times 10^{-3} \text{ h}^{-1} \text{ g-cat}$ and $3.5 \times 10^{-3} \text{ h}^{-1} \text{ g-cat}$ for unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and 1.4 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$, respectively. Thus, $k_1$, $k_2$, and $k_3$ for the conversion of MAL to MAA, AcOH, and CO$_x$, respectively, could be calculated from Eq. 1 by using the selectivity at 0% conversion. The values are summarized in Table 1.

$$k_n = k_{\text{total}} \times \frac{\text{Selectivity (\% at 0\% conversion)}}{100} \quad (n = 1,2,3) \quad (1)$$

In order to evaluate the influence of the support on successive oxidation
reactions of MAA, we assumed that the reactions of MAA to AcOH and CO\textsubscript{x} and MAL to MAA were first-order reactions. Thus, the yield of MAA could be determined as follows:

\[
\text{Yield of MAA} = \frac{k_1}{-(k_1 + k_2 + k_3) + k_4} \times [\text{MAL}]_0 \times (e^{-(k_1 + k_3)t} - e^{-k_4t})
\] (2)

where \(k_1, k_2, k_3,\) and \(k_4\) are rate constants, \([\text{MAL}]_0\) is the concentration of MAA at the inlet of the reactor and, \(t\) is \(WF^{-1}\). In Fig. 4, the yield of MAA is plotted as a function of \(WF^{-1}\). The experimental yields were fitted in relation to \(k_1, k_2, k_3,\) and an optimized value of \(k_4\) and are also shown in Fig. 4. \(k_4\) and the ratio of \(k_4/k_1\) for H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40} and 1.4 mol\% H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40}/SiO\textsubscript{2} are summarized in Table 1. It is noted that the \(k_4/k_1\) ratio is two-times larger for 1.4 mol\% H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40}/SiO\textsubscript{2} (= 1.3) than it is for unsupported H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40} (= 0.65), indicating that the successive reaction of MAA, which results in a decrease of the maximum MAA yield, is accelerated more greatly over 1.4 mol\% H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40}/SiO\textsubscript{2} than it is over unsupported H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40}. In summary, supporting H\textsubscript{4}PMo\textsubscript{11}VO\textsubscript{40} on SiO\textsubscript{2} promoted both selective and non-selective reactions; however, the non-selective reactions were accelerated to a great extent (Table 1).
3.3. Physical and chemical properties of catalysts

As mentioned above, supporting H₄PMo₁₁VO₄₀ on SiO₂ improved the catalytic activity but lowered selectivity for the formation of MAA. Thus, we next investigated the cause of the increase in the activity and the decrease in the selectivity by using physicochemical characterization techniques.

3.3.1. Pre-catalytic oxidation of MAL

Fig. 5 shows XRD patterns of the catalysts before the reaction. The diffraction pattern of unsupported H₄PMo₁₁VO₄₀ (Fig. 5a) was identical to that of H₄PMo₁₁VO₄₀·14H₂O [42]. In the cases of the supported catalysts, 3.3 mol% H₄PMo₁₁VO₄₀/SiO₂ had a diffraction pattern corresponding to H₄PMo₁₁VO₄₀·14H₂O, but the intensities of the diffraction lines were weaker than those of the unsupported catalyst. The intensities of the diffraction lines gradually decreased with a decrease in the loading amount, and in the case of 0.37 mol% H₄PMo₁₁VO₄₀/SiO₂, no diffraction lines for the crystalline heteropolyacid were observed. Since even a
physical mixture of unsupported H₄PMo₁₁VO₄₀ (0.37 mol%) and SiO₂ (99.63 mol%) showed a clear diffraction pattern due to H₄PMo₁₁VO₄₀·14H₂O (data not shown), H₄PMo₁₁VO₄₀ was highly dispersed on the SiO₂ in the supported catalysts.

Fig. 6 shows Raman spectra of the catalysts before the reaction. In the spectrum for unsupported H₄PMo₁₁VO₄₀ (Fig. 6a), only the four characteristic bands of a Keggin structure were observed: 1000, 907, 624, and 242 cm⁻¹ for νₛ(Mo-Oₐ), νₛ(Mo-O₆-Mo), νₛ(Mo-O₅-Mo), and νₛ(Mo-O₆), respectively [43]. 1.4 and 3.3 mol% H₄PMo₁₁VO₄₀/ SiO₂ showed Raman bands corresponding to H₄PMo₁₁VO₄₀, indicating that at least some H₄PMo₁₁VO₄₀ was retained. It should be emphasized that Raman bands due to H₄PMo₁₁VO₄₀ for the supported catalysts shifted toward lower wavenumbers with a decrease in the loading amount of H₄PMo₁₁VO₄₀. For example, νₛ(Mo-O₅-Mo) was observed at 907 cm⁻¹ for unsupported H₄PMo₁₁VO₄₀, whereas it was observed at 897 and 894 cm⁻¹ for 3.3 and 1.4 mol% H₄PMo₁₁VO₄₀/ SiO₂, respectively. This band shift suggests the presence of strong interactions between H₄PMo₁₁VO₄₀ and the SiO₂ surface. A model for the interaction between H₃PW₁₂O₄₀ and the SiO₂ surface, where the protons of H₃PW₁₂O₄₀ react with OH groups on SiO₂ to form -Si-OH₂⁺--H₂PW₁₂O₄₀⁻, has been proposed on the basis of ¹H NMR studies [44-47]. Similar interactions between
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and the SiO$_2$ surface could be present in the case of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$. Since the Raman bands were shifted in the case of SiO$_2$-supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, the Keggin structure was distorted to some degree. For 0.37 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$, only weak bands were observed, meaning that the peak position could not be determined precisely. However, at least some $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ still had a Keggin structure.

Fig. 7 shows a BN-TPD profile for 1.4 mol% $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$; here, a mass spectrometer was utilized as the detector. BN adsorbs only on the outermost surface of a solid heteropolyacid [48], and thus, the number of protons on the outermost surface of heteropolyacid crystallites can be estimated from BN-TPD profiles. However, as shown in Fig. 7, not only BN ($m/e = 103$) but also H$_2$O, CO, and CO$_2$ ($m/e = 18$, 28, and 44, respectively), which form by the oxidative decomposition of BN with lattice oxygen from $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, were detected in the effluent gas while measuring the TPD profile. Thus, we estimated the amount of BN adsorbed on the catalyst by taking into account the amount of CO and CO$_2$. In Fig. 8, the amounts of adsorbed BN per unit catalyst weight are plotted as a function of the loading amount of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. The amount of adsorbed BN on the unsupported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ was 4.6 $\mu$mol g$^{-1}$. If two molecules of BN are adsorbed
on the outermost surface of a molecule of H₄PMo₁₁VO₄₀, only 0.4% of H₄PMo₁₁VO₄₀ is exposed on the outermost surface of unsupported H₄PMo₁₁VO₄₀. In other words, the mean particle size of unsupported H₄PMo₁₁VO₄₀ is 1200 nm (1.2 μm). The amounts of adsorbed BN for the supported catalysts were larger than that for the unsupported H₄PMo₁₁VO₄₀. 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂ adsorbed the largest amount of BN, i.e. 75 μmol g⁻¹ cat⁻¹, which is 16 times larger than that adsorbed by unsupported H₄PMo₁₁VO₄₀. The amounts of adsorbed BN for 0.37 and 3.3 mol% H₄PMo₁₁VO₄₀/SiO₂ are about 10 times larger than that for unsupported H₄PMo₁₁VO₄₀. The mean particle sizes of the supported catalysts were 11, 20, and 48 nm for 0.37, 1.4, and 3.3 mol% H₄PMo₁₁VO₄₀/SiO₂, respectively. On the basis of these findings, we concluded that microparticles of H₄PMo₁₁VO₄₀ were obtained by supporting H₄PMo₁₁VO₄₀ on SiO₂. As a result, the number of H₄PMo₁₁VO₄₀ available for the reaction is larger, thus improving the catalytic activity. However, the trend in the catalytic activity shown in Fig. 2 does not fully agree with that in the amounts of adsorbed BN in Fig. 8. For example, the maximum catalytic activity was observed at a loading of 3.3 mol%, whereas the maximum number of H₄PMo₁₁VO₄₀ exposed on the outermost surface was observed at a loading of 1.4 mol%. The discrepancy indicates that specific activity per H₄PMo₁₁VO₄₀ exposed
on the outermost surface is lower for the supported catalysts than it is for the unsupported one. In addition, selectivity of the supported catalysts for the formation of MAA was lower. In order to elucidate the cause, the catalyst after the reaction was investigated.

3.3.2. Post-catalytic oxidation of MAL

Fig. 9 shows XRD patterns for the catalysts after 5 h of reaction. Unsupported H₄PMo₁₁VO₄₀ (Fig. 9a) gave a diffraction pattern similar to that before the reaction, although the diffraction lines were less intense and broader. On the other hand, in the case of the supported catalysts (Fig. 9b-d), the diffraction pattern corresponding to H₄PMo₁₁VO₄₀ almost disappeared, and sharp diffraction lines attributed to crystalline MoO₃ appeared.

Decomposition of H₄PMo₁₁VO₄₀ in the supported catalysts after the reaction was clearer from the Raman spectra. Fig. 10 shows Raman spectra of the catalysts after the reaction. Unsupported H₄PMo₁₁VO₄₀ (Fig. 10a) showed bands characteristic of a Keggin structure, and no other bands were detected. Therefore, the Keggin structure of the unsupported H₄PMo₁₁VO₄₀ remained intact even after the
reaction, although the band intensity decreased. On the other hand, in the case of the supported catalysts (Fig. 10b-d), Raman bands attributed to not only H₄PMo₁₁VO₄₀ but also MoO₃ (α-MoO₃: 820 and 660 cm⁻¹; β-MoO₃: 849 and 772 cm⁻¹ [43,49]) were detected. These results agree with the XRD measurements (Fig. 9). In particular, in the spectra of 0.37 mol% H₄PMo₁₁VO₄₀/SiO₂ (Fig. 10d), the Raman bands of H₄PMo₁₁VO₄₀ were very weak, and a Raman band attributed to α-MoO₃ was observed at 820 cm⁻¹. A broad Raman bands at around 900 cm⁻¹ for the supported catalysts were attributable to Mo-V mixed oxide [50], but the intensities were weak. Therefore, we concluded that most of the H₄PMo₁₁VO₄₀ on 0.37 mol% H₄PMo₁₁VO₄₀/SiO₂ decomposed mainly to MoO₃ during the reaction. Destabilization of heteropolyacids after supporting them on SiO₂ has been reported for H₃PMo₁₂O₄₀/SiO₂ [51] and for H₅PMo₁₁V₂O₄₀/SiO₂ [41]. Our results are consistent with previously reported ones.

3.4. Catalytic oxidation of MAL over MoO₃/SiO₂ and unsupported MoO₃

As mentioned in Section 3.3, H₄PMo₁₁VO₄₀ in the supported catalysts decomposed during the reaction to form mainly MoO₃. The formation of MoO₃
could cause the decrease in activity per $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ exposed on the outermost surface and in selectivity for the formation of MAA. Therefore, we prepared 3.96 mol% MoO$_3$/SiO$_2$ and examined its catalytic performance for the oxidation of MAL. The loading amount of MoO$_3$ (3.96 mol%) corresponded to the amount of molybdenum present in 0.37 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$. Catalytic performance of unsupported MoO$_3$ was also evaluated. Catalytic results are summarized in Table 2 together with those of 0.37 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$ and unsupported H$_4$PMo$_{11}$VO$_{40}$. The catalytic activity of 3.96 mol% MoO$_3$/SiO$_2$ was 7 μmol g$^{-1}$ min$^{-1}$, and the selectivity for the formation of MAA was only 18%. In addition, unsupported MoO$_3$ also showed low activity and comparable selectivity for MAA to 0.37 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$. These are much lower than those for unsupported H$_4$PMo$_{11}$VO$_{40}$. Therefore, it was concluded that the formation of MoO$_3$ caused the decrease in the catalytic performance of the supported catalysts, especially of the catalysts with low loadings.

The reaction mechanism for the oxidation of MAL to MAA over unsupported H$_3$PMo$_{12}$O$_{40}$ is proposed as Scheme 2, where the first step reaction is promoted by Brønsted acid sites and then the intermediates having C-O-Mo bonds are oxidized with the lattice oxygen (Mars and van Krevelen mechanism) to form
MAA [11,14,52]. Thus, acid sites are indispensable for the selective formation of MAA. MoO$_3$ possesses acid sites, but they are weak [53]. Therefore, the first step reaction may not be promoted and consequently, the selective oxidation forming MAA was inhibited over MoO$_3$/SiO$_2$ and unsupported MoO$_3$.

3.5. Decomposition process of $H_4PMo_{11}VO_{40}$ on SiO$_2$

During the course of the catalyst preparation, the catalysts were calcined at 523 K and were then pretreated at a higher temperature of 593 K before the reaction. On the basis of the time courses of the reaction shown in Fig. 1, changes in the conversion and selectivity were not so large as a function of time. Thus, it is reasonable that the structure of the catalysts do not change drastically during the catalytic reaction.

We investigated the decomposition process of $H_4PMo_{11}VO_{40}$ under the pretreatment conditions. It is well-known that heteropolyacids undergo decomposition with deprotonation during thermal treatment [46]. Fig. 11 shows XRD patterns of the catalysts obtained after thermal treatment at 573 K for 5 h in a gas flow composed of $O_2$, $H_2O$, and $N_2$, that is, under conditions the same as the
pretreatment conditions. Unsupported H₄PMo₁₁VO₄₀ gave broad diffraction lines (Fig. 11a) compared with fresh catalyst (Fig. 4a), and the XRD pattern was similar to that after the reaction (Fig. 8a). On the other hand, 0.37 mol% H₄PMo₁₁VO₄₀/SiO₂ after treatment showed sharp diffraction lines corresponding to MoO₃ (Fig. 12b). This XRD pattern is similar to that after the catalytic reaction (Fig. 8d). The similarity indicates that the Keggin structure of H₄PMo₁₁VO₄₀ decomposes to form MoO₃ in the pretreatment stage.

Fig. 12 shows XRD patterns of the 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂ after the catalytic oxidation for 5 h in the temperature range of 523–563 K, which is lower than the normal reaction temperature (573 K). In the pattern after the reaction at 523 K (Fig. 12c), diffraction lines corresponding to H₄PMo₁₁VO₄₀ were observed. However, in the pattern at 553 K (Fig. 12b), diffraction lines were barely visible. Furthermore, in the pattern at 563 K, diffraction lines corresponding to MoO₃ appeared. The Raman spectra of these samples are consistent with the XRD patterns (data not shown).

Mestl et al. have revealed by using Raman technique the structural transformation of unsupported H₄PMo₁₁VO₄₀ induced by thermal treatment as follows [54,55]: vanadyl and molybdenyl species are expelled from the Keggin cage
and defective Keggin structures are formed. These defective structures further disintegrate to Mo$_3$O$_{13}$ triads, which finally oligomerize to form crystalline MoO$_3$. On the SiO$_2$ support, the similar transformation may take place. As discussed previously, the decomposition temperature of H$_4$PMo$_{11}$VO$_{40}$ decreased after it was supported on SiO$_2$. As mentioned in Section 3.3.1, the protons of H$_4$PMo$_{11}$VO$_{40}$ interact with SiO$_2$, i.e., \(-\text{SiOH}_2^+\)\(-\text{H}_3\text{PMo}_{11}\text{VO}_{40}\). This may result in the changes in the structure of H$_4$PMo$_{11}$VO$_{40}$, lowering the thermal stability of H$_4$PMo$_{11}$VO$_{40}$. Thus, H$_4$PMo$_{11}$VO$_{40}$ decomposed at lower temperatures.

4. Conclusions

Catalytic activity per unit catalyst weight for the oxidation of MAL significantly increased by supporting H$_4$PMo$_{11}$VO$_{40}$ on SiO$_2$ due to the high dispersion of H$_4$PMo$_{11}$VO$_{40}$ on SiO$_2$. In particular, 3.3 mol\% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$ had an activity that was five-times higher than that of unsupported H$_4$PMo$_{11}$VO$_{40}$ and a selectivity for the formation of MAA comparable to that of the unsupported catalyst. However, the supported catalysts with low H$_4$PMo$_{11}$VO$_{40}$ loadings (0.37 mol\%) showed only low selectivities for MAA formation. In the case of the SiO$_2$-
supported catalysts, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ decomposed at a lower temperature, and almost all of the $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ decomposed during pretreatment conducted at 573 K before the catalytic reaction. The decomposition of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ results in a decrease in the catalytic performances of the supported catalysts with low loadings.
References


### Table 1
First-order reaction rate constants for the oxidation of MAL over unsupported H$_4$PMo$_{11}$VO$_{40}$ and 1.4 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate constant$^a$$/ \times 10^{-3}$ h$^{-1}$ g$_{\text{cat}}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{\text{total}}$</td>
</tr>
<tr>
<td>H$<em>4$PMo$</em>{11}$VO$_{40}$</td>
<td>0.94</td>
</tr>
<tr>
<td>1.4 mol% H$<em>4$PMo$</em>{11}$VO$_{40}$/SiO$_2$</td>
<td>3.5 (3.7)$^b$</td>
</tr>
</tbody>
</table>

$^a$Reactions for the rate constants are shown in Scheme 1.

$^b$Figures in parenthesis are relative rates for 1.4 mol% H$_4$PMo$_{11}$VO$_{40}$/SiO$_2$ against the corresponding reaction rates for unsupported H$_4$PMo$_{11}$VO$_{40}$. 
**Table 2**  
Catalytic performance of 3.96 mol% MoO₃/SiO₂, unsupported MoO₃, 0.37 mol% H₄PMo₁₁VO₄₀/SiO₂, and unsupported H₄PMo₁₁VO₄₀ for the oxidation of MAL.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activity/Selectivity/Othera (%)</th>
<th>Activity/Selectivity/Othera (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.96 mol% MoO₃/SiO₂</td>
<td>7 μmol h⁻¹ g⁻¹ cat⁻¹ 18 MAA 25 AcOH 47 COₓ 10 others (7)</td>
<td></td>
</tr>
<tr>
<td>MoO₃</td>
<td>7 μmol h⁻¹ g⁻¹ cat⁻¹ 41 MAA 6 AcOH 53 COₓ n.d. (5)</td>
<td></td>
</tr>
<tr>
<td>0.37 mol% H₄PMo₁₁VO₄₀/SiO₂</td>
<td>15 μmol h⁻¹ g⁻¹ cat⁻¹ 43 MAA 11 AcOH 36 COₓ 10 others (8)</td>
<td></td>
</tr>
<tr>
<td>H₄PMo₁₁VO₄₀</td>
<td>13 μmol h⁻¹ g⁻¹ cat⁻¹ 75 MAA 5 AcOH 16 COₓ 4 others (8)</td>
<td></td>
</tr>
</tbody>
</table>

*aOthers were acetone, acetaldehyde, acrolein, and acrylic acid.*  
*bOthers was not detected with a gas chromatograph.*
Fig. 1. Time courses of oxidation of MAL over (a) unsupported H₄PMo₁₁VO₄₀ and (b) 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂. (●) Conversion of MAL and selectivities for (■) methacrylic acid, (◇) acetic acid, and (△) COₓ. Reaction conditions: MAL:O₂:H₂O:N₂ = 3:6:15:76, temperature = 573 K, total pressure = 0.1 MPa, and $W F^{-1} = 101$ and 17 g-cat h mol⁻¹-MAL⁻¹ for unsupported H₄PMo₁₁VO₄₀ and 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂, respectively.

Fig. 2. Effects of the loading amount of H₄PMo₁₁VO₄₀ on SiO₂ on the catalytic activity and selectivity. (●) Activity and selectivities for (■) MAA, (◇) acetic acid, and (△) COₓ. Reaction conditions: MAL:O₂:H₂O:N₂ = 3:6:15:76, temperature = 573 K, pressure = 0.1 MPa, $W F^{-1} = 99$, 28, 29, and 75 g-cat h mol⁻¹-MAL⁻¹ for unsupported H₄PMo₁₁VO₄₀, 3.3 mol% H₄PMo₁₁VO₄₀/SiO₂, 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂, and 0.37 mol% H₄PMo₁₁VO₄₀/SiO₂, respectively.

Activities were calculated from the data at the conversions in the range of 8%–12%.

Selectivities were evaluated using conversions in the range of 8%–12%.

Fig. 3. Relationship between selectivity and conversion for (a) unsupported H₄PMo₁₁VO₄₀ and (b) 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂. (■) MAA, (◇) acetic acid,

Fig. 4. Experimental data (■) and yield of MAA calculated (―) using the optimized reaction rate constant \( k_4 \) for (a) unsupported H₄PMo₁₁VO₄₀ and (b) 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂. Reaction conditions: MAL:O₂:H₂O:N₂ = 3:6:15:76, temperature = 573 K, and total pressure = 0.1 MPa.

Fig. 5. XRD patterns of unsupported and SiO₂-supported H₄PMo₁₁VO₄₀ before the reaction. (a) Unsupported H₄PMo₁₁VO₄₀, SiO₂-supported H₄PMo₁₁VO₄₀ with loadings of (b) 3.3 mol%, (c) 1.4 mol%, and (d) 0.37 mol% and (e) SiO₂.

Fig. 6. Raman spectra of unsupported and SiO₂-supported H₄PMo₁₁VO₄₀ before the reaction. (a) Unsupported H₄PMo₁₁VO₄₀, SiO₂-supported H₄PMo₁₁VO₄₀ with (b) 3.3 mol%, (c) 1.4 mol%, and (d) 0.37 mol%, and (e) SiO₂.

Fig. 7. BN-TPD profiles of 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂. A mass spectrometer was utilized as the detector.
**Fig. 8.** Adsorbed amount of BN per catalyst weight on unsupported and SiO$_2$-supported H$_4$PMo$_{11}$VO$_{40}$.

**Fig. 9.** XRD patterns of unsupported H$_4$PMo$_{11}$VO$_{40}$ and SiO$_2$-supported H$_4$PMo$_{11}$VO$_{40}$ after the reaction for 5 h. (a) Unsupported H$_4$PMo$_{11}$VO$_{40}$ and SiO$_2$-supported H$_4$PMo$_{11}$VO$_{40}$ with loadings of (b) 3.3 mol%, (c) 1.4 mol%, and (d) 0.37 mol%. Reaction conditions: MAL:O$_2$:H$_2$O:N$_2$ = 3:6:15:76, temperature = 573 K, and total pressure = 0.1 MPa.

**Fig. 10.** Raman spectra of unsupported H$_4$PMo$_{11}$VO$_{40}$ and SiO$_2$-supported H$_4$PMo$_{11}$VO$_{40}$ after the catalytic reaction for 5 h. (a) Unsupported H$_4$PMo$_{11}$VO$_{40}$, and SiO$_2$-supported H$_4$PMo$_{11}$VO$_{40}$ with loadings of (b) 3.3 mol%, (c) 1.4 mol%, and (d) 0.37 mol%. Reaction conditions: MAL:O$_2$:H$_2$O:N$_2$ = 3:6:15:76, temperature = 573 K, and total pressure = 0.1 MPa.
**Fig. 11.** XRD patterns of (a) unsupported H₄PMo₁₁VO₄₀ and (b) 0.37mol% H₄PMo₁₁VO₄₀/SiO₂ after thermal treatment for 5 h. Conditions of thermal treatment: O₂:H₂O:N₂ = 6:15:76, temperature = 573 K, and total pressure = 0.1 MPa.

**Fig. 12.** XRD patterns of 1.4 mol% H₄PMo₁₁VO₄₀/SiO₂ after the reaction for 5 h at (a) 563 K, (b) 553 K, and (c) 523 K. Reaction conditions: MAL:O₂:H₂O:N₂ = 3:6:15:76, temperature = 573 K, and total pressure = 0.1 MPa, and $W/F^{-1} = 23 \text{ g-cat h mol-MAL}^{-1}$.

**Scheme 1**  Reaction pathway for the oxidation of MAL over H₄PMo₁₁VO₄₀ catalysts.

**Scheme 2**  Proposed reaction mechanism for the oxidation of MAL over unsupported H₃PMo₁₂O₄₀ [11,14,52].
Fig. 1  
Kanno et al.
Fig. 2
Kanno et al.
Fig. 3
Kanno et al.
Fig. 4

Kanno et al.
Fig. 5
Kanno et al.
Fig. 6
Kanno et al.
\[ m/e = 18 \text{ (H}_2\text{O)} \]
\[ m/e = 28 \text{ (CO)} \]
\[ m/e = 44 \text{ (CO}_2\text{)} \]
\[ m/e = 103 \text{ (Benzonitrile)} \]

Fig. 7
Kanno et al.
Fig. 8
Kanno et al.
Fig. 9
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Fig. 10
Kanno et al.
Fig. 11
Kanno et al.
Fig. 12
Kanno et al.
Scheme 1
Kanno et al.
Scheme 2
Kanno et al.