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The role of steam in selective oxidation of methacrolein over H3PM012O40

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Graphical abstract



Highlights

- Addition of steam to feed gas significantly enhanced activity and selectivity
- Three H_2O per one Keggin unit were absorbed into the bulk of $H_3PMo_{12}O_{40}$ in the

presence of steam

• Increase in pre-exponential factor for methacrylic acid formation with steam due

to smooth activation of methacrolein on H₃PMo₁₂O₄₀

Abstract

Role of steam in selective oxidation of methacrolein with molecular oxygen over $H_3PMo_{12}O_{40}$ catalyst was investigated. Addition of steam to feed gas significantly enhanced both catalytic activity and selectivity to methacrylic acid, which were fivefold and twice increases, respectively, under the optimal steam pressure ($P_{H20} = 0.13$ atm). Kinetic analysis demonstrated that the addition of steam caused 200-fold increase in the pre-exponential factor for the formation

of methacrylic acid, leading to the significant increase in the activity. The steam in the feed gas varied hydrous state of $H_3PMo_{12}O_{40}$ under the reaction conditions, while did not alter redox property, molecular and crystalline structures, and surface area of the catalyst. In the presence of steam at 573 K, three H_2O per one $H_3PMo_{12}O_{40}$ were absorbed and hydrated protons like $[H_3O]^+$ were formed in the bulk of $H_3PMo_{12}O_{40}$. Methacrolein was adsorbed on the surface of the hydrous catalyst, but not on anhydrous one at all. Based on the results, it was concluded that activation of methacrolein readily occurred on the catalyst in the presence of steam, leading to the significant increase in the pre–exponential factor. Quantum chemical calculation supported the smooth activation of methacrolein by the reaction with $[H_3O]^+$ without any transition state.

Keywords: methacrolein oxidation, steam addition, kinetic analysis, pre-exponential factor, methacrolein adsorption

1. Introduction

Polyoxometalate (POM) is a metal-oxygen cluster anion composed of metal-oxygen tetrahedron XO₄ and octahedron YO₆ as the structural building units, which are connected with sharing the corner, edge, and face. Keggin-type POM (Keggin–POM) has the composition of $[XY_{12}O_{40}]^{n-}$, in which the twelve octahedrons comprise four groups of three edge-shared octahedrons Y₃O₁₃ surrounding the central XO₄ tetrahedron. Keggin–POMs have attracted much

attention in applications as catalysts because of simple preparation procedure, high thermal stability, strong acidity, and high redox ability [1-10]. $[PMo_{12}O_{40}]^{3-}$ is one of the members in Keggin–POM family. $H_3PMo_{12}O_{40}$ as well as its salts is known to show excellent catalytic performance for selective oxidation of various compounds such as saturated [1] and unsaturated hydrocarbons [2], alcohols [1], and aldehydes [1, 2] due to high redox ability [10] in the form of homogeneous as well as heterogeneous catalyst.

Solid Keggin-POM is an ionic crystal composed of [XY₁₂O₄₀]^{#-} and cations. The structure of the polyanion itself, i.e. metal-oxygen cluster anion, in the solid Keggin-POM is called a primary structure. A secondary structure is the three-dimensional arrangement of polyanions, cations, and additional molecules like water of crystallization, forming a crystalline structure. An unique character of solid Keggin-POMs is that small polar molecules like water penetrate into the space between the polyanions, namely the molecules are absorbed into the bulk of the solid, when solid Keggin-POMs have small cations like H⁺ and Li⁺. In fact, water [11] and lower alcohols [12] are absorbed into the bulk of solid Keggin-POMs at room temperature and the number of absorbed molecules is more than 100 times larger than that calculated on the assumption that adsorption occurs only on the outer surface [12]. It is known that the absorption of polar small molecules affects catalytic performance of solid Keggin-POMs for reactions in

which those molecules participate as reactants [13–18], because the reaction occurs in the bulk as well as on the surface of the catalyst particle.

In addition to the aforementioned reactions, there is another type of reactions over solid-Keggin POMs that are enhanced by the presence of small polar molecules like water though those molecules are not found in chemical reaction formulae. An exemplary reaction is gas-phase oxidation of methacrolein (MAL) into methacrylic acid (MAA) over $H_3PMo_{12}O_{40}$ (eq. 1).

$$H + \frac{1}{2}O_2 \longrightarrow OH$$
 (eq. 1)

Misono et al. demonstrated that steam added in the feed gas accelerates the formation of MAA [19, 20]. In fact, both MAL consumption rate and selectivity to MAA were increased with steam [19, 20]. Based on the results of water vapor pressure-dependence and of transient response in cessation of steam as well as of O_2 supply, they proposed a reaction mechanism involving water as follows (Scheme 1) [19,20]: In the first step, 1,1-diol is formed by the reaction of MAL with water, which is promoted by Brønsted acids on $H_3PMo_{12}O_{40}$ and successively molybdate ester is formed. Finally, it transforms into MAA. In this mechanism, the formation of 1,1-diol is a key for the selective formation of MAA.

Another plausible role of steam is to suppress thermal decomposition of the catalyst (eq. 2), because the decomposition occurs at around the reaction temperature for MAL oxidation [21].

$$H_3PMo_{12}O_{40} \rightarrow 0.5P_2O_5 + 12MoO_3 + 1.5H_2O$$
 (eq. 2)

As mentioned above, solid Keggin-POM absorbs small polar molecules like water into its bulk at room temperature. Water absorbed in the bulk of H₃PMo₁₂O₄₀ form dimeric H₅O_{2⁺}, giving $[H_5O_2^+]_3[PMO_{12}O_{40}]^3 \cdot nH_2O$, under wet atmosphere at room temperature. Water in $[H_5O_2^+]_3[PMO_{12}O_{40}]^{3-}$ $\cdot nH_2O$ is released in a step-by-step manner with increase in temperature and anhydrous H₃PMo₁₂O₄₀ is formed at about 433 K under dry atmosphere [22]. Since the reaction temperature for MAL oxidation over H₃PMo₁₂O₄₀ is around 573 K, the catalyst must exist as an anhydrous form if steam is not present in the feed gas. However, steam is normally added to the feed gas to promote the reaction. Thus, H₃PMo₁₂O₄₀ could absorbs some water in its bulk under the reaction conditions and consequently hydrous state could have an impact on the catalytic performance as Misono et al. mentioned that steam may affect the state of the "pseudo-liquid phase" without any direct evidence [19]. However, there is no study on quantitative evaluation of the number of absorbed water in the presence of steam at high temperature and it is unclear how the absorbed water in the bulk participate in the reaction over $H_3PMo_{12}O_{40}$.

In the present study, to give a new insight into the role of steam in MAL oxidation over $H_3PMo_{12}O_{40}$, firstly we conducted kinetic study for the reaction and compared the kinetic parameters (apparent activation energy and pre–exponential factor) in the presence of steam to those in the absence of steam. In addition, the number of water absorbed in $H_3PMo_{12}O_{40}$ under the atmosphere with steam (wet conditions) was quantified at 573 K. Sorption amounts of MAL in dry and wet conditions were also evaluated. Finally, we propose a role of steam for the reaction based on the results of the kinetic study, absorption behavior of MAL under the wet conditions as well as the changes in the chemical and physical properties of the catalyst under the dry and wet conditions.

2. Experimental

2.1 Material

Hydrous 12–molybdophosphoric acid ($H_3PMo_{12}O_{40} \cdot nH_2O$) was supplied by Nippon Inorganic Colour and Chemical Co., Ltd. $H_3PMo_{12}O_{40} \cdot nH_2O$ was extracted from the aqueous solution of $H_3PMo_{12}O_{40}$ with diethyl ether. Finally, $H_3PMo_{12}O_{40} \cdot nH_2O$ was recrystallized in the aqueous solution, which was prepared with the extracted $H_3PMo_{12}O_{40} \cdot nH_2O$, and dried overnight at 333 K.

Impurities in MAL (Tokyo Chem. Ind. Co., Ltd.) were removed by extraction with water. The purified MAL was put in a freezer to remove water as ice and stored with a small amount of hydroquinone (Wako Pure Chem. Ind.).

2.2 Catalytic oxidation of methacrolein

Catalytic oxidation of MAL was performed in a continuous flow reactor at atmospheric pressure. After pretreatment of the catalyst at 593 K with a mixture of O₂ (0.11 atm), H₂O (0.18 atm), and N₂ (balance) at a total flow rate of 28 mL min⁻¹ for 1 h, the temperature was decreased to 573 K and the mixed gas of MAL (0.03 atm), O₂ (0.06 atm), H₂O (0.13 atm), and N₂ (balance) at a total flow rate of 72 mL min⁻¹ was fed into the reactor to start the catalytic reaction. The reaction products were analyzed by using on-line gas chromatographs. Acetic acid, MAL, and MAA were analyzed by a GC (Shimadzu GC-14B) equipped with a flame ionization detector and a capillary column (GL Sciences TC-FFAP, 0.25 mm, 50 m). For CO and CO₂, the other 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. To prevent interference from organic compounds to analysis with GC-TCD, the effluent gas at outlet of the reactor was passed through a dry-ice trap and then was analyzed by the GC. As an internal standard for GC analysis, CH₄ (31 vol.%) diluted with He was mixed at the outlet of the reactor.

The carbon balance was calculated with eq. 3 and was in the range of 97–103 % for whole the reactions.

Carbon balance (%) =
$$\frac{\text{Total formation rate of all products}}{\text{Feed rate of MAL}} \times 100$$
 (eq. 3)

Yield of and selectivity to each product were calculated based on carbon basis with the following equations.

Yield of MAA (%) =
$$\frac{\text{Formation rate of MAA}}{\text{Feed rate of MAL}} \times 100$$
 (eq. 4)

Yield of acetic acid (%) =
$$\frac{(\text{Formation rate of acetic acid}) \times 2}{\text{Feed rate of MAL}} \times 100$$
 (eq. 5)

Yield of
$$CO_{\chi}$$
 (%) = $\frac{(Formation rate of CO_{\chi}) \times 4}{Feed rate of MAL} \times 100$ (eq. 6)

Selectivity to MAA (%) =
$$\frac{\text{Formation rate of MAA}}{\text{Rate of MAL consumed}} \times 100$$
 (eq. 7)

Selectivity to acetic acid (%) =
$$\frac{(\text{Formation rate of acetic acid}) \times 2}{\text{Rate of MAL consumed}} \times 100$$
 (eq. 8)

Selectivity to
$$CO_{\chi}$$
 (%) = $\frac{(Formation rate of CO_{\chi}) \times 4}{Rate of MAL consumed} \times 100$ (eq. 9)

To observe transient response of the catalytic performance, the feed gas was promptly switched from one to another, while the reaction temperature and the total flow rate were kept constant.

2.3 Characterization

Specific surface area was estimated by the Brunauer–Emmett–Teller (BET) equation applied to adsorption isotherm of nitrogen, which was acquired on a Belsorp-28SA instrument (Bel Japan Inc.) at 77 K. Before measurement, the sample was evacuated at 473 K for 6 h.

Average valence of Mo in the catalyst bulk was determined by redox titration using KMnO₄ solution. At a predetermined time point during the catalytic reaction, the feed gas was switched to nitrogen and the catalyst was rapidly cooled to room temperature. A part of the obtained catalyst (0.30 g) was dissolved in deionized water (250 mL). To a part of the solution (75 mL), 10 mL of 47 % H₂SO₄ (Wako Pure Chem. Ind.) and 20 mL of deionized water were added. The solution was titrated with an aqueous solution of KMnO₄ (Wako Pure Chem. Ind., 5 mM). Mo⁵⁺ in the solution was reacted with MnO₄⁻ in an acidic aqueous solution in accordance with the following equation.

$$5Mo^{5+} + MnO_4^{-} + 8H^+ \rightarrow 5Mo^{6+} + Mn^{2+} + 4H_2O$$
 (eq. 10)

The average valence of Mo (Mo^{n+}) in the catalyst bulk was calculated by using the following equation;

$$Mo^{n+} = 6 - \frac{Amount of Mo^{5+} in the solution (redox titration)}{Total amount of Mo in the solution (ICP-AES)}$$
(eq. 11)

, in which the total amount of Mo in the solution was determined by ICP-AES analysis using a Shimadzu ICPE-9000 spectrometer.

Oxidation state of Mo on the catalyst surface was analyzed by X-ray photoelectron spectroscopy (XPS) using a ULVAC-PHI Quantera II (Al K α radiation). Binding energy was calibrated with respect to C 1s peak of a carbon tape at 284.6 eV. Thermogravimetric (TG) analysis of H₃PMo₁₂O₄₀·*n*H₂O was conducted under He flow on a Rigaku Thermo plus TG8120. Temperature of the sample was increased at a rate of 5 K min⁻¹.

Sorption of water was carried out in a continuous flow reactor (BEL-TPD, Bel Japan Inc.) equipped with a quadrupole mass spectrometer (ANELVA Co., M-QA100F). The catalyst (0.5 g) was pretreated in the reactor at 573 K under a flow of He containing steam ($P_{H20} = 0.13$ atm) at a total flow rate of 40 mL min⁻¹ for 1 h with monitoring the concentration of steam (m/e =18) at the outlet of the reactor by using the mass spectrometer. After the signal of m/e =18 became constant, the gas was switched to dry He. The signal intensity was decreased and finally became almost zero. A blank experiment with an empty reactor was conducted. The difference in the integrated intensities between with the catalyst and with the empty reactor corresponds to the amount of water sorbed in the catalyst under the conditions at $P_{H20} = 0.13$ atm and 573 K.

Sorption of MAL was carried out using the same apparatus as that for the water sorption experiment. The catalyst (0.5 g) was pretreated in the reactor at 573 K under a flow of He containing steam ($P_{H20} = 0.13$ atm) at a total flow rate of 40 mL min⁻¹ for 1 h and the temperature was decreased to 433K while flowing the gas. Then sorption of MAL was conducted at 433 K by injecting MAL at regular interval with monitoring the mass signals of m/e = 70 (MAL) and 18 (water). The reason for conducting the sorption experiment at 433 K was to prevent oxidation of MAL by the lattice oxygen of the catalyst. The pulse size of each MAL injection was 2.6 µmol and injections were continued up to 12 times. The sorption experiment with the catalyst pretreated under dry He at 573 K was also conducted as a comparison.

IR spectra were taken at 573 K under dry He or H₂O/He ($P_{H2O} = 0.13$ atm) on a FT/IR– 230 spectrometer (JASCO Co., Japan). The aqueous solution of H₃PMo₁₂O₄₀ was put on a Si wafer (2 cm in diameter). The solution on the wafer was dried up at 333 K and the resulting wafer was applied to IR measurement. An IR spectrum was measured at 573 K with a flow of dry He (15 mL min⁻¹). Then the flowing gas was switched to wet He and IR spectra were measured, while keeping the temperature at 573 K.

3. Results and Discussion

3.1 Catalytic performances in the absence and presence of steam

Figure 1 shows dependence of the catalytic performance of H₃PMo₁₂O₄₀ on the partial pressure of water vapor. Main products were MAA, acetic acid, and CO_x regardless of presence or absence of steam. Only little CO₂ was formed under the reaction conditions and thus CO was dominant. The reaction proceeded even in the absence of steam ($P_{H2O} = 0$ atm). However, the addition of steam to the feed gas greatly enhanced the reaction rates, which is consistent with the previous papers [19, 20]. The yields of every product increased with the increase in P_{H2O} , but degree of the improvement differed from one product to another. The improvement in the yield of MAA by steam was the most prominent of all the products. Thus, the selectivity to MAA increased with increase in P_{H2O} (Fig. 1(b)), and inversely those to acetic acid and CO_x decreased. Since selectivities became almost constant at $P_{H2O} = 0.13$ atm or more, we decided that $P_{H2O} = 0.13$ atm was the standard partial pressure of steam for following experiments.

As Fig. 1 clearly shows, the yield of acetic acid was almost the same as that of CO_x at any P_{H2O} including $P_{H2O} = 0$ atm. In addition, as will be described later, apparent activation energies for the formations of acetic acid and CO_x were the almost same each other for any P_{H2O} . These results suggest that one molecule of acetic acid was formed from one molecule of MAL accompanying with the formation of two molecules of CO_x . Thus, the reaction network starting from MAL is as that shown in Scheme 2.

We further investigated reaction kinetics in the presence and absence of steam for deeper understanding of the influence of steam on the reaction. In order to suppress the conversion of MAL to 20% or less, which corresponds to differential reaction conditions, catalyst weight to flow rate (W/F) were adjusted to 69 and 173 g_{-cat} h mol⁻¹ for the reactions in the presence and absence of steam, respectively. All the data were taken under the steady state conditions. We assumed that the reactions to form each product had a first-order dependence on the partial pressure of MAL. In addition, it can be assumed that the successive oxidations of MAA and acetic acid into CO_x were negligible since conversion of MAL was enough low. The first-order reaction rate constants for the formations of MAA, acetic acid, and CO_x were estimated from the yields at each reaction temperature. The natural logarithms of the rate constants were plotted against inverse of the reaction temperature, namely Arrhenius plot, in Fig. 2. From the slopes and intercepts of the approximation lines, apparent activation energies and pre-exponential factors were estimated (Table 1). For all the products, the apparent activation energies in the presence of steam were about 1.5 times larger than those in the absence of steam, suggesting that the reaction mechanism or the rate-determining step was different for the reactions in the absence and presence of steam. In addition, it should be noted that the addition of steam caused a substantial increase in the preexponential factors (A), e.g. A for MAA formation in the presence of steam was about two orders of magnitude greater than that in the absence of steam. The large pre-exponential factors led to

the substantial enhancement in the formation rates in the presence of steam. The increases in the pre–exponential factors with steam suggest that i) sticking probability of MAL on the surface of $H_3PMo_{12}O_{40}$, that is, probability of the effective collision of MAL with the surface, was increased or ii) the number of active sites on the catalyst was increased. Those will be discussed later in detail.

3.2 Effect of steam on redox property of the catalyst

It is reported that the selective oxidation of MAL over $H_3PMo_{12}O_{40}$ proceeds with Mars– Van Krevelen mechanism, in which lattice oxygen of the catalyst oxidizes MAL [19, 20]. It is possible that the amount of lattice oxygen in the catalyst involved in the redox cycle was increased by steam, thereby the catalytic activity was increased. In order to test this hypothesis, the reaction was carried out without any supply of O₂ to estimate the amounts of lattice oxygen being able to participate in MAL oxidation. The amount of those lattice oxygen was estimated from the total amount of products formed after the stop of O₂ supply. After the reaction reached near steady state under the reaction conditions, supply of O₂ to the reactor was stopped while the supply of MAL was continued. The results are shown in Fig. 3, where the reactions were conducted in the different *W/F* in the presence and absence of steam, being *W/F*= 173 and 345 g h mol⁻¹, respectively, to obtain similar conversions. As Fig. 3 clearly demonstrates, the reactions continued even after the

stop of O_2 supply even in the absence of steam, indicating that the reaction in the absence of steam proceeds with Mars–Van Krevelen mechanism as that in the presence of steam. The main products were MAA, acetic acid and CO_x even after the stop of O_2 supply. The yields gradually decreased with time and the reaction was completely stopped at 200 ~ 300 min after the stop of O_2 supply. For the reaction in the presence of steam, 2.1×10^{-4} , 1.2×10^{-4} , and 2.0×10^{-4} mol of MAA, acetic acid, and CO_x , respectively, were formed after the stop of O_2 supply. Assuming that MAA, acetic acid, and CO_x (mainly CO) were formed according to eqs. 12, 13, and 14, respectively, the number of oxygen atoms necessary for their formations can be calculated and the sum of them was 7.2×10^{-4} mol g⁻¹, which corresponds to $1.4 O_{lattice}$ per one Keggin unit. Misono et al. reported that the about two lattice oxygens per one Keggin unit of H₃PMo₁₂O₄₀ were consumed for the MAL oxidation after the stop of O₂ supply [19, 20], which was about the same number in the present study.

$$C_4H_6O + [O] \rightarrow C_4H_6O_2 \qquad (eq. 12)$$

$$C_4H_6O + 4[O] \rightarrow C_2H_4O_2 + 2CO + H_2O \qquad (eq. 13)$$

$$\text{CO} + [\text{O}] \rightarrow \text{CO}_2$$
 (eq. 14)

[O]: lattice oxygen (Olattice)

For the reaction in the absence of steam, the lattice oxygen involved in the reaction was $1.3 \text{ O}_{\text{lattice}}$ per one Keggin unit, which is almost the same as that in the presence of steam. In addition, there was no difference in the average valence of Mo after the reaction, which was Mo^{5.8+} regardless of the presence and absence of steam. Based on these results, it was concluded that the addition of steam did not alter the redox property of H₃PMo₁₂O₄₀.

3.3 Reversibility of effect of steam on the catalytic performance

Fig. 4 shows the transient response in the catalytic performance for the MAL oxidation over H₃PMo₁₂O₄₀. In the initial 400 min, the reaction was conducted at $P_{H20} = 0$ atm and then the feed gas was switched to that with $P_{H20} = 0.13$ atm. After the switching, the yield of MAA was gradually increased with time and reached a steady state after 60 min of the switching. As mentioned in the introduction, Misono et al. proposed that MAL is hydrated to produce 1,1–diol, which is an intermediate, with the aid of Brønsted acids in the presence of steam. If the production of 1,1-diol is the sole role of steam, the reaction must reach the steady state immediately after the switching the feed gas. In fact, however, about 60 min was necessary to reach the steady state, indicating that the influence of steam was related to somewhat slow process. After the reaction reached steady state at $P_{H20} = 0.13$ atm, the feed gas was switched back to that without steam ($P_{H20} = 0$ atm) at 760 min, whereupon the yield of MAA decreased to almost the same value as

original one at $P_{\text{H2O}} = 0$ atm. We also conducted the experiment in the reverse order of the feed gas ($P_{\text{H2O}} = 0.13$ atm $\rightarrow 0$ atm $\rightarrow 0.13$ atm), the latter yield of MAA at $P_{\text{H2O}} = 0.13$ atm was almost the same as the initial one (Fig. S1). These results clearly indicate that the influence of steam was reversible phenomenon.

To investigate the changes in the catalyst structure during the transient response experiments, the reaction was quenched in the middle of the reactions under the same reaction conditions shown in Figs. 4 and S1, and then the catalysts were analyzed by using IR (Fig. S2), powder XRD (Fig. S3), nitrogen adsorption (Table S1), redox titration (Table S1), and XPS (Fig. S4). However, little difference was found between the fresh catalyst and the spent ones taken in the middle of the reaction runs. Hence, the large difference in the catalytic data between in the presence and absence of steam was impossible to be rationalized by the structural changes in the catalyst. Therefore, dynamic (reversible) change in the catalyst structure occurring in the presence of steam brought about the enhancement in the catalytic performance with steam.

3.4 Hydration of $H_3PMo_{12}O_{40}$ under the reaction conditions

Figure 5 shows TG profile of hydrous $H_3PMo_{12}O_{40} \cdot nH_2O$ used in this study in dry He. The number of water was 12 (= *n* in $H_3PMo_{12}O_{40} \cdot nH_2O$) at room temperature, and a part of water was released at around 323 K to turn to be *n* = 8, and finally anhydrous $H_3PMo_{12}O_{40}$ was formed

at around 423 K. According to the TG profile, the catalyst must exist as anhydrous $H_3PMo_{12}O_{40}$ under dry atmosphere at the reaction temperature (573 K) of the MAL oxidation. However, since anhydrous $H_3PMo_{12}O_{40}$ reversibly returned back to hydrous $H_3PMo_{12}O_{40} \cdot nH_2O$ if it was put under wet atmosphere at room temperature (Fig. S5), it is presumable that the catalyst has a certain number of water of crystallization at the reaction temperature if the feed gas contains steam.

Thus, we determined the amount of water contained in H₃PMo₁₂O₄₀ at 573 K and $P_{H2O} =$ 0.13 atm with the procedure described in the section 2.3 and the result is shown in Fig. 6. For the blank test with an empty reactor, the signal intensity due to H₂O (*m/e* = 18) immediately decreased to the baseline level after switching the gas from wet He ($P_{H2O} = 0.13$ atm) to dry one. On the other hand, when the catalyst was present in the reactor, H₂O had continued to desorb till about 10 min after switching to dry He. The total amount of H₂O desorbed from the catalyst was 1.4 mmol g⁻¹, which corresponds to H₃PMo₁₂O₄₀·3H₂O. This is the first report to demonstrate that H₃PMo₁₂O₄₀ contains a certain amount of water in the bulk of Keggin-POM at high temperature under wet atmosphere.

It was also confirmed from IR spectra that $H_3PMo_{12}O_{40}$ was present as a hydrous form at 573 K in the presence of steam ($P_{H2O} = 0.13$ atm). Fig. 7 shows the IR spectrum of $H_3PMo_{12}O_{40}$ at 573 K under dry He, and those after switching the flowing gas to wet He ($P_{H2O} = 0.13$ atm) while keeping the temperature at 573 K. Under dry He (0 min in Fig. 7), the absorption band at

3250 cm⁻¹ due to O–H stretching vibration in H₃PMo₁₂O₄₀ and those at 794 cm⁻¹ (ν Mo–O–Mo), 883 cm⁻¹ (v Mo–O–Mo), 982 cm⁻¹ (v Mo=O), and 1063 cm⁻¹ (v P–O) due to framework vibrations of [PMo₁₂O₄₀]³⁻ were observed, which are consistent with a previous report [23]. After switching the flowing gas to wet He, the broad absorption band at 3300 - 3400 cm⁻¹ assignable to O-Hstretching vibration of H₂O [24, 25] became intense with time (5-30 min in Fig. 7). In addition, slight change in the framework vibrations was also observed after the gas switching, supporting that the catalyst was hydrated at 573 K in the presence of steam. It is noted that the change in the IR spectra was nearly completed in 30 min after the gas switching. This time length was almost the same as that to reach a steady state in the transient response for the MAL oxidation shown in Fig. 3. Those analogous behavior for time strongly suggested that hydration of H₃PMo₁₂O₄₀ under the reaction conditions was responsible for the high catalytic performance in the presence of steam. We speculated that three H_2O were coordinated to each of the three H^+ to form monomeric $[H_3O]^+$, or dimeric [H₂O---H---OH₂]⁺, though still under investigation on how water is present in H₃PMo₁₂O₄₀·nH₂O (n = 3) under the reaction conditions with steam.

3.5 Effect of steam on adsorption property for methacrolein

The hydration of $H_3PMo_{12}O_{40}$ had a large impact on adsorption of MAL on the catalyst. We compared the adsorption amounts of MAL at 433 K for anhydrous ($H_3PMo_{12}O_{40}$) and hydrous

(H₃PMo₁₂O₄₀·3H₂O) catalysts by a pulse method. The results are shown in Fig. 8. On the hydrous catalyst, MAL was adsorbed up to 7 pulses without any ejection of water from the catalyst. The total amount of adsorbed MAL was 10.4 μ mol g⁻¹, corresponding to 0.019 MAL per one Keggin unit in the bulk. The powder XRD pattern of the catalyst after the experiment showed no change in the lattice constant. The surface area of the catalyst estimated from nitrogen adsorption isotherm was 10 m² g⁻¹. Since one Keggin unit occupies about 1.44 nm² [26], the number of H₃PMo₁₂O₄₀ exposed on the surface was calculated to be 12 µmol g⁻¹. This value was almost the same as the adsorption amount of MAL estimated by the pulse experiment. Based on these results, it is concluded that MAL adsorbed only on the outer surface of the catalyst particle but was not absorbed in the bulk. In contrast to the hydrous catalyst, anhydrous H₃PMo₁₂O₄₀ did not adsorb MAL at all (Fig. 8b).

3.6 Role of steam in the oxidation of methacrolein over H₃PMo₁₂O₄₀

Based on the results mentioned above, we propose a mechanism for the enhancement in the MAA formation over $H_3PMo_{12}O_{40}$ by steam as follows (Scheme 3). Under the reaction conditions in the presence of steam, three H_2O per one $H_3PMo_{12}O_{40}$ is absorbed into the bulk of $H_3PMo_{12}O_{40}$ to form hydrated proton like monomeric $[H_3O]^+$ (**A** in Scheme 3). MAL is activated by the hydrated proton (**B**), forming 1,1–diol on the surface (**C**). Then, it is oxidized with the

lattice oxygen of $H_3PMo_{12}O_{40}$ to produce MAA and consequently hydrated proton is regenerated (**D**). Finally, the reduced catalyst is re-oxidized with gas phase O_2 to complete the catalyst cycle. As the MAL adsorption experiment demonstrated, adsorption of MAL on the surface, which may form 1,1–diol, proceeds smoothly in the presence of steam, leading to the significant increase in the pre–exponential factor. Quantum chemical calculation suggests that the activation of MAL through the reaction with $[H_3O]^+$ proceeds without any high energy state (Fig. S6), supporting the mechanism proposed above.

Conversely, in the absence of steam, the intermediates of \mathbf{B} and \mathbf{C} do not form on the catalyst and thus the lattice oxygen would directly oxidize MAL. It is plausible that this direct oxidation is hard to occur comparing with the activation of MAL on the hydrated catalyst in the presence of steam. Thus pre–exponential factor was low and non–selective oxidation occurred in the absence of steam.

In selective oxidation of acrolein to acrylic acid over Mo-V-W-O_x catalyst, it is proposed that steam promote to hydrolyze acrylic acid ester (M–O(C=O)C₂H₃) on the catalyst surface to give acrylic acid accompanying with the regeneration of surface hydroxyl group (Scheme 4) [27]. If the MAL oxidation over H₃PMo₁₂O₄₀ proceeds with the same reaction mechanism as the oxidation of acrolein, formation of MAA is promoted with steam by hydrolysis of methacrylic acid ester on the surface, that is, desorption of MAA from the surface is facilitated

with steam. Such smooth desorption of product MAA may lower the chance for overoxidation of the surface species due to less prolonged stay on the catalyst, while it is still unknow how acetic acid and CO_x are formed. Consequently, steam promotes the MAA formation much more than those of acetic acid and CO_x , leading to the improved selectivity for MAA formation in the presence of steam.

4. Conclusion

Addition of steam with optimal partial pressure ($P_{H2O} = 0.13$ atm) to the feed gas led to fivefold and twice increases in the yield of and selectivity to MAA, respectively. Kinetic analysis demonstrated that the addition of steam brought about 200-fold increase in the pre-exponential factor for MAA formation, leading to the significant increase in the formation rate of MAA. The steam in the feed gas varied hydrous state of H₃PMo₁₂O₄₀ under the reaction conditions, while did not alter the redox property, molecular and crystalline structures, and surface area of the catalyst. In the presence of steam at 573 K, three H₂O per one H₃PMo₁₂O₄₀ were absorbed into the bulk of the catalyst to form hydrated proton like [H₃O]⁺. On the hydrous catalyst, activation of methacrolein readily occurred with a formation of 1,1-diol on the surface. The promotion of the MAL activation was the reason for the significant increase in the pre–exponential factor and consequently improvement in the catalytic performance in the presence of steam.

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Table 1 Apparent activation energies and pre-exponential factors estimated from Arrhenius plots

in the presence or absence of steam.

	$E^{a}/kJ mol^{-1}$		A ^b / h ⁻¹	
Product	P _{H2O} /atm		P _{H2O} /atm	
	0.13	0.00	0.13	0.00
MAA ^c	86	64	3.4×10 ⁴	1.4×10 ²
Acetic acid	170	120	1.1×10 ¹²	6.5×10 ⁶
CO _x	160	120	1.2×10 ¹¹	1.6×10 ⁷

^a Apparent activation energy

^b Pre-exponential factor

^c Methacrylic acid



Scheme 1 Reaction mechanism involving water proposed in [19, 20].



Scheme 2 Possible reaction routes in the oxidation of methacrolein (MAL) over $H_3PMo_{12}O_{40}$



Scheme 3 Proposed reaction mechanism for selective oxidation of methacrolein over $H_3PMo_{12}O_{40}$

in the presence of steam.



Scheme 4 A proposed role of steam for selective oxidation of acrolein over Mo-V-W-O_x catalyst

[27].



Figure 1 Influence of steam on (a) yields and (b) selectivities for the oxidation of methacrolein over H₃PMo₁₂O₄₀. (\bullet) Methacrylic acid, (\triangle) acetic acid, and (\Box) CO_x. Reaction conditions: catalyst weight; 0.4 g, methacrolein:O₂:H₂O:N₂ = 0.03:0.06:0–0.15:balance; total flow rate; 72 mL min⁻¹, total pressure, atmospheric pressure; and temperature, 573 K. Data were taken after at least 3 h from the beginning of the reaction.



Figure 2 Arrhenius plots for the oxidation of methacrolein over $H_3PMo_{12}O_{40}$ in the presence of (closed symbol) and absence of steam (open symbol). (\bullet , \bigcirc) Methacrylic acid, (\blacktriangle , \triangle) acetic acid, and (\blacksquare , \Box) CO_x. Reaction conditions: methacrolein:O₂:H₂O:N₂ = 0.03:0.06:0.13:balance and 0.03:0.06:0:balance for the reactions in the presence and absence of steam, respectively; total pressure, atmospheric pressure; and temperature, 563, 573, and 583 K.



Figure 3 Transient response for the oxidation of methacrolein over $H_3PMo_{12}O_{40}$ (left) in the presence of ($P_{H20} = 0.13$ atm) and (right) absence of steam by changing the feed gas from (**A**) in the presence of to (**B**) in the absence of O₂ at 400 and 580 min, respectively. (\bigcirc) Methacrylic acid, (\triangle) acetic acid, and (\square) CO_x. Reaction conditions: methacrolein:O₂:H₂O:N₂ = (**A**(a)) 0.03:0.06:0.13:balance, (**B**(a)) 0.03:0:0.13:balance, (**A**(b)) 0.03:0.06:0:balance, and (**B**(b)) 0.03:0:0:balance. Total flow rate; 72 mL min⁻¹, total pressure, atmospheric pressure; temperature, 573 K; and catalyst weight; (left) 1.0 g and (right) 2.0 g.



Figure 4 Transient response for the oxidation of methacrolein over $H_3PMo_{12}O_{40}$ with changing the feed gas from (**A**) in the absence of to (**B**) in the presence of steam at 400 min and subsequently from (**B**) to (**A**) at 760 min. (**•**) Methacrylic acid, (\triangle) acetic acid, and (\Box) CO_x. Reaction conditions: catalyst weight; 0.4 g, methacrolein:O₂:H₂O:N₂ = (**A**) 0.03:0.06:0:balance and (**B**) 0.03:0.06:0.13:balance; total flow rate; 72 mL min⁻¹, total pressure, atmospheric pressure; and temperature, 573 K.



Figure 5 TG curve of $H_3PMo_{12}O_{40} \cdot nH_2O$ in dry He.



Figure 6 Time courses of concentration of water vapor in the gas phase at the outlet of the column filled with (—) H₃PMo₁₂O₄₀ and (---) without catalyst (blank experiment). The gas fed to the column was switched from wet He ($P_{H2O} = 0.13$ atm) to dry one ($P_{H2O} = 0$ atm) at 3 min. Experimental conditions: weight of H₃PMo₁₂O₄₀, 0.5 g; temperature, 573 K; total flow rate, 40 mL min⁻¹; and total pressure, atmospheric pressure.



Figure 7 IR spectrum of $H_3PMo_{12}O_{40}$ under dry He (0 min) and those after switching the flowing gas to wet He ($P_{H2O} = 0.13$ atm). All spectra were measured at 573 K. Experimental conditions: weight of $H_3PMo_{12}O_{40}$, 7 mg; temperature, 573 K; total flow rate of He, 15 mL min⁻⁻¹; and total pressure, atmospheric pressure.



Figure 8 Sorption of methacrolein for $H_3PMo_{12}O_{40}$ at 433 K by intermittent injection of methacrolein in (a) the presence of ($P_{H2O} = 0.13$ atm) and (b) the absence of steam. $H_3PMo_{12}O_{40}$ was pretreated under wet He ($P_{H2O} = 0.13$ atm) at 573K for 1 h. For the experiment (b), the catalyst was further treated at 573 K under dry He for 6 h to remove water sorbed on/in $H_3PMo_{12}O_{40}$. Conditions: pulse size, 2.6 µmol methacrolein; weight of $H_3PMo_{12}O_{40}$, 0.5 g; temperature, 433 K; flow gas, (a) H_2O :He = 0.13:0.87 and (b) only He; total flow rate, 40 mL min⁻¹; and total pressure,

atmospheric pressure.