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Elucidating the role of H₂O in promoting the formation of methacrylic acid during the oxidation of methacrolein over heteropolyacid compounds

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Abstract:

The involvement of water in the selective oxidation of MAL to MAA over a pure Keggin-type H₃PMoO₁₂O₄₀ catalyst was investigated using an *in-situ* DRIFTS reactor coupled with a mass spectrometer for the first time to elucidate the reaction pathway associated with water. By comparing the spectra and activity data using D₂O instead of H₂O during transient switching experiments has allowed us to evaluate the possible active sites where D₂O is activated. It has been found that, during the cycling switches of D₂O in and out of MAL+O₂ gas feed at 320 °C, the formation of MAA-OD product is increased and decreased when D₂O is added and removed, respectively. This suggests that the deuterium from D₂O is involved in the production of gas phase MAA-OD. In addition, the *in-situ* DRIFTS-MS results obtained from the isotopic switches between D₂O and H₂O reveal changes in the characteristic infrared bands of Keggin unit between 1200 and 600 cm⁻¹. It is found that the isotopic exchange possibly occurs on the bridging oxygen of Mo–O–Mo unit, where water is activated for the formation of MAA. Based on the *in-situ* DRIFTS-MS analysis from the transient switching experiments, the reaction mechanism associated with the effect of water on the selective oxidation of MAL to MAA over Keggin-type H₃PMoO₁₂O₄₀ catalyst is proposed.

Keywords:

Methacrolein, Methacrylic acid, Heteropolyacid, *in-situ* DRIFTS-MS, Selective oxidation, Isotopic switches, Keggin unit, H₃PMo₁₂O₄₀

1. Introduction

Heteropolyacids (HPAs) used as oxidation catalysts have been extensively investigated for many decades [1-22] due to their acid and redox properties, high thermal stability, simple preparation procedure and simple physical property modification such as solubility and surface areas [23-34]. In general, the clusters of HPAs are made up by metal-oxygen anions with different molecular sizes, compositions, and structures [1]. One of the HPAs that has been received much attention is the Keggin-type structure with the formula of [XM₁₂O₄₀]ⁿ⁻,

typically composed of a central XO₄ tetrahedral unit surrounded by twelve octahedrons of MO₆ units, linked by corner- and edge-sharing oxygen atoms. [PMo₁₂O₄₀]³⁻ is one of the Keggin-type HPA family. H₃PMo₁₂O₄₀ and its salts have been reported to show excellent catalytic oxidation of various types of hydrocarbons in heterogeneous system [1-22].

The selective oxidation of methacrolein (MAL) to methacrylic acid (MAA) over Keggin-type H₃PMo₁₂O₄₀ (HPMo) compounds has also been extensively studied [1, 2, 8-11, 22], since MAA is an important chemical in the production of methyl methacrylate and materials including polymers. Yet, the reaction mechanism of MAL oxidation to MAA is not fully understood, especially in the presence of water and there have only been a few reaction schemes proposed [2, 12, 19, 22, 35].

Misono et al. [3] also showed that both the MAL consumption rate and selectivity to MAA were increased with the addition of water in the reaction feed and proposed a reaction mechanism associated with water, in which the interaction of MAL and H₂O was promoted by the Brønsted acid sites of H₃PMo₁₂O₄₀. Subsequently, the molybdate ester was formed and finally transformed into MAA.

Recently, Yasuda and co-workers [22] investigated the role of water in the selective oxidation of MAL to MAA over H₃PMo₁₂O₄₀ compound and how the absorbed water in the bulk participates in this particular reaction. It was reported [22] that, under MAL+O₂ reaction with water, three H₂O molecules per one H₃PMo₁₂O₄₀ unit was absorbed into the bulk of H₃PMo₁₂O₄₀ compound to form hydrated proton like monomeric [H₃O]⁺. MAL was then activated by the hydrated proton and the reaction then formed the MAA product. However, it is not yet fully understood where water is activated on Keggin-type H₃PMo₁₂O₄₀ catalyst nor whether the hydrogen atoms in the water play important role in forming the gas phase MAA.

In the present work, the effect of H₂O on the selective oxidation of MAL to MAA over Keggin-type H₃PMo₁₂O₄₀ catalysts has been investigated using the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectrometry (MS). The transient switching experiments using D₂O and/or H₂O have been designed and performed to gain an insight into the reaction mechanism of MAL+O₂ to MAA in the presence of water and to investigate the active sites where water is activated to promote the formation of gas phase MAA product.

2. Experimental

In this study, H₃PMo₁₂O₄₀ (HPMo) catalyst was received from Mitsubishi Chemical Corporation. The catalyst was formed from hydrous 12-molybdophosphoric acid (H₃PMo₁₂O₄₀.xH₂O, Nippon Inorganic Colour and Chemical Co., Ltd.), extracted from an aqueous solution of H₃PMo₁₂O₄₀ and diethyl ether. The H₃PMo₁₂O₄₀.xH₂O was then recrystallised from an aqueous solution and the solid dried at 60 °C overnight [22].

Typically, *in situ* DRIFTS measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N₂-cooled detector. Approximately 40 mg of

H₃PMo₁₂O₄₀ (as received) sample was placed in a ceramic crucible in an *in situ* DRIFTS cell. The exit lines were connected to a Hiden Analytical HPR20 mass spectrometer in order to monitor the gas phase species: H₂O and D₂O ($m/z = 18$), MAL ($m/z = 70$), MAA-OH ($m/z = 86$) and MAA-OD ($m/z = 87$).

Prior to the DRIFTS experiments, the catalyst was pre-treated by heating in Ar at a total flow rate of 50 cm³ min⁻¹ ramping the temperature to 320 °C at a rate of 10 C min⁻¹. Once at temperature the catalyst was held for 60 min. Subsequently, the IR spectrum of treated HPMo catalyst was taken as a background. This procedure was also carried out with KBr powder, in which KBr background was taken and used to recalculate the recorded DRIFTS spectra for further analysis.

The reactant gases used were MAL (95%, Sigma-Aldrich), D₂O (99.99%, Sigma-Aldrich), O₂ (99.99% BOC), Ar (99.99% BOC). O₂ and Ar were fed from independent Aera™ PC-7700C mass flow controllers. MAL and water vapour were introduced to the system by means of separate saturators with Ar as the carrier gas. The MAL saturator was placed in an ice/water bath and the temperature of both H₂O and D₂O saturators was controlled by Grant™ GD120 thermostatic baths. All the lines following the water and MAL saturators were trace heated to prevent condensation. The concentrations of the reactants used were 2 vol% MAL, 4 vol% O₂, 4.0% H₂O (or D₂O), and Ar balance. The total flow rate was 50 cm³ min⁻¹. Gas flows were carefully equilibrated using micrometric needle valves to adjust the pressure between the gas flows on each side of the four-way valve with a high-sensitivity differential pressure detector. This avoided the production of spikes on the MS signal when switching from one mixture to another.

Three different sets of transient switching experiments were performed. The first set of experiments was designed to investigate the promotional effect of D₂O on the surface and gas phase species during the MAL oxidation to MAA. After Ar pre-treatment, the HPMo catalyst was exposed to MAL+O₂ gas feed for 10 min at 320 °C before the cycling switches of D₂O into and out of the MAL+O₂ feed was performed (Figure S1).

The second set of experiments was carried out to study the effect of pre-adsorbing D₂O and the exchange of crystalline water present in the HPMo catalyst. At 320 °C, the catalyst was initially pre-treated under Ar flow and then exposed to the 4 vol% D₂O for 60 min. This allowed the exchange between crystalline H₂O and gas phase D₂O to occur. Thereafter, the HPMo catalyst was purged under Ar flow for 30 min to remove excess gaseous D₂O from the DRIFTS cell before replacing Ar with MAL+O₂ gas feed (Figure S2).

In the final set of experiments (Figure S3), isotopic switches between D₂O and H₂O in and out of MAL+O₂ gas mixture were performed at 320 °C to investigate the involvement of proton in water on the reaction by monitoring the changes of gaseous MAA formation over the HPMo catalyst.

In all cases, the *in-situ* DRIFT spectra were recorded with a resolution of 4 cm⁻¹ and with an accumulation of 128 scans every 60 s and the DRIFTS spectra were analysed by

OPUS software. The IR data are reported as $\log 1/R$ (“absorbance”), with $R = I/I_0$, where R is the sample reflectance, I is the intensity measured under reaction conditions, and I_0 is the intensity measured on the pure HPMo sample or KBr powder under a flow of argon at 320 °C. All *in-situ* DRIFTS spectra presented were measured against the KBr background. It is worth noting that KBr powder was not mixed with HPMo catalyst for the transient *in-situ* DRIFTS-MS measurements.

3. Results and Discussion

3.1 Assignment of IR bands

In the current study, the focus of the DRIFTS study has been on the assignment and changes which occur in the IR fingerprint region of the Keggin-type HPMo catalyst due to the rapid accumulation of large number of surface species, many of which are likely to be spectators. This is shown in Figure S4 which illustrates the typical *in situ* DRIFTS spectra obtained under MAL oxidation over HPMo catalyst in the presence of D₂O at 320 °C. It is clear that there are four distinctive IR regions: (1) the stretching vibration of $-\text{CH}_x$ of hydrocarbons (2700 – 3100 cm^{-1}), (2) the stretching vibration of CO₂ and D₂O (2600 – 2100 cm^{-1}), (3) the stretching vibration of $-\text{C}=\text{O}$ and $-\text{C}=\text{C}-$ functional groups of MAL and MAA (1800 – 1600 cm^{-1}), and (4) fingerprint region of Keggin unit of HPMo catalyst (1200 – 600 cm^{-1}).

Despite the complexity with the accumulation of surface derived HC species and the broad features of IR bands above 1400 cm^{-1} , it is possible to obtain the IR features for the Keggin structure of the HPMo catalyst. The primary structure (see Figure S5) of 12-molybdicphosphoric acid (H₃PMo₁₂O₄₀) containing the Keggin anions can be measured by the infrared in the fingerprint region of 1200 – 600 cm^{-1} , which also includes the interaction of Keggin anions with crystalline water [36].

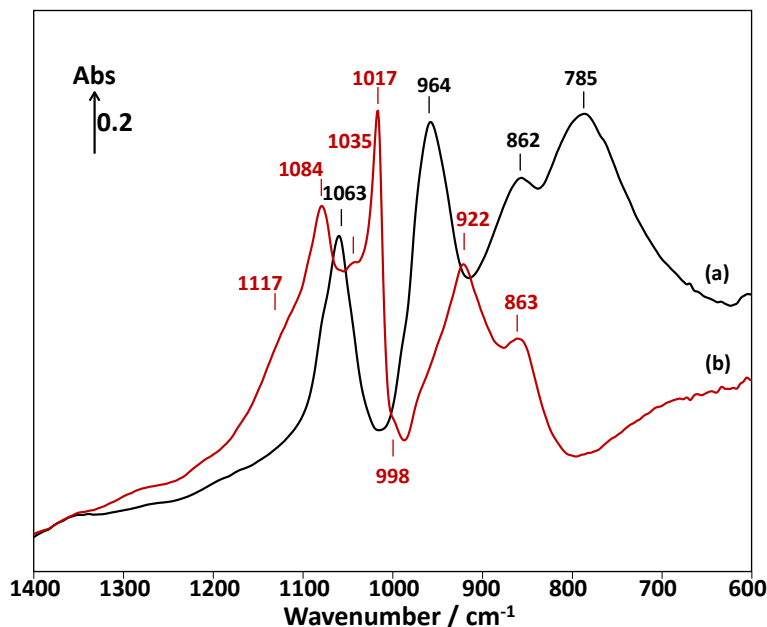


Figure 1 Comparison of *in-situ* DRIFT spectra recorded against KBr background under Ar flow at 320 °C for KBr-diluted (a) and pure (b) H₃PMo₁₂O₄₀ samples.

Figure 1 shows the comparison of *in-situ* DRIFTS spectra calculated against the KBr background and measured under Ar flow at 320 °C. It is evident that there are significant differences in IR band positions and shapes between KBr-mixed HPMo and pure samples. As for KBr-diluted HPMo sample (Figure 1a), it has been widely reported [6, 9-11, 15, 18-22, 33] that there are four distinctive IR bands at 1065-1060, 980-960, 885-860, and 790-780 cm⁻¹, which are assigned to $\nu_{\text{as}}(\text{P}-\text{O}_{\text{p}})$, $\nu_{\text{as}}(\text{Mo}=\text{O}_{\text{t}})$, $\nu_{\text{as}}(\text{Mo}-\text{O}_{\text{c}}-\text{Mo})$, and $\nu_{\text{as}}(\text{Mo}-\text{O}_{\text{e}}-\text{Mo})$, respectively [6, 9-11, 15, 18-22, 33]. However, the DRIFT spectra of pure HPMo (without KBr) show substantial shifts to higher wavenumber and additional IR bands are observed. As shown in Figure 1b in comparison with that of the KBr-diluted HPMo sample, the stretching vibrational bands associated with $\nu_{\text{as}}(\text{P}-\text{O}_{\text{p}})$, $\nu_{\text{as}}(\text{Mo}=\text{O}_{\text{t}})$, $\nu_{\text{as}}(\text{Mo}-\text{O}_{\text{c}}-\text{Mo})$, and $\nu_{\text{as}}(\text{Mo}-\text{O}_{\text{e}}-\text{Mo})$ modes is shifted and split. Herring and McCormick [36] reported detailed *in-situ* DRIFTS study on various Keggin-type H₃PW₁₂O₄₀ (HPW) compounds with and without diluting with KBr. It has been shown that the dilution of HPW with KBr results in the exchange of K ions causing the shift of IR bands [36]. In the current work, the DRIFT spectrum of KBr-diluted HPMo (Figure 1a) is consistent with the report by Herring and McCormick [36] as well as other studies [6, 9-11, 15, 18-22, 33]. Interestingly, it has also been reported [36] that the level of crystalline water in HPW samples also has a significant influence on the Keggin unit. To the best of our knowledge, there are no assignments of *in-situ* DRIFT spectra of pure H₃PMo₁₂O₄₀ (without diluting with KBr). Therefore, the assignment of the *in-situ* DRIFT spectra (Figure 1b) is based on the study reported by Herring and McCormick [36] and the observation during the transient experiments. The broad IR band at 1084 cm⁻¹ is assigned to the stretching vibration of $\nu_{\text{as}}(\text{P}-\text{O}_{\text{p}})$ of PO₄ tetrahedron. The peak at 1017 cm⁻¹ is tentatively assigned to unbound $\nu_{\text{as}}(\text{Mo}=\text{O}_{\text{t}})$ species

since this appears as a sharp feature similar to that of KBr-diluted HPMo sample. There are two IR bands at 1035 cm⁻¹ (strong) and 998 cm⁻¹ (weak) which are thought to be associated with hydrogen-bonded species which is consistent with the changes observed on switching from H₂O to D₂O *vide infra*. Therefore, the two IR bands at 1035 and 998 cm⁻¹ are tentatively assigned to the stretching vibration of ν_{as}(MoO_tH) species. Additionally, there are two types of oxygen atoms which bridge between two Mo₃O₁₃ units. One is located at the corner-sharing bridge which is denoted as Mo–O_c–Mo and is assigned to the feature at 922 cm⁻¹ due to its stretching vibration mode [36]. Another is located at the edge-sharing bridge position with the band appearing at 863 cm⁻¹, attributed to the stretching vibration of ν_{as}(Mo–O_e–Mo) [36].

3.2 D₂O transient switches

Figure 2 shows the effect of D₂O addition on the MAL+O₂ reaction at 320 °C. The evolution of MAA-OH and MAA-OD formation is clearly observed during the switches of D₂O in and out of MAL+O₂ gas feed.

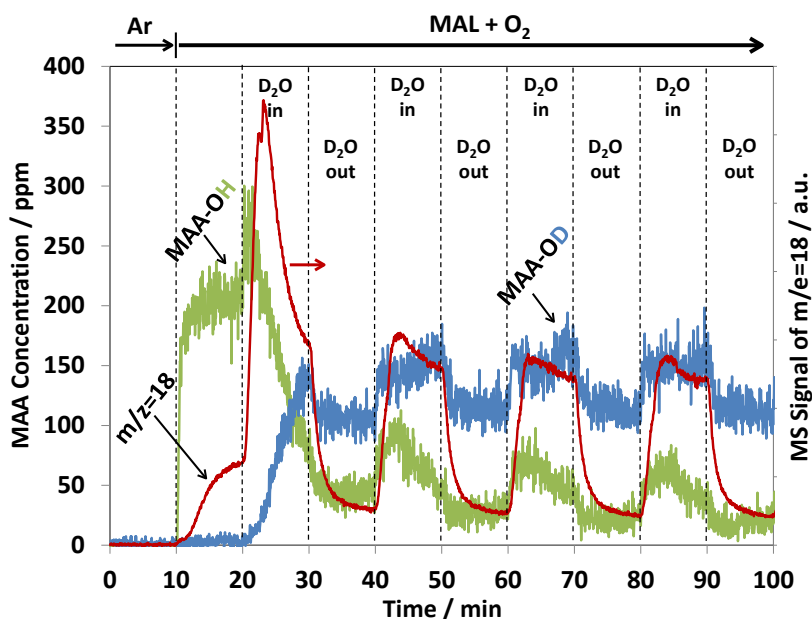


Figure 2 Evolution of MAA formation and added D₂O as a function of time on stream during the cycling switches of D₂O in and out of MAL+O₂ over H₃PMoO₁₂O₄₀ at 320 °C. Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O (when added), and Ar balance and the total flow rate is 50 cm³ min⁻¹.

Prior to the addition of D₂O into the MAL+O₂ feed, the HPMo catalyst was pre-treated under Ar and then exposed to MAL+O₂ for 10 min. Interestingly, the formation of MAA-OH increases rapidly to *ca.* 200 ppm within 3 min, indicating that the oxidation of MAL in the absence of water occurs rapidly. It is also worth noting that, within 10 min of initial exposure to MAL+O₂, there is a slow release of H₂O (m/z=18), suggesting that H₂O, formed during MAL+O₂ reaction, is adsorbed on the HPMo catalyst. This is unlikely to be

due to water from within the as received sample, e.g. crystalline water, as the sample was pre-treated in Ar at 320 °C prior to the introduction of the reactant gas feed.

Upon introduction of D₂O to the MAL+O₂ feed, it is observed that MAA-OH is further released up to 250 ppm and then slowly decreases to 90 ppm within 10 min. This may be due to the introduction of the D₂O displacing MAA which is bound to the surface as a result of competitive adsorption. In addition, there is also a spike in the MS signal of $m/z=18$, probably due to the displacement of D₂O ($m/z=18$) causing the sharp release of H₂O ($m/z=18$).

As the signal for MAA-OH slowly decreases, the formation of MAA-OD gradually increases up to 150 ppm over the course of 10 min under MAL+O₂+D₂O reaction conditions. During this first cycle of D₂O addition, the increase of MAA-OD is gradual and does not match the rapid increase in signal of D₂O. This is due to the fact that active sites on HPMo catalyst are mainly occupied by surface MAL and MAA-OH species, leading to a slow accessibility of D₂O to the active sites to interact with MAL+O₂ to form MAA-OD. Considering the removal of D₂O (Figure 2 between 30 and 40 min), it is clear that the formation of MAA-OH remains decreasing for 3 min and then reaches the steady state value of 45 ppm. It is interesting to note that MAA-OH is produced from MAL+O₂ reaction without water but does not increase as high as previously observed when switching from Ar to MAL+O₂ gas feed. This can be explained by the existence of gas phase MAA-OD formation under MAL+O₂ feed. Despite of the fact that D₂O is removed from MAL+O₂ feed, it is likely that D₂O is retained on HPMo catalyst from the previous cycle and adsorbed D₂O is sufficient to be involved in the MAL oxidation to generate MAA-OD in the next cycle. It is noteworthy that the total concentration of both MAA-OD and MAA-OH formed under MAL+O₂ feed at 30-40 min is ca. 165 ppm (compared to initial concentration of MAA-OH of ca. 200 ppm). This suggests that there is a loss of active sites on HPMo catalyst.

In Figure 2 between 40 and 50 min, the re-introduction of D₂O to MAL+O₂ gas feed results in a further increase in MAA-OD compared with the first cycle. As found in the first cycle, there is a release of gaseous MAA-OH under MAL+O₂+D₂O due to the competitive adsorption. With increasing number of switching cycles, it is evident that the formation of MAA-OD during the D₂O switches is reproducible. However, the formation of MAA-OH during the cycling switches of D₂O in and out of MAL+O₂ decreases with cycling, resulting in a decrease of total concentration of MAA-OH and MAA-OD, also indicating a deactivation of the HPMo catalyst.

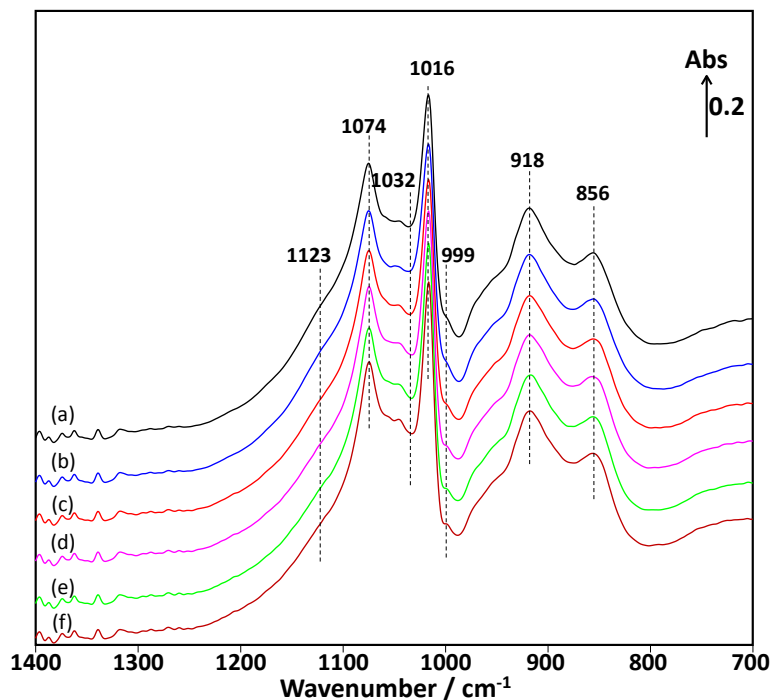


Figure 3 Changes in *in-situ* DRIFT spectra (1400 – 700 cm^{-1}) of Keggin-type $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as a function of time on stream over $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ at 320 °C during the 2nd cycle of switching from MAL+O₂ (a) to MAL+O₂+D₂O feed after 1 min (b), 2 min (c), 3 min (d), 5 min (e), and 10 min (f). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O (when added), and Ar balance and the total flow rate is 50 $\text{cm}^3 \text{min}^{-1}$.

Figure 3 shows selected *in-situ* DRIFT spectra recorded as a function of time on stream during the cycling switches of D₂O in and out of the MAL+O₂ reaction feed over $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ at 320 °C. This corresponds to the cycle shown in Figure 2 between 40 and 50 min. There are significant changes in the Keggin structure of HPMo catalyst, especially in the IR region between 1040 and 840 cm^{-1} . Figure 4 shows the evolution of gas phase MAA-OD and the changes of Mo–O_c–Mo at 918 cm^{-1} . It is seen that, not only does D₂O influence the formation of MAA-OD, but also the change of Keggin unit of HPMo. When D₂O is added to MAL+O₂ feed, the $\nu(\text{Mo}-\text{O}_c-\text{Mo})$ band is decreased perhaps via the interaction of deuterium with the Mo–O_c–Mo oxygen atoms[19].

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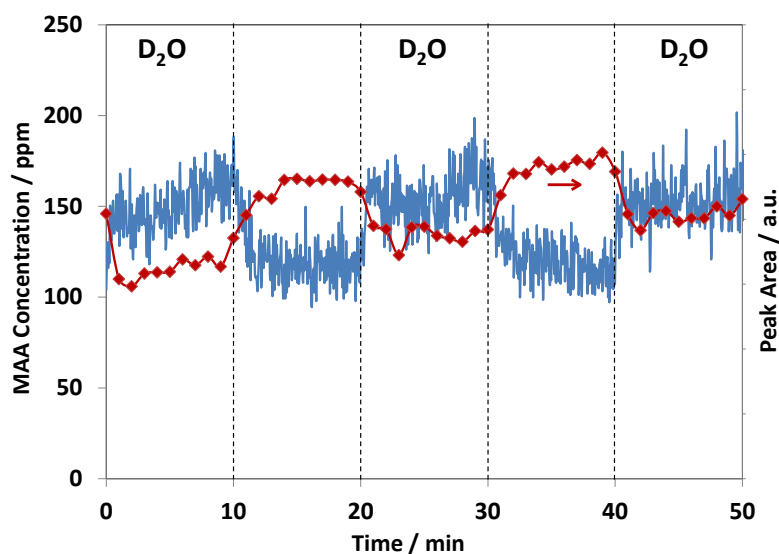


Figure 4 Evolution with time of changes of the DRIFT spectra of Mo–O_c–Mo (918 cm⁻¹) and the corresponding MS signal of gas phase MAA-OD observed during the cycling switches of D₂O in and out of MAL+O₂ over H₃PMoO₁₂O₄₀ at 320 °C. Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O (when added), and Ar balance and the total flow rate is 50 cm³ min⁻¹.

To better understand the behaviour of the formation of MAA and the involvement of water in the selective oxidation of MAL to MAA, D₂O was pre-adsorbed on the HPMo catalyst at 320 °C for 60 min. This procedure allowed the crystalline H₂O to be replaced by D₂O. After purging with Ar to remove gas phase D₂O, the MAL+O₂ gas feed was introduced. The gas phase MAA and the IR bands of the Keggin structure of HPMo catalyst were monitored.

Figure 5a shows the formation of both MAA-OD and MAA-OH after switching from Ar to MAL+O₂ with both products showing different profiles. In the case of MAA-OD formation, it is clear that MAA-OD is immediately produced and peaks at 150 ppm at about 2 min after introducing the MAL+O₂. The formation of MAA-OD remains unchanged for 2 min before gradually decreasing over the course of 30 min as a result of reacting with the reservoir of preadsorbed D₂O. In contrast, the production of MAA-OH is initially suppressed for 3 min and then starts to rise to 200 ppm over 30 min. The MS results shown in Figure 5a suggest that, during the pre-adsorption of D₂O, catalytic active sites are totally occupied by D₂O, which in turn initially suppresses the formation of MAA-OH. Once adsorbed D₂O is consumed by MAL+O₂ to form MAA-OD and the active sites of HPMo catalyst are available and accessible by MAL, MAA-OH is then formed until the steady state under MAL+O₂ conditions is reached.

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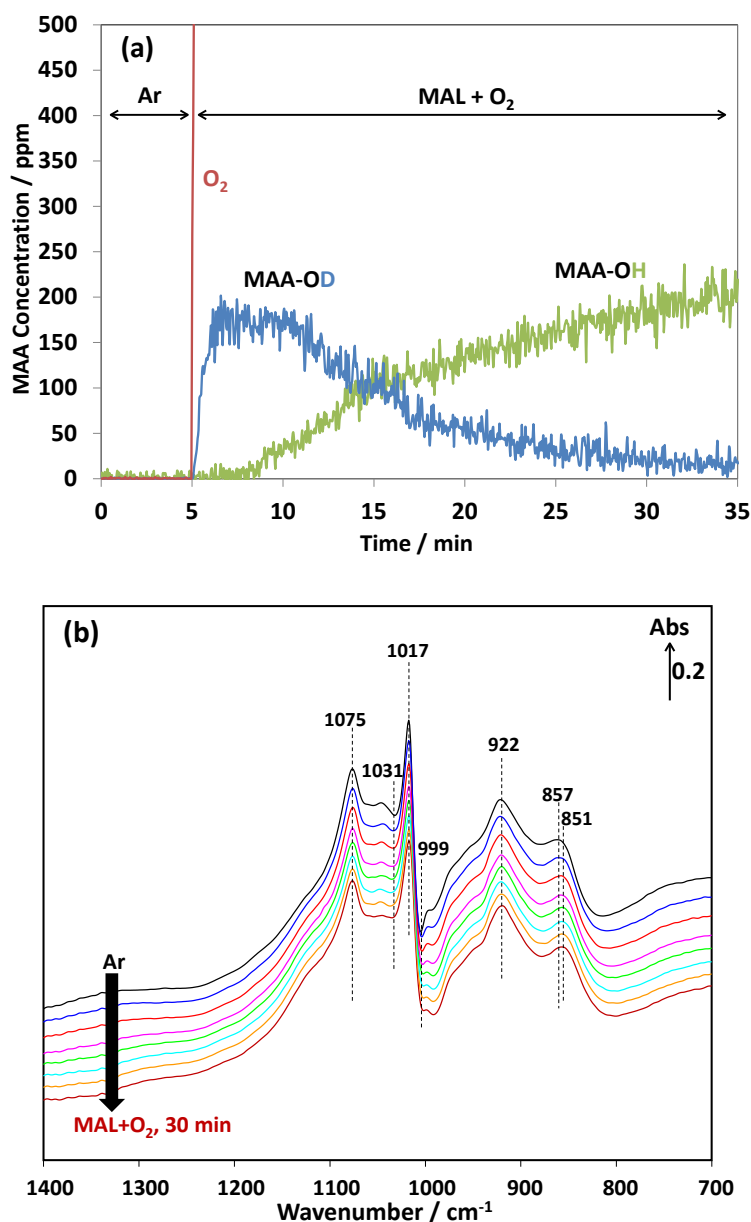


Figure 5 Change in gaseous methacrylic acid (a) and *in situ* DRIFT spectra (b) of Keggin-type H₃PMo₁₂O₄₀ (1400 – 700 cm⁻¹) as a function of time on stream after switching to MAL+O₂ over H₃PMoO₁₂O₄₀ at 320 °C. Prior to the exposure to MAL+O₂ gas feed, H₃PMo₁₂O₄₀ was pre-treated with D₂O feed for 60 min and then purged by Ar for 30 min.

Figure 5b shows the changes in *in-situ* DRIFT spectra of Keggin-type H₃PMo₁₂O₄₀ catalyst (1400 – 700 cm⁻¹), recorded during the same (Figure 5a) 30 min exposure to MAL+O₂ feed at 320 °C. Together with Figure 5, Figure S6 shows a comparison of *in-situ* DRIFTS spectra under different conditions. It is noticeable that there is a difference in IR bands between Ar pre-treatment (Figure S6a) and D₂O pre-adsorption (Figure S6b). The IR bands at 1033 cm⁻¹ and 998 cm⁻¹, tentatively assigned to $\nu_{\text{as}}(\text{MoO}_t\text{H})$, are substantially

decreased, making the IR peak at 1017 cm⁻¹ sharper. Furthermore, there is a shift in the $\nu_{\text{as}}(\text{Mo}-\text{O}_e-\text{Mo})$ band from 863 to 857 cm⁻¹ under the D₂O feed at 320 °C. Therefore, it is reasonable to conclude that the pre-treatment with D₂O has led to the adsorption of D₂O and to the changes of Keggin unit in connection to the loss of hydrogen-bonded $\nu_{\text{as}}(\text{MoO}_t\text{H})$ species.

In Figure 5b, prior to exposure to MAL+O₂ feed, the IR bands at 1033 cm⁻¹ and 998 cm⁻¹ lose their intensity. On the introduction to MAL+O₂, there is an increase in the IR intensity of the two bands at 1033 and 998 cm⁻¹, associated with hydrogen-bonded $\nu_{\text{as}}(\text{MoO}_t\text{H})$ species with the water interacting with the surface probably formed due to the MAL+O₂ reaction. One important feature seen in Figure 5b is that the band assigned to $\nu_{\text{as}}(\text{Mo}-\text{O}_e-\text{Mo})$ is shifted from 857 to 851 cm⁻¹ under MAL+O₂ gas feed. This shift suggests that there is protonation of the (Mo–O_e–Mo) species via H₂O derived from MAL+O₂ reaction.

These DRIFTS-MS results obtained from the transient switching experiments have revealed that hydrogen atom from water is involved in the formation of MAA during the selective oxidation of MAL over HPMo catalyst. Using D₂O in the MAL+O₂ reaction has revealed changes in Keggin unit of HPMo catalyst which match the time dependent gas phase compositional changes. To better understand the role of water and further insight into the pathway of reaction mechanism, the isotopic transient experiments were performed.

3.3 D₂O-H₂O isotopic transient switches

In this section, the isotopic switches between D₂O and H₂O were carried out to elucidate the role and the involvement of water in the selective oxidation of MAL to MAA formation. The implication of these observations is discussed with respect to the various reaction mechanisms proposed in the literature [3, 19, 22, 35].

Figure 6 shows the changes in gas phase MAA and water as a function of time on stream during the isotopic cycling switches between D₂O and H₂O under MAL+O₂ reaction conditions over HPMo catalyst at 320 °C. These MS results show the significant switching of the isotope in the MAL oxidation, further indicating the importance of water in the direct formation of MAA.

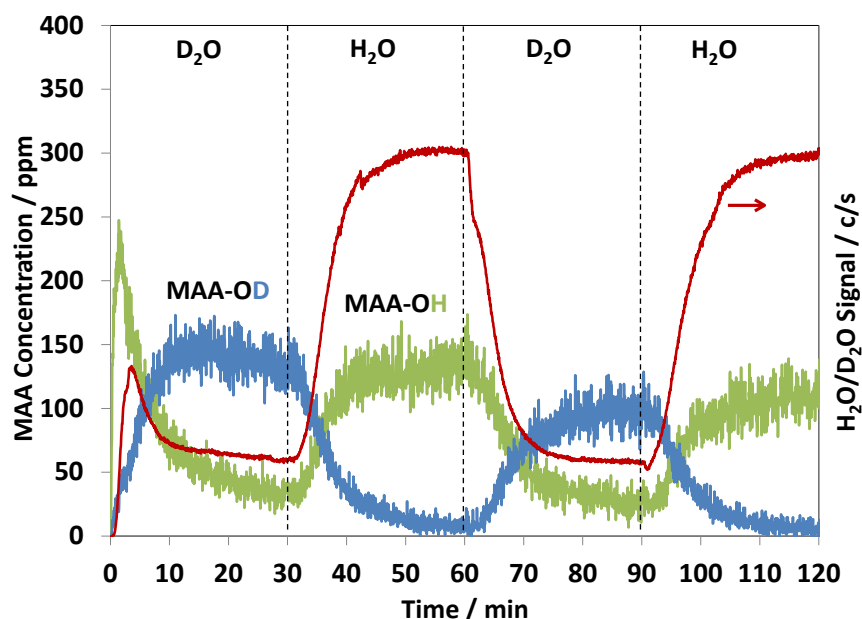


Figure 6 Changes in gaseous methacrylic acid and water as a function of time on stream during the isotopic cycling switches between MAL+O₂+D₂O and MAL+O₂+H₂O over H₃PMoO₁₂O₄₀ at 320 °C. Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O and H₂O (when added), and Ar balance and the total flow rate is 50 cm³ min⁻¹.

During the first cycle of D₂O introduction to MAL+O₂ feed, there is a rapid increase in the formation of gas phase MAA-OH, peaking at ca. 220 ppm within 90 s. Note that the initial concentration of MAA-OH is similar to the results shown in Figure 2 when switching from Ar to MAL+O₂ feed. This similarity indicates that the number of active sites on HPMo is similar and is accessible by MAL+O₂. However, when examining Figure 6 carefully, the difference from Figure 2 is that, when MAL+O₂ gas mix is fed together with D₂O (Figure 6) there is a competition between MAL+O₂ and MAL+O₂+D₂O reactions. Figure 6 shows that the initial concentration of MAA-OH formed under MAL+O₂+D₂O is decreased from 220 to 35 ppm. It is also found that as the MAA-OH decreases, the production of MAA-OD increases, indicating that the presence of D₂O in MAL+O₂ feed starts to be adsorbed competitively with MAL+O₂, leading to the formation of gaseous MAA-OD. In the first 30 min, the concentration of MAA-OD rises to ca. 150 ppm. Upon replacing D₂O with H₂O (Figure 6 between 30-60 min), isotopic signature of the MAA product changes from –OD to –OH and is complete as the MAA-OD decreases to almost 0 ppm and the production of MAA-OH reaches a steady state concentration of approximately 145 ppm (similarly to the MAA-OD concentration observed during the D₂O cycle between 0 and 30 min).

As a result of the change in the MAA from –OD to –OH, the number of sites that are active for the selective oxidation of MAL to form MAA can be calculated. The calculated number of active sites when switching from D₂O to H₂O at 30-40 min is 72.2 μmol g⁻¹. With

increasing number of cycles, the formation of MAA-OH decreases with the number of active sites between 90-120 min under MAL+O₂+H₂O reaction found to be 47.5 $\mu\text{mol g}^{-1}$. One of the possible explanations is that the adsorption of unreacted MAL and/or stored products somewhat causes the blockage of active sites. This is evidenced by the result shown in Figure 2 that there is a release of MAA-OH on the addition of D₂O into MAL+O₂ feed. One would expect that the formation of MAA-OH should decrease immediately in the presence of D₂O. In fact, stored MAA-OH formed under MAL+O₂ without D₂O presence is displaced by the introduction of D₂O, resulting in a release of MAA-OH product. In addition to the adsorption, the presence of water has been reported to be the cause of the deactivation over HPMo catalyst [4] as a result of strongly-adsorbed water.

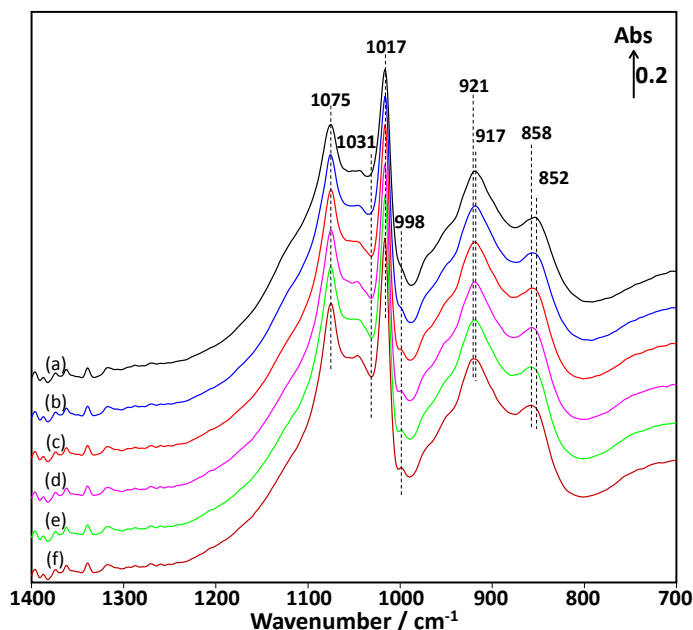


Figure 7 *In situ* DRIFT spectra (1400 – 700 cm^{-1}) of Keggin-type $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as a function of time on stream during the isotopic cycling switches over $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ at 320 °C under $\text{H}_2\text{O}+\text{MAL}+\text{O}_2$ feed (a) and then after 1 min (b), 5 min (c), 10 min (d), 20 min (e), and 30 min (f) after switching to $\text{D}_2\text{O}+\text{MAL}+\text{O}_2$ feed. Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O and H₂O (when added), and Ar balance and the total flow rate is 50 $\text{cm}^3 \text{min}^{-1}$.

Figure 7 shows selected *in-situ* DRIFT spectra of Keggin unit when switching from $\text{MAL}+\text{O}_2+\text{H}_2\text{O}$ to $\text{MAL}+\text{O}_2+\text{D}_2\text{O}$ feed, which correspond to Figure 6 between 60 and 90 min, over HPMo catalyst at 320 °C. It should be noted that there are significant changes of DRIFT spectra upon the switching from H₂O to D₂O. The stretching vibration of Mo–O_c–Mo and Mo–O_e–Mo is shifted from 917 to 921 cm^{-1} and from 852 to 858 cm^{-1} , respectively, due to the influence of D₂O in the reaction (Figure S7). It is important to point out that, although the isotopic change between -OH and -OD is not well-resolved, the small shift of these two IR bands allows the changes to be correlated with the changes in the gas phase MAA-OD and

the relationship with the protonated bridging oxygens in the Keggin units as illustrated in Figure 8.

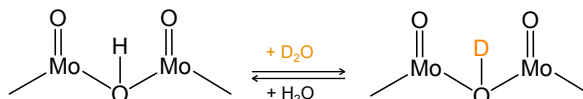


Figure 8 The influence of water on the bridging oxygen in Keggin-type H₃PMo₁₂O₄₀ catalyst

In addition, it is found in Figure 7 that there are changes of Keggin unit observed in the IR region between 1040 and 990 cm⁻¹ when replacing H₂O with D₂O under MAL+O₂ reaction conditions. The IR bands at 1031 and 998 cm⁻¹ thought to be associated with $\nu_{\text{as}}(\text{Mo}=\text{O}_t)$ mode at 1017 cm⁻¹ change in the presence of water (D₂O and H₂O) in the MAL+O₂ gas feed. It is observed that the changes of Keggin unit observed at 1031 and 998 cm⁻¹ are decreased, whereas the IR band of $\nu_{\text{as}}(\text{Mo}=\text{O}_t)$ mode at 1017 cm⁻¹ is increased in the presence of D₂O and vice versa in the presence of H₂O. It is fairly concluded that the presence of water (D₂O and H₂O) has a significant influence on the IR bands between 1040 and 995 cm⁻¹, which are associated with (Mo=O_t) group of Keggin-type HPMo catalyst.

Figure 9 compares the temporal evolution of the relative intensities of *in-situ* DRIFT spectra of $\nu_{\text{as}}(\text{Mo}-\text{O}_c-\text{Mo})$ and $\nu_{\text{as}}(\text{Mo}-\text{O}_e-\text{Mo})$ and the corresponding changes of gas phase MAA-OD and MAA-OH observed under MAL+O₂+D₂O feed over H₃PMoO₁₂O₄₀ at 320 °C. It is evident that the exchange of H to form MAA-OH with D to form MAA-OD occurs slowly. The 50% H-D exchange occurs at about 7 min after switching from MAL+O₂+H₂O to MAL+O₂+D₂O feed, whereas the evolution of the IR bands assigned to $\nu_{\text{as}}(\text{Mo}-\text{O}_c-\text{Mo})$ and $\nu_{\text{as}}(\text{Mo}-\text{O}_e-\text{Mo})$ modes increases faster than the formation of MAA-OD product, suggesting that the exchange rate of H with D over both (Mo-O_c-Mo) and (Mo-O_e-Mo) modes is more rapid than the desorption rate of gas phase MAA. Therefore, it is possible that hydrogen (H and D) from water is activated on the bridging oxygen (both corner-sharing and edge-sharing) of the Keggin unit and readily interacts with MAL+O₂ to form MAA.

In comparison to Figure 9, Figure S9 shows the evolution and correlation between gaseous MAA and the changes of Keggin unit observed at 1031, 1017 and 998 cm⁻¹. Interestingly, the changes of these three IR bands are faster than the formation of gas phase MAA-OD, indicating the rapid H-D exchange during the H₂O-D₂O isotopic switches.

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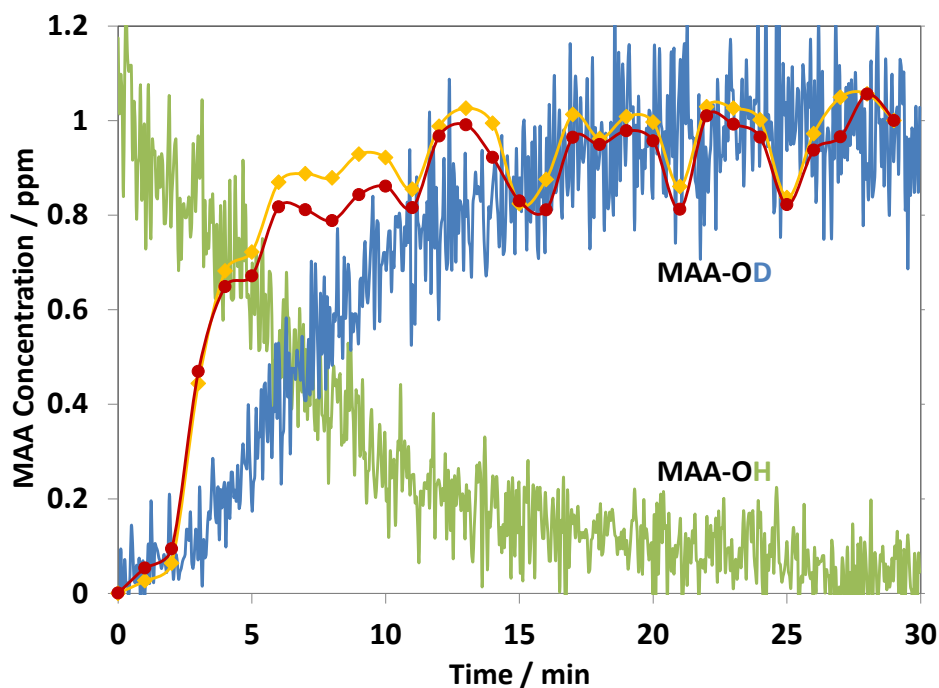


Figure 9 Evolution with time of changes of the relative intensities of the DRIFT spectra of Mo–O_c–Mo (■, 921-918 cm⁻¹) and Mo–O_e–Mo (●, 858-852 cm⁻¹), and the corresponding mass spectrometry signal of gas phase MAA-OD and MAA-OH observed during the isotopic cycling switches over H₃PMoO₁₂O₄₀ at 320 °C under D₂O+MAL+O₂ feed. Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O and H₂O (when added), and Ar balance and the total flow rate is 50 cm³ min⁻¹.

Based on the *in-situ* DRIFTS-MS analysis from these transient switching experiments and previous studies [2, 12, 19, 22, 35], a reaction mechanism associated with the effect of water (D₂O in this study) on the selective oxidation of MAL to MAA over Keggin-type H₃PMoO₁₂O₄₀ catalyst is proposed in Figure 10. Initially, D₂O is molecularly activated on the bridging oxygen (Mo–O–Mo), blocking the H abstraction from MAL. Thereafter, the oxygen on the terminal Mo=O_t functional group interacts with carbon of –C=O group of MAL, followed by the coordination of oxygen of C=O– group of MAL with another Mo=O_t group, resulting in a negative charge on Mo–O_t group. Simultaneously, the –OD group of activated D₂O remove H from MAL to form HOD, which may then hydrogen-bond with negative-charged Mo–O_t group. Finally, gaseous oxygen (O₂) oxidises the reduced Mo^{δ+} to Mo^{δ+} and the coordinated carboxylate (–OC(R)O–) type intermediates reacts with the bridging -OD resulting a release of gas phase MAA-OD as the product.

It is worth pointing out that, in the absence of water, the reaction pathway is similar to that in the presence of water, the difference is that hydrogen atom of MAL is abstracted by

bridging oxygen (Mo–O–Mo) group and then recombined with the coordinated carboxylate (–OC(R)O–) type intermediates to form MAA product [19].

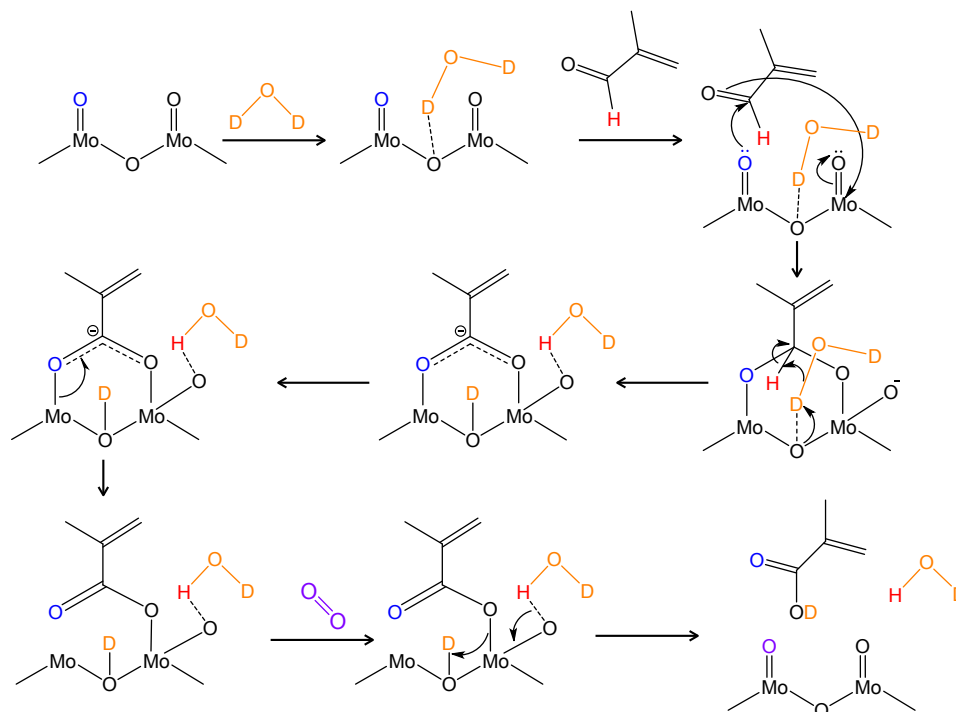


Figure 10 Proposed reaction mechanism of selective oxidation of MAL to MAA in the presence of D₂O over Keggin-type H₃PMo₁₂O₄₀ catalyst.

4. Conclusions

The current work highlights, for the first time, the involvement of water with the selective oxidation of MAL to produce MAA over Keggin-type H₃PMo₁₂O₄₀ catalyst, using *in-situ* DRIFTS-MS. It has been found that, during the cycling of D₂O in and out of MAL+O₂ gas feed at 320 °C, the deuterium is involved in the production of gas phase MAA-OD, which is increased and decreased when D₂O is added and removed, respectively. Moreover, the *in-situ* DRIFTS-MS results obtained from the isotopic switches between D₂O and H₂O reveal that the H-D exchange possibly occurs on the bridging oxygen of Mo–O–Mo unit, where water is activated for the formation of MAA.

Acknowledgements

We gratefully acknowledge the financial support of this work from Mitsubishi Chemical Corporation.

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Supplementary Figures

Elucidating the role of H₂O in promoting the formation of methacrylic acid during the oxidation of methacrolein over heteropolyacid compounds

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Elucidating the role of H₂O in promoting the formation of methacrylic acid during the oxidation of methacrolein over heteropolyacid compounds

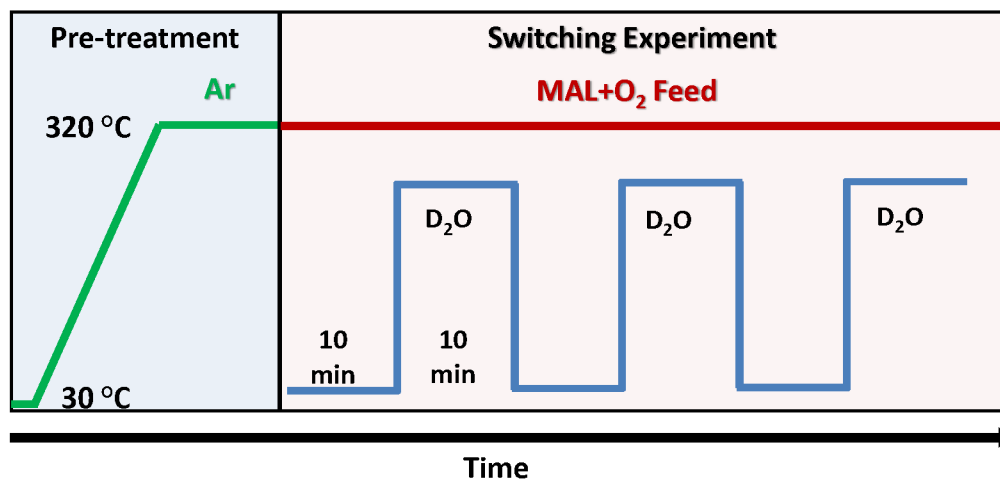


Figure S1 Switching experimental profile with switches of D₂O in and out of MAL+O₂.

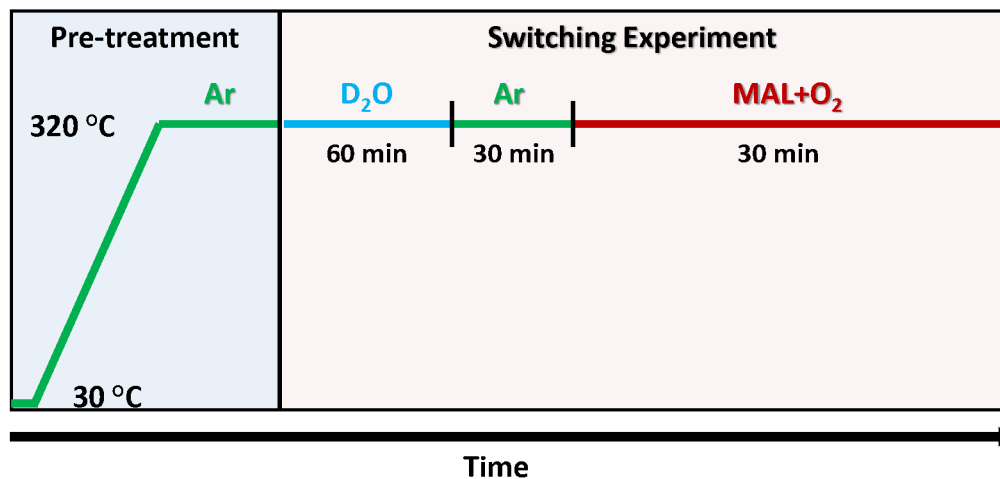


Figure S2 Transient experimental profile and the effect of D₂O pre-adsorption.

Elucidating the role of H₂O in promoting the formation of methacrylic acid during the oxidation of methacrolein over heteropolyacid compounds

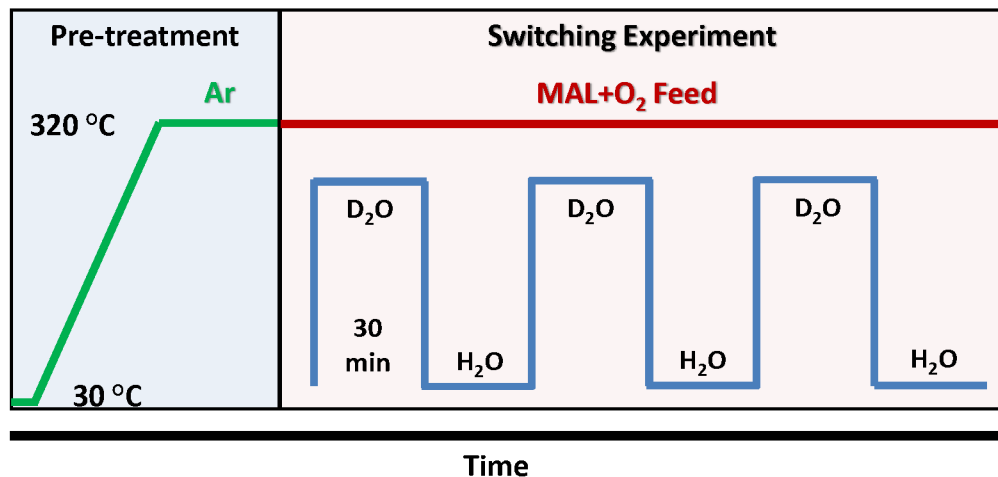


Figure S3 Experimental profile with isotopic switches between D₂O and H₂O.

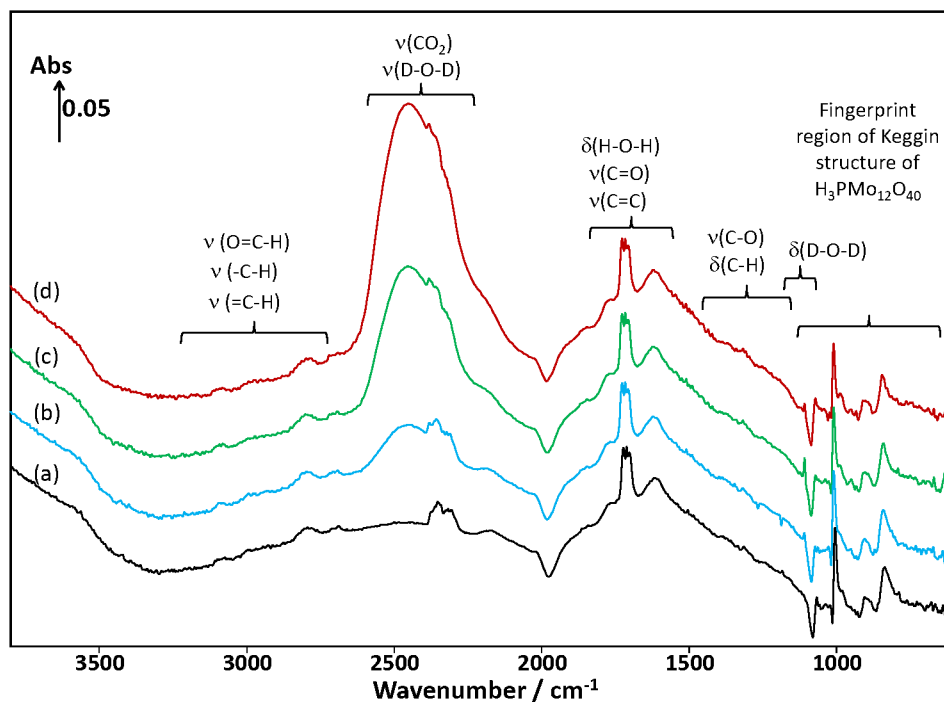


Figure S4 *In-situ* DRIFTS spectra recorded as a function of time on stream under MAL+O₂+H₂O gas feed at 320 °C after 0.5 min (a), 1 min (b), 2 min (c), and 3 min (d). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O, and Ar balance and the total flow rate is 50 cm³ min⁻¹. IR background was taken over H₃PMO₁₂O₄₀ catalyst at 320 °C after 60 min Ar pre-treatment at 320 °C.

Elucidating the role of H₂O in promoting the formation of methacrylic acid during the oxidation of methacrolein over heteropolyacid compounds

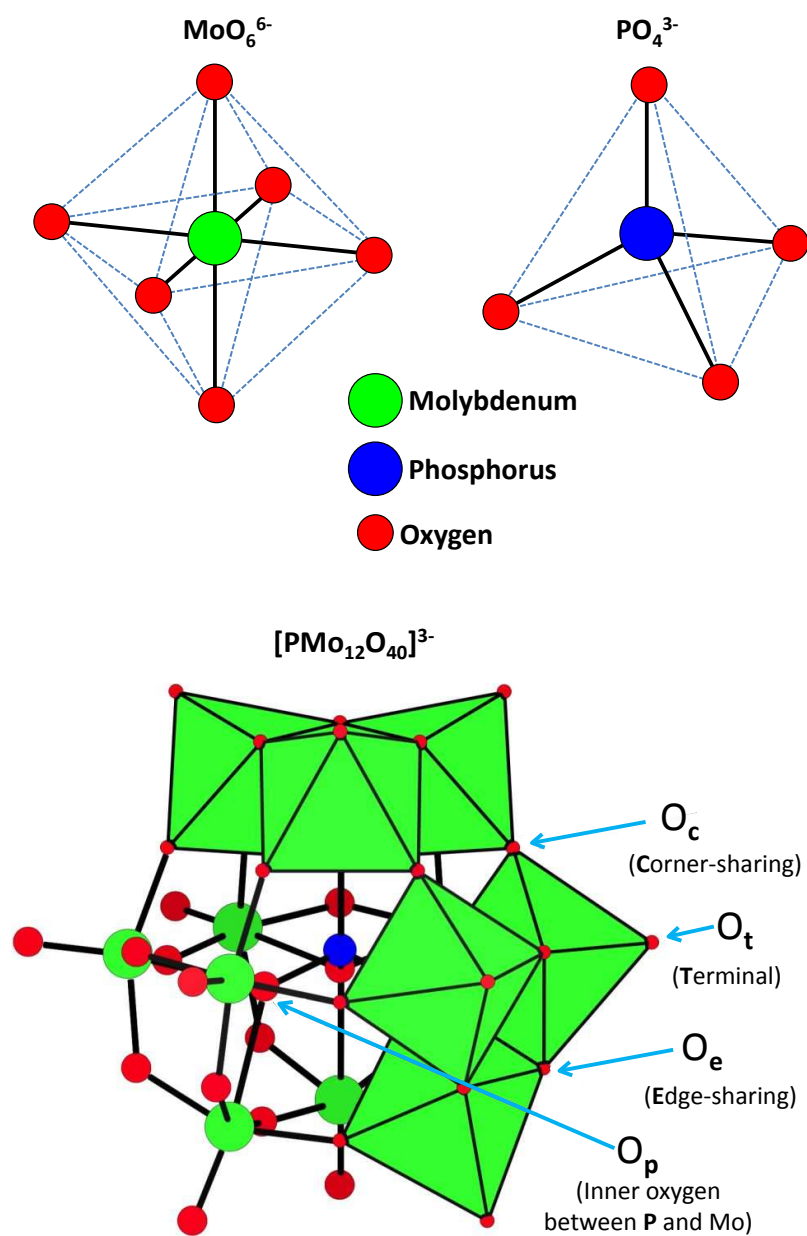


Figure S5 Typical structure of Keggin-type heteropolyacid catalyst.

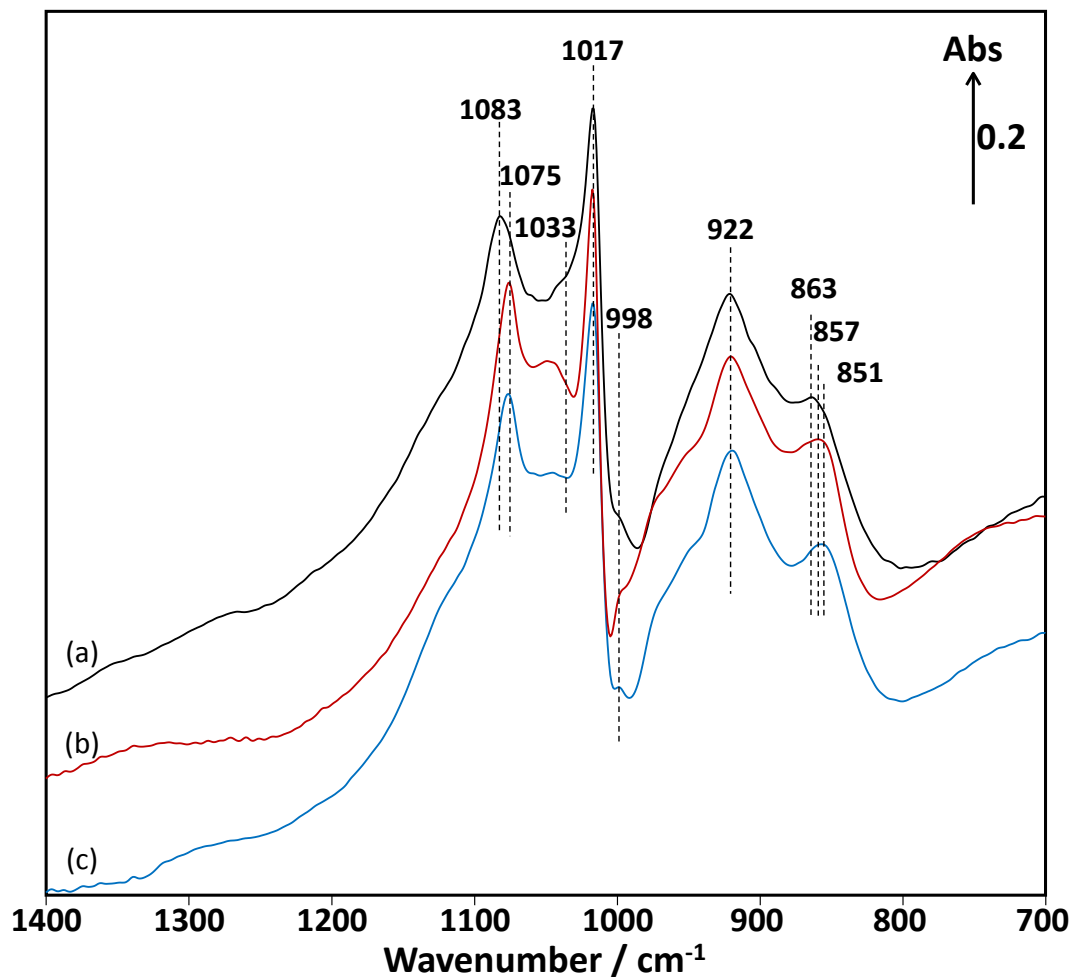


Figure S6 Comparison of *in-situ* DRIFT spectra (1400 – 700 cm⁻¹) of Keggin-type H₃PMo₁₂O₄₀, recorded at 320 °C after 60 min under Ar pre-treatment (a), after 60 min under D₂O pre-adsorption (b), and after 30 min under MAL+O₂ feed (c). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O (when added) and Ar balance and the total flow rate is 50 cm³ min⁻¹.

Elucidating the role of H₂O in promoting the formation of methacrylic acid during the oxidation of methacrolein over heteropolyacid compounds

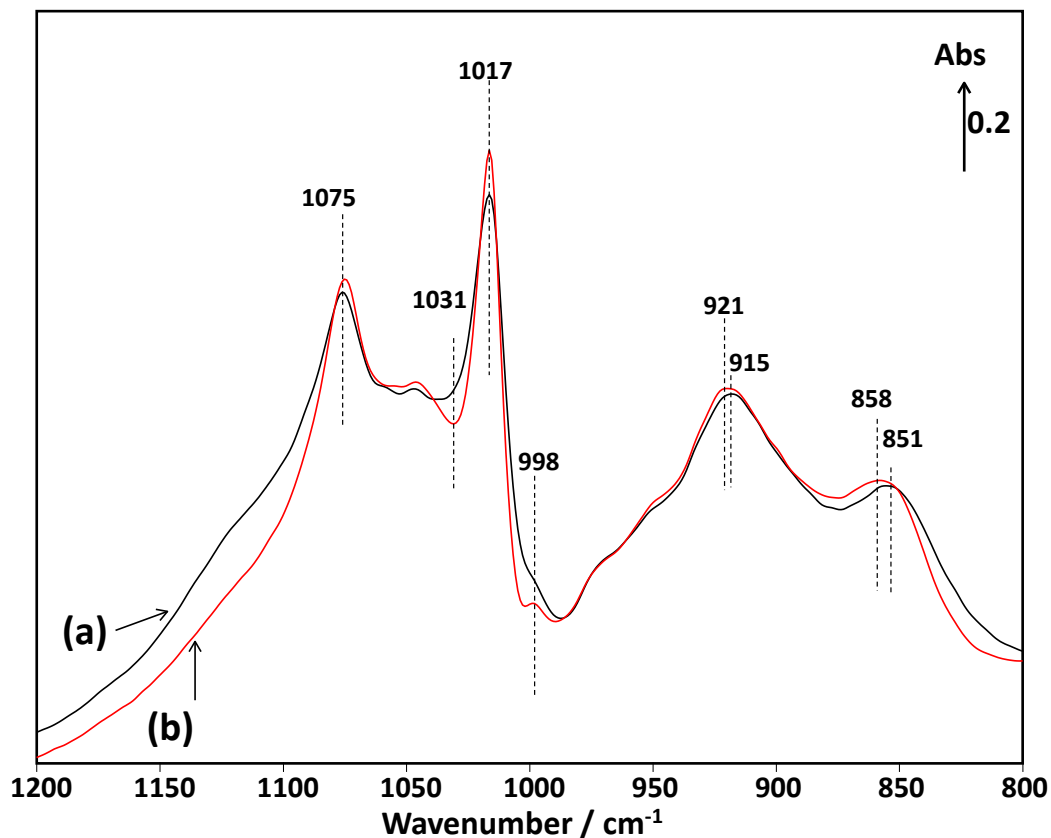


Figure S7 A comparison of *in situ* DRIFTS spectra (1400 – 700 cm⁻¹) of Keggin-type H₃PMo₁₂O₄₀, recorded at 320 °C at steady state conditions under MAL+O₂+H₂O (a) and MAL+O₂+D₂O (b). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O and H₂O (when added), and Ar balance and the total flow rate is 50 cm³ min⁻¹.

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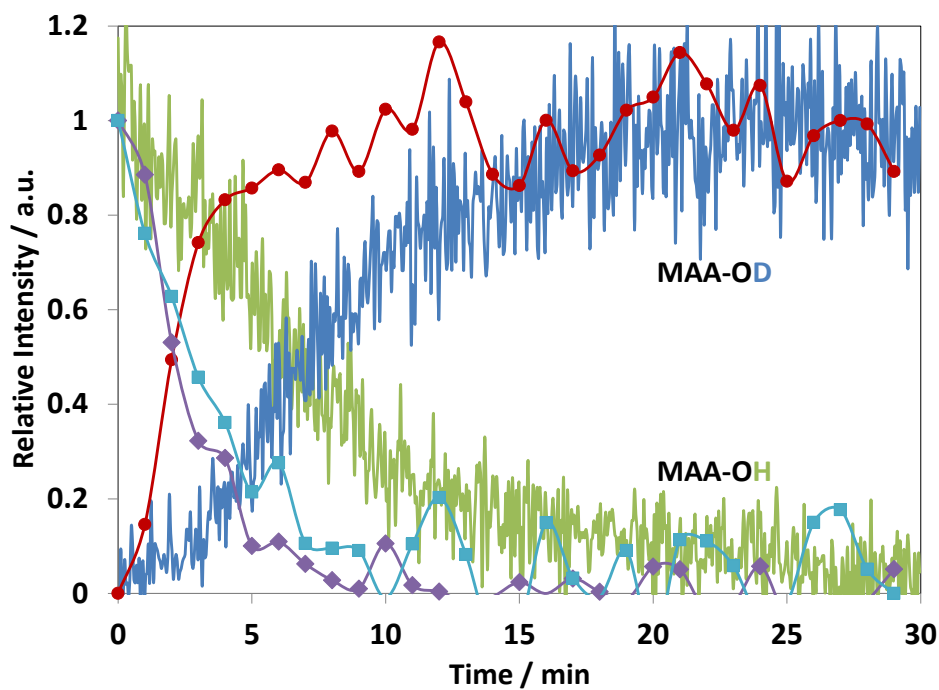


Figure S8 Evolution with time of changes of the relative intensities of the DRIFT spectra of MoO_tH (■, 1031 cm⁻¹), Mo=O_t (●, 1017 cm⁻¹), and MoO_tH (◆, 998 cm⁻¹), and the corresponding mass spectrometry signal of gas phase MAA-OD and MAA-OH observed during the isotopic cycling switches over H₃PMoO₁₂O₄₀ at 320 °C under D₂O+MAL+O₂ feed. Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O and H₂O (when added), and Ar balance and the total flow rate is 50 cm³ min⁻¹.