

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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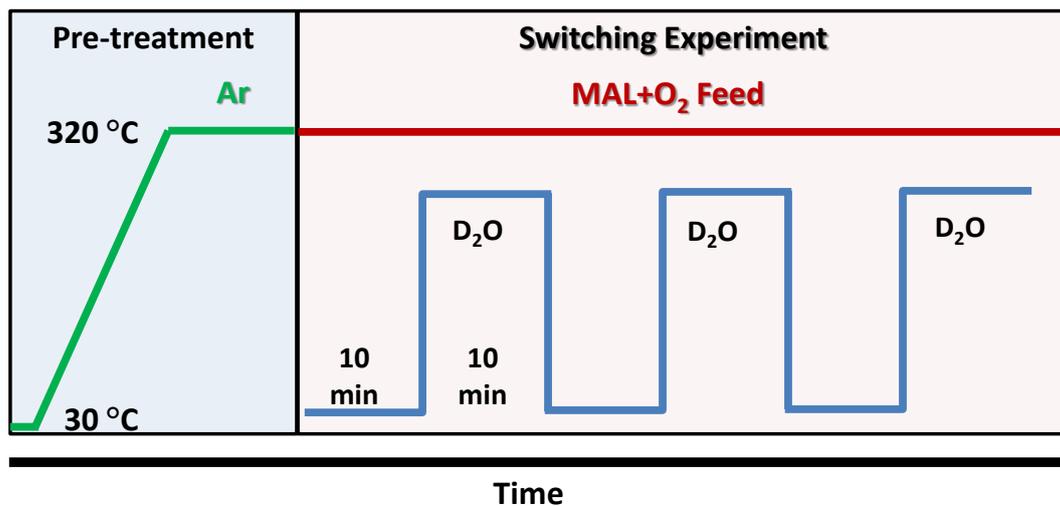


Figure S1 Switching experimental profile with switches of D₂O in and out of MAL+O₂.

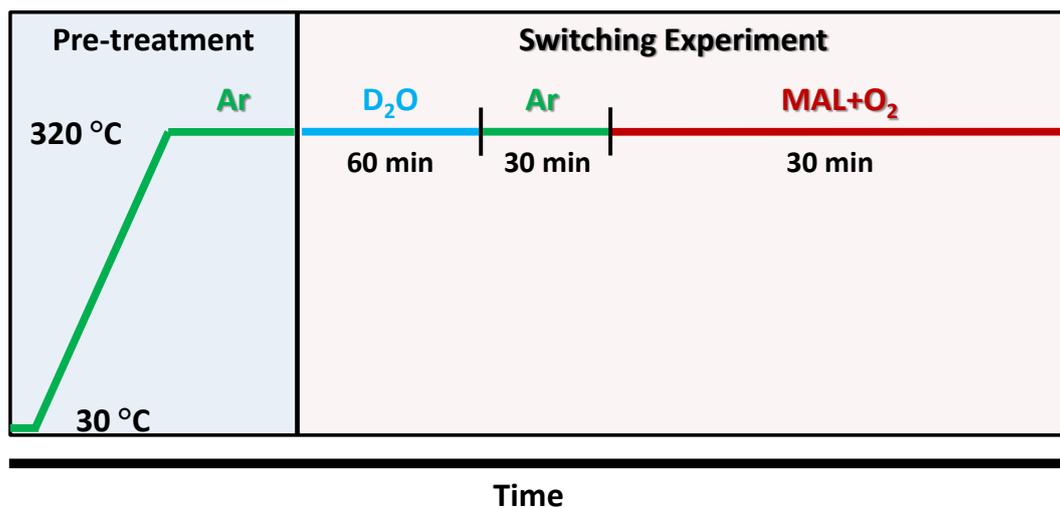


Figure S2 Transient experimental profile and the effect of D₂O pre-adsorption.

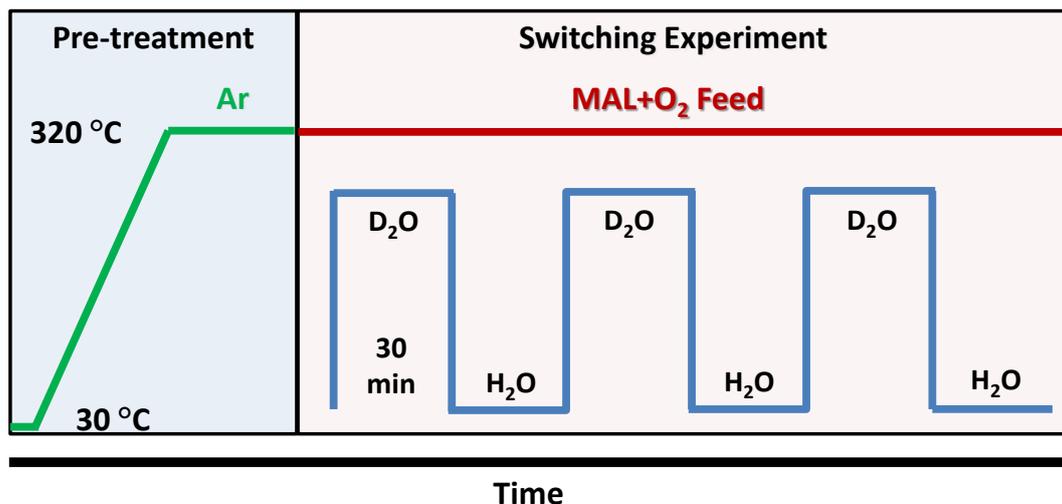


Figure S3 Experimental profile with isotopic switches between D₂O and H₂O.

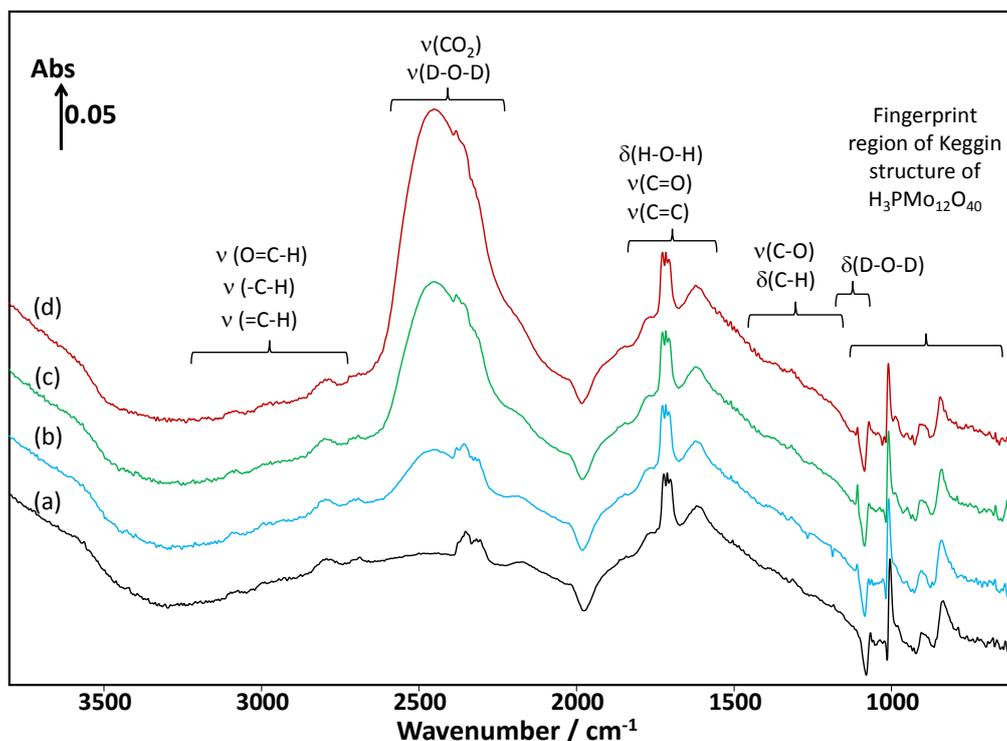


Figure S4 *In-situ* DRIFTS spectra recorded as a function of time on stream under MAL+O₂+H₂O gas feed at 320 °C after 0.5 min (a), 1 min (b), 2 min (c), and 3 min (d). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O, and Ar balance and the total flow rate is 50 cm³ min⁻¹. IR background was taken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

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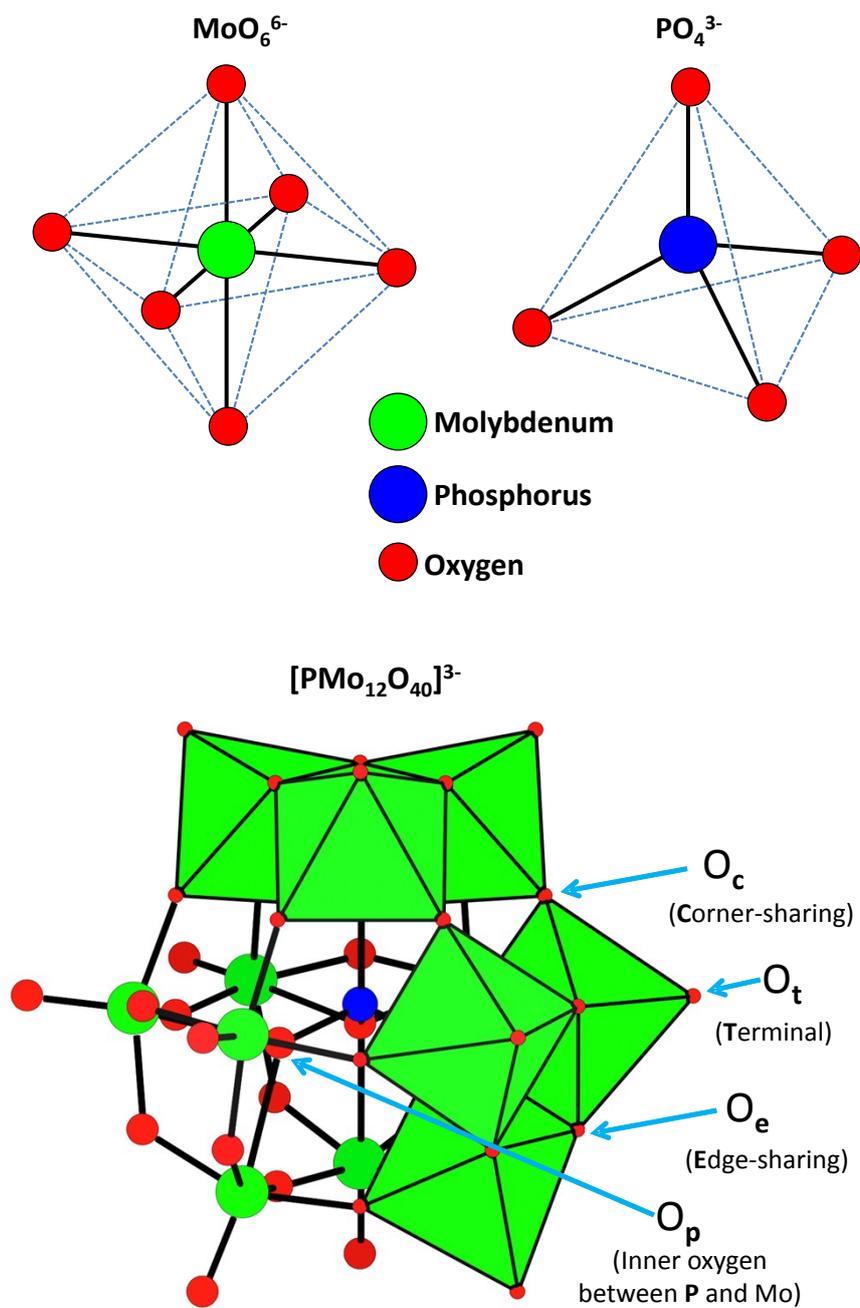


Figure S5 Typical structure of Keggin-type heteropolyacid catalyst.

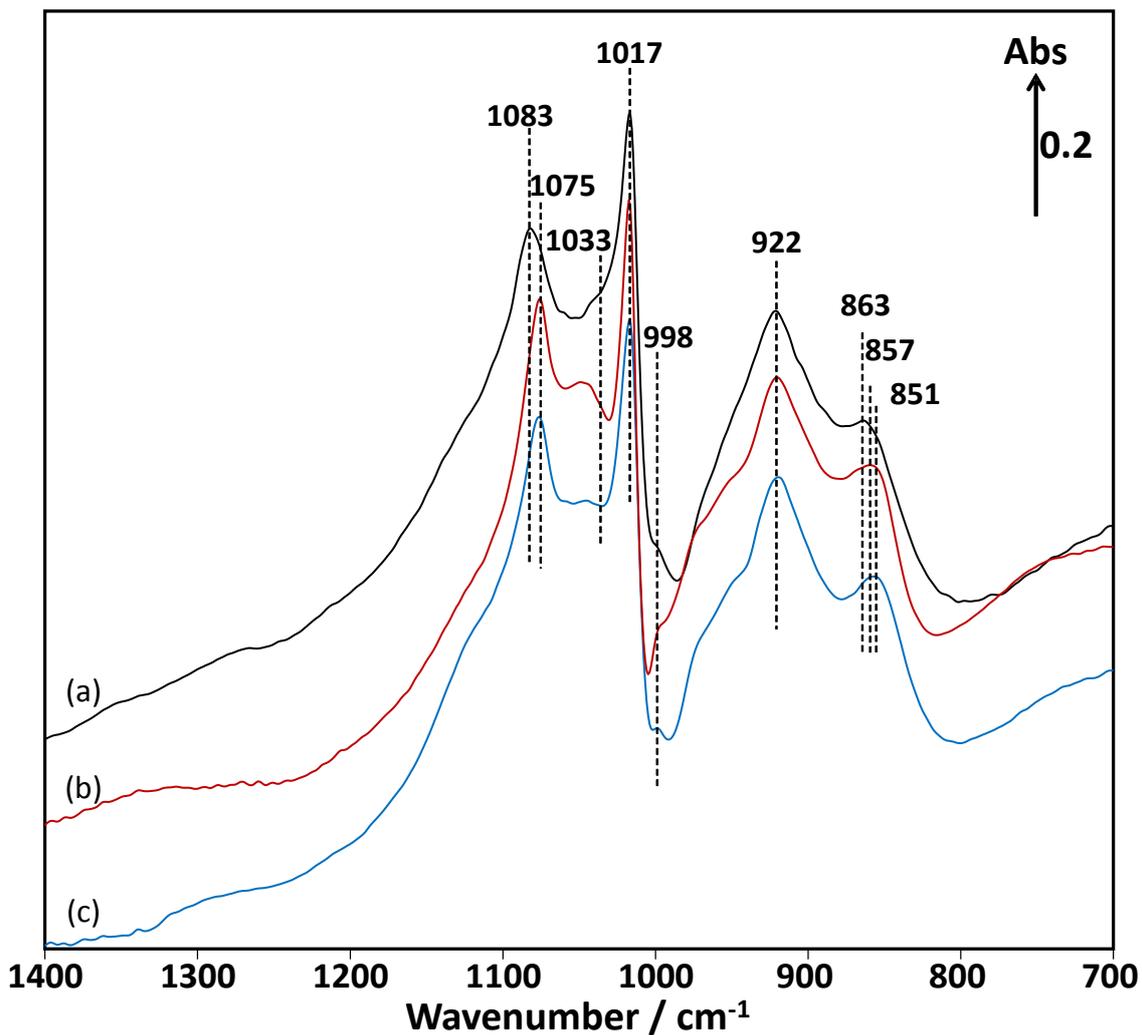


Figure S6 Comparison of *in-situ* DRIFT spectra (1400 – 700 cm⁻¹) of Keggin-type H₃PMo₁₂O₄₀, recorded at 320 °C after 60 min under Ar pre-treatment (a), after 60 min under D₂O pre-adsorption (b), and after 30 min under MAL+O₂ feed (c). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O (when added)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

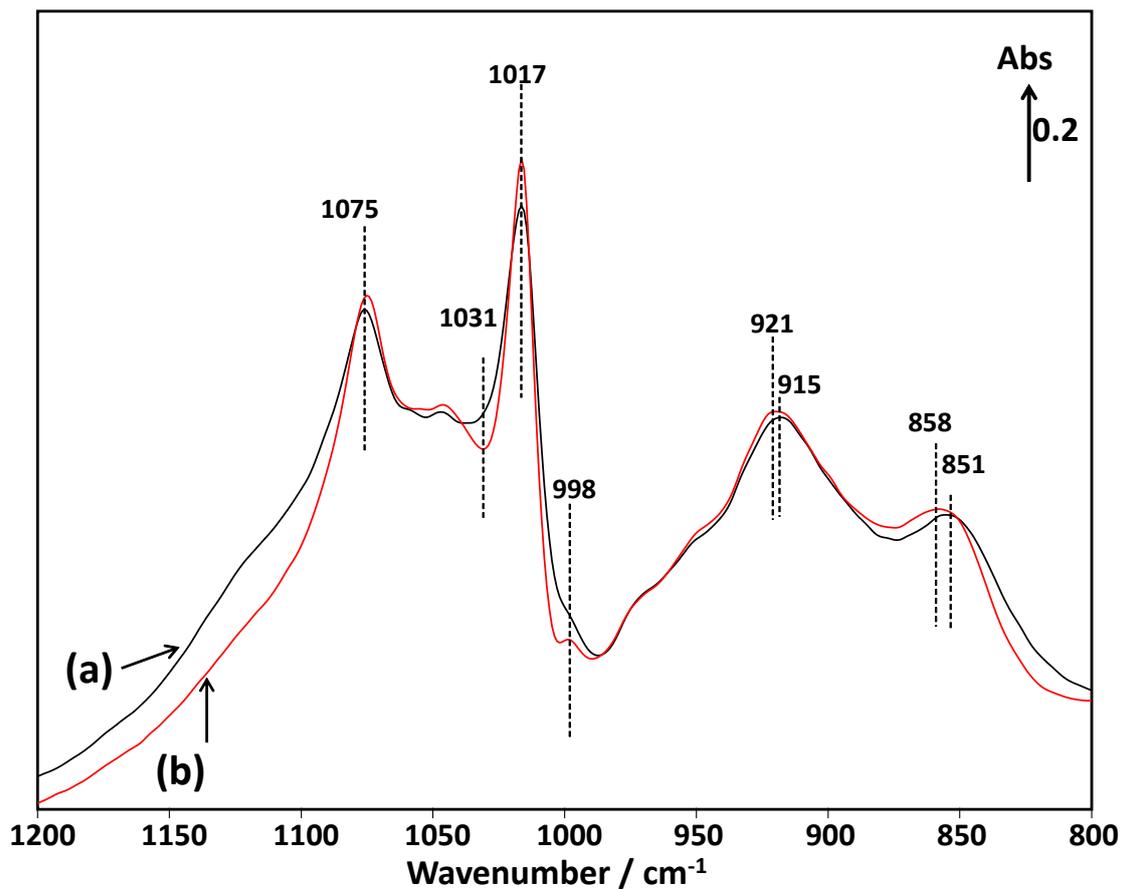


Figure S7 A comparison of *in situ* DRIFTS spectra (1400 – 700 cm⁻¹) of Keggin-type H₃PMo₁₂O₄₀, recorded at 320 °C at steady state conditions under MAL+O₂+H₂O (a) and MAL+O₂+D₂O (b). Feed conditions is composed of 2% MAL, 4% O₂, 4% D₂O and H₂O (when added), and Ar balance and the total flow rate is 50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

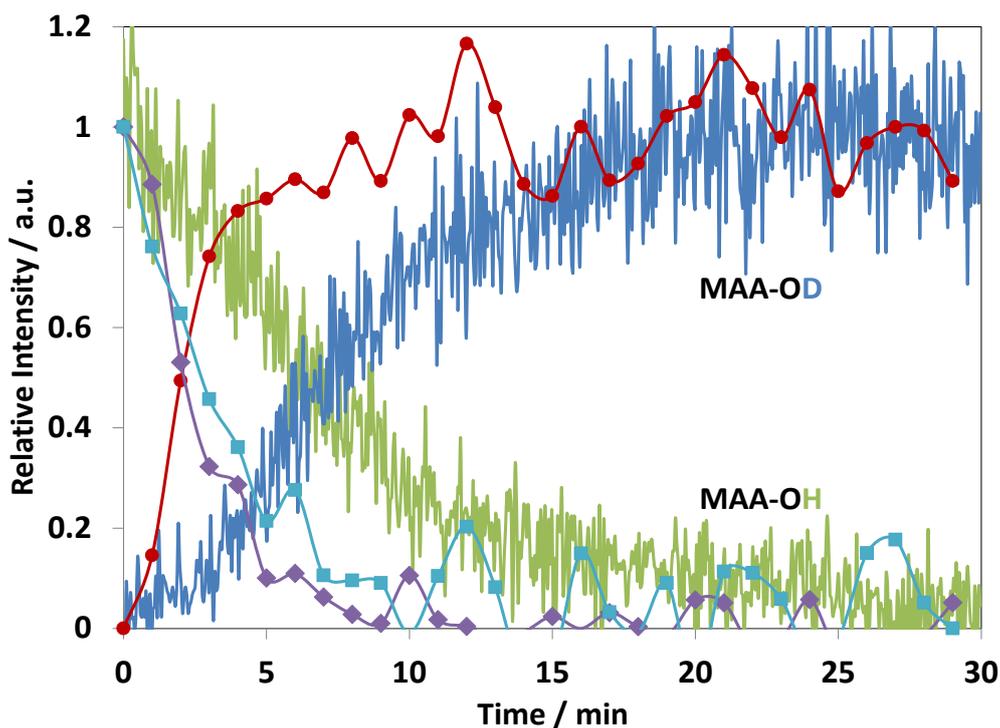


Figure S8 Evolution with time of changes of the relative intensities of the DRIFT spectra of MoO_tH (■, 1031 cm⁻¹), Mo=O_t (●, 1017 cm⁻¹), and MoO_tH (◆, 998 cm⁻¹), and the corresponding mass spectrometry signal of gas phase MAA-OD and MAA-OH observed during the isotopic cycling switches over H₃PMoO₁₂O₄₀ 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.