Supporting Information

An *in-situ* DRIFTS-MS study on elucidating the role of V in the selective oxidation of methacrolein to methacrylic acid over heteropolyacid compounds

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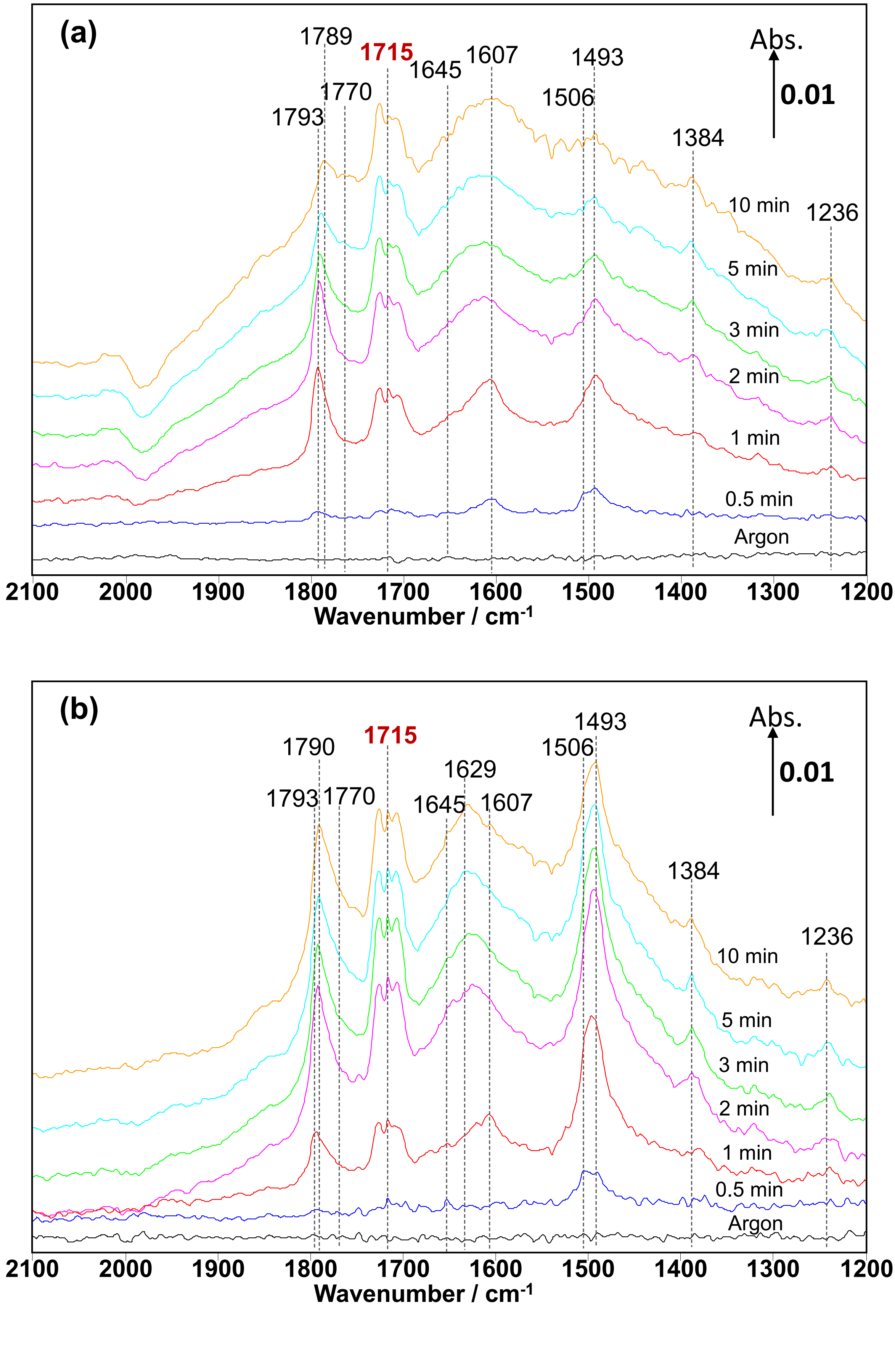

(a)
1789
1715
1645
1607
1493
1770
1506
1793
1384
1236
Abs.
0.01
10 min
5 min
3 min
2 min
1 min
0.5 min
Argon
2100 2000 1900 1800 1700 1600 1500 1400 1300 1200
Wavenumber / cm-1
(b)
1790
1715
1629
1493
1506
1793
1770
1645
1607
1384
1236
Abs.
0.01
10 min
5 min
3 min
2 min
1 min
0.5 min
Argon
2100 2000 1900 1800 1700 1600 1500 1400 1300 1200
Wavenumber / cm-1

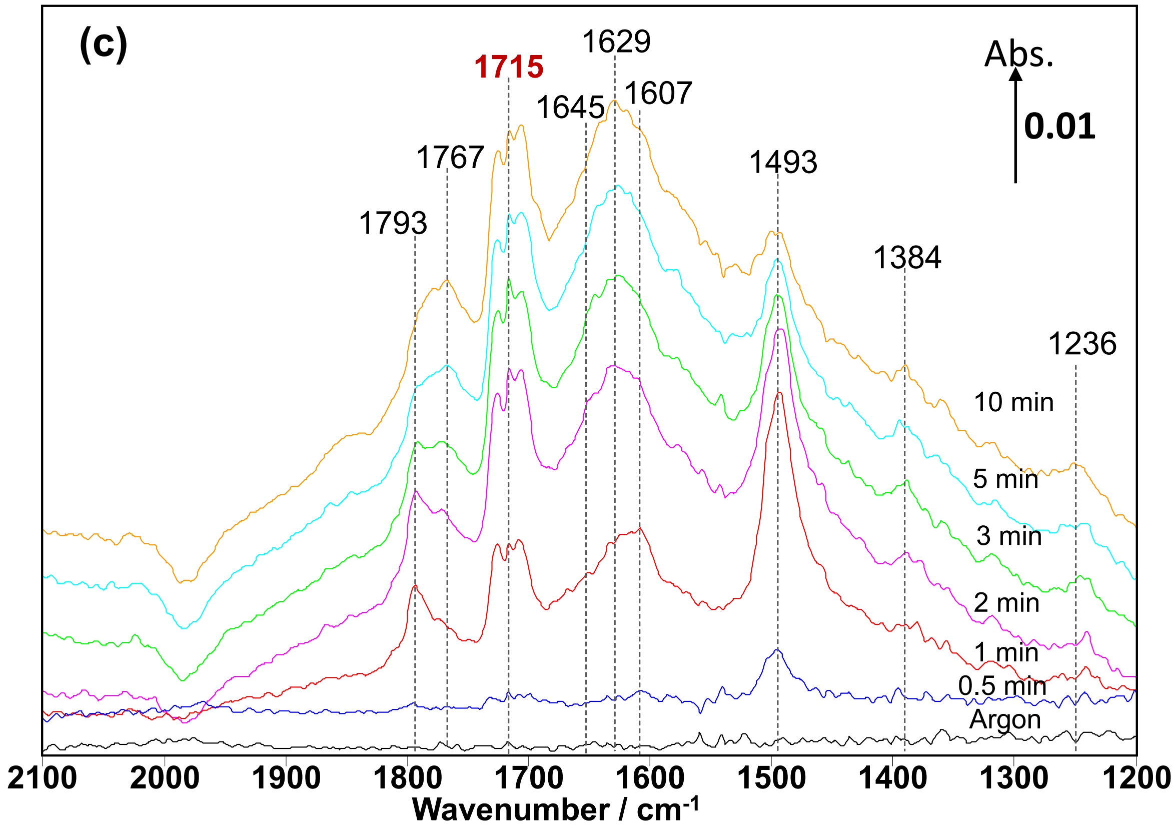
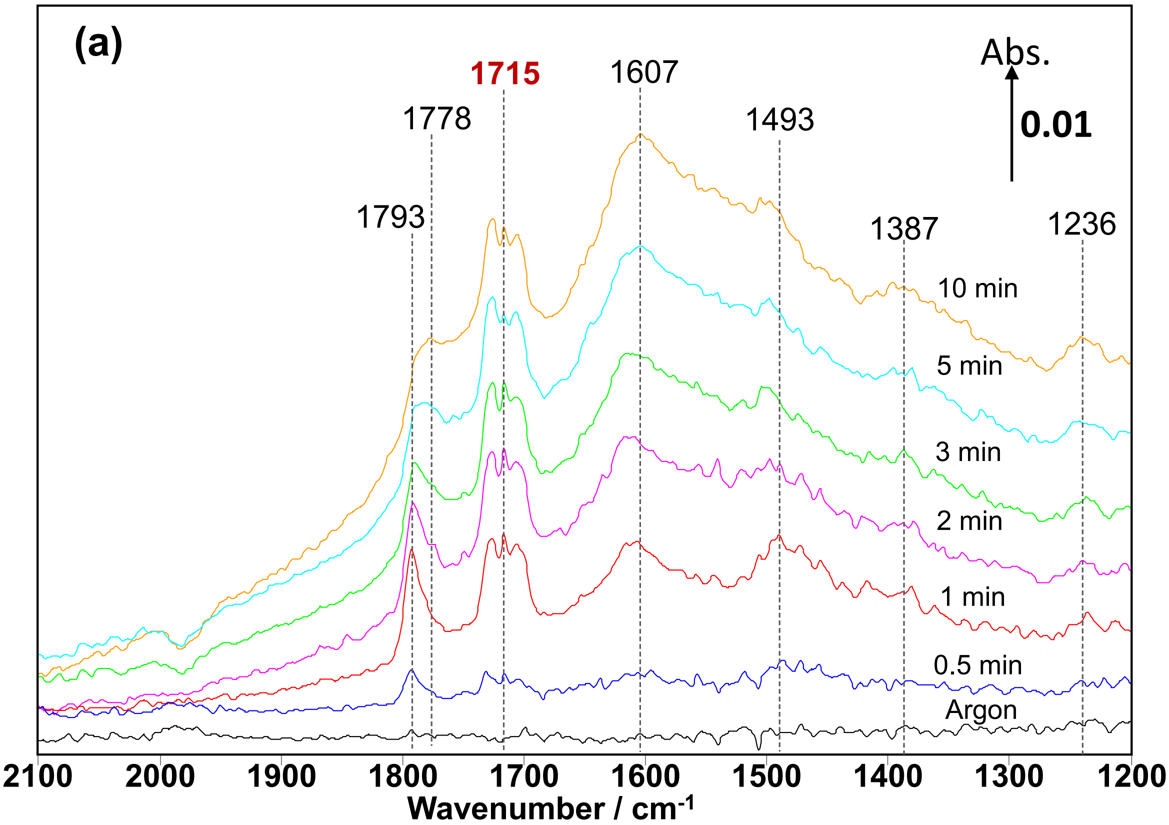
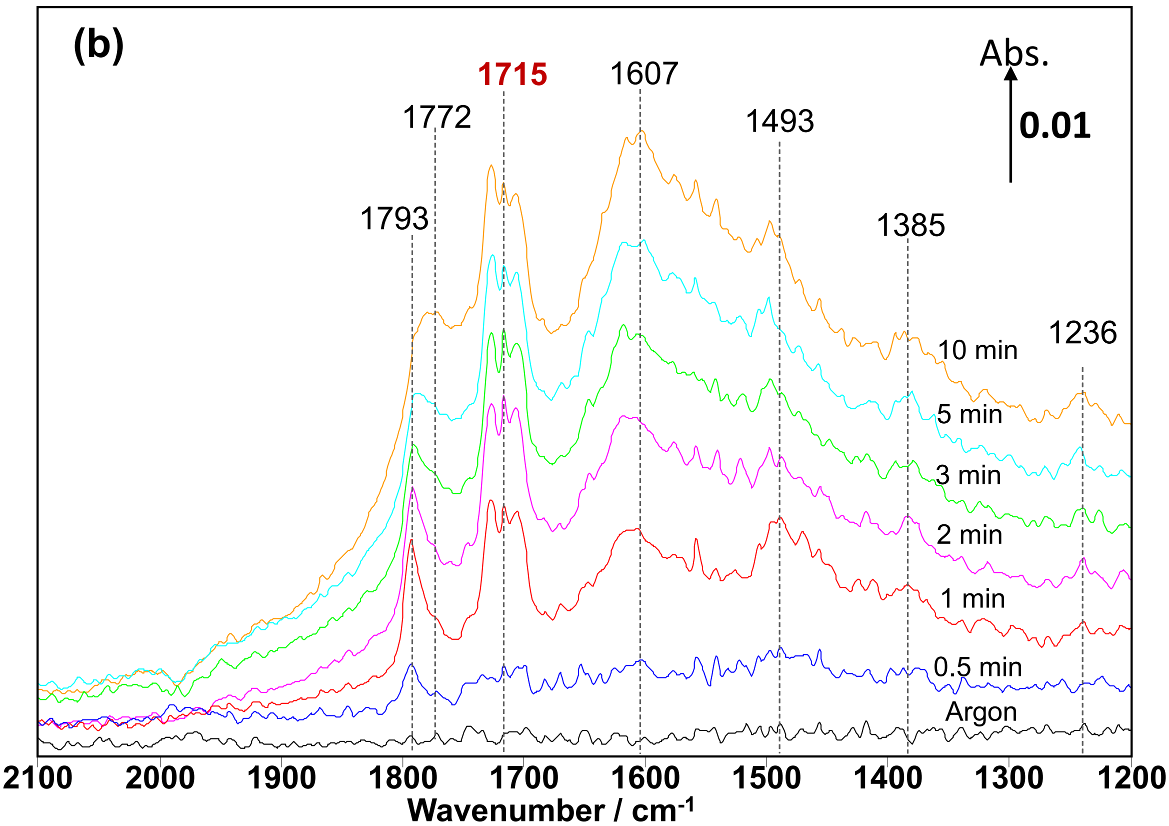


Figure S1 Changes in *in-situ* DRIFT spectra recorded at 320 °C over **HPMo** catalyst within 10 min under MAL (**a**), MAL+O_2 (**b**), and MAL+O_2+H_2O (**c**). Gas feed is composed of 3500 ppm MAL (when added), 7000 ppm O_2 (when added), 7000 ppm H_2O (when added), and Ar balance and the total flow rate is 100 cm^3 min^{-1}.


(a)
1715
1607
1778
1493
1793
1387
1236
Abs.
0.01
10 min
5 min
3 min
2 min
1 min
0.5 min
Argon
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
Wavenumber / cm-1


(b)
1715
1607
1772
1493
1793
1385
1236
Abs.
0.01
10 min
5 min
3 min
2 min
1 min
0.5 min
Argon
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
Wavenumber / cm-1

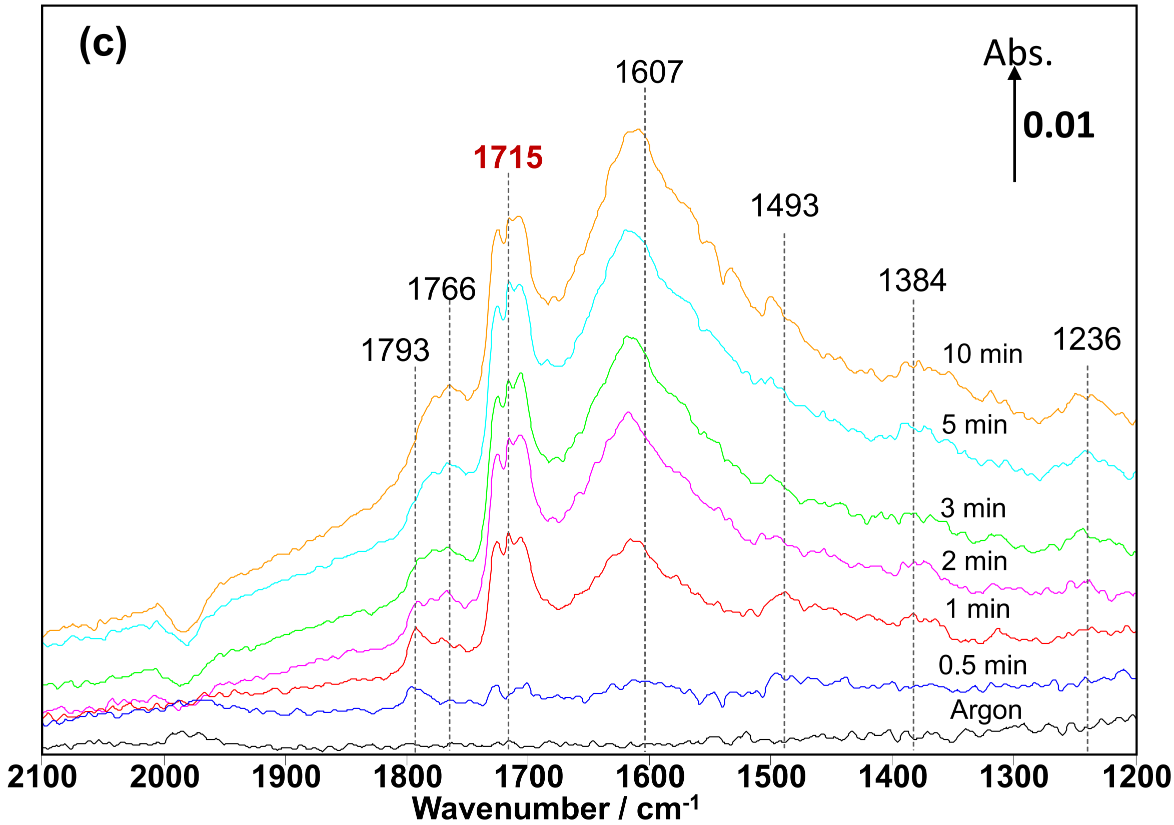
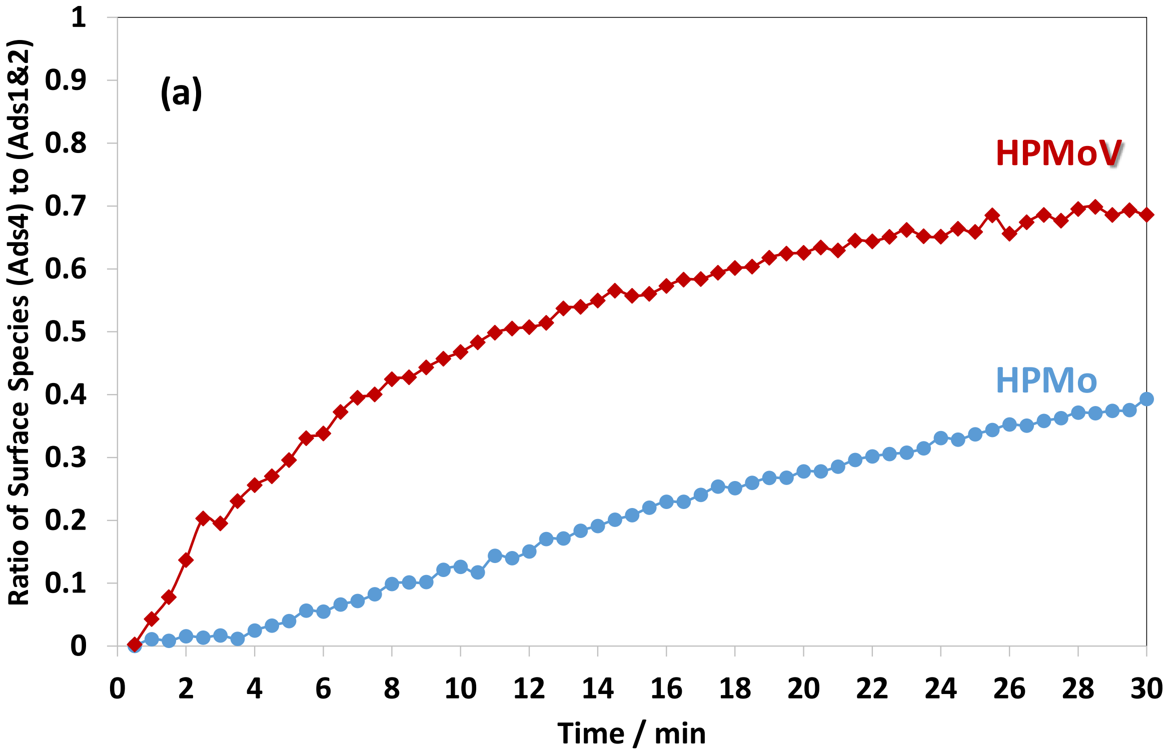
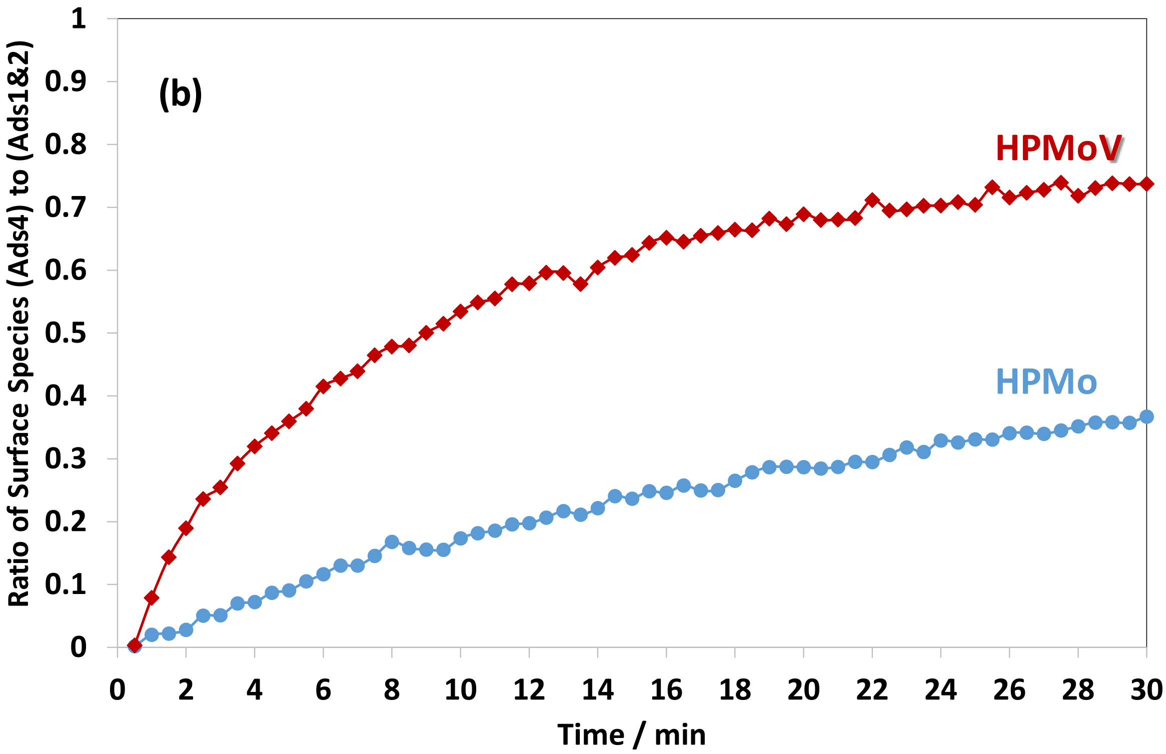


Figure S2 Changes in *in-situ* DRIFT spectra recorded at 320 °C over **HPMoV** catalyst within 10 min under MAL (**a**), MAL+O_2 (**b**), and MAL+O_2+H_2O (**c**). Gas feed is composed of 3500 ppm MAL (when added), 7000 ppm O_2 (when added), 7000 ppm H_2O (when added), and Ar balance and the total flow rate is 100 cm^3 min^{-1}.


(a)
HPMoV
HPMo
Ratio of Surface Species (Ads4) to (Ads1&2)
Time / min
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30


(b)
HPMoV
HPMo
Ratio of Surface Species (Ads4) to (Ads1&2)
Time / min
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

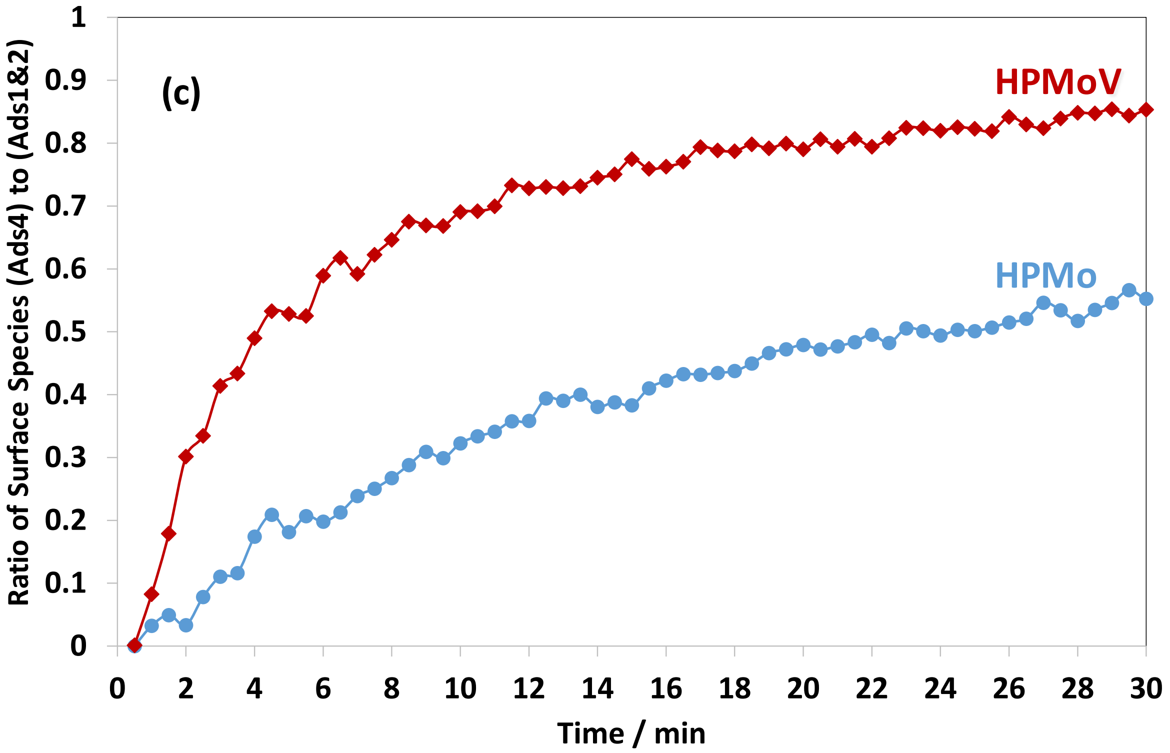
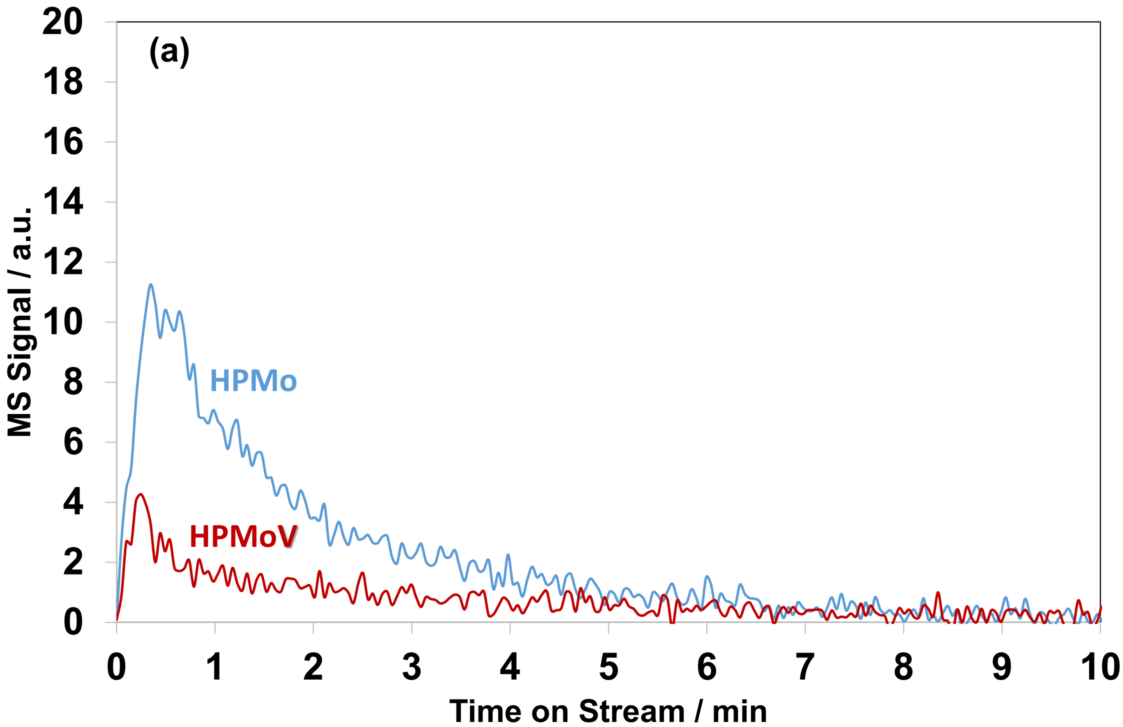


Figure S3 Changes in ratio of monodentate methacrylate adsorbed species (**Ads4**) in the IR range of 1780 – 1760 cm^{-1} to lactone-type adsorbed species (**Ads1** and **Ads2**) in the IR range of 1800 – 1780 cm^{-1} as a function of time on stream at 320 °C over HPMo and HPMoV catalysts under MAL (**a**), MAL+O_2 (**b**), and MAL+O_2+H_2O (**c**) reaction conditions. Gas feed is composed of 3500 ppm MAL (when added), 7000 ppm O_2 (when added), 7000 ppm H_2O (when added), and Ar balance and the total flow rate is 100 cm^3 min^{-1}.



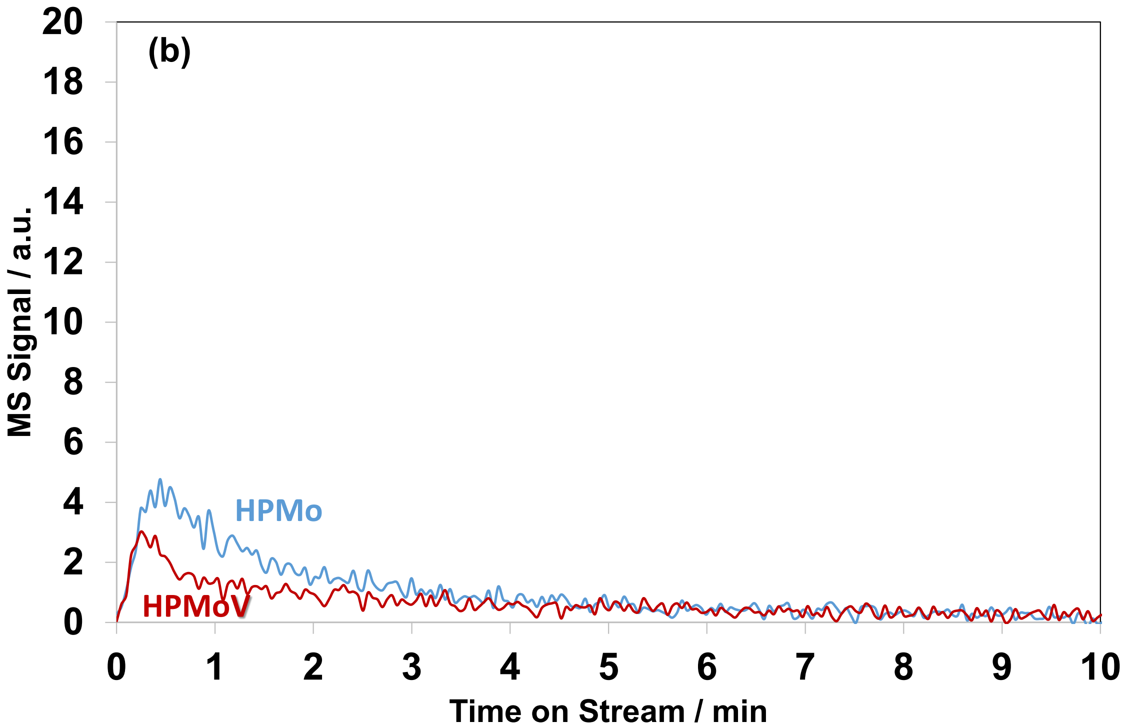


Figure S4 Comparison of the evolution of CO (**a**) and CO_2 (**b**) formation as a function of time on stream at 320 °C over $H_3PMoO_{12}O_{40}$ (HPMo) and $H_4PMoO_{11}VO_{40}$ (HPMoV) under **MAL** adsorption. Gas feed is composed of 3500 ppm MAL and Ar balance and the total flow rate is 100 cm^3 min^{-1}.

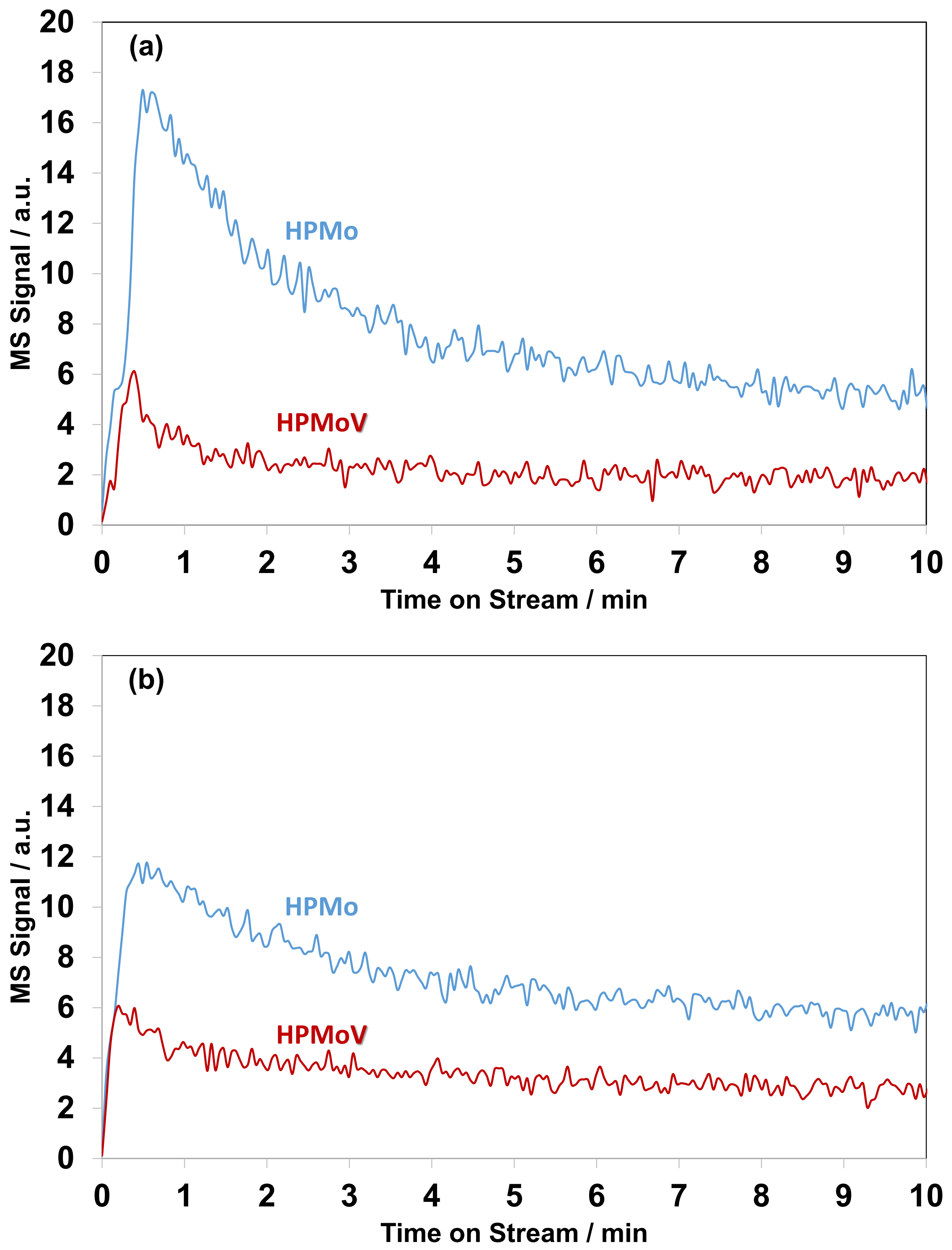


Figure S5 Comparison of the evolution of CO (**a**) and CO_2 (**b**) formation at 320 °C as a function of time on stream over $H_3PMoO_{12}O_{40}$ (HPMo) and $H_4PMoO_{11}VO_{40}$ (HPMoV) under **MAL+O_2** reaction. Gas feed is composed of 3500 ppm MAL, 7000 ppm O_2, and Ar balance and the total flow rate is 100 cm^3 min^{-1}.

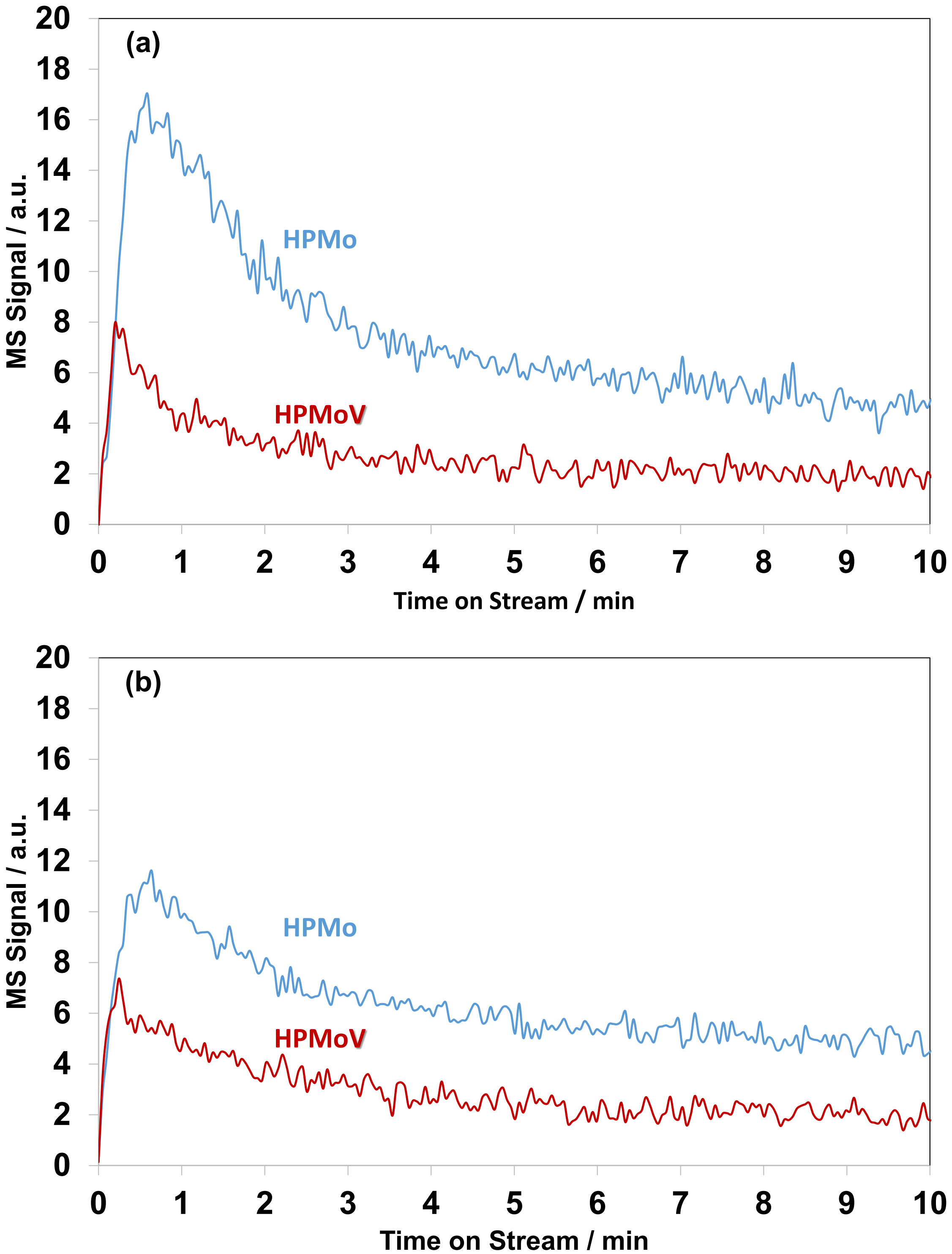
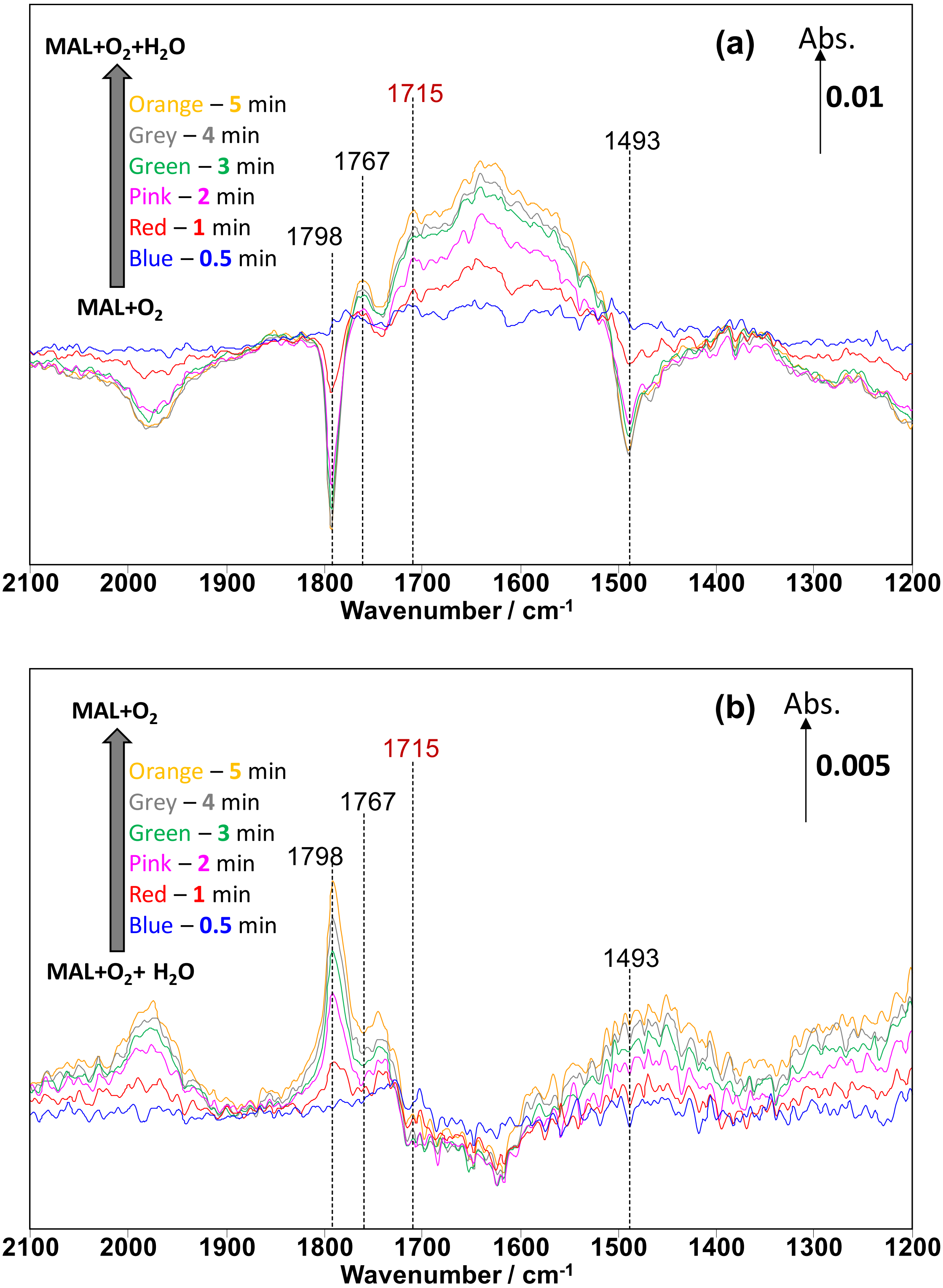


Figure S6 Comparison of the evolution of CO (**a**) and CO_2 (**b**) formation at 320 °C as a function of time on stream over $H_3PMoO_{12}O_{40}$ (HPMo) and $H_4PMoO_{11}VO_{40}$ (HPMoV) under **MAL+O_2+H_2O** reaction. Gas feed is composed of 3500 ppm MAL, 7000 ppm O_2, 7000 ppm H_2O and Ar balance and the total flow rate is 100 cm^3 min^{-1}.



(a)
Abs.
0.01
MAL+O$_2$+H$_2$O
Orange – 5 min
Grey – 4 min
Green – 3 min
Pink – 2 min
Red – 1 min
Blue – 0.5 min
MAL+O$_2$
1798
1767
1715
1493
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
Wavenumber / cm^{-1}
(b)
Abs.
0.005
MAL+O$_2$
Orange – 5 min
Grey – 4 min
Green – 3 min
Pink – 2 min
Red – 1 min
Blue – 0.5 min
MAL+O$_2$+ H$_2$O
1798
1767
1715
1493
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
Wavenumber / cm^{-1}

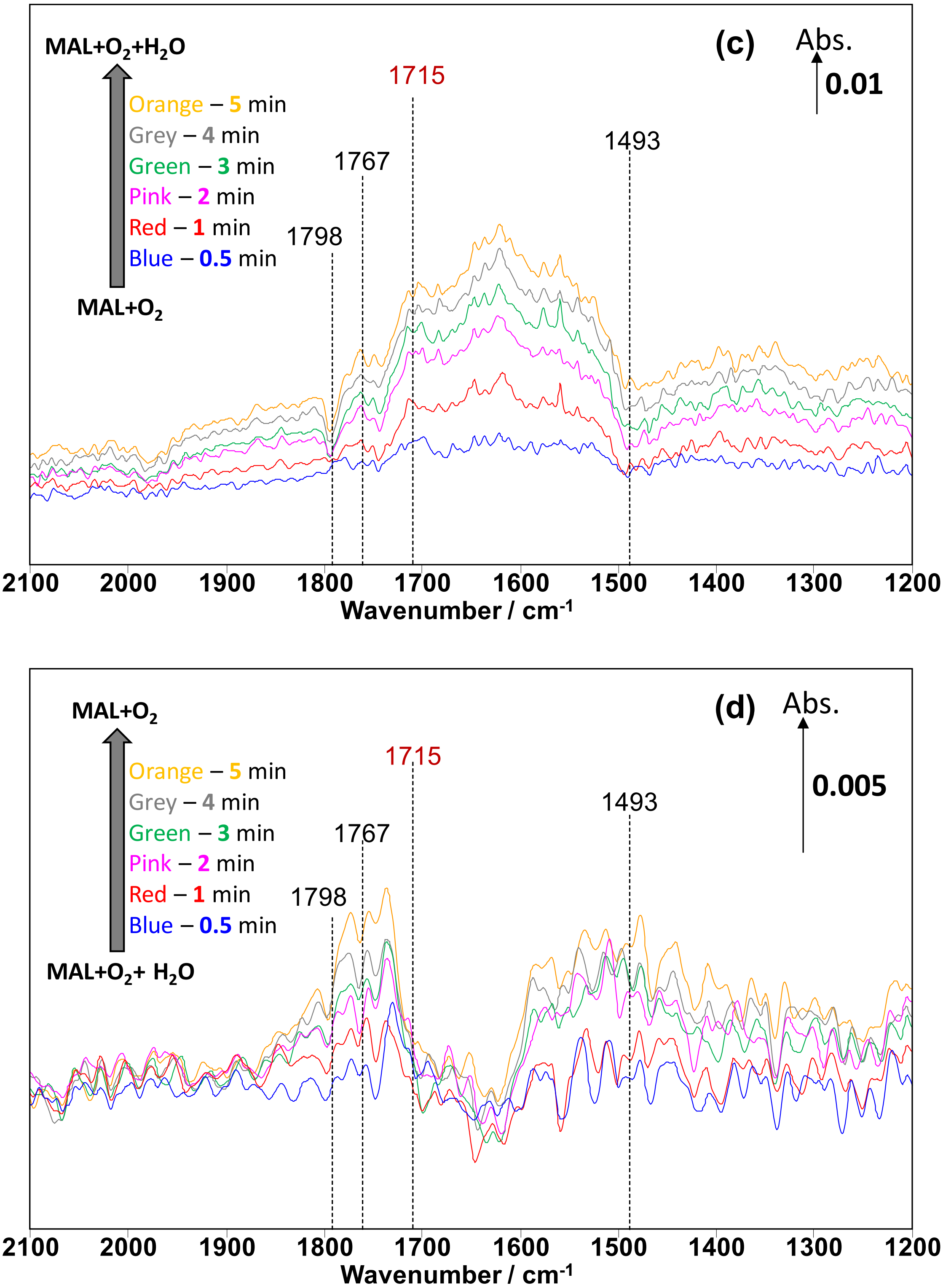


Figure S7 Changes in ***difference*** DRIFT spectra (2100 – 1200 cm^{-1}) corresponding to the formation of MAA formation shown in Figure 3 as a function of time on stream over HPMo (**a, b**) and HPMoV (**c,d**) catalysts at 320 °C during the 2nd cycle of switches of H_2O in and out of MAL+O_2 gas feed. Gas feed is composed of 3500 ppm MAL, 7000 ppm O_2, 7000 ppm H_2O (when added), and Ar balance and the total flow rate is 100 cm^3 min^{-1}.

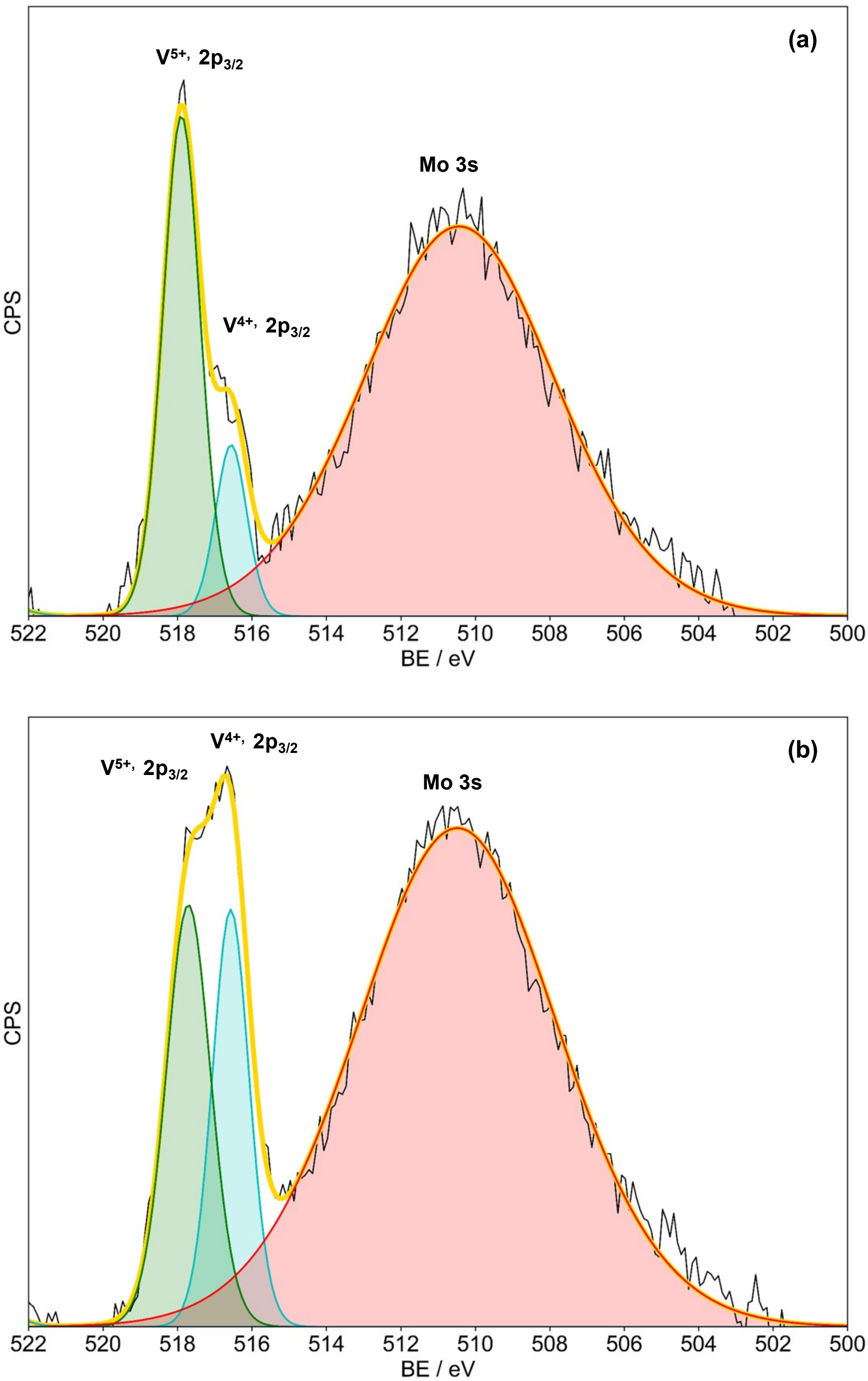
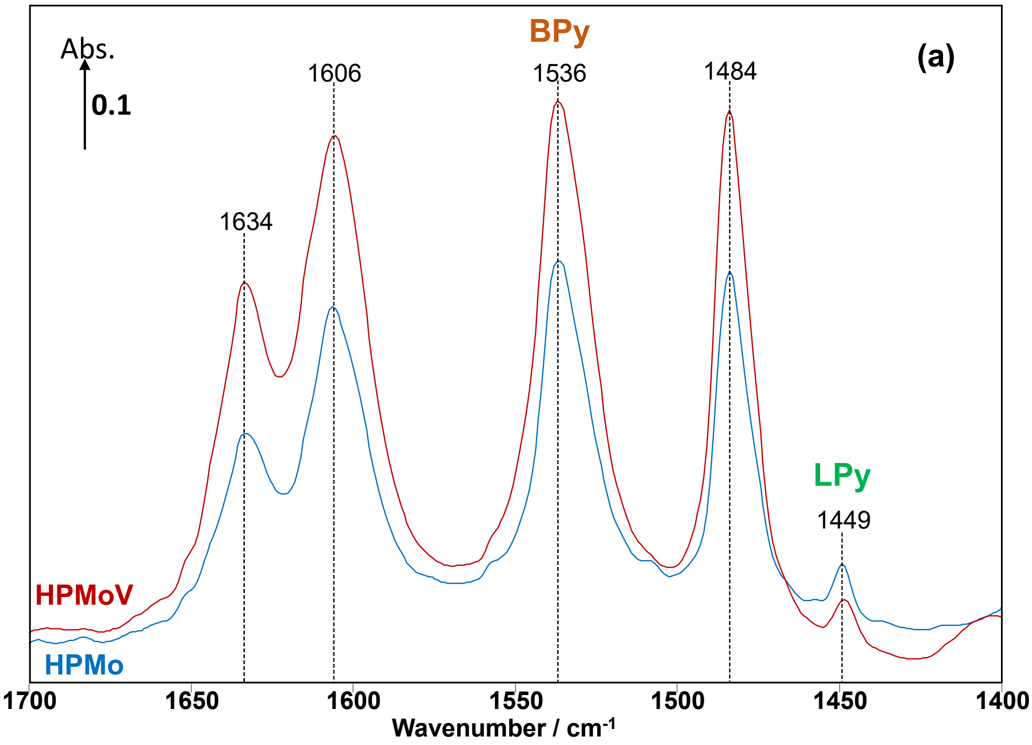


Figure S8 Comparison of V $2p_{3/2}$ XPS spectra of $H_4PMoO_{11}VO_{40}$ (HPMoV) catalyst before (**a**) and after (**b**) MAL+O_2+H_2O reaction at 320 °C for 60 min. Gas feed is composed of 3500 ppm MAL, 7000 ppm O_2, 7000 ppm H_2O and Ar balance and the total flow rate is 100 cm^3 min^{-1}.



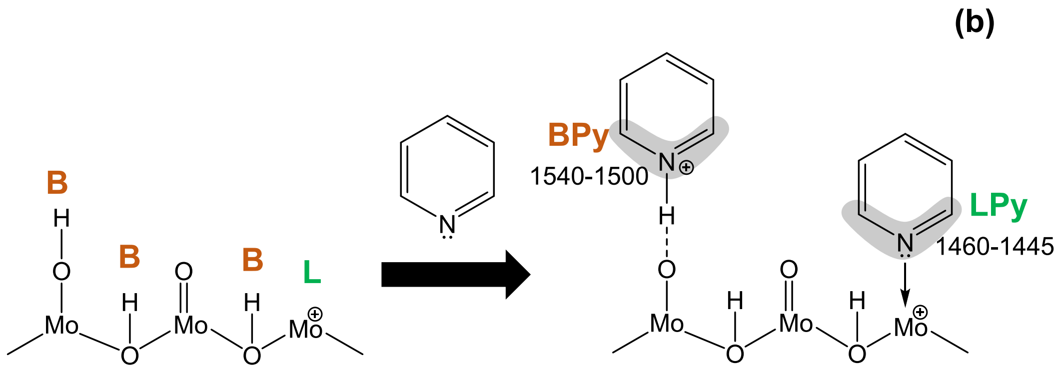


Figure S9 Comparison of *in-situ* DRIFT spectra of pyridine adsorption at 320 °C (**a**) at 10 min under Ar purge after pyridine adsorption at 30 °C for 60 min over $H_3PMoO_{12}O_{40}$ (HPMo) and $H_4PMoO_{11}VO_{40}$ (HPMoV) and the schematic representation of acid sites of heteropoly acids (**b**). Adsorption feed is composed of 3500 ppm pyridine and Ar balance and the total flow rate is 100 cm^3 min^{-1}.