

Supporting Information for

Deactivation Behavior of an Iron-Molybdate Catalyst During Selective Oxidation of Methanol to Formaldehyde†

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Figure S1: Raman spectra of relevant reference phases.

Figure S2: Relative rate for all activity experiments.

Figure S3: Arrhenius plot measured prior to experiments

Figure S4: Carbon mol balance for activity measurements.

Figure S5: XRD patterns of most relevant spectral range of (Figure 2)

Figure S6: Raman spectra of most relevant spectral range (Figure 3)

Figure S7: Test for sample laser damage during Raman spectroscopy for the sample run for 600 h on stream.

Figure S8-S12: SEM-EDS of fresh and spent catalyst (TOS = 10-600 h).

Figure S13-S17: SEM images of fresh and spent catalyst (TOS = 10-600 h).

Figure S18-S27 STEM high-angle annular dark-field images and elemental mapping images.

Figure S28: XPS spectrums of fresh and spent catalyst (TOS = 10-600 h).

Raman spectra: Relevant reference phases.

The Raman spectra of β - MoO_3 are shown in the literature¹ and the other relevant spectra are shown in Figure S1.

1 T. M. McEvoy and K. J. Stevenson, *Langmuir*, 2005, **21**, 3521–8.

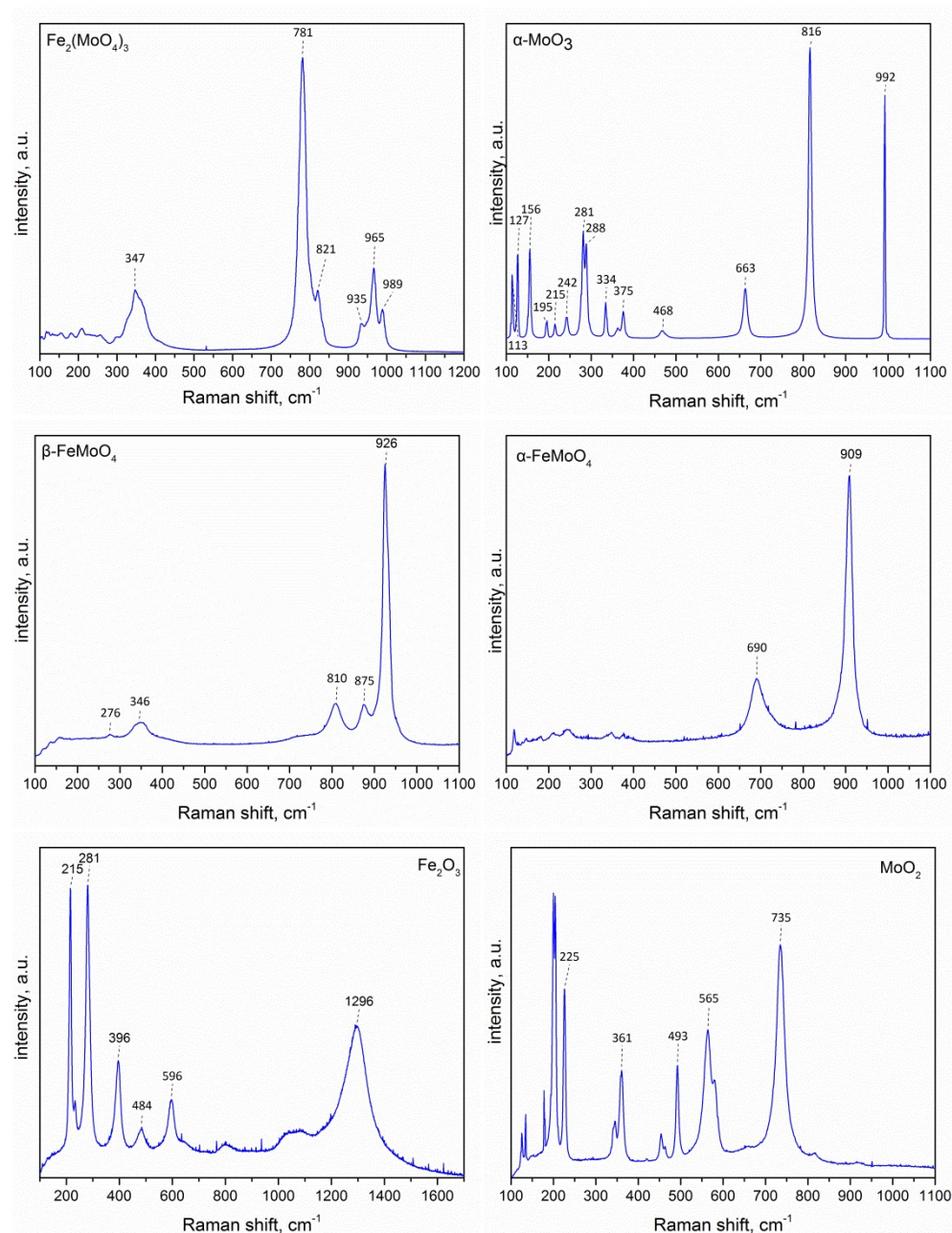


Figure S1 – Raman spectra of $\text{Fe}_2(\text{MoO}_4)_3$, $\alpha\text{-MoO}_3$, $\beta\text{-FeMoO}_4$, $\alpha\text{-FeMoO}_4$, Fe_2O_3 and MoO_2 .

Activity measurement: Comparison of relative rate between all activity experiments, Arrhenius plot and C-mol balances and selectivities.

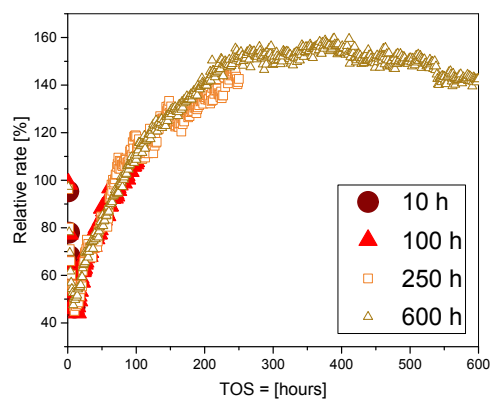


Figure S2 – Relative rates of the catalyst for all activity experiments TOS = 10, 100, 250 and 600 hours.

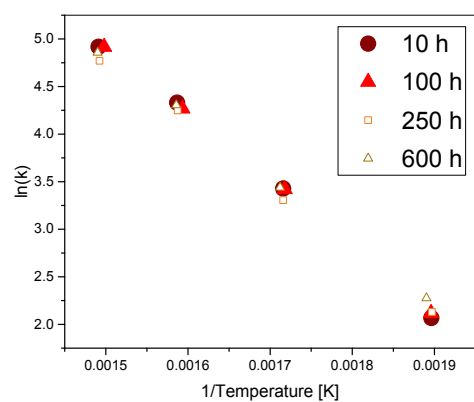


Figure S3– Arrhenius plot of rate constants measured prior to all activity experiments of the catalyst.

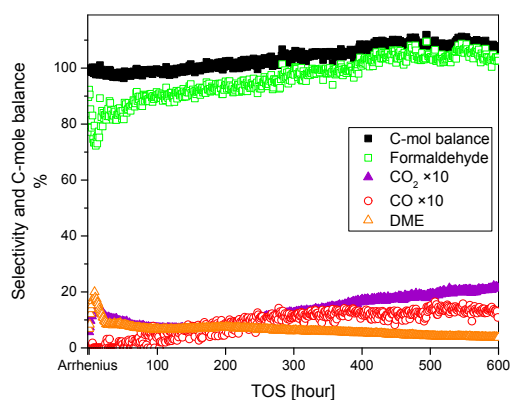
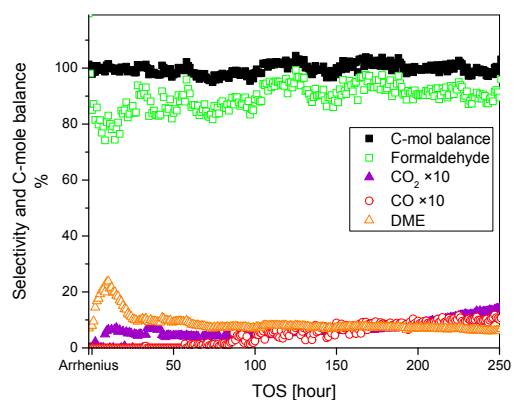
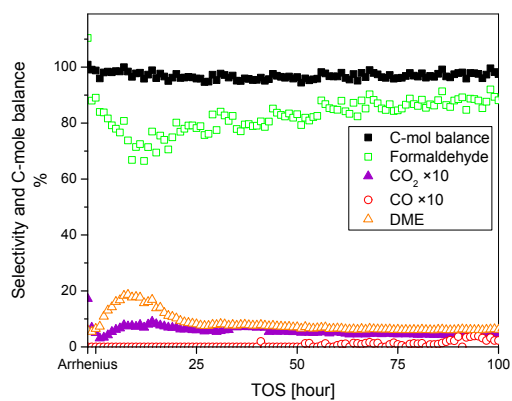
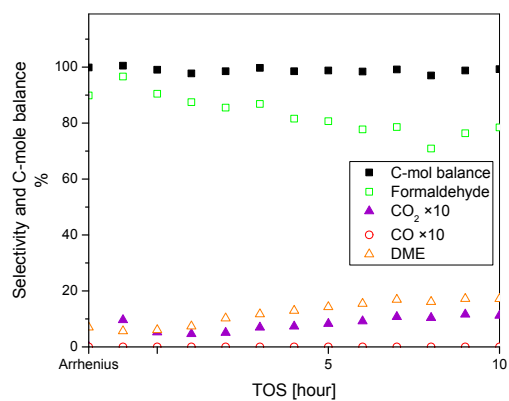


Figure S4 – Carbon mole balances and selectivities of activity experiments TOS = 10, 100, 250 and 600 hours.

XRD patterns and Raman spectra: Zoom-ins of the most relevant spectral ranges

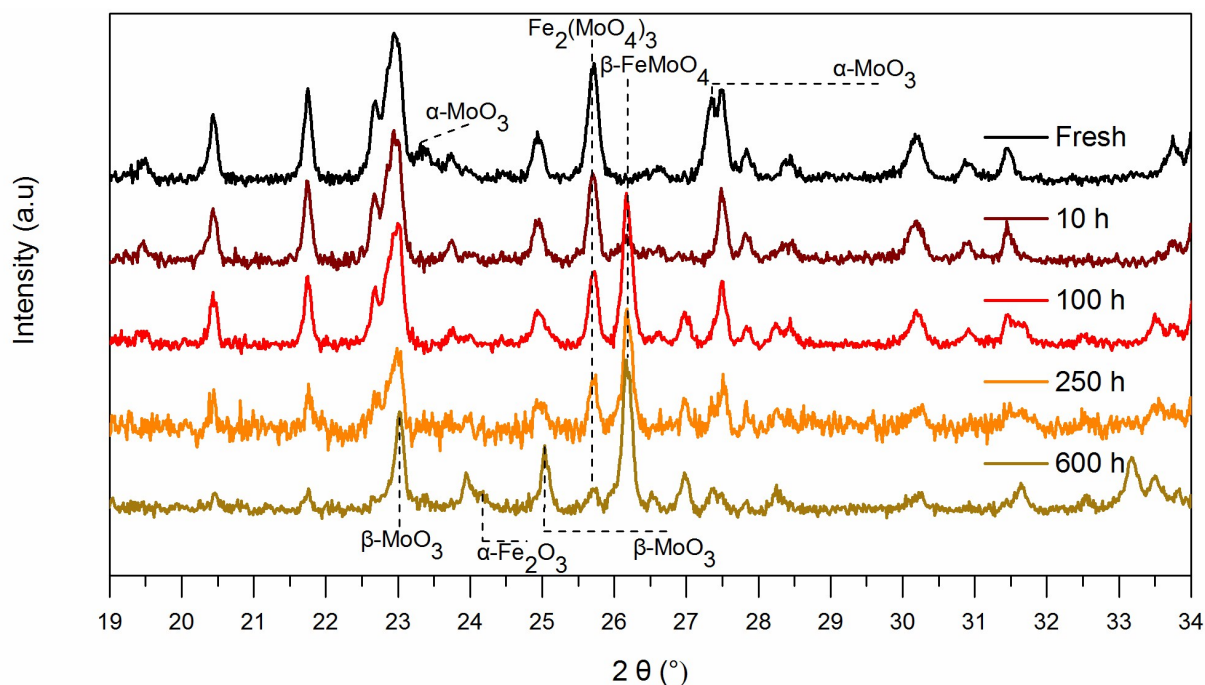


Figure S5 – Zoom-in of Figure 2: XRD patterns of the fresh and spent FeMo catalyst samples (TOS = 10, 100, 250 and 600 h).

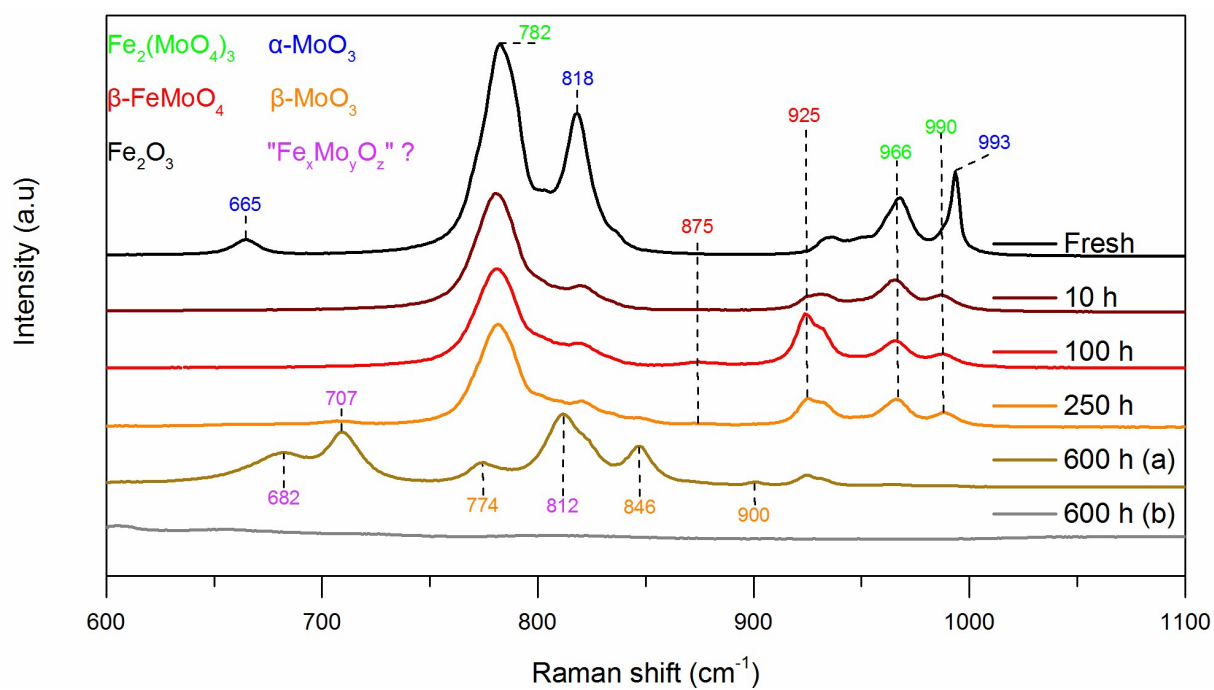


Figure S6 – Zoom-in of Figure 3: Raman spectra of the fresh and spent FeMo catalyst samples (TOS = 10, 100, 250 and 600 h). Due to the inhomogeneous nature of the catalyst after 600 h spectra from two representative positions are shown.

Raman spectroscopy: Test for sample laser damage at increasing laser power for the sample run for 600 h on stream.

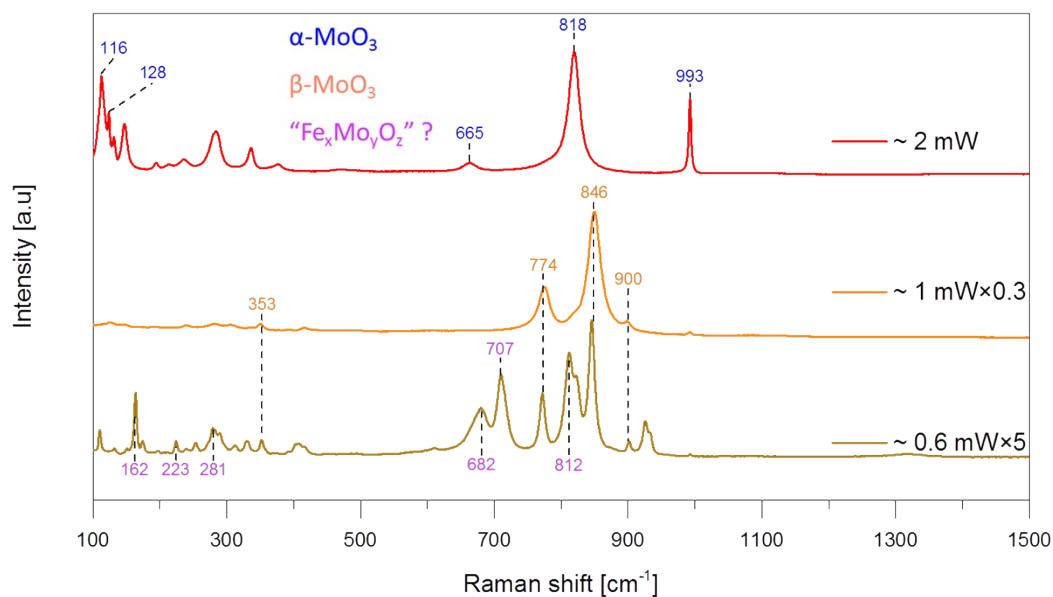


Figure S7 – Raman spectra of the spent FeMo catalyst sample (TOS = 600 h) at varying laser power.

Figure S7 shows Raman spectra of the spent FeMo catalyst after 600 h on stream at increasing laser power. At a laser power of 0.6 mW the bands at 846, 353, 774 and 900 cm^{-1} were assigned to the metastable $\beta\text{-MoO}_3$. However, bands at 682, 707 and 812 cm^{-1} could not be assigned. By increasing the laser power to 1 mW, the non-assigned bands were selectively removed (indicating a high reactivity of this phase), and by increasing the laser power further to 2 mW, the $\beta\text{-MoO}_3$ was transformed into the thermodynamically stable $\alpha\text{-MoO}_3$.

SEM: EDS analysis and Images

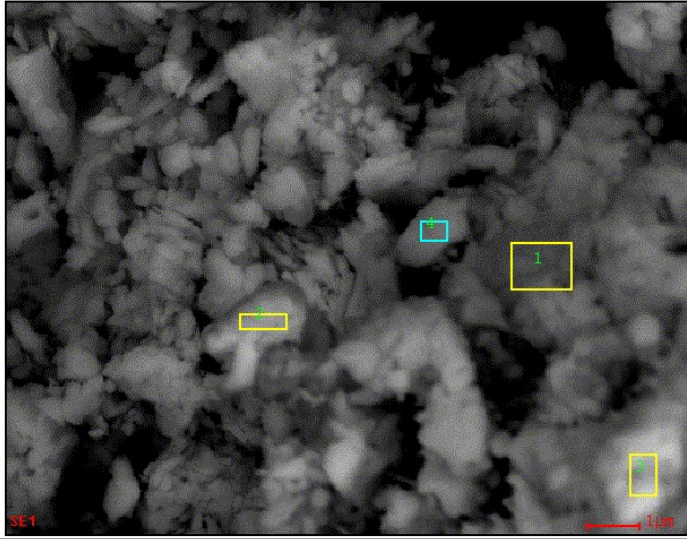
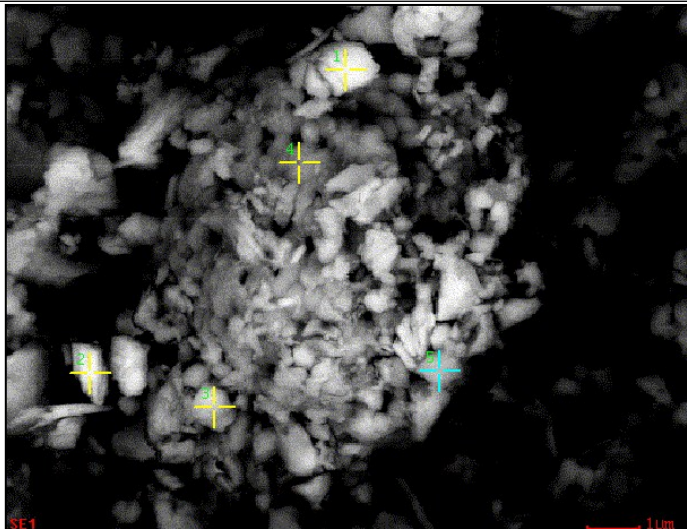
Fresh catalyst (a) Mo/Fe: Area 1 = 1.43 Area 2 = 7.19 Area 3 = 9.03 Area 4 = 7.51	
Fresh catalyst (b) Mo/Fe: Area 1 = 6.47 Area 2 = 4.48 Area 3 = 1.40 Area 4 = 1.52 Area 5 = 1.56	

Figure S8 – SEM-EDS of fresh catalyst.

Spent catalyst TOS = 10 h

Mo/Fe:

Area 1 = 1.22

Area 2 = 1.44

Area 3 = 1.46

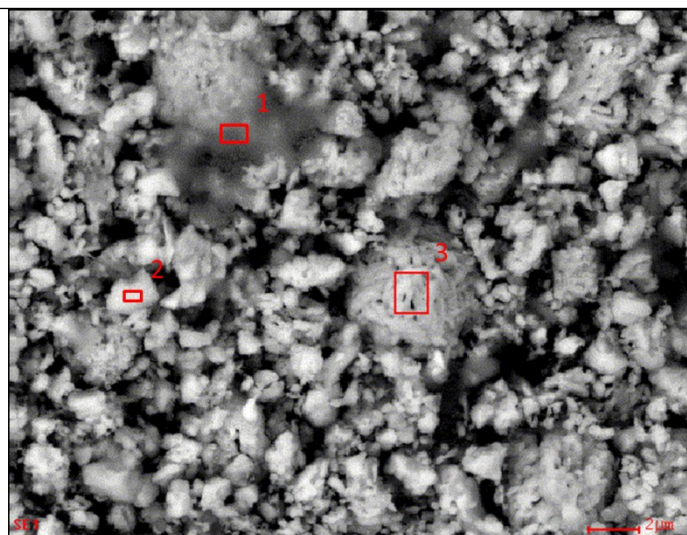


Figure S9 – SEM-EDS of spent catalyst TOS = 10 h.

Spent catalyst TOS = 100 h

Mo/Fe:

Area 1 = 0.67

Area 2 = 1.11

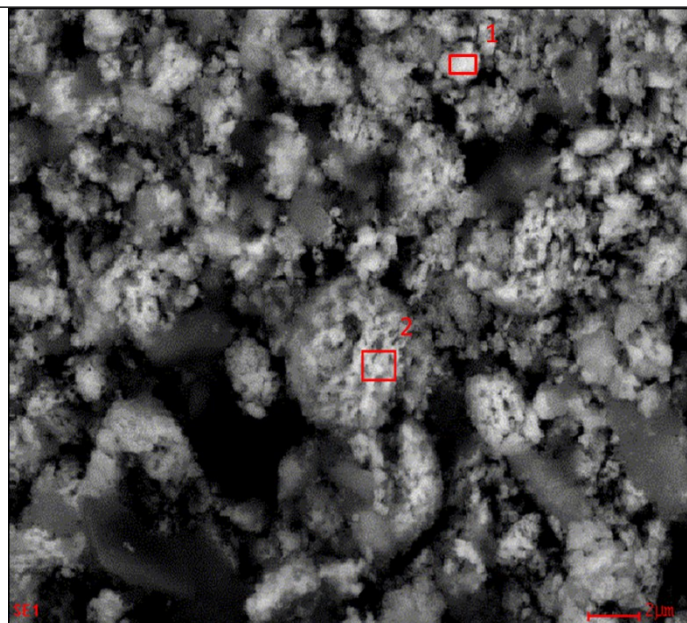


Figure S10 – SEM-EDS of spent catalyst TOS = 100 h.

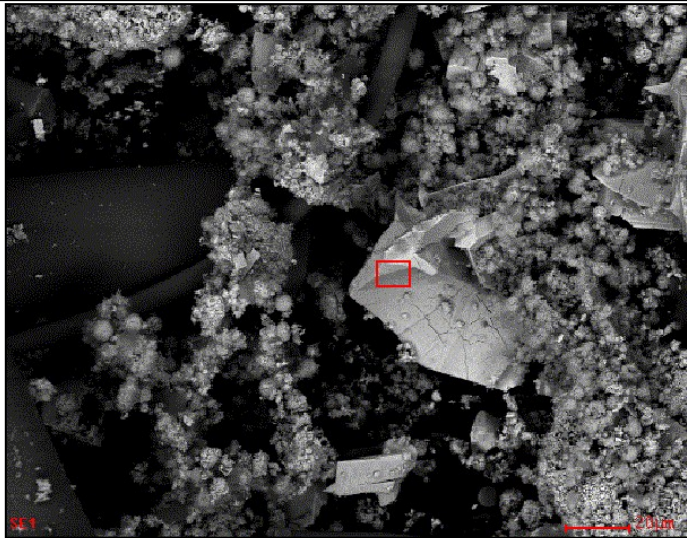
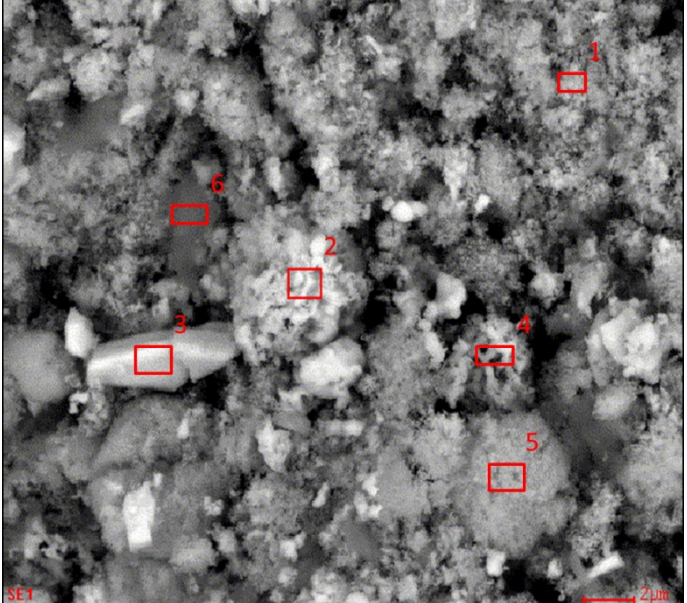
Spent catalyst TOS = 250 h (a) Mo/Fe: Area = 2.07	
Spent catalyst TOS = 250 h (b) Mo/Fe: Area 1 = 0.015 Area 2 = 1.09 Area 3 = 2.33 Area 4 = 0.66 Area 5 = 0.037 Area 6 = 0.091	

Figure S11 – SEM-EDS of spent catalyst TOS = 250 h.

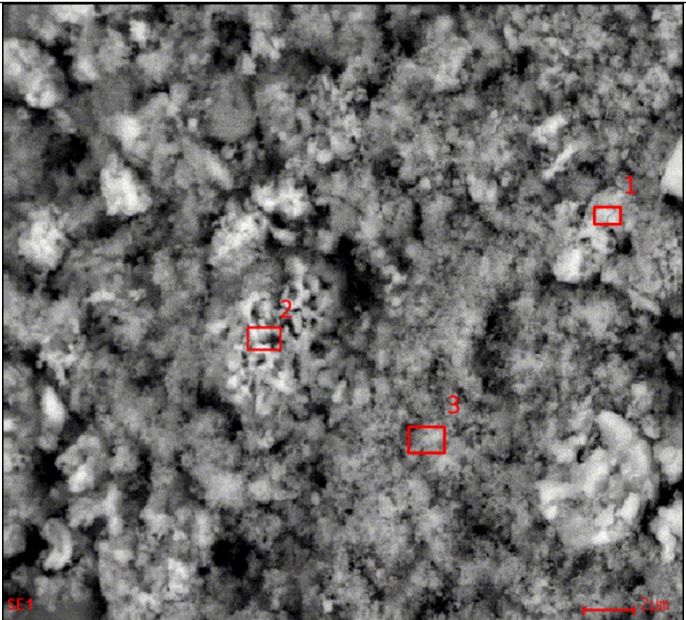
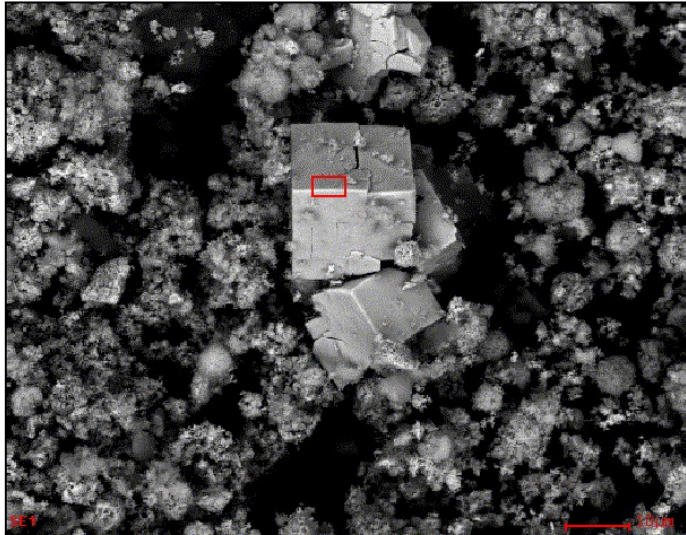
Spent catalyst TOS = 600 h (a) Mo/Fe: Area 1 = 0.56 Area 2 = 0.55 Area 3 = 0.025	
Spent catalyst TOS = 600 h (b) Mo/Fe: Area = 8.37	

Figure S12 – SEM-EDS of spent catalyst TOS = 600 h.

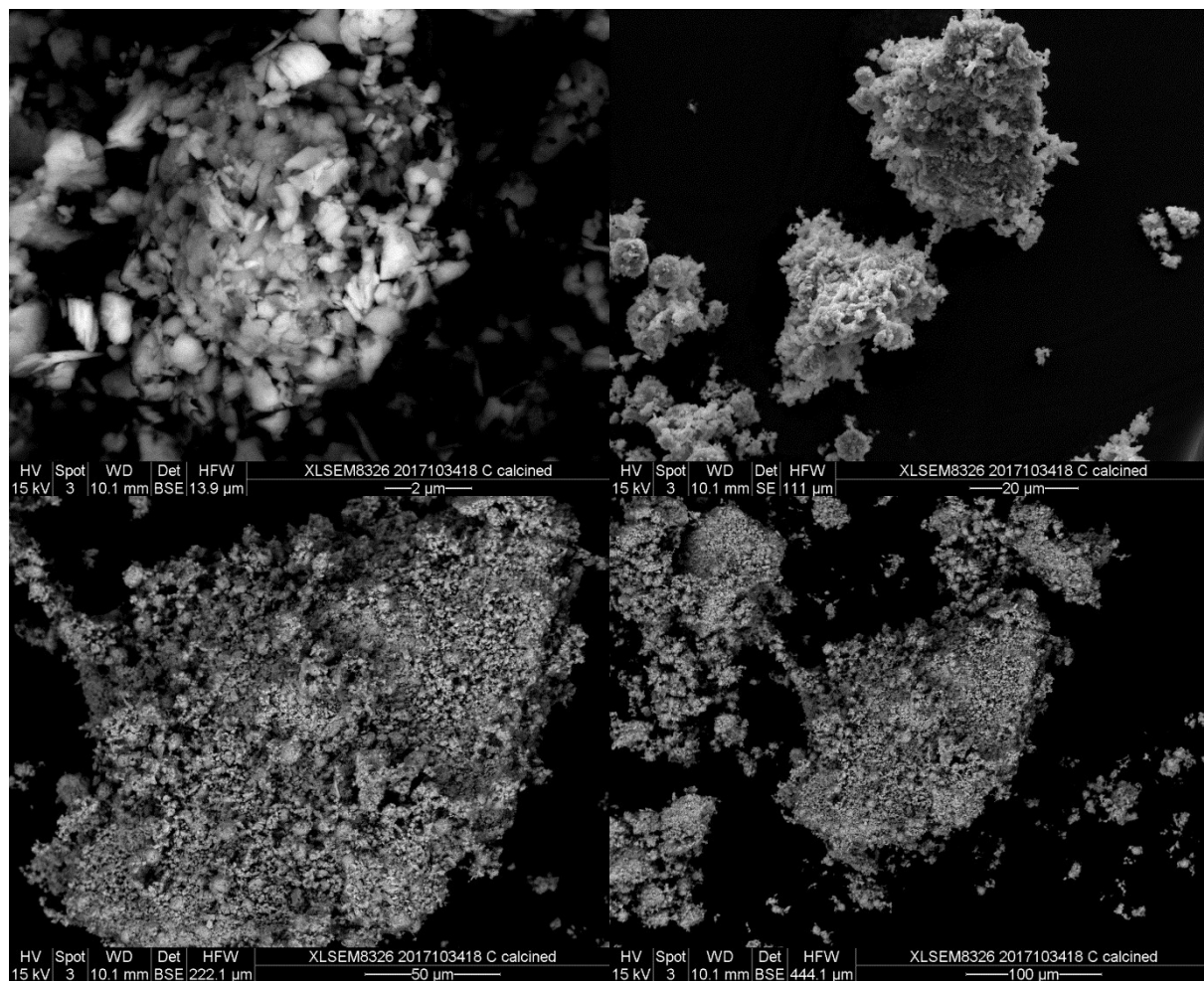


Figure S13 – SEM images of fresh catalyst.

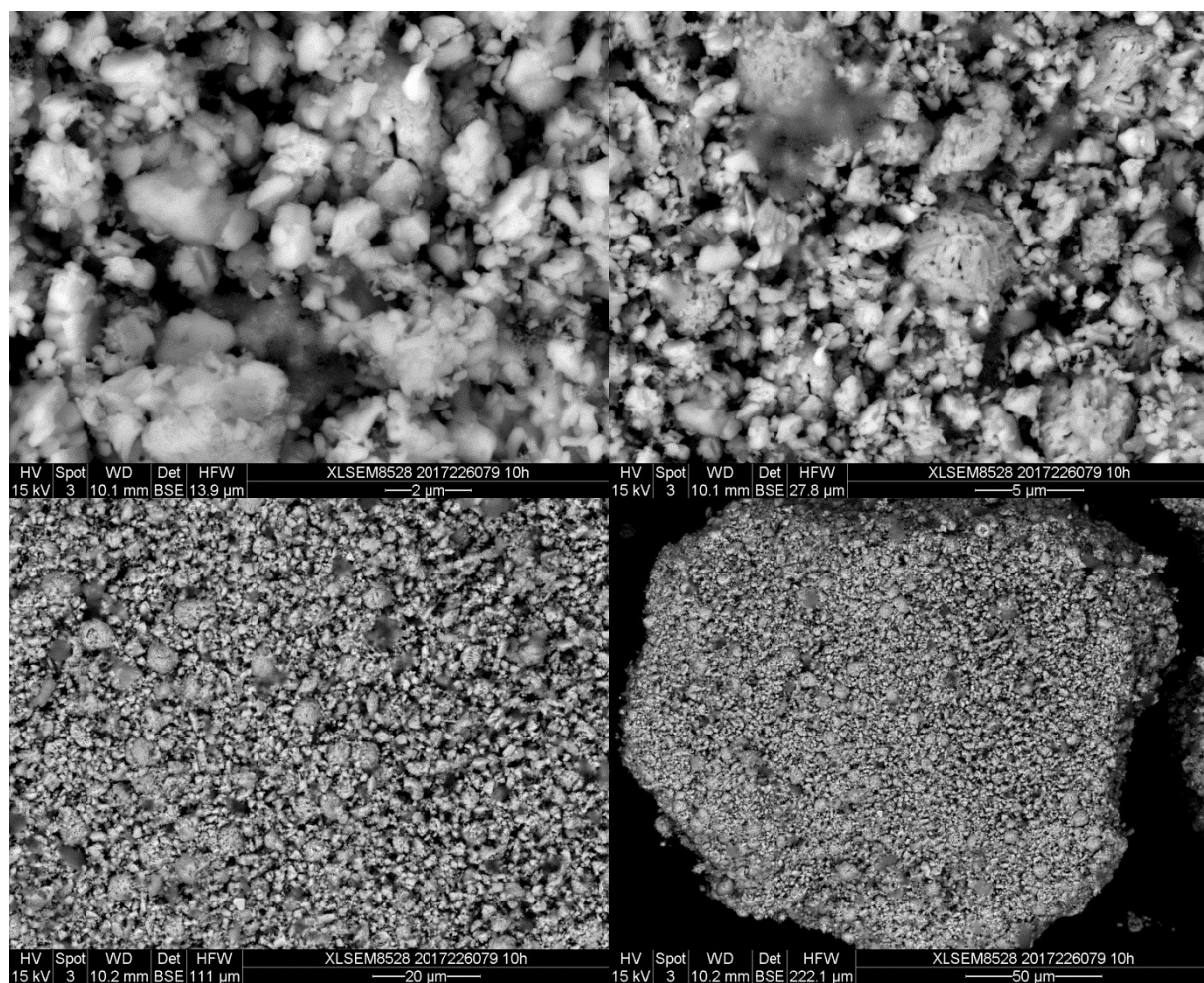


Figure S14 – SEM images of spent catalyst (TOS = 10 h).

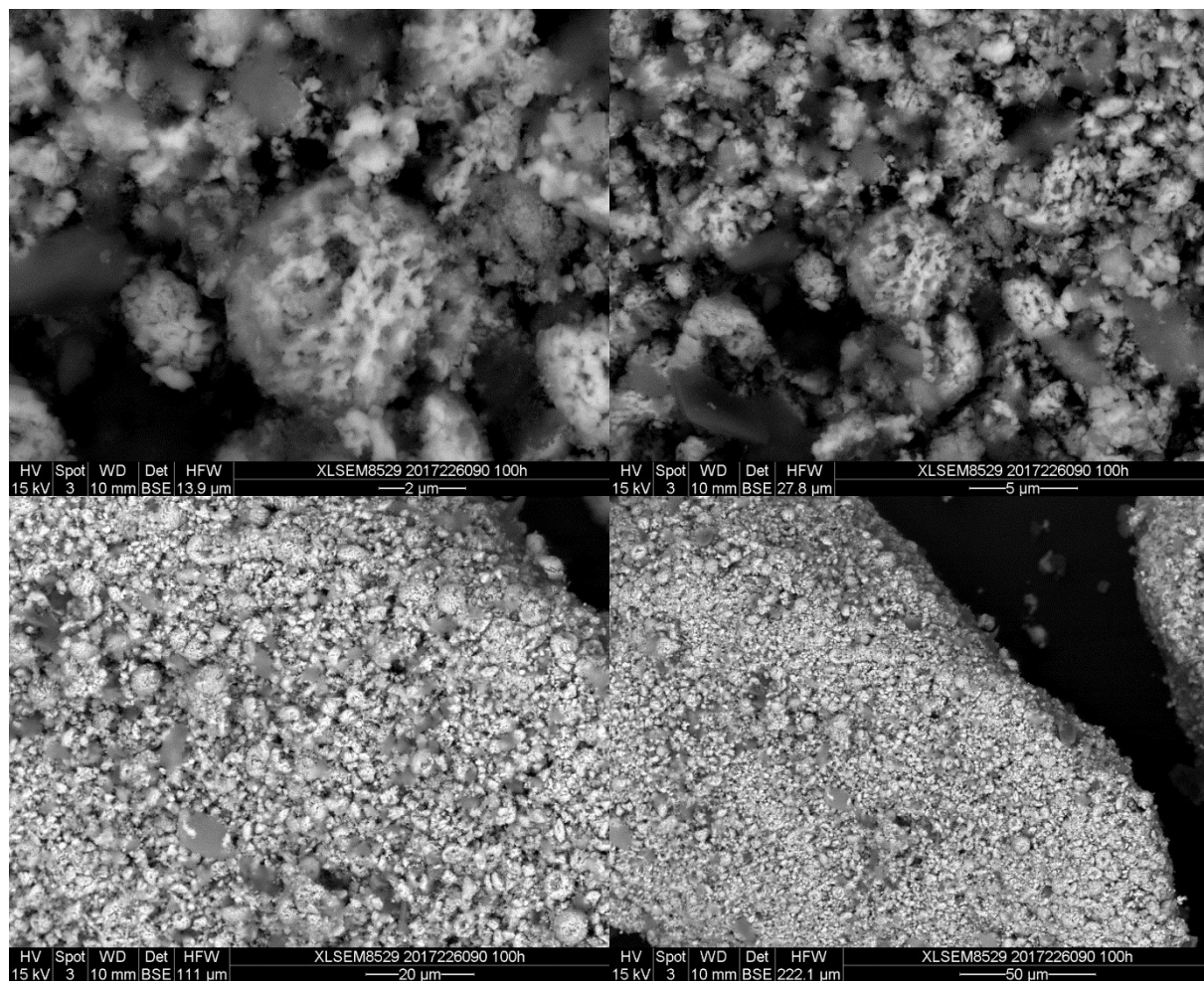


Figure S15 – SEM images of spent catalyst (TOS = 100 h).

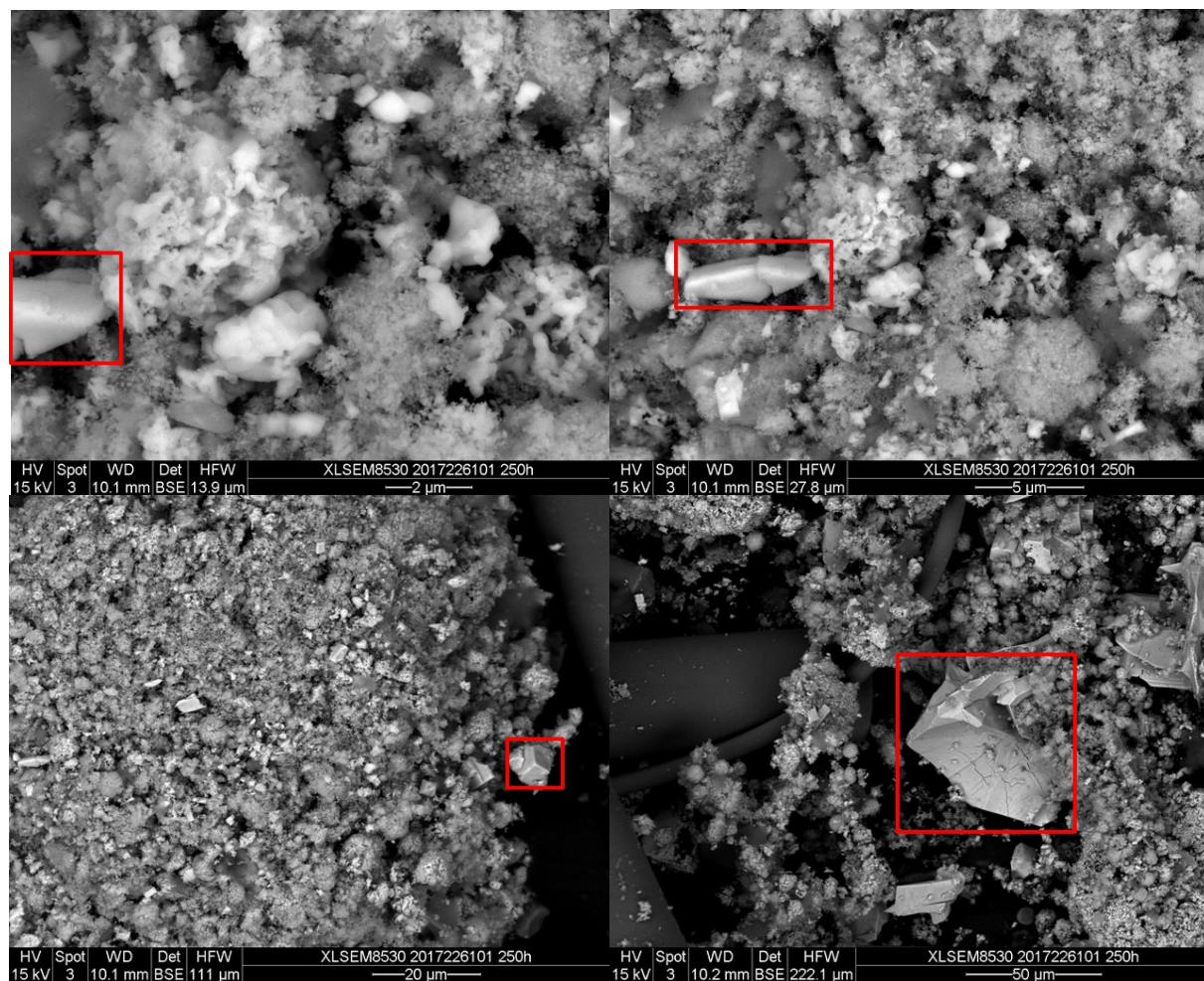


Figure S16 – SEM images of spent catalyst (TOS = 250 h). Marked crystals are MoO_3 .

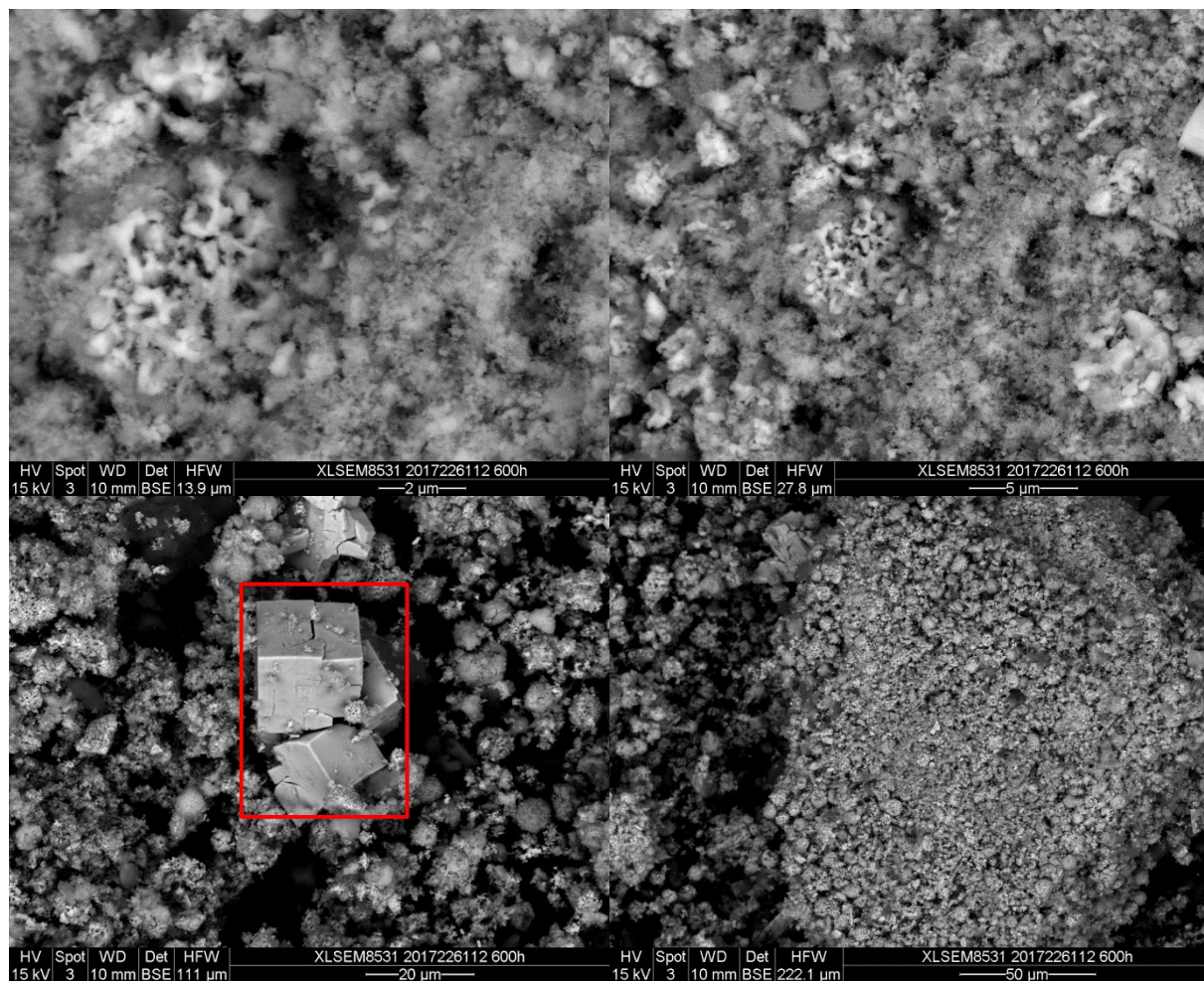


Figure S17 – SEM images of spent catalyst (TOS = 600 h). Marked crystal is MoO_3 .

STEM: High-angle annular dark-field images and elemental mapping images.

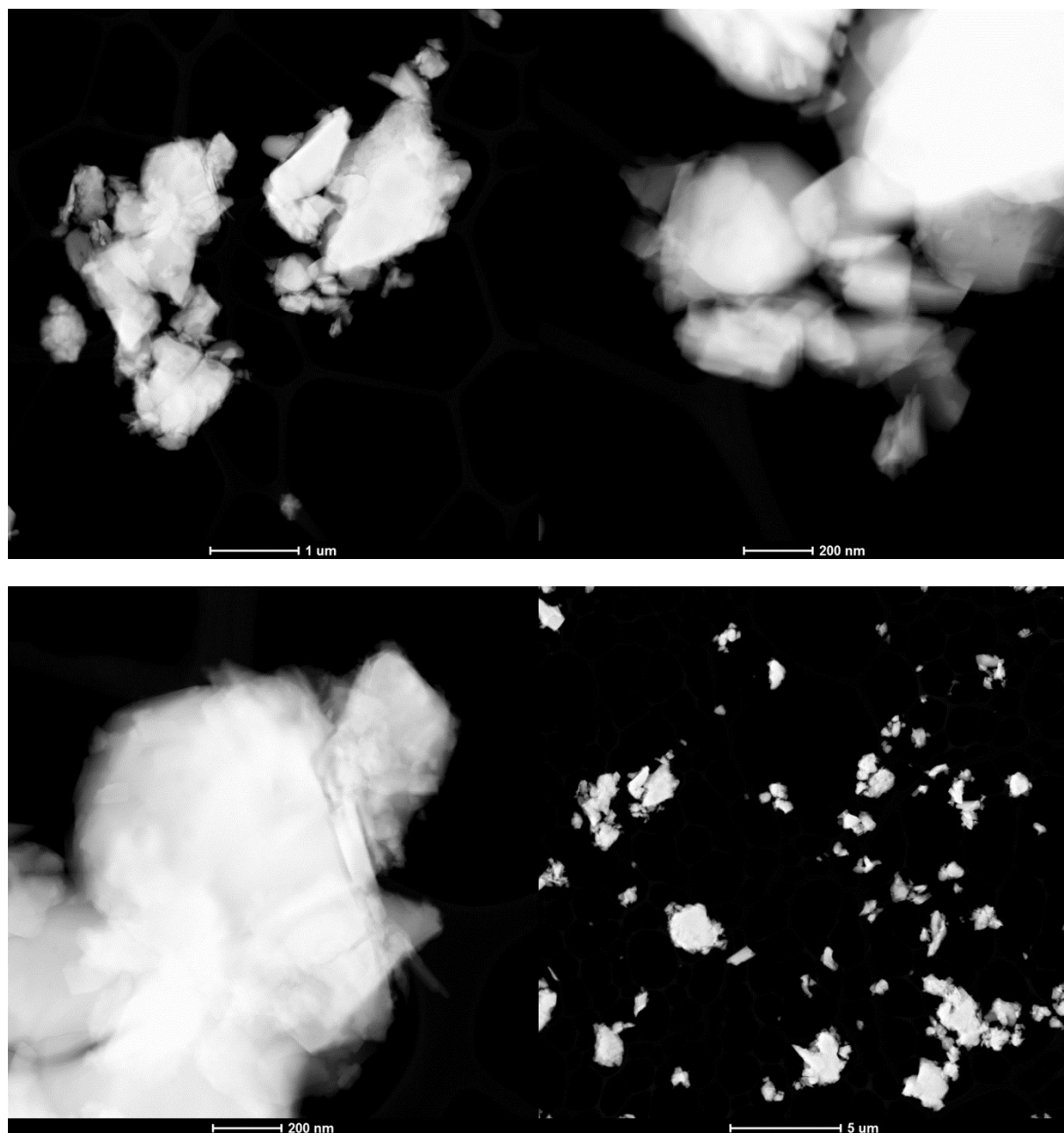


Figure S18 – STEM-HAADF images of fresh catalyst.

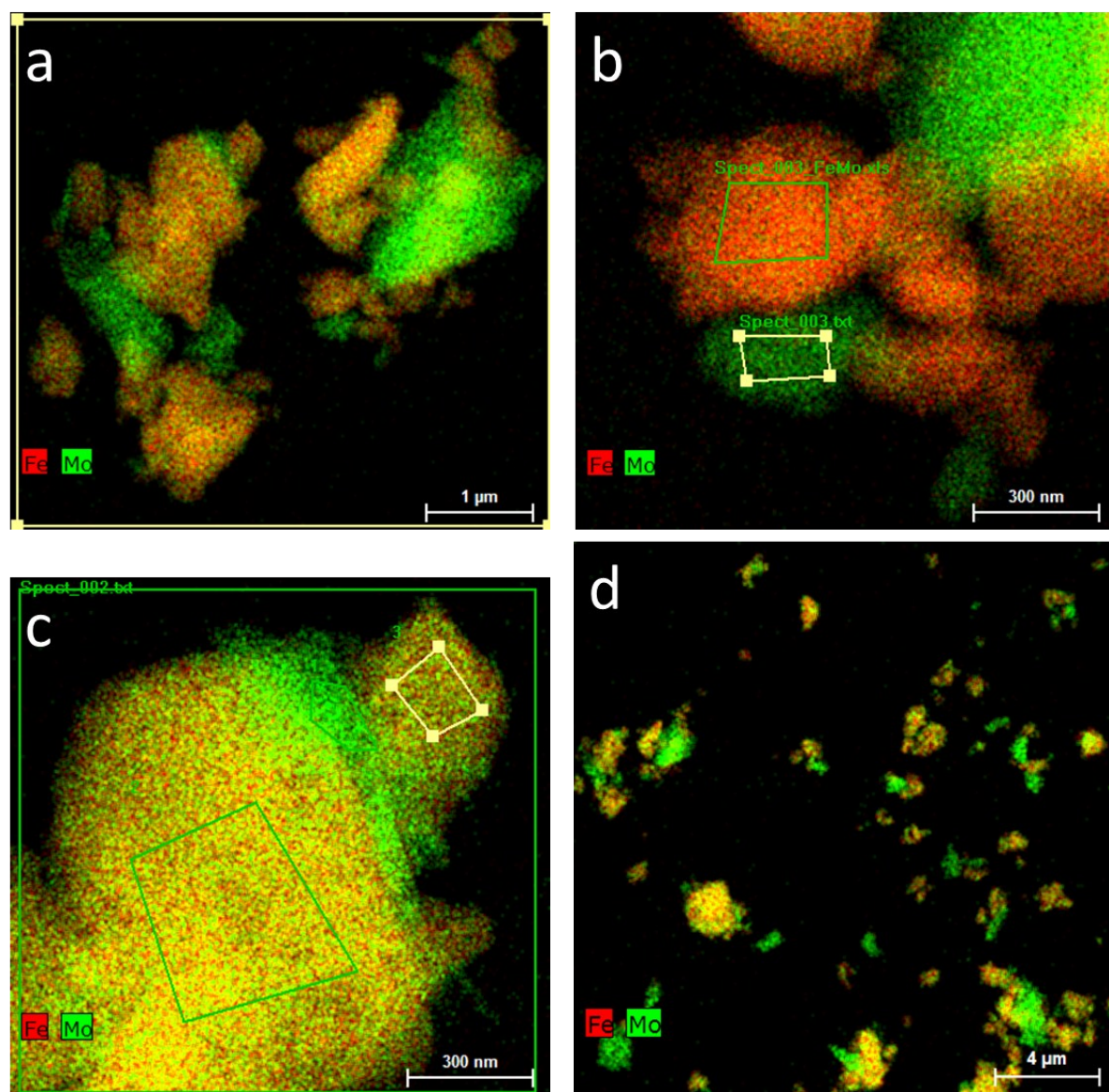


Figure S19 – STEM elemental mapping of fresh catalyst. Mo/Fe ratio: b: spect_003_FeMo = 1.66 and, b: spect_003 = 64.9, c1 = 14.7, c2 = 1.55 and c3 = 1.64.

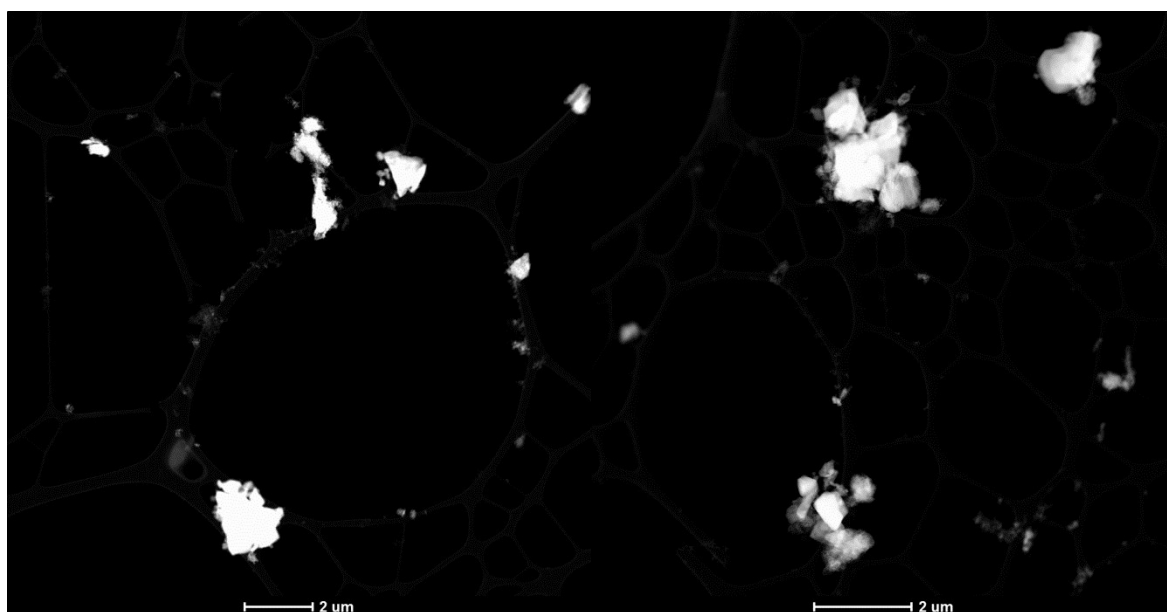
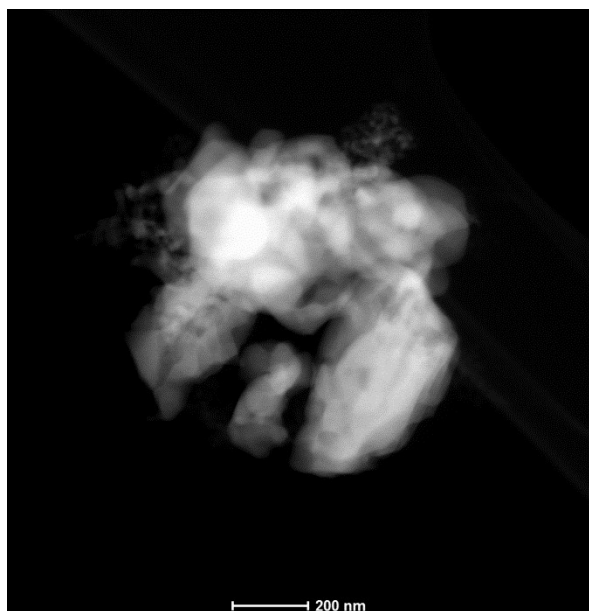


Figure S20 – STEM-HAADF images of spent catalyst (TOS = 10 h).

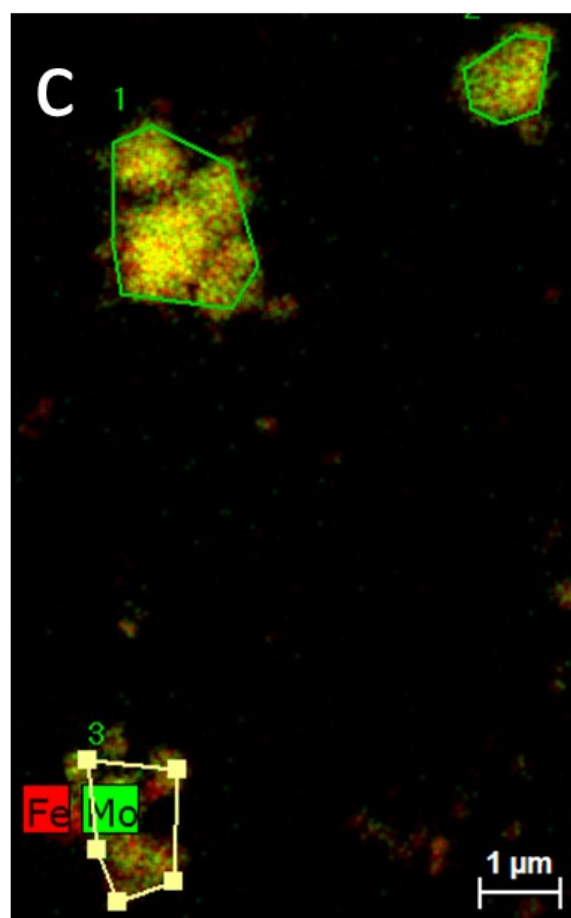
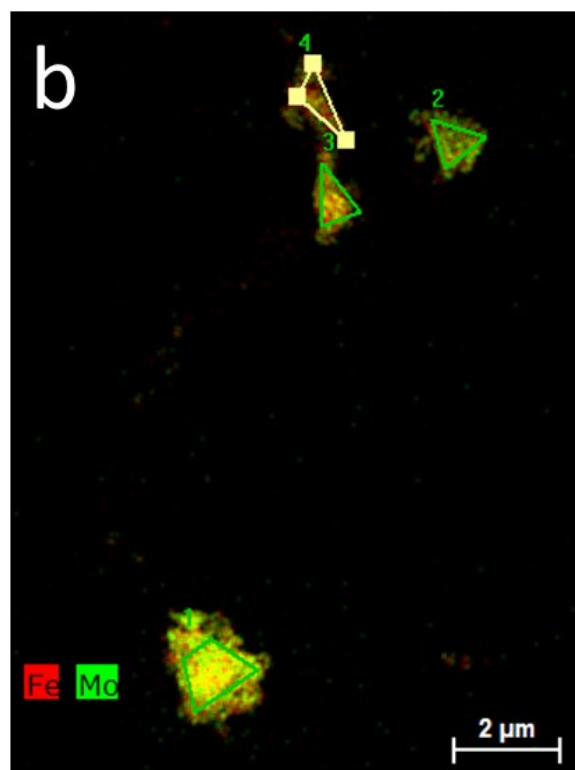
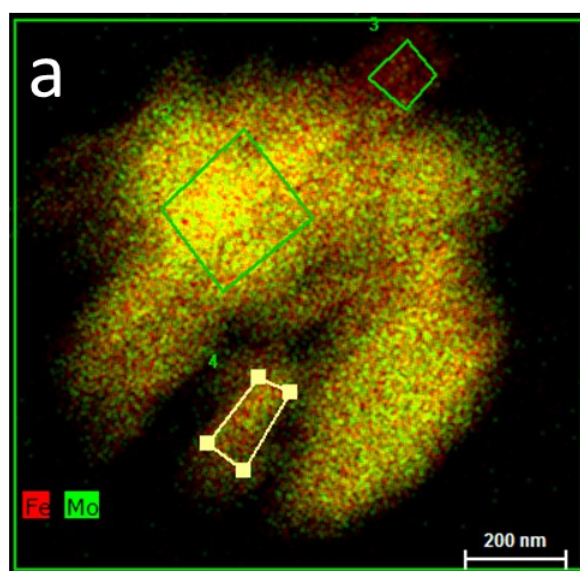


Figure S21 - STEM elemental mapping of spent catalyst (TOS = 10 h). Mo/Fe ratio: a total = 1.12, a2 = 1.25, a3 = 0.13, a4 = 1.00, b1 = 1.33, b2 = 1.44, b3 = 1.05, b4 = 0.90, c1 = 1.31, c2 = 1.49 and c3 = 1.24.

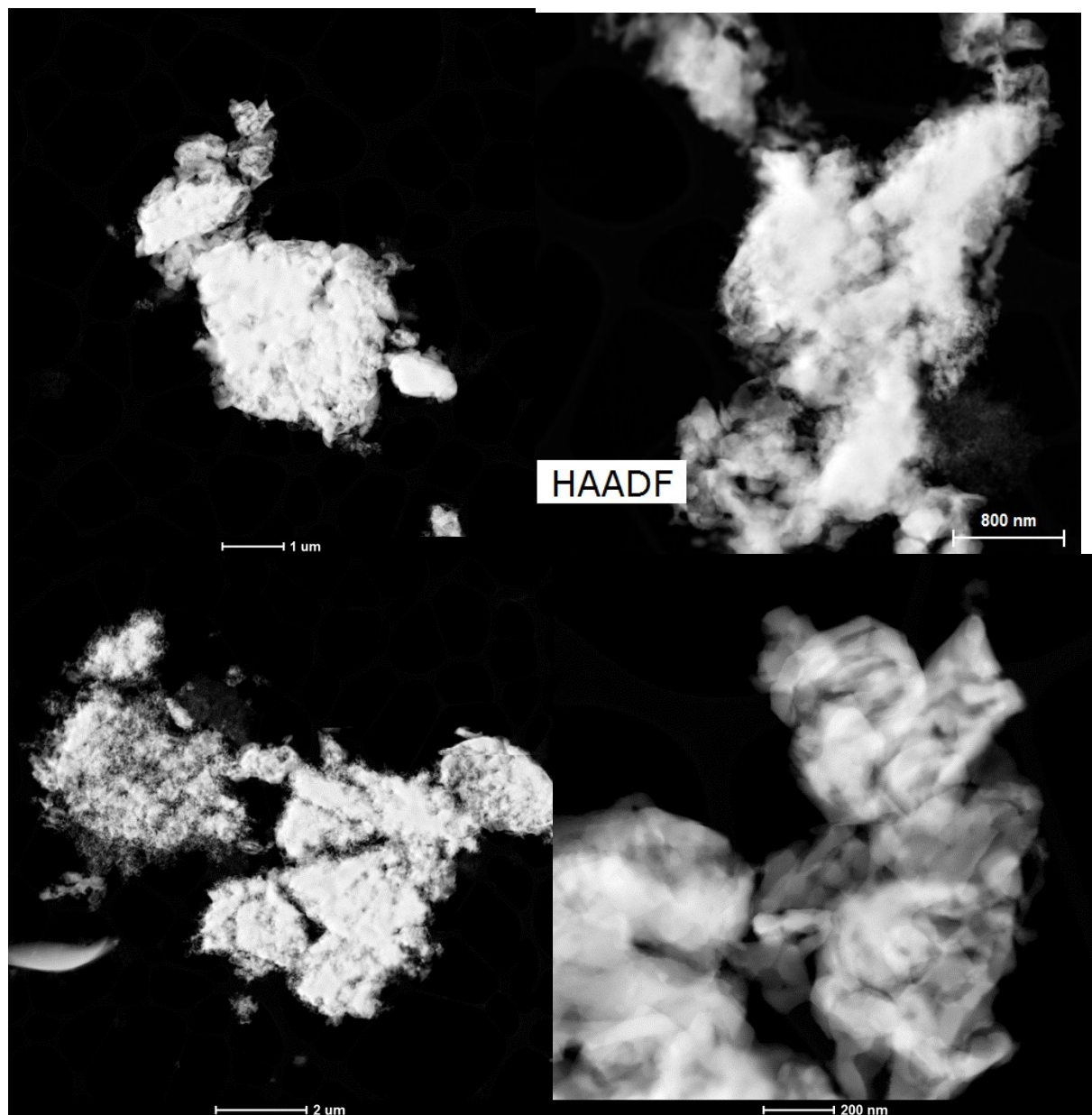


Figure S22 – STEM-HAADF images of spent catalyst (TOS = 100 h).

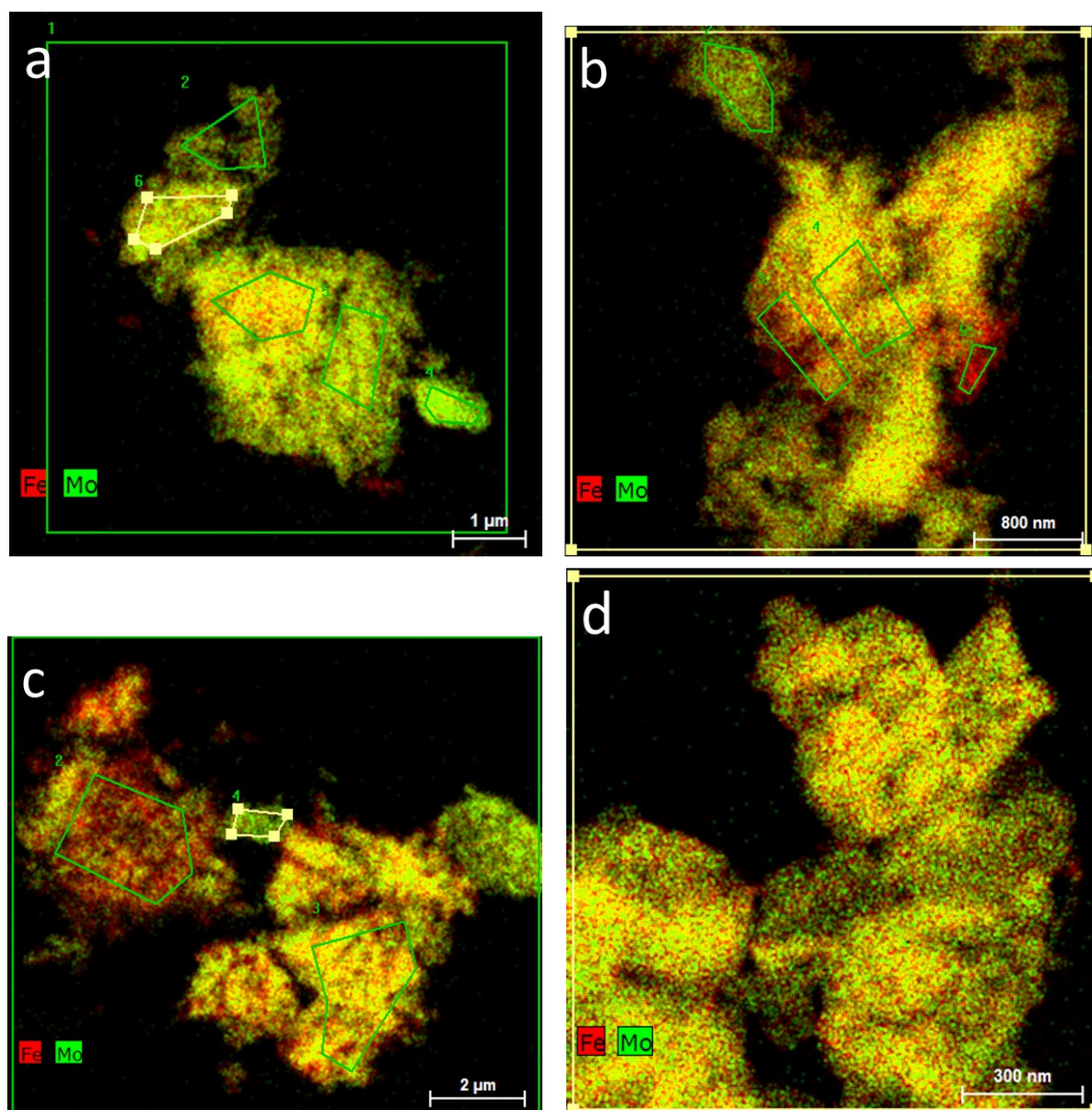


Figure S23 - STEM elemental mapping of spent catalyst (TOS = 100 h). Mo/Fe ratio: a total = 0.81, a2 = 0.83, a3 = 0.65, a4 = 1.36, a5 = 0.81, a6 = 0.84, b total = 0.68, b2 = 0.92, b3 = 0.45, b5 = 0.057, c total = 0.46, c2 = 0.29, c3 = 0.51, c4 = 0.91, c4 = 0.91 and d total = 0.83.



Figure S24 – STEM-HAADF images of spent catalyst (TOS = 250 h).

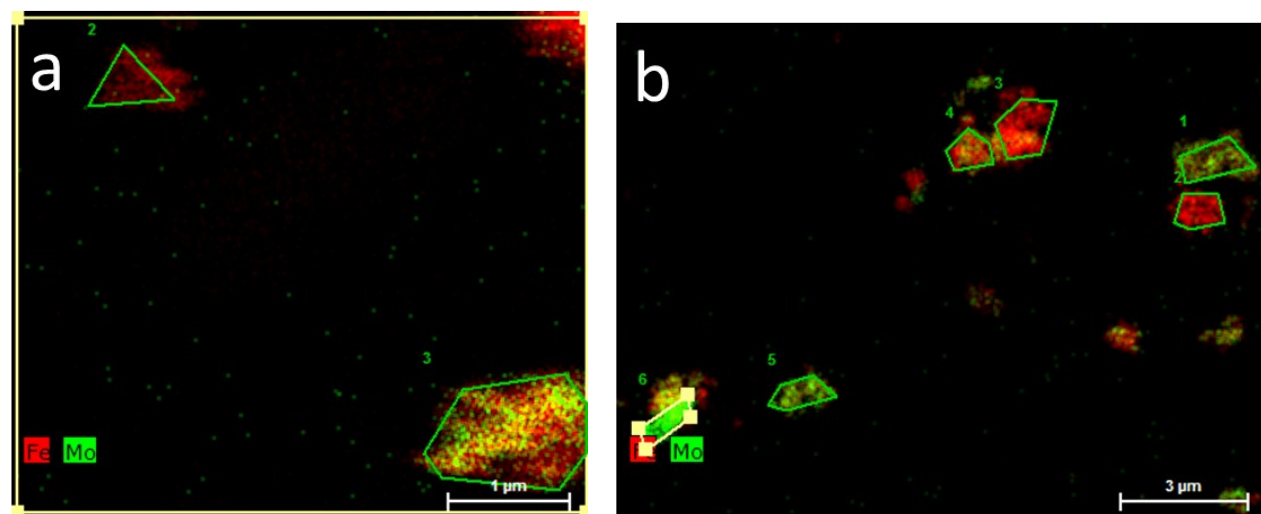


Figure S25 – STEM elemental mapping of spent catalyst (TOS = 250 h). Mo/Fe ratio: a2 = Fe, a3 = 0.43, b1 = 0.66, b2 = 0.0026, b3 = 0.069, b4 = 0.26, b5 = 0.86 and b6 = 4.42.

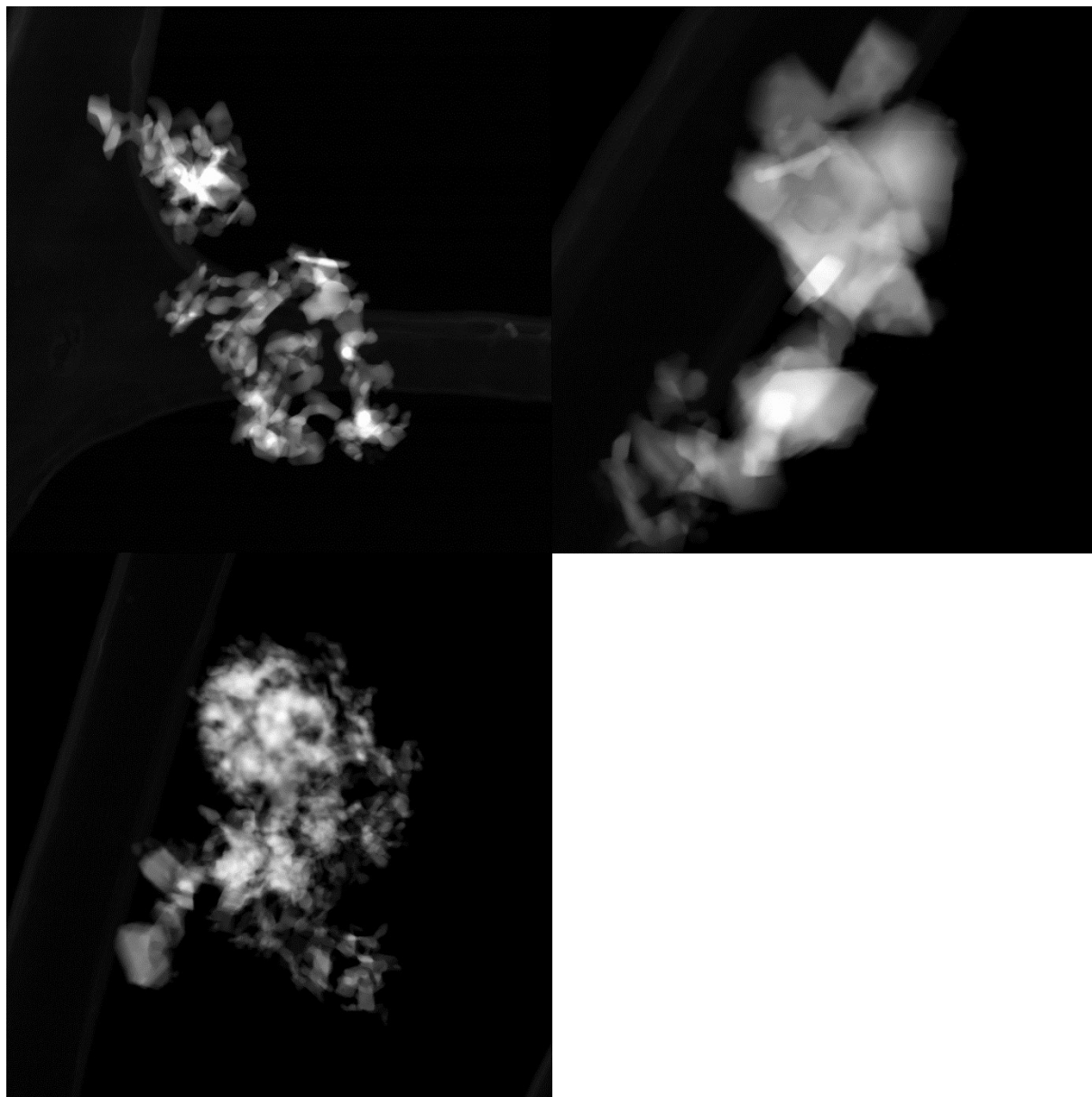


Figure S26 – STEM-HAADF images of spent catalyst (TOS = 600 h).

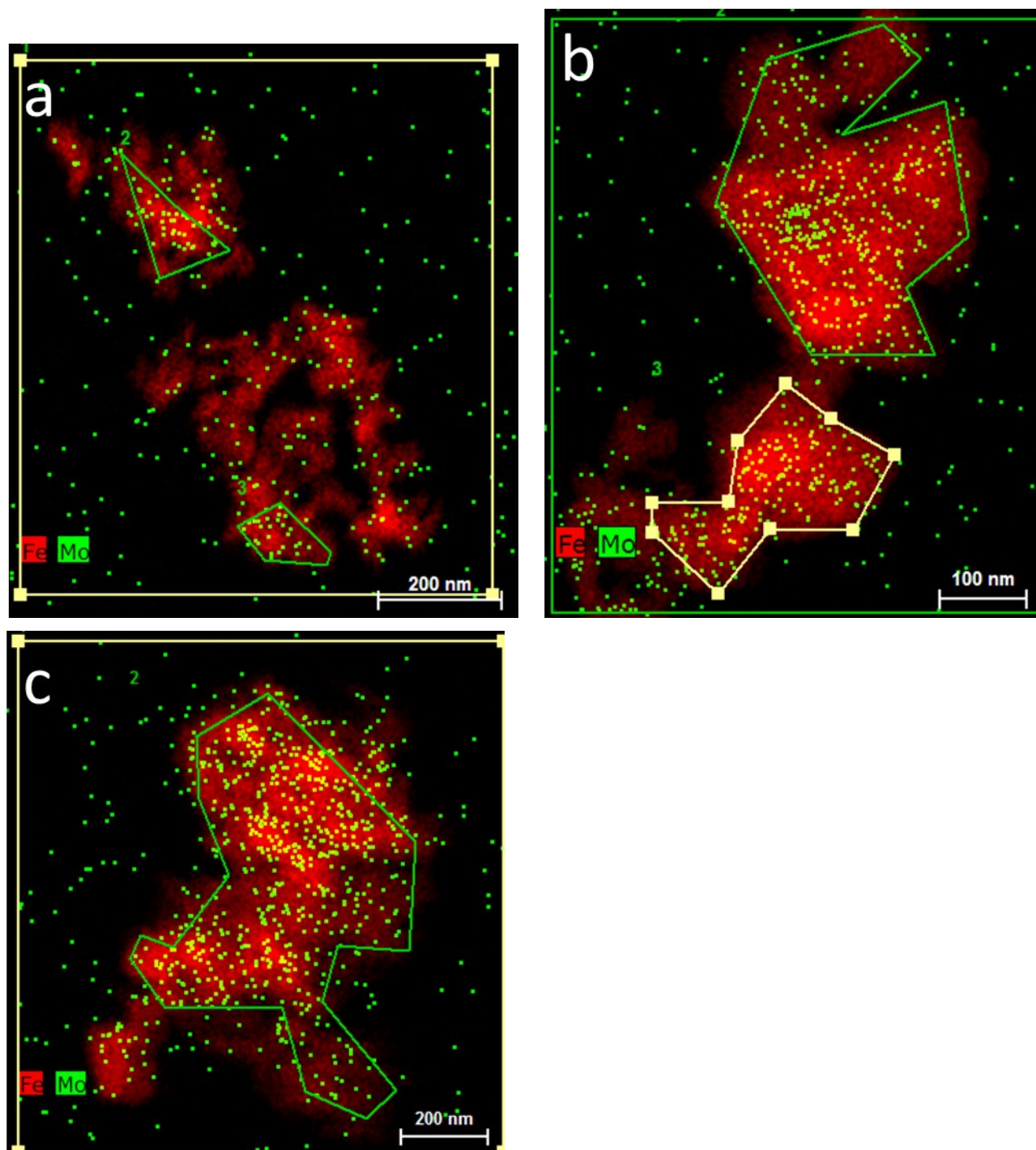


Figure S27 - STEM elemental mapping of spent catalyst (TOS = 600 h). Mo/Fe ratio: a2 = 0.0094, a3 = 0.0041, b2 = 0.0057, b3 = 0.004 and c2 = 0.0090.

XPS: spectra with respect to Molybdenum, Iron and Oxygen.

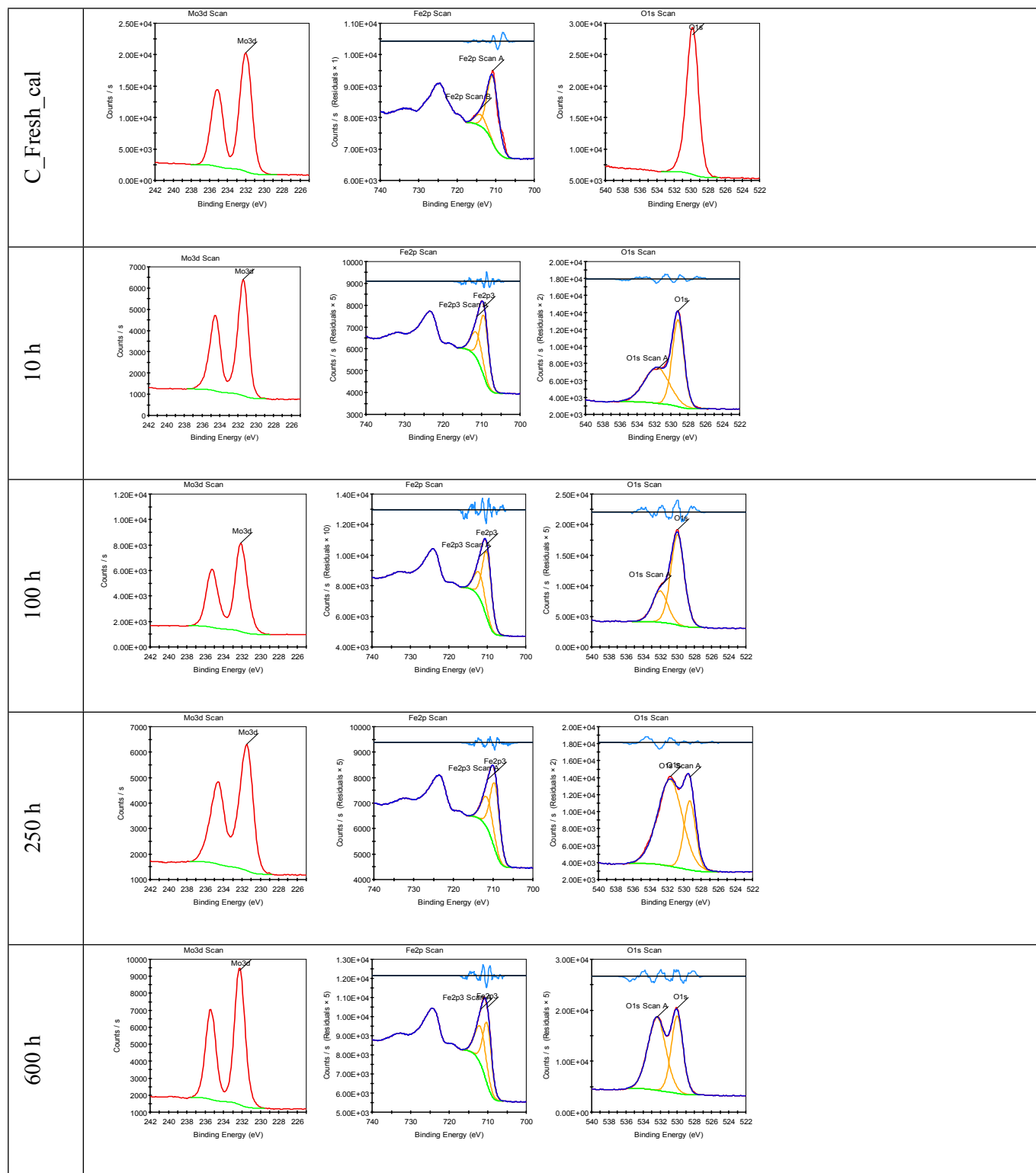


Figure S28 – XPS spectra with respect to molybdenum, iron and oxygen for fresh and spent catalyst. Shirley background is shown.