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Raun, Kristian Viegaard; Lundegaard, Lars Fahl; Chevallier, Jacques; Beato, Pablo; Appel, Charlotte Clausen; Nielsen, Kenneth; Thorhauge, Max; Jensen, Anker Degn; Høj, Martin

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Supporting Information for

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

Kristian Viegaard Raun,a Lars Fahl Lundegaard,b Jacques Chevallier,c Pablo Beato,b Charlotte Clausen Appel,b Kenneth Nielsen,d Max Thorhauge,b Anker Degn Jensena and Martin Høj* a

aDTU Chemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark. E-mail: mh@kt.dtu.dk, Tel: +45 45252842

bHaldor Topsøe A/S, 2800 Kgs. Lyngby, (Denmark)

cDepartment of Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark

dDepartment of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

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 $\beta$-MoO$_3$ are shown in the literature$^1$ and the other relevant spectra are shown in Figure S1.


*Figure S1 – Raman spectra of Fe$_3$(MoO$_4$)$_3$, $\alpha$-MoO$_3$, $\beta$-FeMoO$_4$, $\alpha$-FeMoO$_4$, Fe$_2$O$_3$ 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 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 $\beta$-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 $\beta$-MoO\(_3\) was transformed into the thermodynamically stable $\alpha$-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 MoO₃.
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: \text{spect\_003\_FeMo} = 1.66 and, b: \text{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: $a_{\text{total}} = 0.81$, $a_2 = 0.83$, $a_3 = 0.65$, $a_4 = 1.36$, $a_5 = 0.81$, $a_6 = 0.84$, $b_{\text{total}} = 0.68$, $b_2 = 0.92$, $b_3 = 0.45$, $b_5 = 0.057$, $c_{\text{total}} = 0.46$, $c_2 = 0.29$, $c_3 = 0.51$, $c_4 = 0.91$, $c_4 = 0.91$ and $d_{\text{total}} = 0.83$. 
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: $a_2 = Fe$, $a_3 = 0.43$, $b_1 = 0.66$, $b_2 = 0.0026$, $b_3 = 0.069$, $b_4 = 0.26$, $b_5 = 0.86$ and $b_6 = 4.42$. 
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: $a_2 = 0.0094, a_3 = 0.0041, b_2 = 0.0057, b_3 = 0.004$ and $c_2 = 0.0090$. 
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.