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Supporting Information

Activity, Selectivity and Initial Degradation of Iron Molybdate in the Oxidative Dehydrogenation of Ethanol

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Access to data files

The complete data sets are available as comma-separated values (.csv) files through an open access repository provided by the Technical University of Darmstadt (TUdatalib). They are accessible via DOI:

- EtOH ODH: Time resolved conversion and selectivities for bm-$Fe_2(MoO_4)_3$ (Figure 1a): *DOI will be added after acceptance*
- EtOH ODH: Time resolved conversion and selectivities for p-$Fe_2(MoO_4)_3$ (Figure 1b): *DOI will be added after acceptance*
- EtOH ODH: Steady-state values of conversion and selectivities for bm-$Fe_2(MoO_4)_3$ (Figure 1c): *DOI will be added after acceptance*
- EtOH ODH: Steady-state values of conversion and selectivities for p-$Fe_2(MoO_4)_3$ (Figure 1d): *DOI will be added after acceptance*
- EtOH ODH: Long-term measurement at 280 °C for bm-$Fe_2(MoO_4)_3$ (Figure 1e): *DOI will be added after acceptance*
- EtOH ODH: Long-term measurement at 280 °C for p-$Fe_2(MoO_4)_3$ (Figure 1f): *DOI will be added after acceptance*
- MeOH ODH: Steady-state values of conversion and selectivities for bm-$Fe_2(MoO_4)_3$ (Figure 2a): *DOI will be added after acceptance*
- MeOH ODH: Steady-state values of conversion and selectivities for p-$Fe_2(MoO_4)_3$ (Figure 2b): *DOI will be added after acceptance*
- Raman spectra of bm-$Fe_2(MoO_4)_3$ (Figure 4): *DOI will be added after acceptance*
- Raman spectra of spent bm-$Fe_2(MoO_4)_3$ (Figure 4): *DOI will be added after acceptance*
- Raman spectra of p-$Fe_2(MoO_4)_3$ (Figure 4): *DOI will be added after acceptance*
- Raman spectra of spent p-$Fe_2(MoO_4)_3$ (Figure 4): *DOI will be added after acceptance*
- Mössbauer data of bm-$Fe_2(MoO_4)_3$ (Figure 5a): *DOI will be added after acceptance*
- Mössbauer data of p-$Fe_2(MoO_4)_3$ (Figure 5b): *DOI will be added after acceptance*
- Mössbauer data of spent bm-$Fe_2(MoO_4)_3$ (Figure 5c): *DOI will be added after acceptance*
- Mössbauer data of spent p-$Fe_2(MoO_4)_3$ (Figure 5d): *DOI will be added after acceptance*
- X-ray powder diffraction data of bm-$Fe_2(MoO_4)_3$ (Figure 6a): *DOI will be added after acceptance*
- X-ray powder diffraction data of spent bm-$Fe_2(MoO_4)_3$ (Figure 6a): *DOI will be added after acceptance*
- X-ray powder diffraction data of bm-$Fe_2(MoO_4)_3$ (Figure 6b): *DOI will be added after acceptance*
- X-ray powder diffraction data of spent bm-$Fe_2(MoO_4)_3$ (Figure 6b): *DOI will be added after acceptance*
- EtOH ODH: Time resolved conversion and selectivities of induction period (280 °C) for bm-$Fe_2(MoO_4)_3$ (Figure S1a): *DOI will be added after acceptance*
- EtOH ODH: Time resolved conversion and selectivities of induction period (280 °C) for p-$Fe_2(MoO_4)_3$ (Figure S1b): *DOI will be added after acceptance*
- EtOH ODH: Long-term measurement at 250 °C for bm-$Fe_2(MoO_4)_3$ (Figure S2a): *DOI will be added after acceptance*
- EtOH ODH: Long-term measurement at 250 °C for p-$Fe_2(MoO_4)_3$ (Figure S2b): *DOI will be added after acceptance*
- MeOH ODH: Time resolved conversion and selectivities of temperature variation for bm-$Fe_2(MoO_4)_3$ (Figure S3a) *DOI will be added after acceptance*

- MeOH ODH: Time resolved conversion and selectivities of temperature variation for p-$Fe_2(MoO_4)_3$ (Figure S3b): *DOI will be added after acceptance*
- EtOH ODH: Conversion/Yield diagram for bm- and p-$Fe_2(MoO_4)_3$ (Figure S4): *DOI will be added after acceptance*
- XPS data of bm-$Fe_2(MoO_4)_3$: *DOI will be added after acceptance*
- XPS data of spent bm-$Fe_2(MoO_4)_3$: *DOI will be added after acceptance*
- XPS data of p-$Fe_2(MoO_4)_3$: *DOI will be added after acceptance*
- XPS data of spent p-$Fe_2(MoO_4)_3$: *DOI will be added after acceptance*
- NH_3-TPD data for p-$Fe_2(MoO_4)_3$: *DOI will be added after acceptance*
- NH_3-TPD data for p-$Fe_2(MoO_4)_3$: *DOI will be added after acceptance*

Induction period in ethanol ODH

Figure S1 shows the induction period of the precipitated (p) and ball-milling solid-state synthesized (bm) $Fe_2(MoO_4)_3$ catalysts at a reaction temperature of 280 °C. Figure S2 shows a long-term measurement after pre-treating at 280 °C.

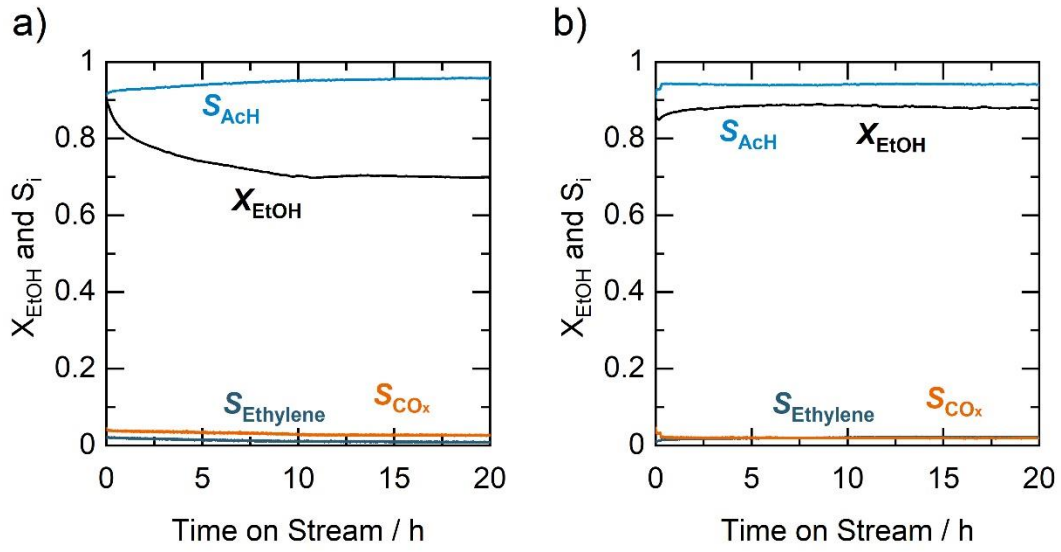


Figure S1: Induction period of investigated catalysts at 280 °C. Conversion of ethanol (EtOH) and selectivities to acetaldehyde (AcH), ethylene and CO_x for: a) 150 mg bm-$Fe_2(MoO_4)_3$ and b) 100 mg p-$Fe_2(MoO_4)_3$. Reaction conditions: 5 vol% EtOH, 10 vol% O_2, 85 vol% He, $\dot{V}_{total}$ = 20 ml_{STP} min^{-1}, 280 °C.

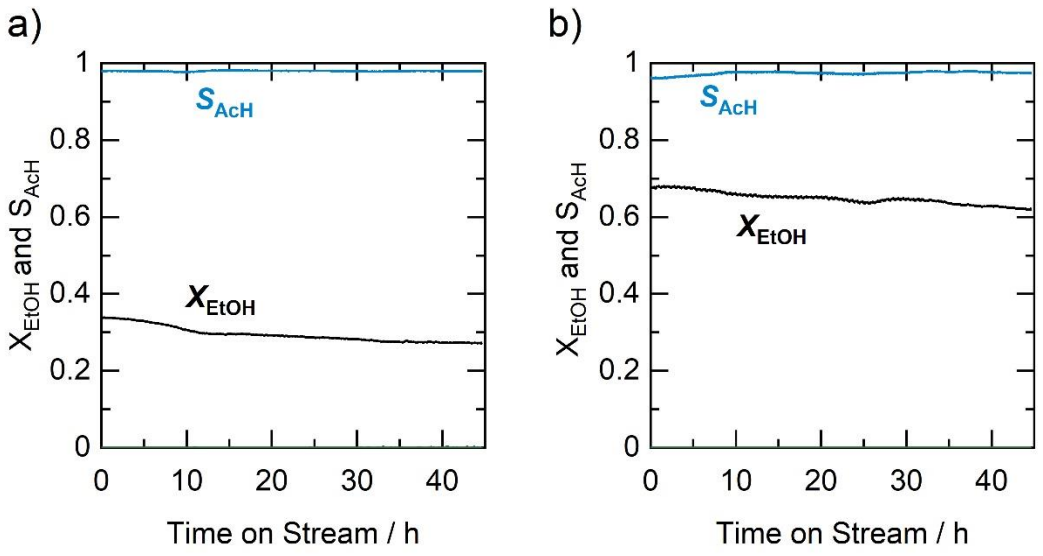


Figure S2: Long-term measurements at 250 °C. Conversion of ethanol (EtOH) and selectivitiy to acetaldehyde (AcH) for: a) 150 mg bm-$Fe_2(MoO_4)_3$ and b) 100 mg p-$Fe_2(MoO_4)_3$. Reaction conditions: 5 vol% EtOH, 10 vol% O_2, 85 vol% He, $\dot{V}_{total}$ = 20 ml_{STP} min^{-1}, 250 °C.

Methanol ODH

Figure S3 shows the time-resolved conversion and selectivities to reaction products during temperature variation in methanol ODH.

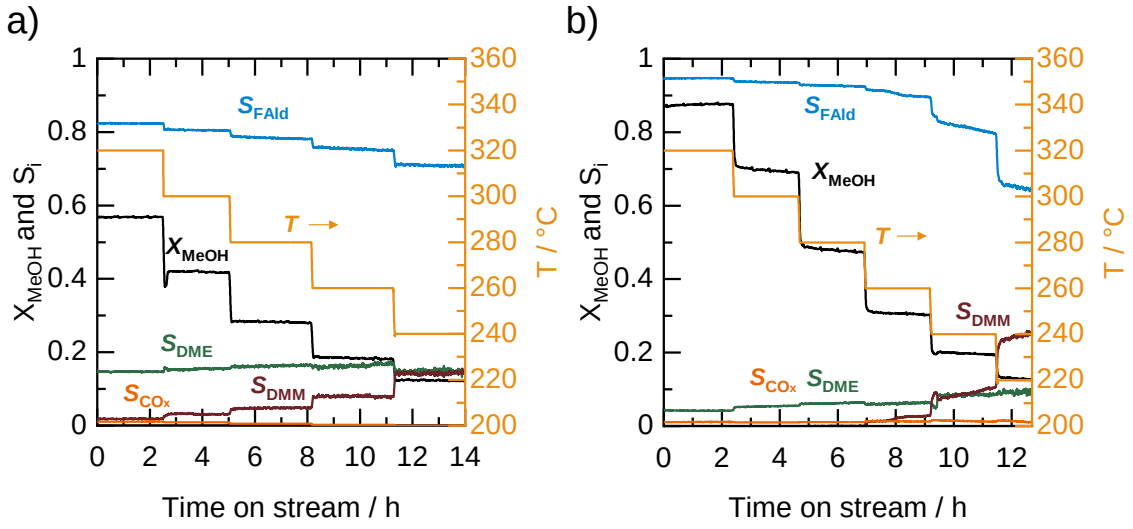


Figure S3: Conversion of methanol (MeOH) and selectivities to formaldehyde (FAld), dimethyl ether (DME), dimethoxy methane (DMM) and CO_x for a) 100 mg bm-$Fe_2(MoO_4)_3$ and b) 100 mg p-$Fe_2(MoO_4)_3$. Reaction conditions: 10 vol% MeOH, 10 vol% O_2, 80 vol% He, $\dot{V}_{total}$= 20 ml_{STP} min^{-1}.

Ethanol ODH: X_{EtOH}/Y_{AcH} diagram

Figure S4 shows the yield of acetaldehyde depending on the conversion of ethanol for both materials.

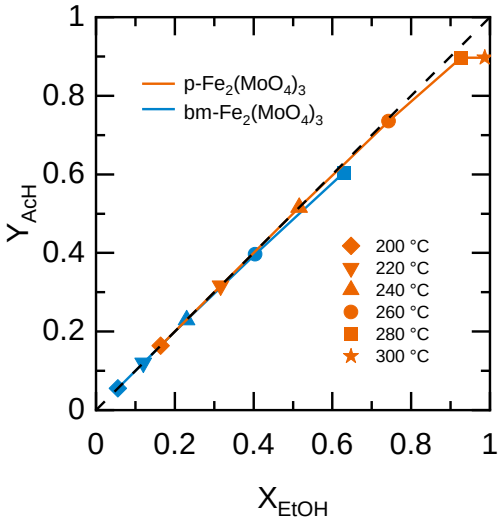


Figure S4: Yield of acetaldehyde (AcH) versus conversion of ethanol (EtOH). Dashed line: Angle bisector (for orientation)

XPS Spectra

Figure S5 shows the survey and high resolution XPS spectra of the catalysts prior and after catalysts.

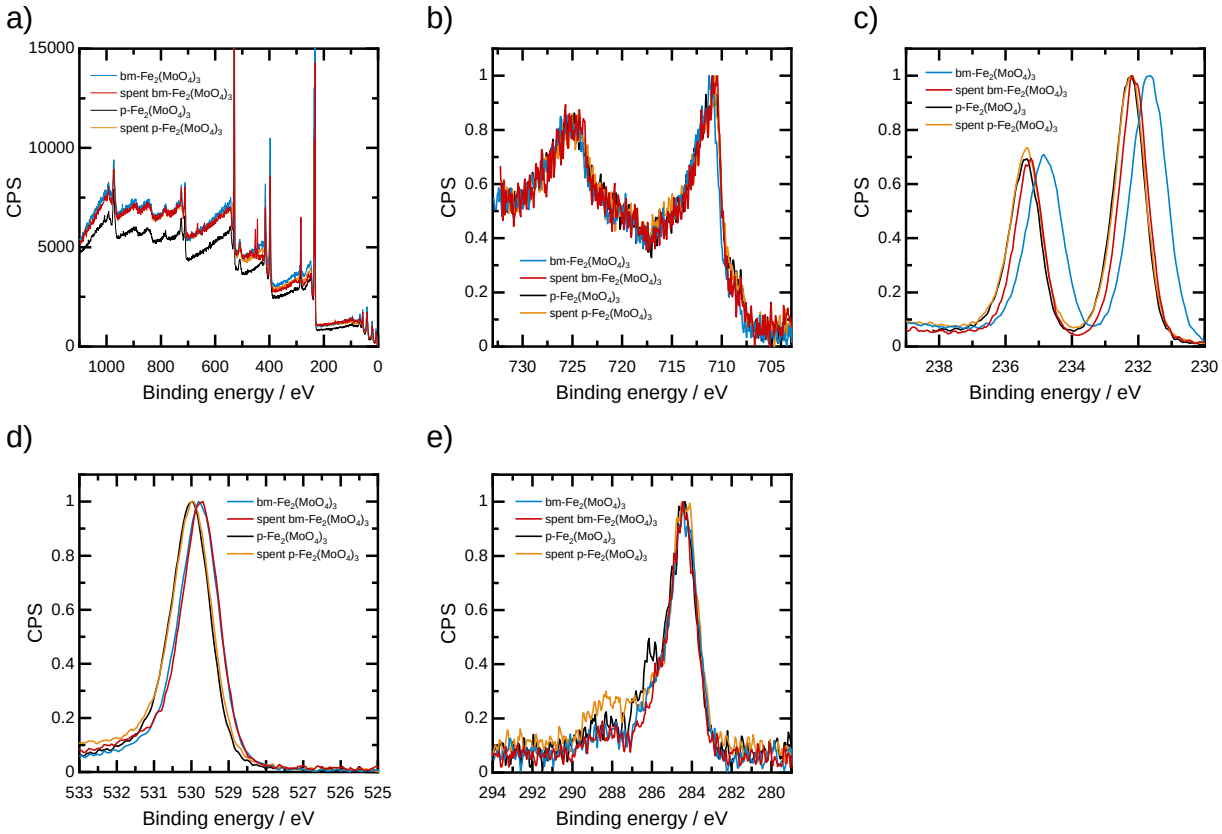


Figure S5: XPS spectra of pristine and spent catalysts: a) Survey spectra, b) Fe 2p, c) Mo 3d, d) O 1s and e) C 1s spectra.

NH_3 TPD:

Figure S6 shows the NH_3 TPD measurements of both catalysts and the total amount of desorbed NH_3.

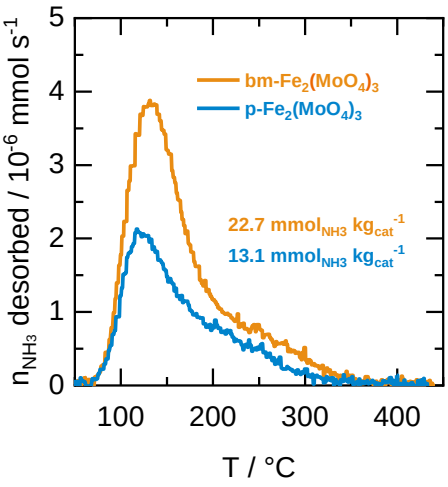
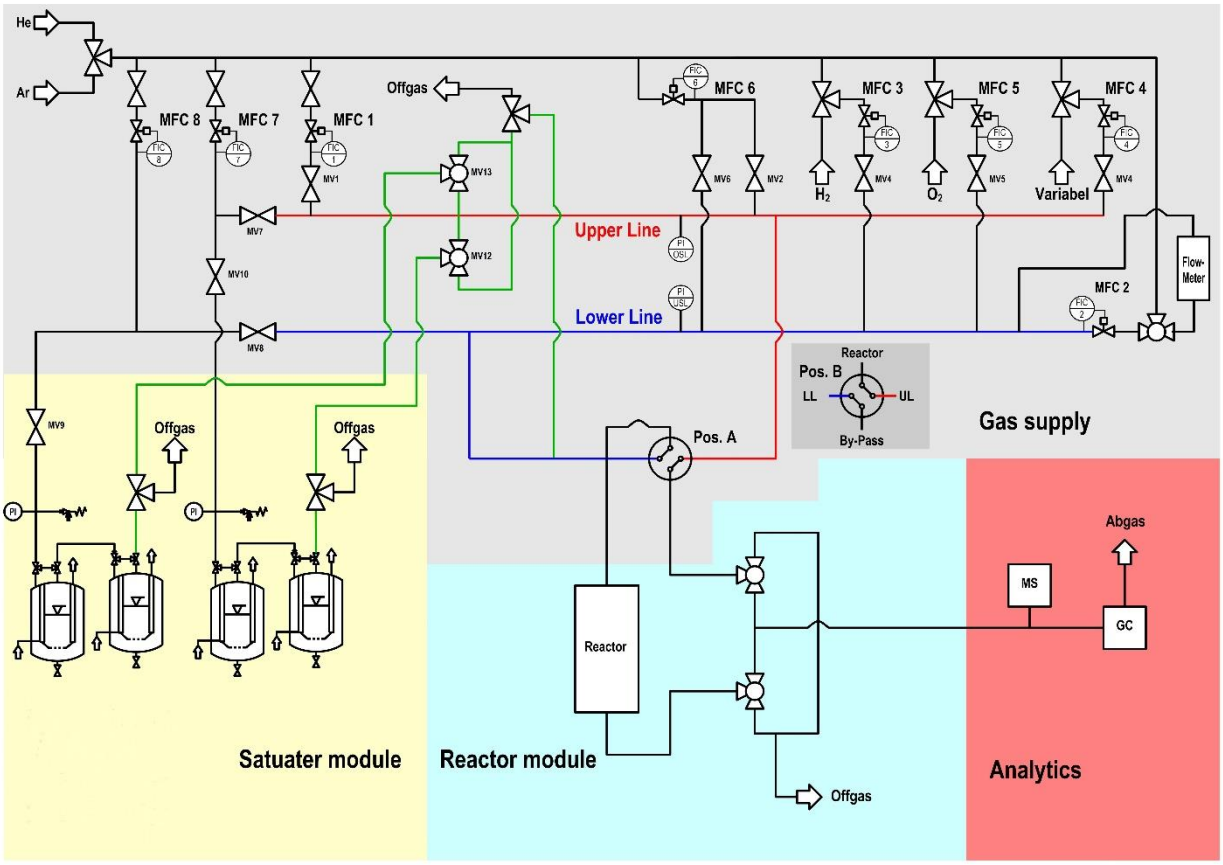


Figure S6: NH_3-TPD spectra of bm-$Fe_2(MoO_4)_3$ (orange) and p-$Fe_2(MoO_4)_3$ (blue). (100 mg, Heating rate: 5 K min^{-1}, N_2 volume flow: 100 ml min^{-1} (STP), analytics: FTIR spectrometer)

Sheme S7 shows a simplified flow sheet of the reaction setup including a saturator module, gas supply module, reactor module and analytics.



Scheme S7: Simplified flow sheet of the used reaction setup for the methanol and ethanol ODH measurements. Gases are dosed by mass flow controllers and liquids components are evaporated using a double saturator station. Analytics is done using an online quadrupole mass spectrometer and a gas chromatograph equipped with a FID and TCD detector.