

Supplementary materials

Iron-Molybdenum Sulfide Electrocatalysts for the Hydrogen Evolution

Reaction: An *Operando* XAS study

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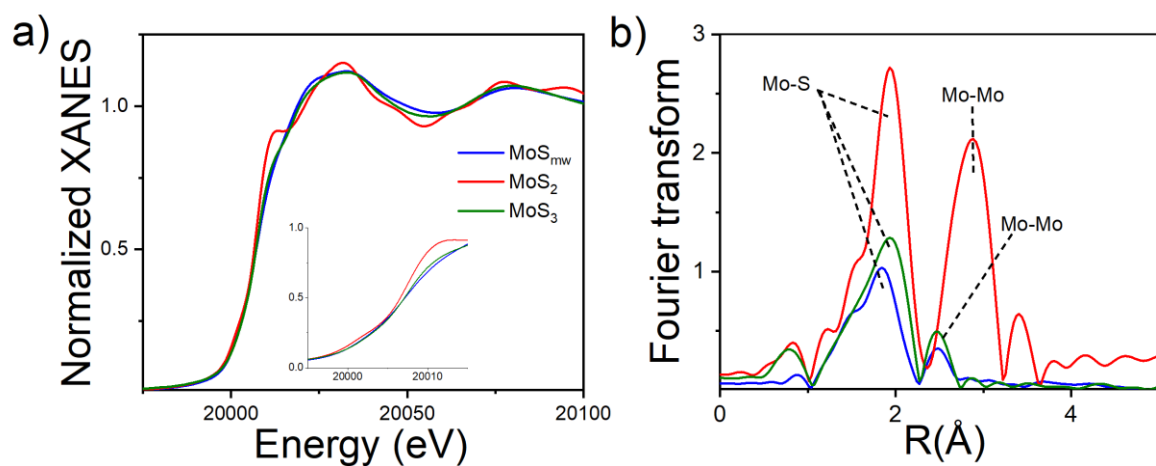


Figure S1. Comparison between the Mo K-edge (a) XANES and (b) FT-EXAFS spectra of MoS_{mw} (blue line) and the reference compounds MoS₂ (red line) and MoS₃ (green line). The inset in (a) shows a magnification of the edge features.

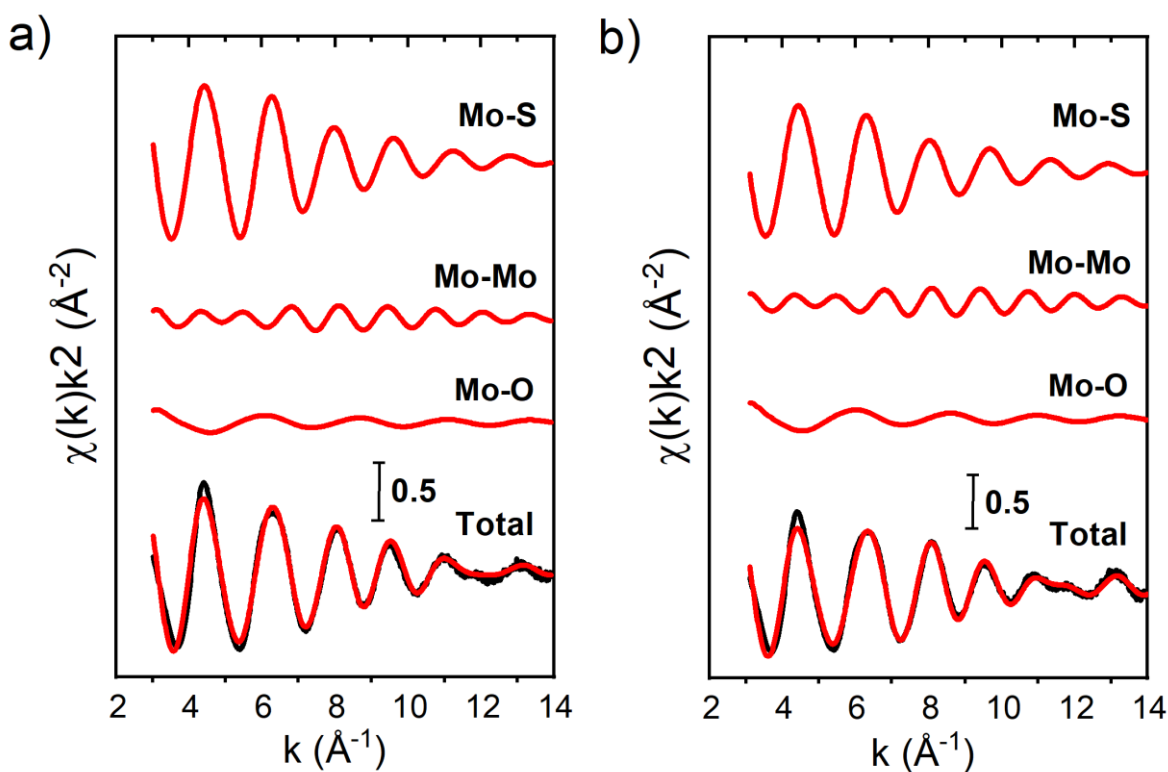


Figure S2. Mo K-edge EXAFS analysis of (a) MoS_{mw} and (b) FeMoS_{mw} catalysts. From the top of each panel: Mo-S, Mo-Mo and Mo-O $\gamma^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line).

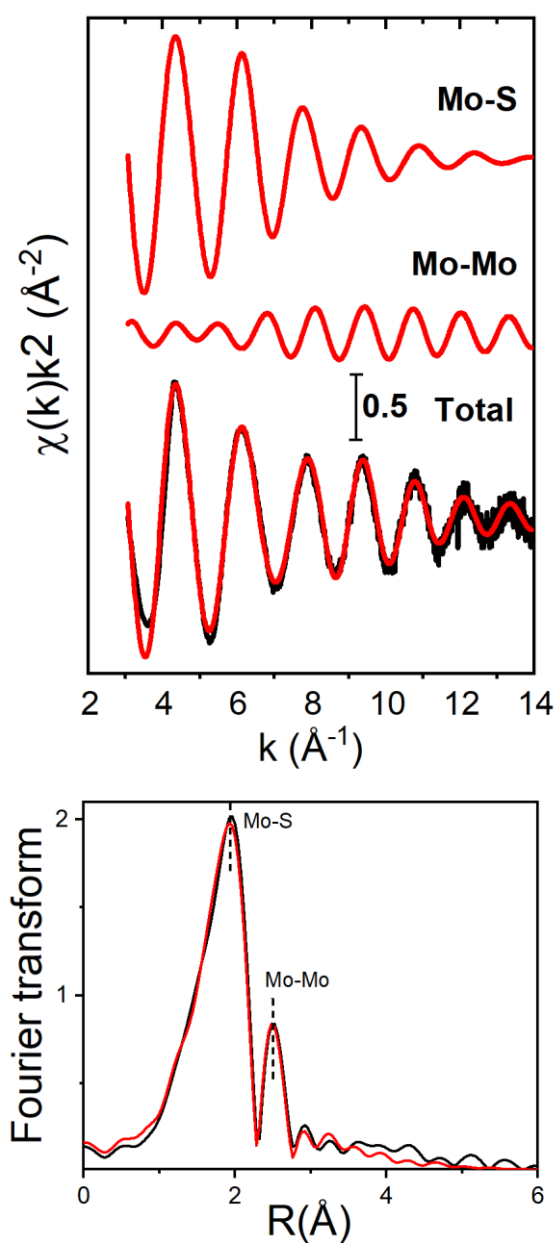


Figure S3. Mo K-edge EXAFS analysis of MoS₃ reference compound. Upper panel: Mo-S, and Mo-Mo $\chi^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line). Lower panel: the fit in the Fourier transformed space.

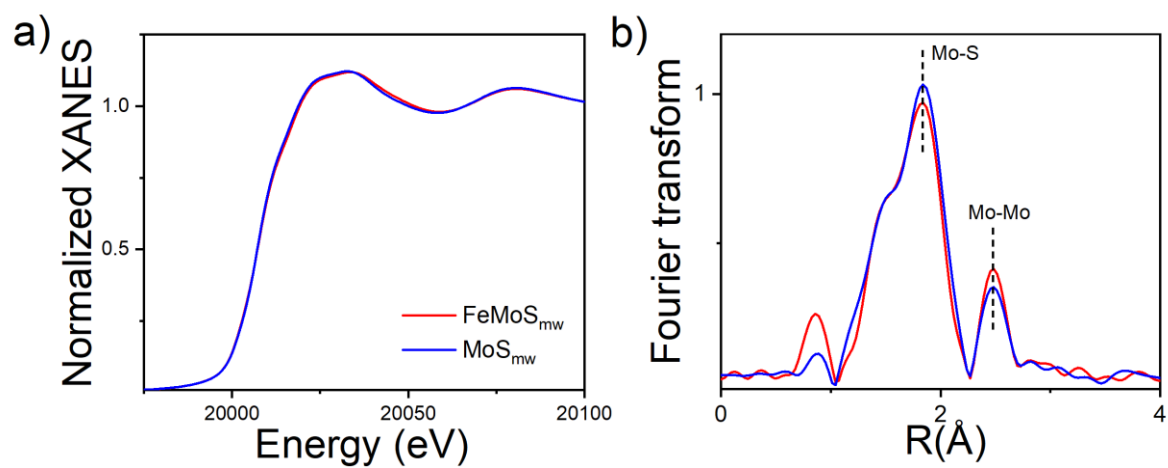


Figure S4. Comparison between the Mo K-edge (a) XANES and (b) FT-EXAFS spectra of FeMoS_{mw} (red line) and MoS_{mw} (blue line)

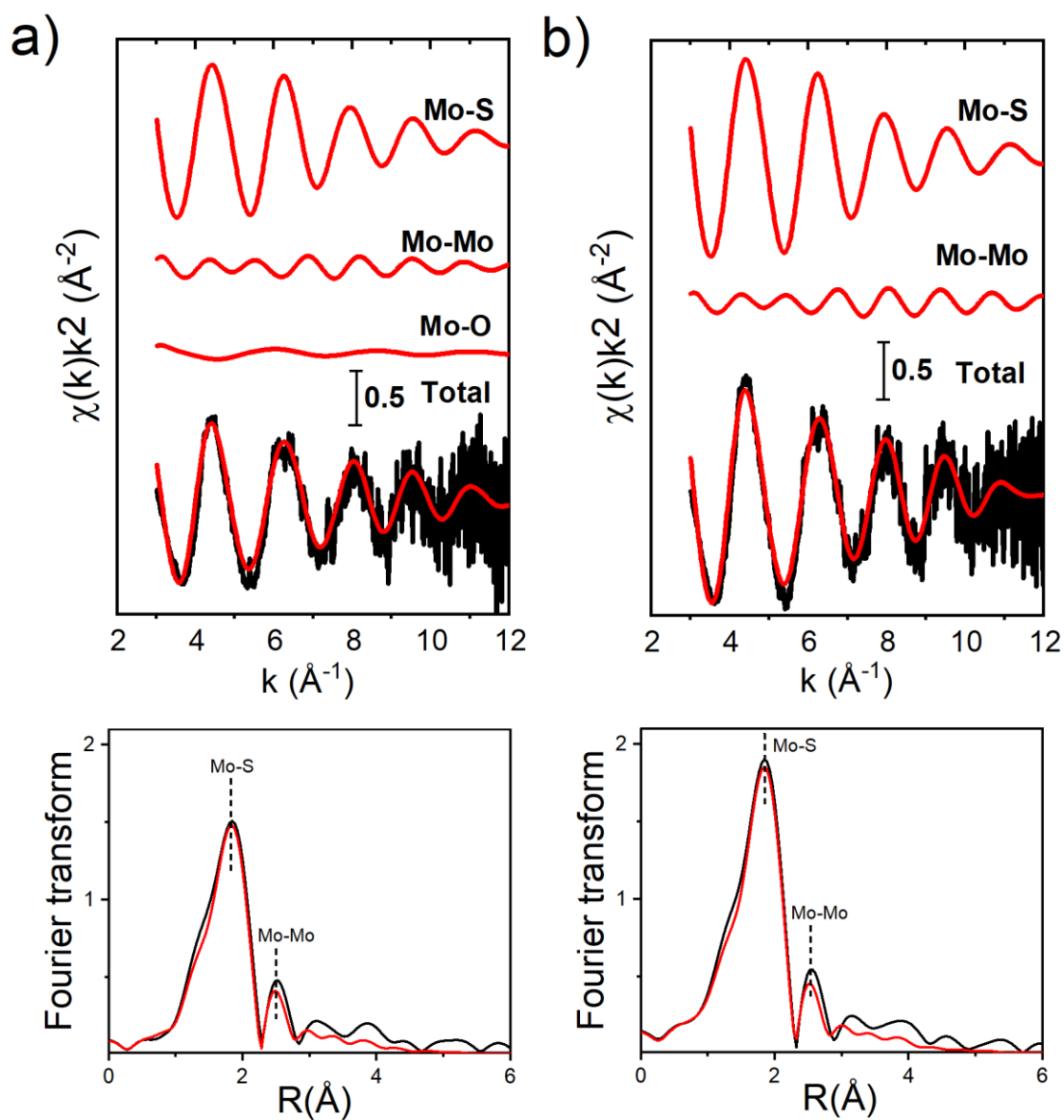


Figure S5. Mo K-edge EXAFS analysis of MoS_{mw} at (a) OCP and (b) at -0.21V . Upper left panel: Mo-S, Mo-Mo and Mo-O $\gamma^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line). Upper right panel: Mo-S and Mo-Mo $\gamma^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line). Lower panels: the fits in the Fourier transformed space.

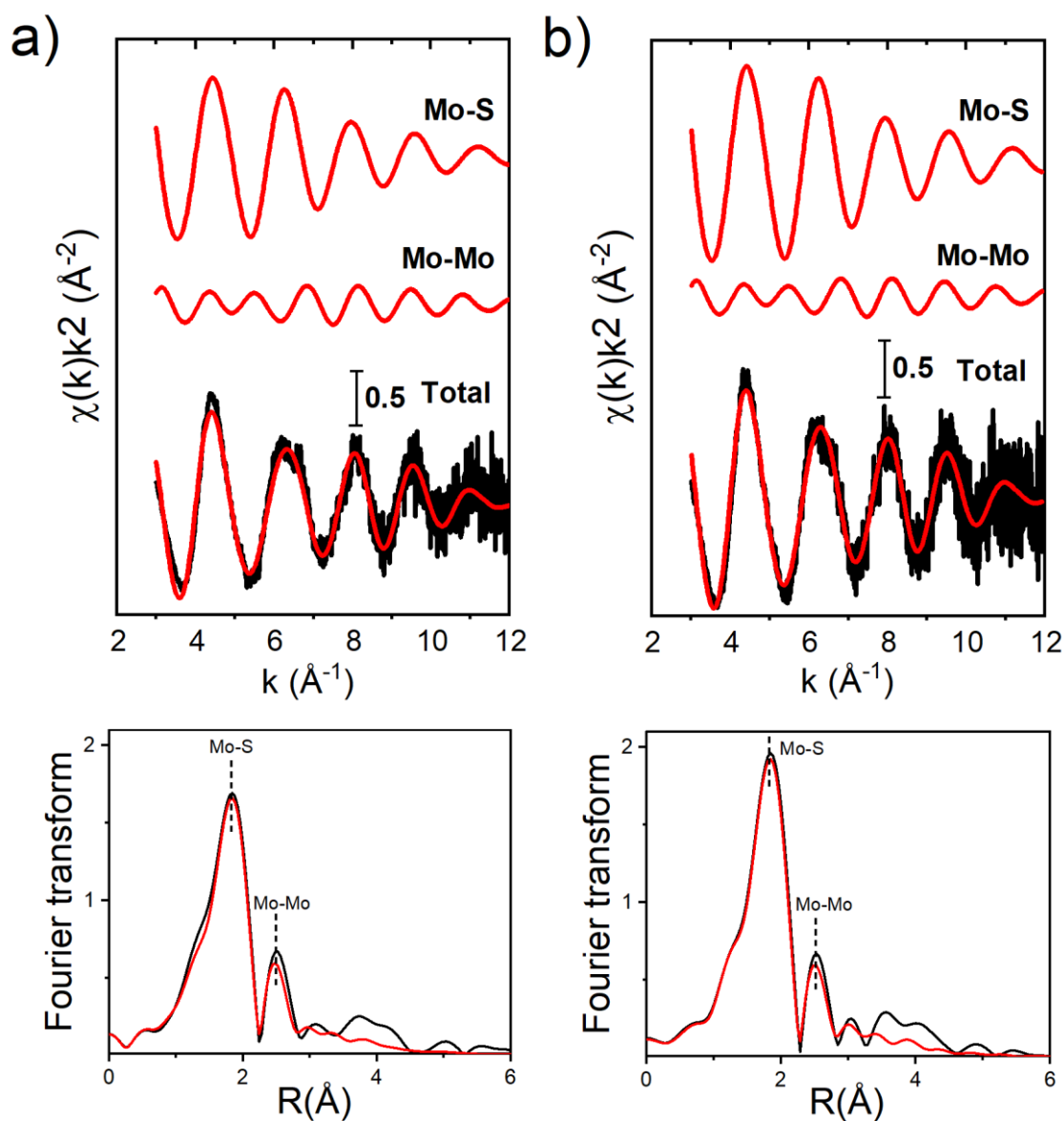


Figure S6. Mo K-edge EXAFS analysis of FeMoS_{mw} at (a) OCP and (b) at -0.21V . Upper panels: Mo-S and Mo-Mo $\gamma^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line). Lower panels: the fits in the Fourier transformed space.

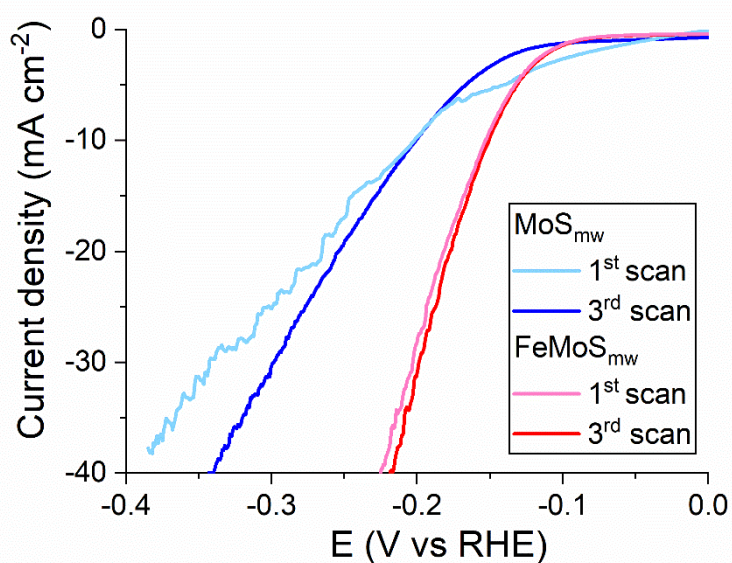


Figure S7. Polarization curve for HER on MoS_{mw} and FeMoS_{mw} electrocatalysts (catalyst loading: 0.82 mg·cm⁻²). Conditions: N₂-saturated 0.1 M H₂SO₄, scan rate 5 mV·s⁻¹, Ti wire counter electrode.

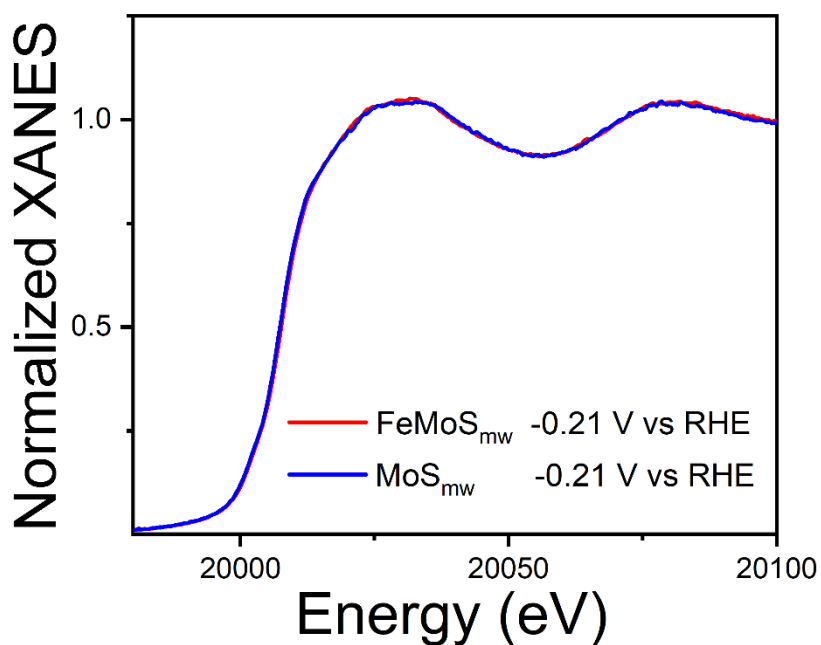


Figure S8. Mo K-edge XANES spectra of FeMoS_{mw} (red line) and MoS_{mw} (blue line) under catalytic conditions.

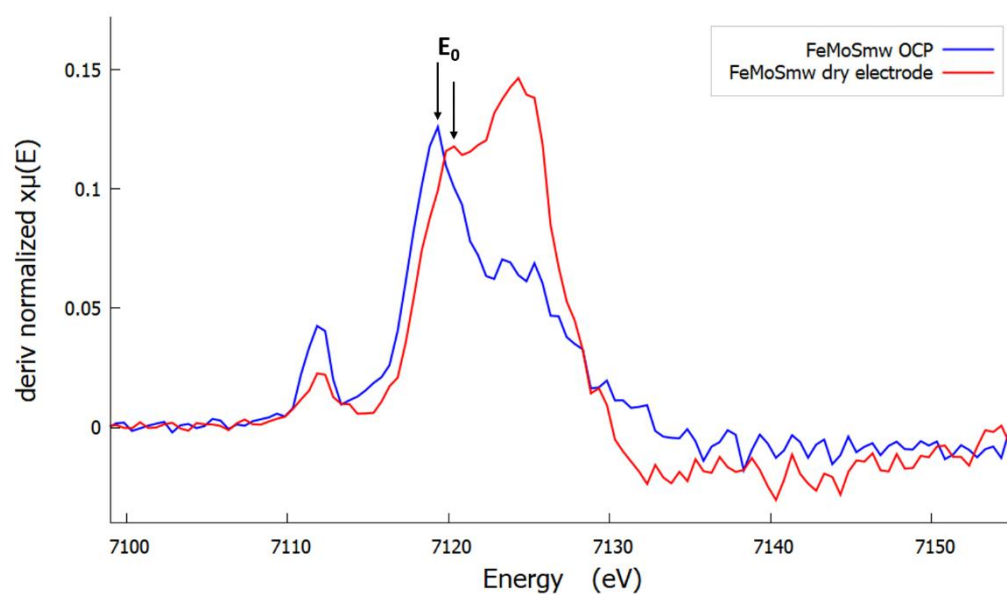


Figure S9. Fe K-edge first derivative of XAS spectra of FeMoS_{mw} for the dry electrode (red line) and at OCP (blue line). The experimental edge positions, E₀, is indicated by the arrows.

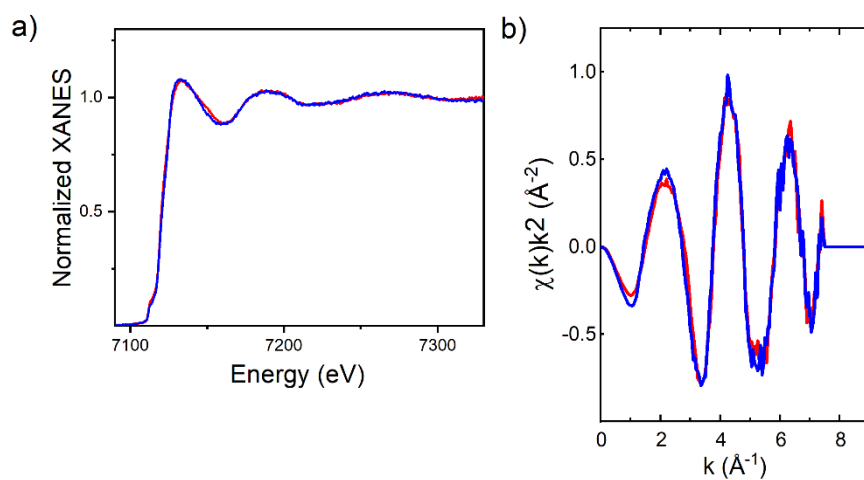


Figure S10. Fe K-edge a) XAS spectra and b) EXAFS spectra of FeMoS_{mw} at OCP (red line) and under catalytic conditions (blue line).

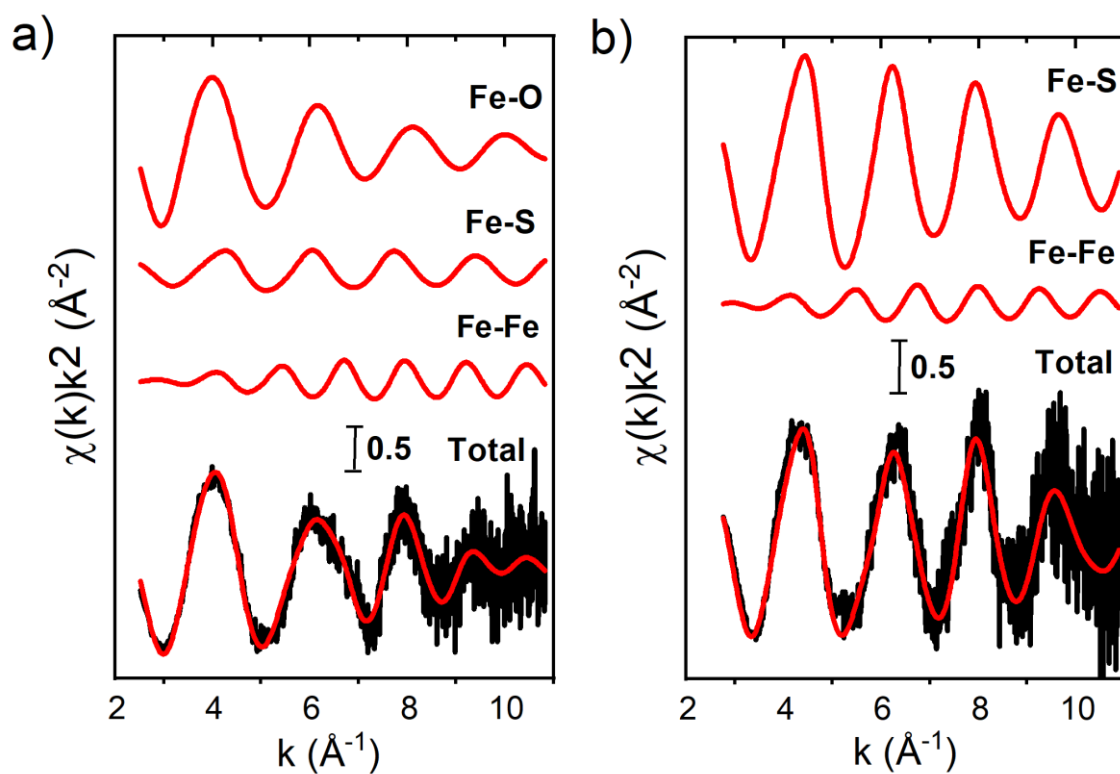


Figure S11. Fe K-edge EXAFS analysis of FeMoS_{mw} for the (a) dry electrode and (b) at OCP. Left panel: Fe-O, Fe-S and Fe-Fe $\gamma^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line). Right panel: Fe-S and Fe-Fe $\gamma^{(2)}$ two-body signals included in the fit, the total signal (red line) superimposed to the experimental one (black line).