Sulfur Substitution in Fe-MOF-74: Implications for Electrocatalytic CO_2 and CO Reduction from an ab initio Perspective

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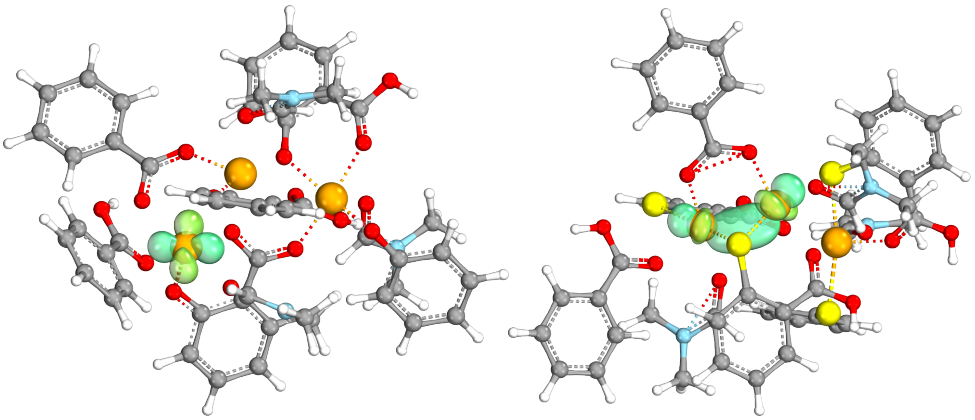
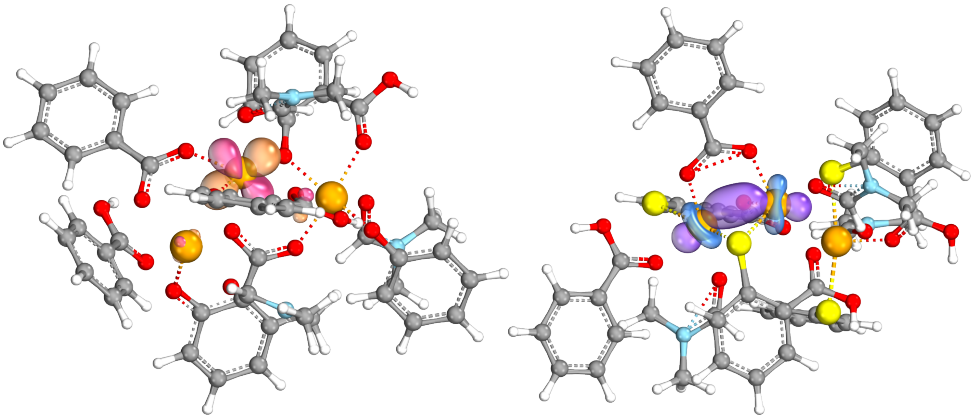
SUPPLEMENTARY INFORMATION

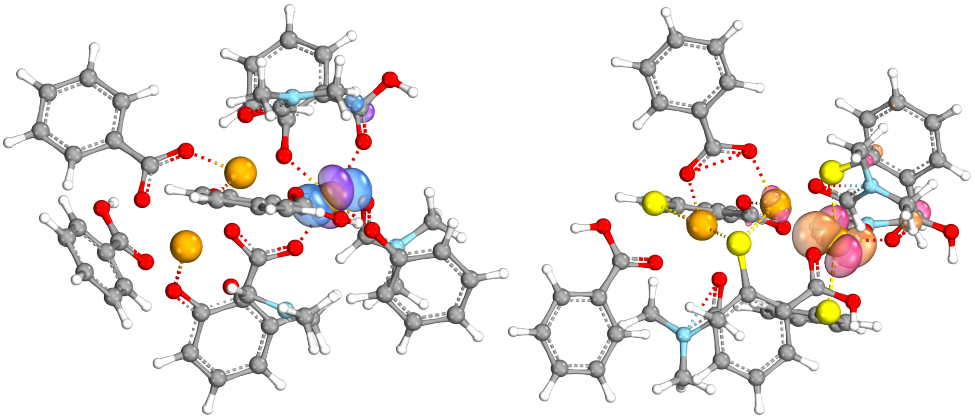
List of Figures



(a) E_{MO} = -0.7069 (b) E_{MO} = -0.4120



(c) E_{MO} = -0.6947 (d) E_{MO} = -0.4088



(e) E_{MO} = -0.5437 (f) E_{MO} = -0.4087

Figure S1: Localized molecular orbitals of the highest occupied β orbitals for the Fe centers of Fe_2DOBDC (left) and Fe_2DSBDC (right) clusters. Orbital energies (eV) are given below each figure. Color code: C (grey), N (blue), O (red), S (yellow), Fe (gold). Rendered using IboView.

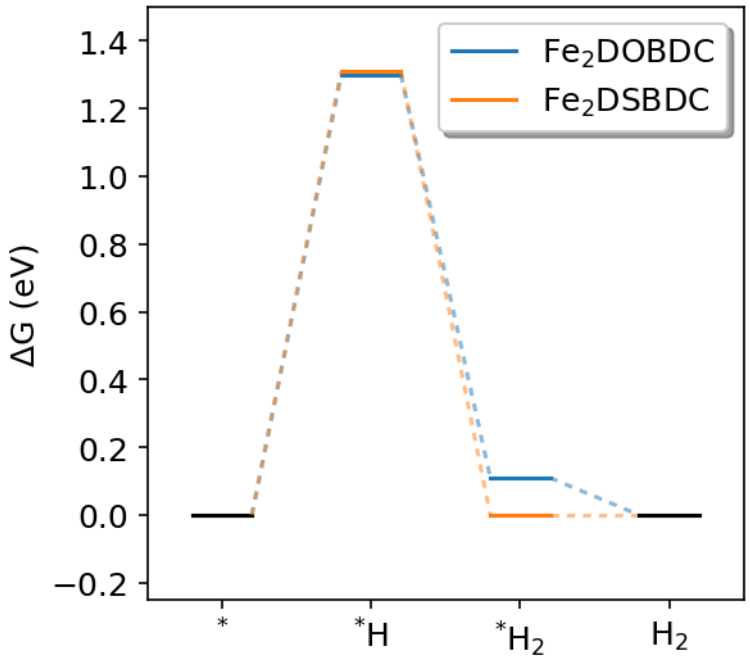


Figure S2: Reaction coordinate diagram of hydrogen reduction on the Fe_2DOBDC and Fe_2DSBDC clusters.

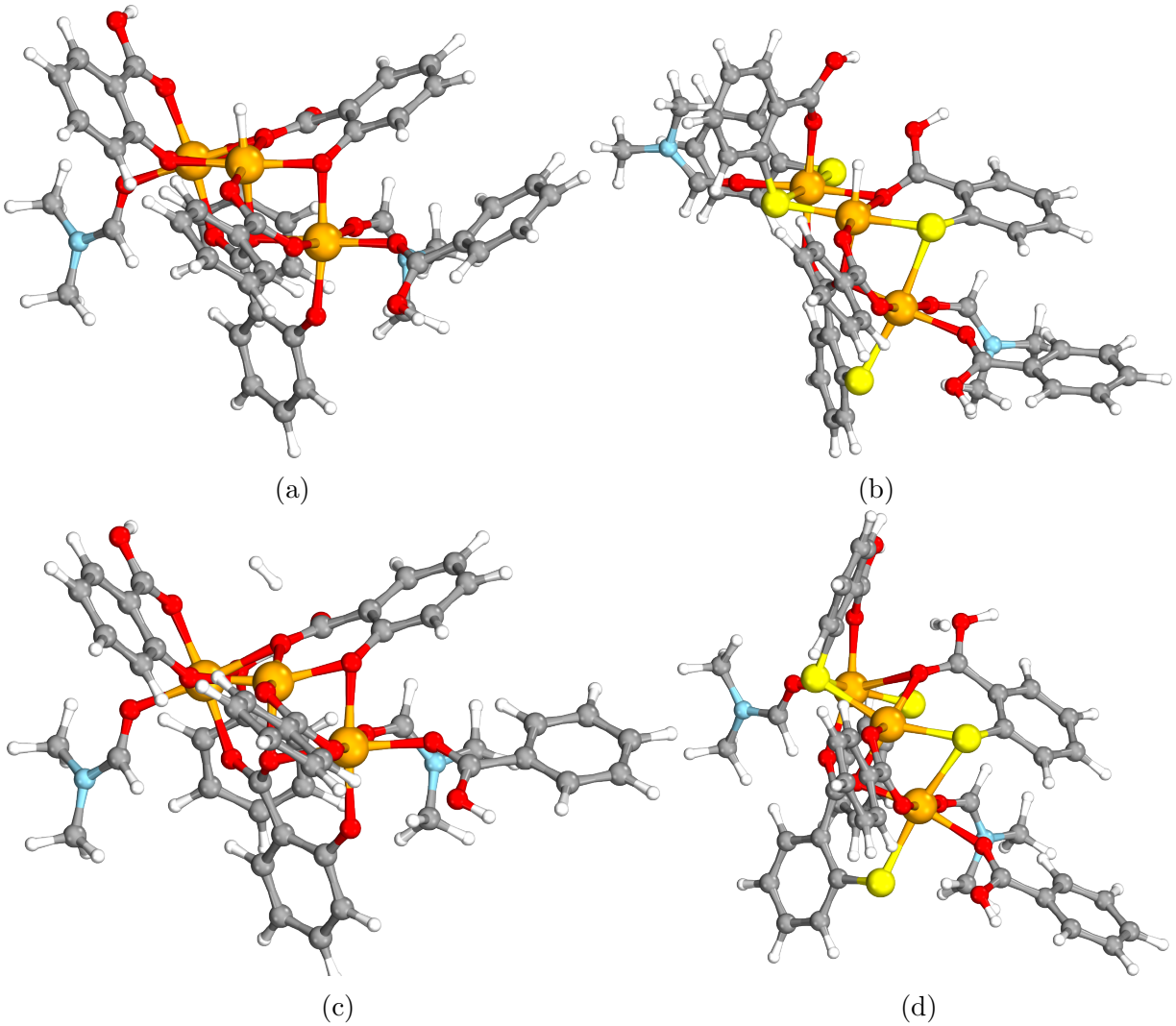
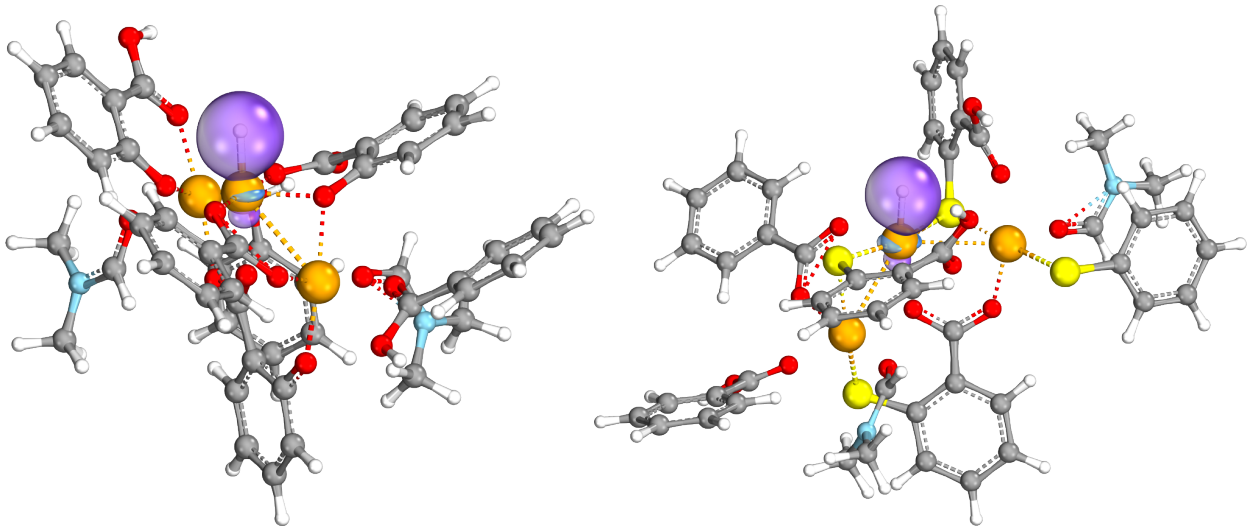


Figure S3: Molecular structures of the a) Fe_2DOBDC-H, b) Fe_2DSBDC-H, c) Fe_2DOBDC-H_2, and Fe_2DSBDC-H_2 intermediates. Color code: H (white), C (grey), N (blue) O (red), S (yellow), Fe (gold).



(a) E_{MO} = -0.25 eV (b) E_{MO} = -0.25 eV

Figure S4: Localized molecular orbitals comprised of the Fe-H bonds for the a) Fe_2DOBDC and b) Fe_2DSBDC clusters. Color code: H (white), C (grey), N (blue), O (red), S (yellow), Fe (gold).

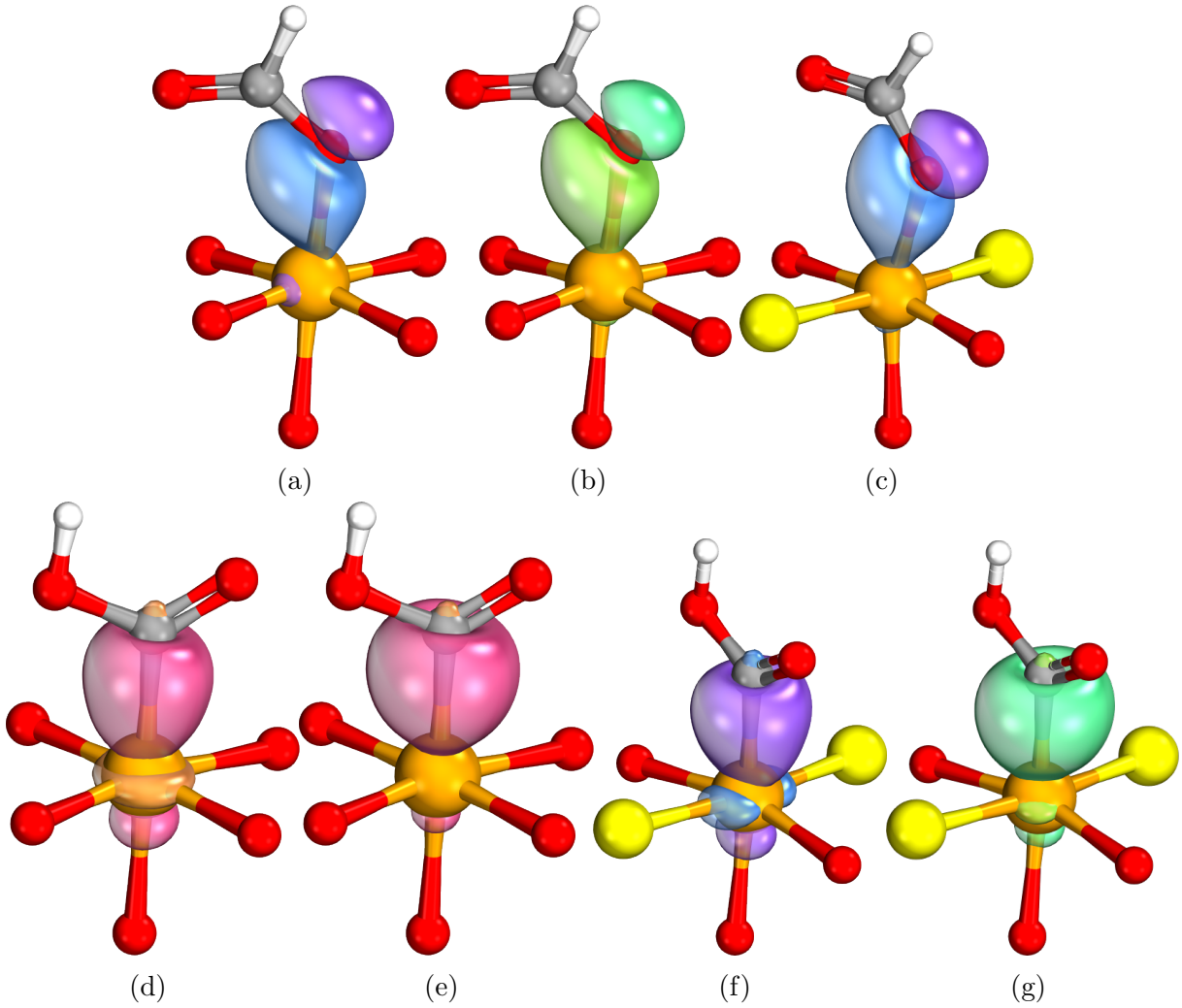
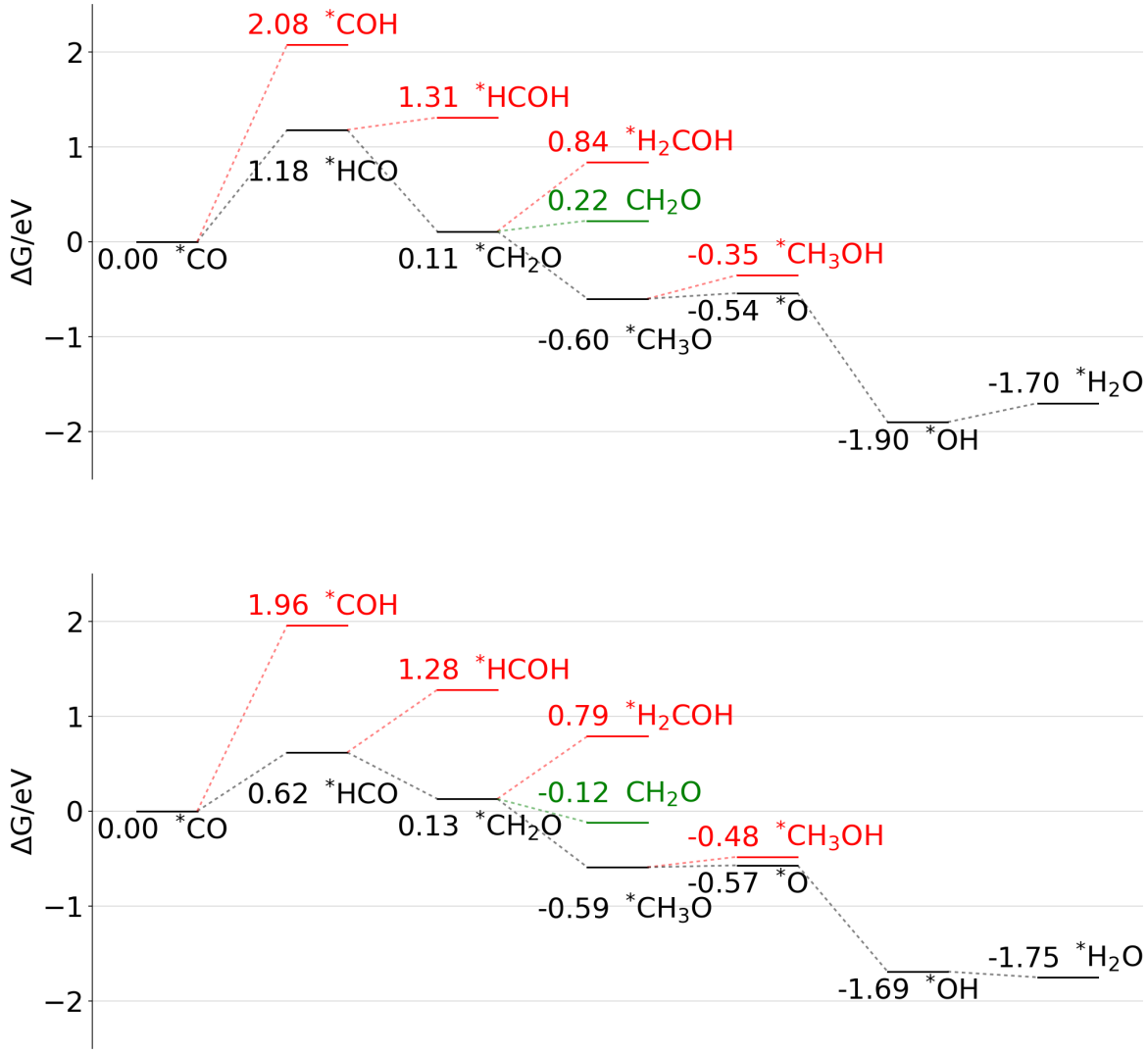


Figure S5: Localized molecular orbitals for the *OCHO (top) and *OCOH (bottom) intermediates. Color code: H (white), C (grey), N (blue) O (red), S (yellow), Fe (gold).



(a)

Figure S6: Free energy reaction mechanism for the reduction of CO to CH_4 on the (top) Fe_2DOBDC and (bottom) Fe_2DSBDC clusters. All energy values are relative to *CO for each respective cluster. Color code - favorable reduction (black), unfavorable reduction (red), desorption (green).