Supporting Information for

Di- and Tetrameric Molybdenum Sulfide Clusters Activate and Stabilize Dihydrogen as Hydrides

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S1. Methodology for the Calculation of Thermochemical Properties

Standard thermodynamics equations were used for computing the thermochemical properties of the system. The free energy of a system at any given temperature (T) is defined as:

\[ G = H - TS, \]  

(1)

where \( H \) is the enthalpy of the system and \( S \) is the total entropy of the system. The free energy of a gas-phase species at a non-standard partial pressure (\( p \)) was calculated according to the following relation:

\[ G = G^0 + k_B T \ln p, \]  

(2)

where \( G^0 \) is the standard free energy of the gas-phase species computed at 1 bar and \( k_B \) is the Boltzmann constant.

The enthalpy of a system is defined as:

\[ H = U + k_B T, \]  

(3)

where \( U \) is the internal energy of the system which was calculated according to the following equation:

\[ U = E_{el} + E_{ZPE} + E_{vib} + E_{rot} + E_{tr}, \]  

(4)

where \( E_{el} \) is the electronic energy of the system (obtained from single-point energy calculations), \( E_{ZPE} \) is the zero-point-energy (ZPE) correction to the internal energy of the system, and \( E_{vib}, E_{rot}, \) and \( E_{tr} \) are the contributions to internal energy of the system due to its vibrations, rotation, and translation, respectively.

The contribution to the internal energy of the system due to its translation at a finite temperature is:

\[ E_{tr} = \frac{3}{2} RT \]  

(5)

The contribution to the internal energy of the system due to its rotation at a finite temperature is:

\[ E_{rot} = RT, \text{ for a linear molecule, and } \]
\[ E_{rot} = \frac{3}{2} RT, \text{ for a general polyatomic molecule. } \]  

(6a, 6b)
Finally, the contribution to the internal energy of the system from zero-point vibrational energy and molecular vibrations at a finite temperature were calculated using the following equations:

\[ E_{\text{ZPE}} = k_B \sum_k \frac{1}{2} \Theta_{\nu,k}, \text{ and} \]

\[ E_{\text{vib}} = k_B \sum_k \frac{\Theta_{\nu,k}}{e^{\Theta_{\nu,k}/k_B T} - 1}, \]

where \( \Theta_{\nu,k} = \frac{h \nu_k}{k_B} \) is the characteristic temperature of a vibrational mode \( k \) (obtained from vibrational frequency calculations), \( \nu_k \) is the frequency of the vibrational mode, and \( h \) is the Planck’s constant. Each of the \( 3N - 6 \) vibrational modes for minima (\( 3N - 5 \) vibrational modes for linear molecules and \( 3N - 7 \) vibrational modes for transition states) were considered for calculating the \( E_{\text{ZPE}} \) and \( E_{\text{vib}} \). The frequencies obtained from DFT calculations were not scaled and were used as computed.

The total entropy of a system is defined as:

\[ S = S_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{tr}}, \]

where \( S_{\text{el}}, S_{\text{vib}}, S_{\text{rot}}, \) and \( S_{\text{tr}} \) are the contributions to the total entropy of the system from electronic, vibrational, rotational, and translational motions, respectively.

The entropy of a species due to its electronic degeneracy is defined as:

\[ S_{\text{el}} = k_B \ln \omega, \]

where \( \omega \) is the total electron spin-multiplicity of the system.

The entropy of the system due to its rotational motion can be obtained using the following equations:

\[ S_{\text{rot}} = k_B \left( \ln \left( \frac{1}{\sigma_r \Theta_r} \right) + 1 \right), \text{ for a diatomic molecule, and} \]

\[ S_{\text{rot}} = k_B \left( \ln \left( \frac{\pi^{0.5}}{\sigma_r} \left( \frac{\tau^{1.5}}{\Theta_{r,x} \Theta_{r,y} \Theta_{r,z}} \right)^{0.5} \right) + \frac{3}{2} \right), \text{ for a general polyatomic molecule}, \]

where \( \Theta_r = \frac{h^2}{8\pi^2 I k_B} \) is the characteristic rotational temperature of the system, \( \sigma_r \) is the rotational symmetry number, and \( I \) is the moment of inertia of the molecule.

The entropy of the system due to translational motion at a given temperature, \( T \), and partial pressure, \( p \), was obtained using the Sackur-Tetrode equation:
\[ S_{fr} = k_B \left( \ln \left( \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{1.5} \frac{k_B T}{p} + \frac{s}{2} \right) \right). \]  \hspace{1cm} (12)

Finally, the contribution to the entropy of a system due to its vibrational motion was determined using the rigid-rotor harmonic oscillator (RRHO) approximation:

\[ S_{vib} = k_B \left( \sum_k \left( \frac{\Theta_{v,k}/T}{e^{\Theta_{v,k}/T} - 1} - \ln \left( 1 - e^{\Theta_{v,k}/T} \right) \right) \right). \]  \hspace{1cm} (13)

Following the approach by Cramer and Truhlar, all frequencies below the 100 cm\(^{-1}\) were uniformly shifted up to the cut-off value for computing the vibrational entropy of the system.
S2. Infrared (IR) Spectroscopy of Adsorbed CO

Figure S2.1. Example of peak deconvolution of IR spectra of adsorbed CO on (a) Mo$_2$S$_4$/NaY (~3.2 wt.-% Mo), (b) Mo$_2$S$_4$/NaY (~3.2 wt.-% Mo), and (c) MoS$_2$/γ-Al$_2$O$_3$ (~8.8 wt.-% Mo), after cooling to 173 K in either vacuum (left) or hydrogen (right). Background corrected difference spectra were deconvoluted to three Gaussian bands (~2105 cm$^{-1}$, ~2095 cm$^{-1}$, and ~2055 cm$^{-1}$ for MoS$_2$/γ-Al$_2$O$_3$ and ~2085 cm$^{-1}$, ~2075 cm$^{-1}$, and ~2035 cm$^{-1}$ for Mo$_2$S$_4$/NaY catalysts) using Origin 2020 software package. Half-widths of all peaks were kept constant within ±10% throughout the fitting process.
Figure S2.2. CO adsorption isotherms (between 0.01 mbar and 2 mbar) on (a) Mo$_2$S$_4$/NaY (~3.2 wt.-% Mo), (b) Mo$_4$S$_4$/NaY (~3.2 wt.-% Mo), and (c) MoS$_2$/γ-Al$_2$O$_3$ (~8.8 wt.-% Mo), after cooling to 173 K in vacuum (left) or hydrogen (right). The deconvoluted CO adsorption data were fitted to Langmuir-type isotherms.
Table S2.1. Adsorption constants (K) and maximum CO uptake ($q_{\text{max}}$, normalized to catalyst wafer mass and size) for the deconvoluted IR spectra of adsorbed CO on (a) Mo$_2$S$_4$/NaY (~3.2 wt.% Mo), (b) Mo$_4$S$_4$/NaY (~3.2 wt.% Mo), and (c) MoS$_2$/γ-Al$_2$O$_3$ (~8.8 wt.% Mo), after cooling to 173 K in either vacuum or hydrogen.

(a) Mo$_2$S$_4$/NaY (~3.2 wt.% Mo)

| Band position | 2085 cm$^{-1}$ | 2075 cm$^{-1}$ | 2035 cm$^{-1}$ | Total CO adsorbed |
|---------------|----------------|----------------|----------------|-------------------|
| Cooled in     | K [cm·g$^{-1}$] | K [cm·g$^{-1}$] | K [cm·g$^{-1}$] | $q_{\text{max}}$ [cm·g$^{-1}$] | [%] |
| Vacuum        | 30             | 920            | 5              | 115               | 30   | 420 | 1455 | 100 |
| Hydrogen (1 bar) | 13            | 430            | 7              | 25                | 17   | 140 | 595  | 41  |

(b) Mo$_4$S$_4$/NaY (~3.2 wt.% Mo)

| Band position | 2085 cm$^{-1}$ | 2075 cm$^{-1}$ | 2035 cm$^{-1}$ | Total CO adsorbed |
|---------------|----------------|----------------|----------------|-------------------|
| Cooled in     | K [cm·g$^{-1}$] | K [cm·g$^{-1}$] | K [cm·g$^{-1}$] | $q_{\text{max}}$ [cm·g$^{-1}$] | [%] |
| Vacuum        | 30             | 900            | 7              | 200               | 30   | 660 | 1760 | 100 |
| Hydrogen (1 bar) | 15            | 445            | 7              | 100               | 15   | 320 | 865  | 49  |

(c) MoS$_2$/γ-Al$_2$O$_3$ (~8.8 wt.% Mo)

| Band position | 2105 cm$^{-1}$ | 2095 cm$^{-1}$ | 2055 cm$^{-1}$ | Total CO adsorbed |
|---------------|----------------|----------------|----------------|-------------------|
| Cooled in     | K [cm·g$^{-1}$] | K [cm·g$^{-1}$] | K [cm·g$^{-1}$] | $q_{\text{max}}$ [cm·g$^{-1}$] | [%] |
| Vacuum        | 13             | 740            | 5              | 950               | 13   | 1230 | 2920 | 100 |
| Hydrogen (1 bar) | 15            | 680            | 5              | 860               | 16   | 1240 | 2780 | 95  |
Table S2.2. Adsorption constants (K) and maximum CO uptake ($q_{\text{max}}$; normalized to catalyst wafer mass and size) for the deconvoluted IR spectra of adsorbed CO on (a) Mo$_2$S$_x$/NaY (~3.2 wt.-% Mo), and (b) Mo$_x$S$_y$/NaY (~3.2 wt.-% Mo), after cooling to 173 K in either vacuum, ethene, or a mixture of ethene and hydrogen.

(a) Mo$_2$S$_4$/NaY (~3.2 wt.-% Mo)

| Cooled in (mbar) | Band position | Total CO adsorbed |
|------------------|---------------|-------------------|
|                  | 2085 cm$^{-1}$ | 2075 cm$^{-1}$ | 2035 cm$^{-1}$ | $K$ | $q_{\text{max}}$ | $K$ | $q_{\text{max}}$ | $K$ | $q_{\text{max}}$ | [%] |
| Vacuum           | 35            | 930              | 20              | 328 | 35             | 450 | 1708            | 100 |
| C$_2$H$_4$ (100) | 8             | 170              | 6               | 25  | 6              | 47  | 242             | 14  |
| Vacuum           | 35            | 830              | 20              | 420 | 35             | 485 | 1735            | 100 |
| H$_2$ (960) + C$_2$H$_4$ (50) | 11          | 165              | 7               | 60  | 8              | 110 | 335             | 19  |

(b) Mo$_x$S$_y$/NaY (~3.2 wt.-% Mo)

| Cooled in (mbar) | Band position | Total CO adsorbed |
|------------------|---------------|-------------------|
|                  | 2085 cm$^{-1}$ | 2075 cm$^{-1}$ | 2035 cm$^{-1}$ | $K$ | $q_{\text{max}}$ | $K$ | $q_{\text{max}}$ | $K$ | $q_{\text{max}}$ | [%] |
| Vacuum           | 16            | 970              | 22              | 440 | 28             | 320 | 1730            | 100 |
| C$_2$H$_4$ (1000) | 10           | 90               | 10              | 65  | 7              | 50  | 205             | 11  |
| H$_2$ (960) + C$_2$H$_4$ (50) | 14          | 285              | 7               | 100 | 8              | 110 | 495             | 28  |
**S3. CO Adsorption on MoₓSᵧ Clusters**

![Image](image.png)

**Figure S3.1.** DFT/B3LYP/def2-TZVP-optimized geometries of (a) Mo₂S₄, and (b) Mo₄S₄ clusters, with multiple CO molecules (three per Mo) adsorbed on Mo atoms. The average C–O bond lengths in the adsorbed CO molecules were computed to be ~1.131 Å in the dimer and ~1.137 Å in the tetramer. The Mayer bond orders for the C–O bond were computed to be 2.31−2.40 in Mo₂S₄ and 2.27−2.34 in Mo₄S₄. The C–O bond length and Mayer bond order for gas-phase CO species were computed to be ~1.125 Å and ~2.44, respectively. Optimized geometries and structural parameters obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; C: gray; O: red.
Figure S3.2. Average free energy change (ΔG) per adsorbed CO molecule on Mo$_2$S$_4$ and Mo$_4$S$_4$ clusters as a function of number of adsorbed CO molecules, computed at T = 173 K and p$_{CO}$ = 2 mbar, with (i) DFT/B3LYP/def2-TZVPP (filled symbols), and (ii) DFT/PBE0/def2-TZVPP (open symbols). Error bars correspond to ±½D gas-phase translational entropy of CO at 173 K.
S4. Hydrogen Adsorption on Mo$_2$S$_4$

Figure S4.1. DFT/B3LYP/def2-TZVP-optimized geometries of Mo$_2$S$_4$ clusters with gas-phase H$_2$ ([1a]) or physisorbed H$_2$ ([2a]) centered on Mo, and Mo$_2$S$_4$ clusters with dissociatively adsorbed H$_2$ (as hydride or sulfhydryl species) on (i) single Mo atom ([3a]), (ii) two Mo atoms ([4a]), (iii) one Mo atom and one bridging S atom ([5a]), (iv) two bridging S atoms ([6a]), and (v) single bridging S atom ([7a]). The optimized structures of the transition states between [2a] and [3a], i.e., [2-3a]$^\ddagger$, and between [3a] and [4a], i.e., [3-4a]$^\ddagger$, are also shown. The reported spin-multiplicities (ω) correspond to the thermodynamically most stable configurations (Table S4.1). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; H: pink.
Table S4.1. Relative enthalpies (ΔH) and free energies (ΔG) of Mo$_2$S$_4$ clusters with gas-phase, physisorbed, or dissociatively adsorbed H$_2$, computed at T = 473 K and p$_{H_2}$ = 1 bar, using (a) DFT/B3LYP/def2-TZVPP and (b) DFT/PBE0/def2-TZVPP. The corresponding structures are depicted in Figure S4.1.

(a) DFT/B3LYP/def2-TZVPP

| Spin-multiplicity (ω) | ΔH$_{473K}$ /kJ·mol$^{-1}$ | ΔG$_{473K}$ /kJ·mol$^{-1}$ |
|-----------------------|-----------------------------|-----------------------------|
|                       | 1   | 3   | 5   | 1   | 3   | 5   |
| [1a]                  | 0.0$^a$ | -32.2 | -10.4 | 0.0$^a$ | -35.1 | -24.0 |
| [2a]                  | -70.5 | -90.9 | -7.6$^b$ | -15.3 | -41.0 | 31.1$^b$ |
| [2-3]$^1$             | -d  | -78.3 | -e  | -d  | -26.9 | -e  |
| [3a]                  | -120.9 | -81.2 | -c  | -61.0 | -37.1 | -c  |
| [3-4]$^1$             | 79.6 | 34.2 | -e  | 142.2 | 87.6 | -e  |
| [4a]                  | -156.5 | -140.1 | 59.9 | -100.8 | -93.2 | 93.3 |
| [5a]                  | -32.8 | -52.5 | -17.9$^c$ | 20.5 | -4.3 | 22.4$^c$ |
| [6a]                  | 8.9 | 71.4 | 66.1 | 60.6 | 118.0 | 108.2 |
| [7a]                  | 109.6 | 134.2 | 150.0 | 163.5 | 184.3 | 195.6 |

(b) DFT/PBE0/def2-TZVPP

| Spin-multiplicity (ω) | ΔH$_{473K}$ /kJ·mol$^{-1}$ | ΔG$_{473K}$ /kJ·mol$^{-1}$ |
|-----------------------|-----------------------------|-----------------------------|
|                       | 1   | 3   | 5   | 1   | 3   | 5   |
| [1a]                  | 0.0$^a$ | -39.9 | -27.6 | 0.0$^a$ | -42.9 | -42.6 |
| [2a]                  | -72.4 | -109.4 | -30.2$^b$ | -19.5 | -59.8 | 7.1$^b$ |
| [2-3]$^1$             | -d  | -96.7 | -e  | -d  | -46.1 | -e  |
| [3a]                  | -130.7 | -89.1 | -c  | -71.6 | -46.8 | -c  |
| [3-4]$^1$             | 73.6 | 28.5 | -e  | 135.6 | 82.7 | -e  |
| [4a]                  | -162.5 | -145.3 | 58.9 | -106.9 | -100.0 | 88.5 |
| [5a]                  | -40.5 | -69.8 | -43.6$^c$ | 12.5 | -22.4 | -4.7$^c$ |
| [6a]                  | -1.6 | 51.9 | 34.6 | 49.6 | 98.2 | 75.6 |
| [7a]                  | 95.0 | 107.6 | 114.7 | 149.0 | 160.7 | 159.5 |

$^a$ The enthalpy and free energy of [1a] with spin-multiplicity, $ω = 1$ (i.e., no unpaired electrons) was used as the standard and was set to zero.

$^b$ The lowest energy structure was the trans form with terminal S atoms pointing in opposite direction.

$^c$ The optimized structure with non-imaginary vibrational frequency modes was not achieved.

$^d$ No climbing image was found indicating a barrier-less transition.

$^e$ Transition-state optimization was not performed for this structure.
Figure S4.2. Free energy diagram of Mo\textsubscript{2}S\textsubscript{4} configurations, with spin-multiplicity $\omega = 1$ and $\omega = 3$, showing the transitions from [2a] to [3a] and from [3a] to [4a], computed at $T = 473$ K and $p_{H_2} = 1$ bar, using (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The corresponding structures are shown in Figure S4.1. Error bars correspond to $\pm \frac{1}{2}D$ gas-phase translational entropy of the H\textsubscript{2} at 473 K. Values shown in the figure are in kJ\cdot mol\textsuperscript{-1}. Values shown in parentheses are the imaginary frequencies of the corresponding transition state structures.
Table S4.2. Mayer bond orders and bond lengths of relevant bonds in the thermodynamically most-stable Mo$_2$S$_4$ configurations with gas-phase, physisorbed, or dissociatively adsorbed H$_2$, computed with (i) DFT/B3LYP/def2-TZVPP, and (ii) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S4.1.

| Structure (spin-multiplicity) | Bond                  | Mayer bond order | Bond length /Å |
|-------------------------------|-----------------------|------------------|----------------|
|                               |                       | B3LYP | PBE0 | B3LYP | PBE0 |
| [1a] ($\omega = 3$)           | H$_1$ - H$_2$         | 1.000 | 1.000 | 0.744 | 0.746 |
| [2a] ($\omega = 3$)           | Mo$_1$ - H$_1$        | 0.251 | 0.257 | 1.935 | 1.897 |
|                               | Mo$_1$ - H$_2$        | 0.307 | 0.335 | 1.936 | 1.903 |
|                               | H$_1$ - H$_2$         | 0.678 | 0.652 | 0.811 | 0.827 |
| [2-3]$^\dagger$ ($\omega = 3$) | Mo$_1$ - H$_1$        | 0.640 | 0.675 | 1.707 | 1.690 |
|                               | Mo$_1$ - H$_2$        | 0.718 | 0.761 | 1.707 | 1.690 |
|                               | H$_1$ - H$_2$         | 0.217 | 0.180 | 1.247 | 1.330 |
| [3a] ($\omega = 1$)           | Mo$_1$ - H$_1$        | 0.826 | 0.831 | 1.684 | 1.676 |
|                               | Mo$_1$ - H$_2$        | 0.826 | 0.831 | 1.683 | 1.676 |
|                               | H$_1$ - H$_2$         | - a  | - a  | 1.768 | 1.719 |
| [3-4a]$^\dagger$ ($\omega = 3$) | Mo$_1$ - H$_1$        | 0.850 | 0.854 | 1.684 | 1.685 |
|                               | Mo$_1$ - H$_2$        | 0.596 | 0.553 | 1.803 | 1.840 |
|                               | Mo$_2$ - H$_2$        | 0.259 | 0.293 | 2.171 | 2.120 |
| [4a] ($\omega = 1$)           | Mo$_1$ - H$_1$        | 0.868 | 0.877 | 1.713 | 1.705 |
|                               | Mo$_2$ - H$_2$        | 0.868 | 0.877 | 1.713 | 1.705 |
| [5a] ($\omega = 3$)           | Mo$_1$ - H$_1$        | 0.883 | 0.895 | 1.708 | 1.701 |
|                               | S$_1$ - H$_2$         | 0.957 | 0.953 | 1.354 | 1.353 |
| [6a] ($\omega = 1$)           | S$_1$ - H$_1$         | 0.961 | 0.956 | 1.358 | 1.358 |
|                               | S$_2$ - H$_2$         | 0.961 | 0.956 | 1.358 | 1.358 |
| [7a] ($\omega = 1$)           | S$_1$ - H$_1$         | 0.948 | 0.942 | 1.345 | 1.346 |
|                               | S$_1$ - H$_2$         | 0.848 | 0.856 | 1.382 | 1.381 |
|                               | H$_1$ - H$_2$         | - a  | - a  | 1.982 | 1.978 |

$^a$ The computed bond order was < 0.1.
Table S4.3. Net Hirshfeld charges in the thermodynamically most-stable Mo$_2$S$_4$ configurations with gas-phase, physisorbed, or dissociatively adsorbed H$_2$, computed using (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S4.1.

(a) DFT/B3LYP/def2-TZVPP

| Structure | [1a] | [2a] | [2-3a]$^\ddagger$ | [3a] | [3-4a]$^\ddagger$ | [4a] | [5a] | [6a] | [7a] |
|-----------|------|------|----------------|------|----------------|------|------|------|------|
| Spin-multiplcity ($\omega$) | 3     | 3    | 3              | 1    | 3              | 1    | 3    | 1    | 1    |
| Mo$_2$S$_4$ | 0.000 | -0.060 | 0.088           | 0.202 | 0.209          | 0.264 | 0.089 | -0.098 | -0.155 |
| H$_2$H$_2$ | 0.000 | 0.060 | -0.088         | -0.202 | -0.209          | -0.264 | -0.089 | 0.098  | 0.155  |

(b) DFT/PBE0/def2-TZVPP

| Structure | [1a] | [2a] | [2-3a]$^\ddagger$ | [3a] | [3-4a]$^\ddagger$ | [4a] | [5a] | [6a] | [7a] |
|-----------|------|------|----------------|------|----------------|------|------|------|------|
| Spin-multiplcity ($\omega$) | 3     | 3    | 3              | 1    | 3              | 1    | 3    | 1    | 1    |
| Mo$_2$S$_4$ | 0.000 | -0.065 | 0.090          | 0.182 | 0.212          | 0.248 | 0.074 | -0.112 | -0.167 |
| H$_2$H$_2$ | 0.000 | 0.065 | -0.090         | -0.182 | -0.212          | -0.248 | -0.074 | 0.112  | 0.167  |
S5. Hydrogen Adsorption on Mo₄S₄

Figure S5.1. DFT/B3LYP/def2-TZVP-optimized geometries of Mo₄S₄ clusters with gas-phase H₂ ([1b]) or physisorbed H₂ ([2b]) centered on Mo, and Mo₂S₄ clusters with dissociatively adsorbed H₂ (as hydride or sulfhydryl species) on (i) single Mo atom ([3b]), (ii) two Mo atoms ([4b]), (iii) one Mo atom and one bridging S atom ([5b]), (iv) two bridging S atoms ([6b]), and (v) single bridging S atom ([7b]). The optimized structures of transition states between [2b] and [3b], i.e., [2-3b]‡, and between [3b] and [4b], i.e., [3-4b]‡, are also shown. The reported spin-multiplicities (ω) correspond to the thermodynamically most stable configurations (Table S5.1). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; H: pink.
Table S5.1. Relative enthalpies ($\Delta H$) and free energies ($\Delta G$) of Mo₄S₄ clusters with gas-phase, physisorbed, or dissociatively adsorbed H₂, computed at $T = 473$ K and $p_{H_2} = 1$ bar, with (a) DFT/B3LYP/def2-TZVPP and (b) DFT/PBE0/def2-TZVPP. The corresponding structures are depicted in Figure S5.1.

(a) DFT/B3LYP/def2-TZVPP

| Multiplicity ($\omega$) | $\Delta H_{473K} / kJ \cdot mol^{-1}$ | $\Delta G_{473K} / kJ \cdot mol^{-1}$ |
|------------------------|---------------------------------------|--------------------------------------|
|                        | 1  | 3  | 5  | 7  | 1  | 3  | 5  | 7  |
| [1b]                   | 0.0⁠¹ | 11.7 | 6.6 | 43.4 | 0.0⁠¹ | -4.1 | -11.0 | 22.4 |
| [2b]                   | -43.3 | -70.5 | -59.6 | 2.1 | 3.5 | -31.5 | -27.0 | 36.2 |
| [2-3b]¹                  | -51.6 | -⁠b | -45.6 | -⁠c | 0.4 | -⁠b | -7.2 | -⁠c |
| [3b]                   | -75.7 | -108.3 | -55.7 | -2.7 | -23.5 | -61.0 | -17.8 | 30.5 |
| [3-4b]¹                  | 54.9 | 49.3 | 54.6 | -⁠c | 108.6 | 89.4 | 94.7 | -⁠c |
| [4b]                   | -99.7 | -115.9 | -69.9 | -44.0 | -47.6 | -72.3 | -32.9 | -13.7 |
| [5b]                   | 81.9 | -49.8 | 16.3 | 61.9 | 131.4 | -15.4 | 49.4 | 83.6 |
| [6b]                   | -⁠d | 156.5 | 145.9 | -⁠d | -⁠d | 188.2 | 177.3 | -⁠d |
| [7b]                   | -⁠d | 173.7 | 193.8 | 228.2 | -⁠d | 202.4 | 228.2 | 254.3 |

(b) DFT/PBE0/def2-TZVPP

| Multiplicity ($\omega$) | $\Delta H_{473K} / kJ \cdot mol^{-1}$ | $\Delta G_{473K} / kJ \cdot mol^{-1}$ |
|------------------------|---------------------------------------|--------------------------------------|
|                        | 1  | 3  | 5  | 7  | 1  | 3  | 5  | 7  |
| [1b]                   | 0.0⁠¹ | 5.0 | -5.9 | 25.6 | 0.0⁠¹ | -7.2 | -23.5 | 4.3 |
| [2b]                   | -59.5 | -83.6 | -88.7 | -31.2 | -11.1 | -47.7 | -55.5 | 3.5 |
| [2-3b]¹                  | -69.9 | -⁠b | -71.5 | -⁠c | -16.1 | -⁠b | -34.7 | -⁠c |
| [3b]                   | -90.5 | -131.8 | -76.4 | -23.9 | -37.5 | -84.3 | -38.3 | 8.9 |
| [3-4b]¹                  | 53.8 | 21.7 | 57.3 | -⁠c | 109.1 | 64.9 | 98.2 | -⁠c |
| [4b]                   | -118.9 | -140.1 | -94.1 | -52.1 | -65.9 | -96.4 | -58.2 | -20.5 |
| [5b]                   | 68.2 | -61.0 | 29.5 | 52.9 | 119.8 | -27.5 | 61.5 | 79.7 |
| [6b]                   | -⁠d | 121.1 | 136.6 | -⁠d | -⁠d | 154.2 | 176.2 | -⁠b |
| [7b]                   | -⁠d | 173.2 | 182.4 | 218.8 | -⁠d | 202.0 | 217.2 | 242.5 |

⁠¹The enthalpy and free energy of [1b] with spin-multiplicity, $\omega = 1$ (i.e., no unpaired electrons) was used as the standard and was set to zero.

⁠b No climbing image was found suggesting a barrier-less transition.

⁠c Transition-state optimization was not performed for this structure.

d The optimized structure with non-imaginary vibrational frequency modes was not achieved.
Figure S5.2. Free energy diagram of Mo₄S₄ configurations, with spin-multiplicity ω = 3 and ω = 5, showing the transition from [2b] to [3b] and from [3b] to [4b], computed at T = 473 K and p_H₂ = 1 bar, with (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The corresponding structures are shown in Figure S5.1. Error bars correspond to ±½D gas-phase translational entropy of H₂ at 473 K. Values shown in the figure are in kJ mol⁻¹. Values shown in parentheses are the imaginary frequencies of the corresponding transition state structures.
Table S5.2. Mayer bond orders and bond lengths of relevant bonds in the thermodynamically most stable Mo$_4$S$_4$ configurations with gas-phase, physisorbed, or dissociatively adsorbed H$_2$, computed with (i) DFT/B3LYP/def2-TZVPP, and (ii) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S5.1.

| Structure (spin-multiplicity) | Bond          | Mayer bond order | Bond length /Å |
|-------------------------------|---------------|------------------|----------------|
|                               |               | B3LYP | PBE0 | B3LYP | PBE0 |
| [1b] ($\omega = 5$)           | H$_1$ - H$_2$ | 1.000 | 1.000 | 0.744 | 0.746 |
| [2b] ($\omega = 3$)           | Mo$_1$ - H$_1$ | 0.448 | 0.284$^a$ | 1.825 | 1.931$^a$ |
|                               | Mo$_1$ - H$_2$ | 0.461 | 0.284$^a$ | 1.829 | 1.931$^a$ |
|                               | H$_1$ - H$_2$ | 0.428 | 0.682$^a$ | 0.936 | 0.822$^a$ |
| [2-3b]$^\dagger$ ($\omega = 5$) | Mo$_1$ - H$_1$ | 0.654 | 0.647 | 1.734 | 1.732 |
|                               | Mo$_1$ - H$_2$ | 0.654 | 0.666 | 1.734 | 1.721 |
|                               | H$_1$ - H$_2$ | 0.229 | 0.228 | 1.225 | 1.227 |
| [3b] ($\omega = 3$)           | Mo$_1$ - H$_1$ | 0.836 | 0.849 | 1.719 | 1.712 |
|                               | Mo$_1$ - H$_2$ | 0.836 | 0.849 | 1.719 | 1.712 |
|                               | H$_1$ - H$_2$ | -$^b$ | -$^b$ | 1.980 | 1.948 |
| [3-4b]$^\dagger$ ($\omega = 3$) | Mo$_1$ - H$_1$ | 0.738 | 0.752 | 1.739 | 1.736 |
|                               | Mo$_1$ - H$_2$ | 0.419 | 0.578 | 1.940 | 1.815 |
|                               | Mo$_2$ - H$_2$ | 0.419 | 0.250 | 1.973 | 2.151 |
| [4b] ($\omega = 3$)           | Mo$_1$ - H$_1$ | 0.848 | 0.861 | 1.752 | 1.744 |
|                               | Mo$_2$ - H$_2$ | 0.848 | 0.861 | 1.752 | 1.744 |
| [5b] ($\omega = 3$)           | Mo$_1$ - H$_1$ | 0.523 | 0.524 | 1.850 | 1.857 |
|                               | Mo$_2$ - H$_1$ | 0.356 | 0.365 | 1.979 | 1.978 |
|                               | S$_1$ - H$_2$ | 0.982 | 0.979 | 1.348 | 1.347 |
| [6b] ($\omega = 5$)           | S$_1$ - H$_1$ | 0.942 | 0.931$^c$ | 1.369 | 1.361$^c$ |
|                               | S$_2$ - H$_2$ | 0.942 | 0.931$^c$ | 1.369 | 1.362$^c$ |
| [7b] ($\omega = 3$)           | S$_1$ - H$_1$ | 0.906 | 0.907 | 1.356 | 1.361 |
|                               | S$_1$ - H$_2$ | 0.923 | 0.927 | 1.360 | 1.355 |
|                               | H$_1$ - H$_2$ | -$^b$ | -$^b$ | 1.973 | 1.961 |

$^a$ Data reported is for spin-multiplicity, $\omega = 5$.
$^b$ The computed bond order was < 0.1.
$^c$ Data reported is for spin-multiplicity, $\omega = 3$. 
Table S5.3. Net Hirshfeld charges in the thermodynamically most stable Mo<sub>4</sub>S<sub>4</sub> configurations with gas-phase, physisorbed, or dissociatively adsorbed H<sub>2</sub>, computed using (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S5.1.

(a) DFT/B3LYP/def2-TZVPP

| Structure | [1b] | [2b] | [2-3b]<sup>‡</sup> | [3b] | [3-4b]<sup>‡</sup> | [4b] | [5b] | [6b] | [7b] |
|-----------|------|------|----------------|------|----------------|------|------|------|------|
| Mo<sub>4</sub>S<sub>4</sub> | 0.000 | 0.310 | 0.328 | 0.305 | 0.402 | 0.123 | -0.030 | -0.127 |
| H<sub>2</sub>H<sub>2</sub> | 0.000 | -0.310 | -0.328 | -0.305 | -0.402 | -0.123 | 0.030 | 0.127 |

(b) DFT/PBE0/def2-TZVPP

| Structure | [1b] | [2b] | [2-3b]<sup>‡</sup> | [3b] | [3-4b]<sup>‡</sup> | [4b] | [5b] | [6b] | [7b] |
|-----------|------|------|----------------|------|----------------|------|------|------|------|
| Mo<sub>4</sub>S<sub>4</sub> | 0.000 | 0.292 | 0.312 | 0.296 | 0.386 | 0.113 | -0.053 | -0.137 |
| H<sub>2</sub>H<sub>2</sub> | 0.000 | -0.292 | -0.312 | -0.296 | -0.386 | -0.113 | 0.053 | 0.137 |
S6. Multiple Hydrogen Adsorption on Mo₄S₄

Figure S6.1. DFT/B3LYP/def2-TZVP-optimized geometries of Mo₄S₄ clusters with one ([3b]), two ([8b]), three ([9b]), or four ([10b]) H₂ molecule(s) dissociatively adsorbed on Mo. The optimized geometry of bare Mo₄S₄ cluster with gas-phase ethene ([1b]) is also shown for comparison. The reported spin-multiplicities (ω) correspond to the thermodynamically most-stable configurations (Tables S6.1 and S6.2). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; H: pink.
Table S6.1. Enthalpies ($\Delta H$) and free energies ($\Delta G$) of Mo$_4$S$_4$ clusters with (multiple) H$_2$ molecule(s) dissociatively adsorbed on Mo, computed at (a) $T = 473$ K and $p_{H_2} = 1$ bar, and (b) $T = 173$ K and $p_{H_2} = 1$ bar, with DFT/B3LYP/def2-TZVPP. The corresponding structures are shown in Figure S6.1.

(a) $T = 473$ K and $p_{H_2} = 1$ bar

| Spin-multiplicity ($\omega$) | $\Delta H^{473K}$/kJ·mol$^{-1}$ | $\Delta G^{473K}$/kJ·mol$^{-1}$ |
|-----------------------------|---------------------------------|---------------------------------|
| [1b]                        | 0.0$^a$ 11.7 6.6 43.4           | 0.0$^a$ -4.1 -11.0 22.4         |
| [3b]                        | -75.7 -108.3 -55.7 -2.7         | -23.5 -61.0 -17.8 30.5         |
| [8b]                        | -146.0 -127.3 -100.5 -38.1      | -37.2 -28.1 -2.6 55.8          |
| [9b]                        | -147.5 -150.4 -101.9            | 16.8 3.2 43.6 -b               |
| [10b]                       | -144.7 -b -b -b                 | 74.2 -b -b -b                   |

(b) $T = 173$ K and $p_{H_2} = 1$ bar

| Spin-multiplicity ($\omega$) | $\Delta H^{173K}$/kJ·mol$^{-1}$ | $\Delta G^{173K}$/kJ·mol$^{-1}$ |
|-----------------------------|---------------------------------|---------------------------------|
| [1b]                        | 0.0$^a$ 10.4 5.1 41.8           | 0.0$^a$ 5.5 -0.3 35.2           |
| [3b]                        | -73.4 -106.2 -54.8 -2.3         | -55.9 -90.3 -41.6 9.5           |
| [8b]                        | -140.8 -123.1 -95.9 -33.4       | -104.5 -89.7 -63.2 -2.1         |
| [9b]                        | -139.3 -143.7 -97.1            | -84.7 -92.1 -47.3 -b            |
| [10b]                       | -133.8 -b -b -b                 | -61.1 -b -b -b                   |

$^a$The enthalpy and free energy of [1b] with spin-multiplicity, $\omega = 1$ (i.e., no unpaired electrons) was used as the standard and was set to zero.

$^b$Optimized structure with only non-imaginary vibrational frequency modes was not achieved.
Table S6.2. Enthalpies (ΔH) and free energies (ΔG) of Mo$_4$S$_4$ clusters with (multiple) H$_2$ molecule(s) dissociatively adsorbed on Mo, computed at (a) $T = 473$ K and $p_{H_2} = 1$ bar, and (b) $T = 173$ K and $p_{H_2} = 1$ bar, with DFT/PBE0/def2-TZVPP. The corresponding structures are shown in Figure S6.1.

(a) $T = 473$ K and $p_{H_2} = 1$ bar

| Spin-multiplicity (ω) | $\Delta H^{473K}$/kJ·mol$^{-1}$ | $\Delta G^{473K}$/kJ·mol$^{-1}$ |
|-----------------------|---------------------------------|---------------------------------|
|                       | 1  | 3  | 5  | 7  | 1  | 3  | 5  | 7  |
| [1b]                  |    |    |    |    | 0.0$^a$ |    |    |    | 0.0$^a$ | -7.2 | -23.5 | 4.3 |
| [3b]                  | -90.5 | -131.8 | -76.4 | -23.9 | -37.5 | -84.3 | -38.3 | 8.9 |
| [8b]                  | -178.1 | -160.9 | -136.8 | -70.3 | -68.0 | -59.9 | -39.5 | 14.9 |
| [9b]                  | -179.4 | -195.8 | -137.3 | -   b | -15.3 | -33.9 | 8.3 | -   b |
| [10b]                 | -204.6 | -   b | -   b | -   b | 18.1 | -   b | -   b | -   b |

(b) $T = 173$ K and $p_{H_2} = 1$ bar

| Spin-multiplicity (ω) | $\Delta H^{173K}$/kJ·mol$^{-1}$ | $\Delta G^{173K}$/kJ·mol$^{-1}$ |
|-----------------------|---------------------------------|---------------------------------|
|                       | 1  | 3  | 5  | 7  | 1  | 3  | 5  | 7  |
| [1b]                  | 0.0$^a$ | 4.0 | -7.6 | 23.8 | 0.0$^a$ | 0.2 | -12.9 | 17.2 |
| [3b]                  | -88.2 | -129.8 | -75.6 | -23.6 | -70.3 | -113.8 | -62.3 | -11.9 |
| [8b]                  | -172.7 | -156.4 | -132.4 | -68.4 | -136.1 | -122.5 | -99.8 | -38.7 |
| [9b]                  | -171.4 | -186.8 | -132.6 | -   b | -116.8 | -133.5 | -82.7 | -   b |
| [10b]                 | -192.3 | -   b | -   b | -   b | -118.9 | -   b | -   b | -   b |

$^a$The enthalpy and free energy of [1b] with spin-multiplicity, $ω = 1$ (i.e., no unpaired electrons) was used as the standard and was set to zero.

$^b$Optimized structure with only non-imaginary vibrational frequency modes was not achieved.
Table S6.3. Mayer bond orders and bond lengths of relevant bonds in the thermodynamically most-stable Mo$_4$S$_4$ configurations with (multiple) H$_2$ molecule(s) dissociatively adsorbed on Mo, computed with (i) DFT/B3LYP/def2-TZVPP, and (ii) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S6.1.

| Structure (spin-multiplicity) | Bond | Mayer bond order | Bond length /Å |
|-------------------------------|------|------------------|----------------|
|                               |      | B3LYP           | PBE0           |
|                               |      | B3LYP           | PBE0           |
| [1b] (ω = 5)                  | H$_1$ - H$_2$ | 1.000 | 1.000 | 0.744 | 0.746 |
|                               | Mo$_1$ - H$_1$ | 0.836 | 0.849 | 1.719 | 1.712 |
| [3b] (ω = 3)                  | Mo$_1$ - H$_2$ | 0.836 | 0.849 | 1.719 | 1.712 |
|                               | H$_1$ - H$_2$ | -$^{b}$ | -$^{b}$ | 1.980 | 1.948 |
| [8b] (ω = 1)                  | Mo$_2$ - H$_3$ | 0.837 | 0.850 | 1.722 | 1.715 |
|                               | Mo$_2$ - H$_4$ | 0.847 | 0.856 | 1.710 | 1.704 |
|                               | H$_3$ - H$_4$ | -$^{b}$ | -$^{b}$ | 1.984 | 1.949 |

$^{a}$ The computed bond order was < 0.1.
Table S6.4. Net Hirshfeld charges in the thermodynamically most-stable Mo₄S₄ configurations with (multiple) H₂ molecule(s) dissociatively adsorbed on Mo, computed with (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S6.1.

(a) DFT/B3LYP/def2-TZVPP

| Structure | Net Hirshfeld charges | Spin-multiplicity (ω) |
|-----------|-----------------------|-----------------------|
|           | [1b] | [3b] | [8b] | 5 | 3 | 1 |
| Mo₄S₄     | 0.000 | 0.328 | 0.606 |
| H₁H₂      | -    | -0.328 | -0.303 |
| H₃H₄      | -    | -    | -0.303 |

(b) DFT/PBE0/def2-TZVPP

| Structure | Net Hirshfeld charges | Spin-multiplicity (ω) |
|-----------|-----------------------|-----------------------|
|           | [1b] | [3b] | [8b] | 5 | 3 | 1 |
| Mo₄S₄     | 0.000 | 0.312 | 0.575 |
| H₁H₂      | -    | -0.312 | -0.287 |
| H₃H₄      | -    | -    | -0.287 |
S7. Ethene Adsorption on Mo$_2$S$_4$

**Figure S7.1.** DFT/B3LYP/def2-TZVP-optimized geometries of Mo$_2$S$_4$ clusters with one ([11a]) or two ([12a]) ethene molecules adsorbed on Mo. The optimized geometry of bare Mo$_2$S$_4$ cluster with gas-phase ethene [1a] is also shown for comparison. The reported spin-multiplicities (ω) correspond to the thermodynamically most stable configurations (Tables S7.1 and S7.2). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; H: pink; C: gray.
Table S7.1. Enthalpies (ΔH) and free energies (ΔG) of Mo₂S₄ clusters with (multiple) ethene molecule(s) adsorbed on Mo, computed at (a) T = 473 K and pC₂H₄ = 50 mbar, and (b) T = 173 K and pC₂H₄ = 1 bar, with DFT/B3LYP/def2-TZVPP. The corresponding structures are shown in Figure S7.1.

(a) T = 473 K and pC₂H₄ = 50 mbar

| Spin-multiplicity (ω) | ΔH₄₇₃K /kJ·mol⁻¹ | ΔG₄₇₃K /kJ·mol⁻¹ |
|-----------------------|------------------|------------------|
|                       | 1     | 3    | 5    | 1     | 3    | 5    |
| [1a]                  | 0.0ᵃ  | -32.2| -10.4| 0.0   | -35.1| -24.0|
| [11a]                 | -213.6| -185.3| -113.0| -107.5| -89.0| -24.8|
| [12a]                 | -356.8| -311.0| -184.0| -148.6| -113.8| 3.3  |

(b) T = 173 K and pC₂H₄ = 1 bar

| Spin-multiplicity (ω) | ΔH¹₇₃K /kJ·mol⁻¹ | ΔG¹₇₃K /kJ·mol⁻¹ |
|-----------------------|------------------|------------------|
|                       | 1     | 3    | 5    | 1     | 3    | 5    |
| [1a]                  | 0.0ᵃ  | -32.0| -11.0| 0.0ᵃ  | -33.2| -15.6|
| [11a]                 | -216.0| -188.3| -116.9| -184.7| -160.2| -91.2|
| [12a]                 | -362.3| -317.5| -191.7| -300.7| -259.3| -136.4|

ᵃ The enthalpy and free energy of [1a] with spin-multiplicity, ω = 1 (i.e., no unpaired electrons) was used as the standard and was set to zero.
Table S7.2. Enthalpies (ΔH) and free energies (ΔG) of Mo$_2$S$_4$ clusters with (multiple) ethene molecule(s) adsorbed on Mo, computed at (a) $T = 473$ K and $p_{C_2H_4} = 50$ mbar, and (b) $T = 173$ K and $p_{C_2H_4} = 1$ bar, with DFT/PBE0/def2-TZVPP. The corresponding structures are shown in Figure S7.1.

(a) $T = 473$ K and $p_{C_2H_4} = 50$ mbar

| Spin-multiplicity ($\omega$) | $\Delta H^{473K}$/kJ·mol$^{-1}$ | $\Delta G^{473K}$/kJ·mol$^{-1}$ |
|-----------------------------|---------------------------------|---------------------------------|
|                             | 1                               | 3                               | 5                               |
| [1a]                        | 0.0$^a$                         | -39.9                           | -27.6                           |
| [11a]                       | -236.6                          | -212.8                          | -143.5                          |
| [12a]                       | -397.9                          | -353.1                          | -223.3                          |

(b) $T = 173$ K and $p_{C_2H_4} = 1$ bar

| Spin-multiplicity ($\omega$) | $\Delta H^{173K}$/kJ·mol$^{-1}$ | $\Delta G^{173K}$/kJ·mol$^{-1}$ |
|-----------------------------|---------------------------------|---------------------------------|
|                             | 1                               | 3                               | 5                               |
| [1a]                        | 0.0$^a$                         | -39.7                           | -28.4                           |
| [11a]                       | -238.8                          | -215.7                          | -147.5                          |
| [12a]                       | -403.2                          | -359.4                          | -231.0                          |

$^a$ The enthalpy and free energy of [1a] with spin-multiplicity, $\omega = 1$ (i.e., no unpaired electrons) was used as the standard and was set to zero.
Table S7.3. Mayer bond orders and bond lengths of relevant bonds in the thermodynamically most-stable Mo$_2$S$_4$ configurations with (multiple) ethene molecule(s) adsorbed on Mo computed with (i) DFT/B3LYP/def2-TZVPP, and (ii) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S7.1.

| Structure (spin-multiplicity) | Bond | Mayer bond order | Bond length /Å |
|------------------------------|------|------------------|----------------|
|                              |      | B3LYP | PBE0 | B3LYP | PBE0 |
| [1a] ($\omega = 3$)          | C$_1$ - C$_2$ | 1.910 | 1.946 | 1.325 | 1.323 |
| [11a] ($\omega = 1$)         | Mo$_1$ - C$_1$$(^{1})$ | 0.683 | 0.707 | 2.203 | 2.174 |
|                              | Mo$_1$ - C$_2$$(^{1})$ | 0.683 | 0.707 | 2.202 | 2.174 |
|                              | C$_{1}$(^{1})$ - C$_2$$(^{1})$ | 1.063 | 1.075 | 1.420 | 1.420 |
| [12a] ($\omega = 1$)         | Mo$_2$ - C$_1$$(^{2})$ | 0.604 | 0.644 | 2.238 | 2.200 |
|                              | Mo$_2$ - C$_2$$(^{2})$ | 0.510 | 0.543 | 2.314 | 2.271 |
|                              | C$_{1}$(^{2})$ - C$_2$$(^{2})$ | 1.171 | 1.176 | 1.398 | 1.400 |
Table S7.4. Net Hirshfeld charges in the thermodynamically most-stable Mo$_2$S$_4$ configurations with (multiple) ethene molecule(s) adsorbed on Mo, computed with (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S7.1.

(a) DFT/B3LYP/def2-TZVPP

| Structure | Net Hirshfeld charges | [1a] | [11a] | [12a] |
|-----------|------------------------|------|------|------|
|            | Spin-multiplicity (ω)  | 3    | 1    | 1    |
| Mo$_2$S$_4$|                        | 0.000| 0.095| 0.011|
| C$_2$H$_4^{(1)}$|                    | -    | -0.095| -0.005|
| C$_2$H$_4^{(2)}$|                        | -    | -0.006|      |

(b) DFT/PBE0/def2-TZVPP

| Structure | Net Hirshfeld charges | [1a] | [11a] | [12a] |
|-----------|------------------------|------|------|------|
|            | Spin-multiplicity (ω)  | 3    | 1    | 1    |
| Mo$_2$S$_4$|                        | 0.000| 0.098| 0.018|
| C$_2$H$_4^{(1)}$|                    | -    | -0.098| -0.009|
| C$_2$H$_4^{(2)}$|                        | -    | -    | -0.010|
S8. Ethene Adsorption on Mo₄S₄

Figure S8.1. DFT/B3LYP/def2-TZVP-optimized geometries of Mo₄S₄ clusters with one ([11b]), two ([12b]), three ([13b]), or four ([14b]) ethene molecule(s) adsorbed on Mo. The optimized geometry of bare Mo₄S₄ cluster with gas-phase ethene ([1b]) is also shown for comparison. The reported spin-multiplicities (ω) correspond to the thermodynamically most-stable configurations (Tables S8.1 and S8.2). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; H: pink; C: gray.
Table S8.1. Enthalpies (ΔH) and free energies (ΔG) of Mo₄S₄ clusters with (multiple) ethene molecule(s) adsorbed on Mo, computed with DFT/B3LYP/def2-TZVPP at (a) T = 473 K and pC₂H₄ = 50 mbar, and (b) T = 173 K and pC₂H₄ = 1 bar. The corresponding structures are shown in Figure S8.1.

(a) T = 473 K and pC₂H₄ = 50 mbar

| Spin-multiplicity (ω) | ΔH₁⁴⁷³K /kJ·mol⁻¹ | ΔG₁⁴⁷³K /kJ·mol⁻¹ |
|-----------------------|---------------------|---------------------|
| [1b]                  | 0.0° 11.7 6.6 43.4 |
| [11b]                 | -154.8 -185.4 -145.4 -87.5 |
| [12b]                 | -325.4 -316.8 -278.2 -218.1 |
| [13b]                 | -451.9 -450.1 -395.8 -372.5 |
| [14b]                 | -567.1 -496.1 -531.5 -466.4 |

(b) T = 173 K and pC₂H₄ = 1 bar

| Spin-multiplicity (ω) | ΔH₁⁷³K /kJ·mol⁻¹ | ΔG₁⁷³K /kJ·mol⁻¹ |
|-----------------------|---------------------|---------------------|
| [1b]                  | 0.0° 10.4 5.1 41.8 |
| [11b]                 | -158.6 -189.6 -150.3 -91.4 |
| [12b]                 | -332.6 -324.3 -286.5 -226.6 |
| [13b]                 | -462.5 -460.5 -406.9 -384.0 |
| [14b]                 | -580.3 -510.1 -545.5 -481.8 |

°The enthalpy and free energy of [1b] with spin-multiplicity, ω = 1 (i.e., no unpaired electrons) was used as the standard and was set to zero.
Table S8.2. Enthalpies (ΔH) and free energies (ΔG) of Mo₄S₄ clusters with (multiple) ethene molecule(s) adsorbed on Mo, computed with DFT/PBE0/def2-TZVPP at (a) T = 473 K and pC₂H₄ = 50 mbar, and (b) T = 173 K and pC₂H₄ = 1 bar. The corresponding structures are shown in Figure S8.1.

(a) T = 473 K and pC₂H₄ = 50 mbar

| Spin-multiplicity (ω) | ΔH⁴₇₃K /kJ·mol⁻¹ | ΔG⁴₇₃K /kJ·mol⁻¹ |
|------------------------|-------------------|-------------------|
|                        | 1                 | 3                 | 5                 | 7                 | 1                 | 3                 | 5                 | 7                 |
| [1b]                   | 0.0ₐ              | 5.0               | -5.9              | 25.6              | 0.0               | -7.2              | -23.5             | 4.3               |
| [11b]                  | -184.0            | -225.6            | -181.6            | -130.9            | -85.4             | -125.9            | -98.5             | -48.9             |
| [12b]                  | -381.4            | -376.7            | -343.1            | -282.1            | -181.9            | -184.4            | -157.5            | -101.3            |
| [13b]                  | -533.9            | -531.6            | -482.7            | -464.8            | -232.7            | -235.3            | -192.9            | -179.5            |
| [14b]                  | -673.7            | -601.1            | -641.4            | -579.1            | -267.3            | -203.3            | -247.8            | -193.0            |

(b) T = 173 K and pC₂H₄ = 1 bar

| Spin-multiplicity (ω) | ΔH¹⁷₃K /kJ·mol⁻¹ | ΔG¹⁷₃K /kJ·mol⁻¹ |
|------------------------|-------------------|-------------------|
|                        | 1                 | 3                 | 5                 | 7                 | 1                 | 3                 | 5                 | 7                 |
| [1b]                   | 0.0ₐ              | 4.0               | -7.6              | 23.8              | 0.0ₐ              | 0.2               | -12.9             | 17.2              |
| [11b]                  | -187.7            | -227.4            | -186.5            | -135.5            | -158.4            | -198.7            | -162.0            | -107.3            |
| [12b]                  | -388.6            | -384.1            | -351.2            | -290.6            | -329.2            | -327.2            | -296.3            | -228.5            |
| [13b]                  | -544.2            | -541.8            | -493.7            | -476.2            | -454.7            | -454.1            | -407.9            | -378.8            |
| [14b]                  | -686.4            | -614.8            | -655.2            | -594.0            | -565.9            | -496.8            | -538.7            | -462.3            |

ₐThe enthalpy and free energy of [1b] with spin-multiplicity, ω = 1 (i.e., no unpaired electrons) was used as the standard and was set to zero.
Table S8.3. Mayer bond orders and bond lengths of relevant bonds in the thermodynamically most-stable Mo₄S₄ configurations with (multiple) ethene molecule(s) adsorbed on Mo, computed with (i) DFT/B3LYP/def2-TZVPP, and (ii) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S8.1.

| Structure (spin-multiplicity) | Bond | Mayer bond order | Bond length /Å |
|------------------------------|------|------------------|----------------|
|                              |      | **B3LYP** | PBE0 | **B3LYP** | PBE0 |
| [1b] (ω = 5)                 | C₁ - C₂ | 1.910  | 1.946 | 1.325  | 1.323 |
| [11b] (ω = 3)                | Mo₁ - C₁ (1) | 0.611  | 0.643 | 2.216  | 2.188 |
|                              | Mo₁ - C₂ (1) | 0.674  | 0.698 | 2.194  | 2.169 |
|                              | C₁ (1) - C₂ (1) | 1.104  | 1.121 | 1.427  | 1.428 |
| [12b] (ω = 3)                | Mo₁ - C₁ (1) | 0.684  | 0.707 | 2.186  | 2.164 |
|                              | Mo₁ - C₂ (1) | 0.601  | 0.630 | 2.218  | 2.192 |
|                              | C₁ (1) - C₂ (1) | 1.106  | 1.125 | 1.425  | 1.425 |
|                              | Mo₂ - C₁ (2) | 0.600  | 0.630 | 2.219  | 2.192 |
|                              | Mo₂ - C₂ (2) | 0.683  | 0.707 | 2.189  | 2.184 |
|                              | C₁ (2) - C₂ (2) | 1.106  | 1.125 | 1.425  | 1.425 |
| [13b] (ω = 3)                | Mo₁ - C₁ (1) | 0.640  | 0.662 | 2.207  | 2.182 |
|                              | Mo₁ - C₂ (1) | 0.637  | 0.660 | 2.209  | 2.184 |
|                              | C₁ (1) - C₂ (1) | 1.120  | 1.144 | 1.422  | 1.421 |
|                              | Mo₂ - C₁ (2) | 0.639  | 0.662 | 2.207  | 2.182 |
|                              | Mo₂ - C₂ (2) | 0.635  | 0.659 | 2.210  | 2.184 |
|                              | C₁ (2) - C₂ (2) | 1.121  | 1.145 | 1.421  | 1.421 |
|                              | Mo₃ - C₁ (3) | 0.594  | 0.620 | 2.238  | 2.208 |
|                              | Mo₃ - C₂ (3) | 0.593  | 0.619 | 2.238  | 2.208 |
|                              | C₁ (3) - C₂ (3) | 1.170  | 1.189 | 1.407  | 1.408 |
| [14b] (ω = 1)                | Mo₁ - C₁ (1) | 0.595  | 0.641 | 2.241  | 2.201 |
|                              | Mo₁ - C₂ (1) | 0.505  | 0.553 | 2.284  | 2.245 |
|                              | C₁ (1) - C₂ (1) | 1.155  | 1.149 | 1.408  | 1.412 |
|                              | Mo₂ - C₁ (2) | 0.670  | 0.704 | 2.181  | 2.153 |
|                              | Mo₂ - C₂ (2) | 0.585  | 0.622 | 2.231  | 2.203 |
|                              | C₁ (2) - C₂ (2) | 1.095  | 1.110 | 1.427  | 1.428 |
|                              | Mo₃ - C₁ (3) | 0.640  | 0.665 | 2.217  | 2.190 |
|                              | Mo₃ - C₂ (3) | 0.635  | 0.657 | 2.203  | 2.179 |
|                              | C₁ (3) - C₂ (3) | 1.120  | 1.143 | 1.416  | 1.415 |
|                              | Mo₄ - C₁ (4) | 0.622  | 0.638 | 2.216  | 2.193 |
|                              | Mo₄ - C₂ (4) | 0.624  | 0.647 | 2.212  | 2.187 |
|                              | C₁ (4) - C₂ (4) | 1.136  | 1.161 | 1.412  | 1.409 |
Table S8.4. Net Hirshfeld charges in the thermodynamically most-stable Mo$_2$S$_4$ configurations with (multiple) ethene molecule(s) adsorbed on Mo, computed with (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The nomenclature of atoms corresponds to the structures shown in Figure S8.1.

(a) DFT/B3LYP/def2-TZVPP

| Structure   | [1b] | [11b] | [12b] | [13b] | [14b] |
|-------------|------|-------|-------|-------|-------|
| Spin-multiplicity (ω) | 5    | 3     | 3     | 3     | 1     |
| Mo$_2$S$_4$  | 0.000| 0.220 | 0.328 | 0.463 | 0.567 |
| C$_2$H$_4$\(^{(1)}\) | -    | -0.220| -0.119| -0.170| -0.120|
| C$_2$H$_4$\(^{(2)}\) | -    | -     | -0.209| -0.169| -0.191|
| C$_2$H$_4$\(^{(3)}\) | -    | -     | -     | -0.124| -0.137|
| C$_2$H$_4$\(^{(4)}\) | -    | -     | -     | -     | -0.119|

(b) DFT/PBE0/def2-TZVPP

| Structure   | [1b] | [11b] | [12b] | [13b] | [14b] |
|-------------|------|-------|-------|-------|-------|
| Spin-multiplicity (ω) | 5    | 3     | 3     | 3     | 1     |
| Mo$_2$S$_4$  | 0.000| 0.224 | 0.328 | 0.461 | 0.566 |
| C$_2$H$_4$\(^{(1)}\) | -    | -0.224| -0.118| -0.169| -0.132|
| C$_2$H$_4$\(^{(2)}\) | -    | -     | -0.210| -0.169| -0.194|
| C$_2$H$_4$\(^{(3)}\) | -    | -     | -     | -0.124| -0.132|
| C$_2$H$_4$\(^{(4)}\) | -    | -     | -     | -     | -0.108|
S9. Competitive Adsorption between Hydrogen and Ethene on Mo₂S₄

Figure S9.1. DFT/B3LYP/def2-TZVP-optimized geometries of Mo₂S₄ clusters with (simultaneously) adsorbed ethene and hydrogen. The reported spin-multiplicities (ω) correspond to the thermodynamically most stable configurations (Table S9.1). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; C: gray; H: pink.
Table S9.1. Enthalpies (ΔH) and free energies (ΔG) of Mo$_2$S$_4$ clusters with (simultaneously) adsorbed ethene and hydrogen, computed at $T = 473$ K, $p_{C_2H_4} = 50$ mbar, and $p_{H_2} = 1$ bar, with (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The corresponding structures are shown in Figure S9.1.

(a) DFT/B3LYP/def2-TZVPP

|     | $\Delta H^{473K}$ /kJ∙mol$^{-1}$ | $\Delta G^{473K}$ /kJ∙mol$^{-1}$ |
|-----|----------------------------------|----------------------------------|
|     | Spin-multiplicity ($\omega$)     | 1      | 3      | 5      | 1      | 3      | 5      |
| [1a] | 0.0$^a$                          | -32.2  | -10.4  |        | 0.0    | -35.1  | -24.0  |
| [3a] | -120.9                           | -81.2  | -7.6   | -61.0  | -37.1  | 31.1   |
| [15a]| -248.3                           | -207.4 | -       | -87.4  | -56.3  | -       |
| [12a]| -356.8                           | -311.0 | -184.0 | -148.6 | -113.8 | 3.3    |

(b) DFT/PBE0/def2-TZVPP

|     | $\Delta H^{473K}$ /kJ∙mol$^{-1}$ | $\Delta G^{473K}$ /kJ∙mol$^{-1}$ |
|-----|----------------------------------|----------------------------------|
|     | Spin-multiplicity ($\omega$)     | 1      | 3      | 5      | 1      | 3      | 5      |
| [1a] | 0.0$^a$                          | -39.9  | -27.6  |        | 0.0    | -42.9  | -42.6  |
| [3a] | -130.7                           | -97.4  | -30.2  | -71.6  | -46.2  | 7.1    |
| [15a]| -279.1                           | -236.0 | -       | -119.2 | -85.7  | -       |
| [12a]| -397.9                           | -353.1 | -223.3 | -188.9 | -155.4 | -36.3  |

$^a$ The enthalpy and free energy of [1a] with spin-multiplicity, $\omega = 1$ (i.e., no unpaired electrons) was used as the standard and was set to zero.

$^b$ The optimized structure with non-imaginary vibrational frequency modes was not achieved.
S10. Competitive Adsorption between Hydrogen and Ethene on Mo₄S₄

Figure S10.1. DFT/B3LYP/def2-TZVP-optimized geometries of Mo₄S₄ clusters with (simultaneously) adsorbed ethene and hydrogen. The reported spin-multiplicities (ω) correspond to the thermodynamically most stable configurations (Table S10.1). Optimized geometries obtained using DFT/PBE0/def2-TZVP were similar. S: yellow; Mo: blue; C: gray; H: pink.
Table S10.1. Enthalpies (ΔH) and free energies (ΔG) of Mo₄S₄ clusters with (simultaneously) adsorbed ethene and hydrogen, computed at T = 473 K, pC₂H₄ = 50 mbar, and pH₂ = 1 bar, with (a) DFT/B3LYP/def2-TZVPP, and (b) DFT/PBE0/def2-TZVPP. The corresponding structures are shown in Figure S10.1.

(a) DFT/B3LYP/def2-TZVPP

| Spin-multiplicity (ω) | ΔH₄⁷₃K /kJ·mol⁻¹ | ΔG₄⁷₃K /kJ·mol⁻¹ |
|-----------------------|------------------|------------------|
| [1b]                  |                  |                  |
| 0.0                   | 11.7             | -4.1             |
| 3                     | 6.6              | -11.0            |
| 5                     | 43.4             | 22.4             |
| [15b]                 |                  |                  |
| -376.2                | -351.7           | -271.3           |
| -375.6                | -75.5            | -61.3            |
| [16b]                 |                  |                  |
| -457.7                | -442.3           | -101.4           |
| -465.0                | -113.5           | -103.7           |
| -381.1                | -45.4            |                  |
| [14b]                 |                  |                  |
| -567.1                | -531.5           | -162.8           |
| -496.1                | -100.2           | -139.4           |
| -646.4                | -83.0            |                  |

(b) DFT/PBE0/def2-TZVPP

| Spin-multiplicity (ω) | ΔH₄⁷₃K /kJ·mol⁻¹ | ΔG₄⁷₃K /kJ·mol⁻¹ |
|-----------------------|------------------|------------------|
| [1b]                  |                  |                  |
| 0.0                   | 5.0              | -7.2             |
| 3                     | -5.9             | -23.5            |
| 5                     | 25.6             | 4.3              |
| [15b]                 |                  |                  |
| -447.3                | -431.2           | -135.3           |
| -450.8                | -348.7           | -150.3           |
| [16b]                 |                  |                  |
| -546.6                | -535.3           | -187.8           |
| -560.0                | -477.1           | -207.1           |
| [14b]                 |                  |                  |
| -673.7                | -641.4           | -267.3           |
| -601.1                | -579.1           | -203.3           |
| -641.4                | -247.8           | -193.0           |

* The enthalpy and free energy of [1b] with spin-multiplicity, ω = 1 (*i.e.*, no unpaired electrons) was used as the standard and was set to zero.
S11. X-ray Absorption Spectroscopy (XAS) Measurements

XAS measurements were performed at the P65 beamline of the German Electron Synchrotron (DESY) in Hamburg, Germany. The storage ring operated at 6 GeV energy and 100 mA current. A water-cooled Si311 double crystal monochromator (DCM) was used for obtaining monochromatic X-rays. Two Rh-coated plane mirrors were installed in front of the DCM to reject higher harmonics. The DCM was calibrated to Mo K-edge energy by measuring a reference Mo foil and setting the first major inflection point to 20 000 eV. The beam spot-size was 200 μm (vertical) × 1.6 mm (horizontal) on the sample and the energy resolution of incident X-rays is estimated to be ~2 eV (ΔE/E ~1.0 × 10⁻⁴) at Mo K-edge energy.

The carbonyl containing catalyst precursors were placed in a quartz capillary (WJM Glas, 1 mm outer diameter, 20 μm thickness) supported between two quartz wool plugs. The capillary was heated from below with a hot-air gas-blower (Oxford FMB). Gas flow rates were controlled using electronic mass flow controllers (Bronkhorst) and the pressure was monitored using a pressure gauge (Omega). All experiments were performed at ambient pressure. The catalyst precursors were sulfided in situ in a flow of 10 mL·min⁻¹ H₂S (10 vol.% in H₂) at 673 K for 2 h to form the sulfided Mo₂S₄/NaY catalyst. This sample was then treated in 10 mL·min⁻¹ H₂ at 673 K for 2 h to form the reduced Mo₄S₄/NaY catalyst. After performing sulfidation/reduction, the catalysts were exposed to ethene hydrogenation reaction conditions (T ≈ 473 K, p_H₂ ≈ 950 mbar, p_C₂H₄ ≈ 50 mbar) for at least 2 h. The capillary was then cooled down to room temperature and placed on the sample stage for XAS measurements, whilst maintaining the ethene/H₂ gas flow. The data were monitored for any signs of X-ray beam damage. Several successive scans were averaged to reduce signal-to-noise ratio and improve the data quality.

The XAS spectra were measured between 19 800 and 21 000 eV in total fluorescence yield (TFY) mode using a passivated implanted planar silicon (PIPS) detector. For extended X-ray absorption fine structure (EXAFS) analyses, spectra were background subtracted, normalized, k³-weighted, and Fourier-transformed (FT) between k = 3 and k = 12 Å⁻¹. The EXAFS fitting was performed in k-space between 3 and 12 Å⁻¹ simultaneously on the k¹-, k²-, and k³-weighted data. The fitting was performed using Artemis software package. E₀ was set such that energy shift (ΔE₀) obtained during the fit was less than 1 eV. A reference Mo foil was first fitted to Mo bcc structure and the Mo–Mo coordination number was set to 8 and 6 (theoretical values based on the bcc structure) for the first and second coordination shells, respectively, to obtain the amplitude reduction factor (S₀²) which was then used in the subsequent fits.
Figure S11.1. $k^3$-weighted EXAFS (a, c) and Fourier-transformed EXAFS (b, d) of Mo$_2$S$_4$/NaY (blue) and Mo$_4$S$_4$/NaY (red), after 2 h time-on-stream under ethene hydrogenation reaction conditions ($T \approx 473$ K, $p_{C_2H_4} \approx 50$ mbar, and $p_{H_2} \approx 960$ mbar). Experimental data are shown as closed symbols and the fitted data are shown as solid black lines.
Table S11.1. EXAFS fitting parameters: coordination numbers (CN), interatomic distances ($d$), and Debye-Waller factors ($\sigma^2$), for Mo-S and Mo-Mo paths, in (a) Mo$_2$S$_4$/NaY, and (b) Mo$_4$S$_4$/NaY, after 2 h time-on-stream under ethene hydrogenation conditions ($T \approx 473$ K, $p_{C_2H_4} \approx 50$ mbar, and $p_{H_2} \approx 960$ mbar). The (previously reported) CN$_{Mo-Mo}$, CN$_{Mo-S}$, $d_{Mo-Mo}$, and $d_{Mo-S}$ for fresh Mo$_x$S$_y$/NaY catalysts are also shown for comparison.

(a) Mo$_2$S$_4$/NaY

| Path   | CN   | $d$/Å | $\sigma^2 \times 1000$ /Å$^2$ |
|--------|------|-------|-----------------------------|
| Fresh catalyst |     |       |                             |
| Mo–S   | 3.9$^a$ | 2.42$^a$ |                             |
| Mo–Mo  | 1.3$^a$ | 2.77$^a$ |                             |
| After reaction |     |       |                             |
| Mo–S   | 3.1 ± 0.8 | 2.39 ± 0.02 | 8.1 ± 2.4                  |
| Mo–Mo  | 1.3 ± 2.4 | 2.77 ± 0.04 | 13.7 ± 13                   |

(b) Mo$_4$S$_4$/NaY

| Path   | CN   | $d$/Å | $\sigma^2 \times 1000$ /Å$^2$ |
|--------|------|-------|-----------------------------|
| Fresh catalyst |     |       |                             |
| Mo–S   | 2.6$^a$ | 2.47$^a$ |                             |
| Mo–Mo  | 3.3$^a$ | 2.66$^a$ |                             |
| After reaction |     |       |                             |
| Mo–S   | 2.9 ± 2.3 | 2.44 ± 0.09 | 7.2 ± 9.1                  |
| Mo–Mo  | 3.0 ± 3.2 | 2.66 ± 0.06 | 7.2 ± 5.3                   |

$^a$ Data from Weindl et al.$^4$
Figure S12.1. Standard enthalpy diagram of Langmuir–Hinshelwood (LH) type reaction pathway for ethene hydrogenation on Mo$_2$S$_4$ cluster with spin-multiplicity ω = 1, showing the reaction between an adsorbed H$_2$ and an adsorbed ethene, computed with (i) DFT/B3LYP/def2-TZVP, and (ii) DFT/PBE0/def2-TZVP. Values shown in the figure are in kJ·mol$^{-1}$. Values shown in parentheses are the imaginary frequencies of the corresponding transition state structures. Displayed structures were optimized with B3LYP. Optimized geometries obtained using PBE0 were similar. S: yellow; Mo: blue; H: pink; C: gray.
Figure S12.2. Standard enthalpy diagram of Eley–Rideal (ER) type reaction pathway for ethene hydrogenation on Mo$_2$S$_4$ cluster with spin-multiplicity $\omega = 1$, showing the reaction between an adsorbed H$_2$ and a gas-phase ethene, computed with (i) DFT/B3LYP/def2-TZVP, and (ii) DFT/PBE0/def2-TZVP. Values shown in the figure are in kJ·mol$^{-1}$. Values shown in parentheses are the imaginary frequency of the corresponding transition state structures. Displayed structures were optimized with B3LYP. Optimized geometries obtained using PBE0 were similar. S: yellow; Mo: blue; H: pink; C: gray.
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