

Supporting information for

Hydrodesulfurization of methanethiol over Co-promoted MoS<sub>2</sub> model catalysts

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## S1 The ReactorSTM setup

The high-pressure scanning tunneling microscope (STM) setup (the ReactorSTM) [10] comprises the STM instrument, the reactor volume, and the sample holder (see Figure S1). When the sample holder presses against the STM body, it forms a reactor volume of 50 microliters. This reactor is sealed vacuum-tight from the rest of the assembly and the ultra-high vacuum (UHV) components using two chemically inert elastomer O-rings. The sample, which has a hat-shaped design, is electrically isolated from the holder and features a rear-mounted filament for radiative heating. K-type thermocouples welded onto the sample allow for direct temperature measurement. Bellows are utilized to press the sample, the Kalrez O-ring, and the STM together, effectively establishing a closed reactor cell. Within the reactor, capillary-sized channels facilitate gas flow, connecting to a dedicated gas cabinet and a quadrupole mass spectrometer for control and monitoring. The setup can operate at pressures of up to 6 bar. A single piezotube serves for both coarse Z-approach and raster scanning motion, facilitating the establishment of the tunneling junction. The STM tip is housed in a gold-coated stainless steel holder (slider), actuated by an SmCo magnet against gold-coated tracks (guiding rails) to ensure optimal stick-slip behavior and chemical inertness. For image acquisition, the setup employs video-rate scanning electronics [11], enabling up to 1 image per second at a resolution of 256x256 square pixels. Typically, operando images are obtained at a resolution of 512x512 square pixels with a time resolution of 10-20 seconds.

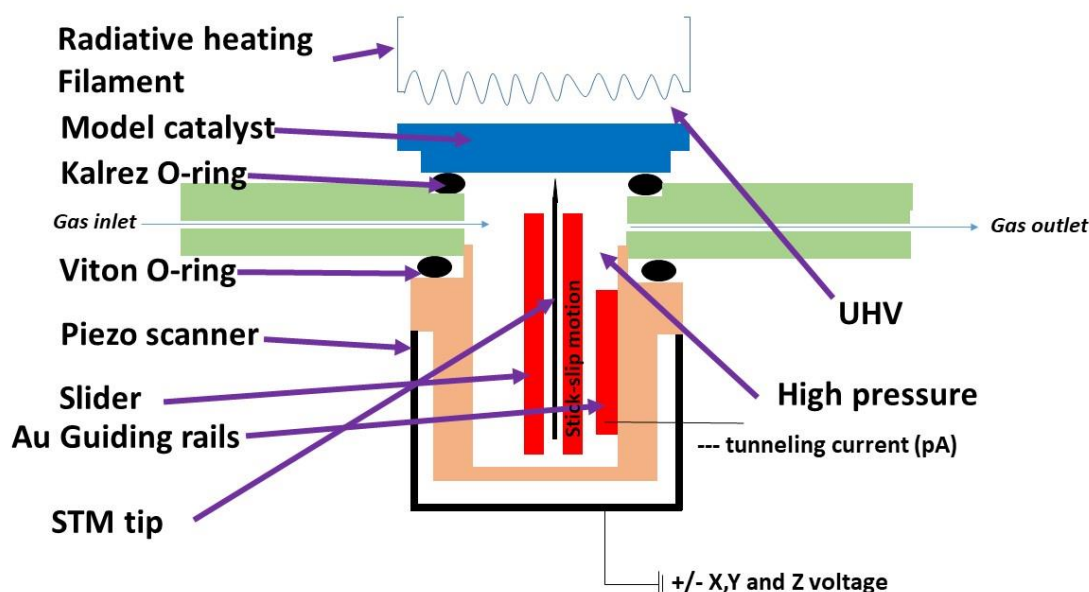


Figure S1: **ReactorSTM setup**. Schematic of the high-pressure ReactorSTM, based on [12], chapter 2, Figure 3.

## S2 Semi-infinite CoMoS slab model used for DFT calculations

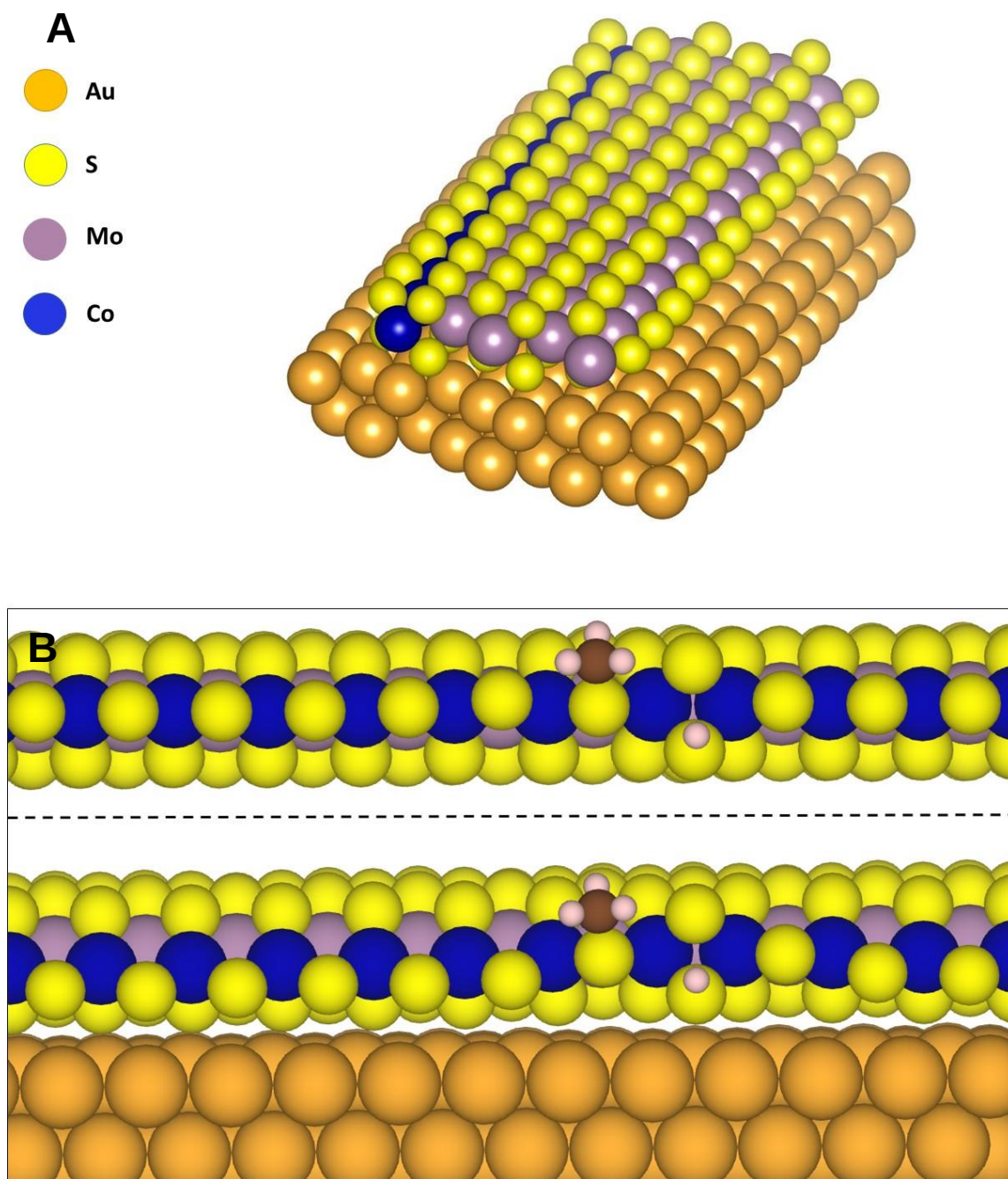
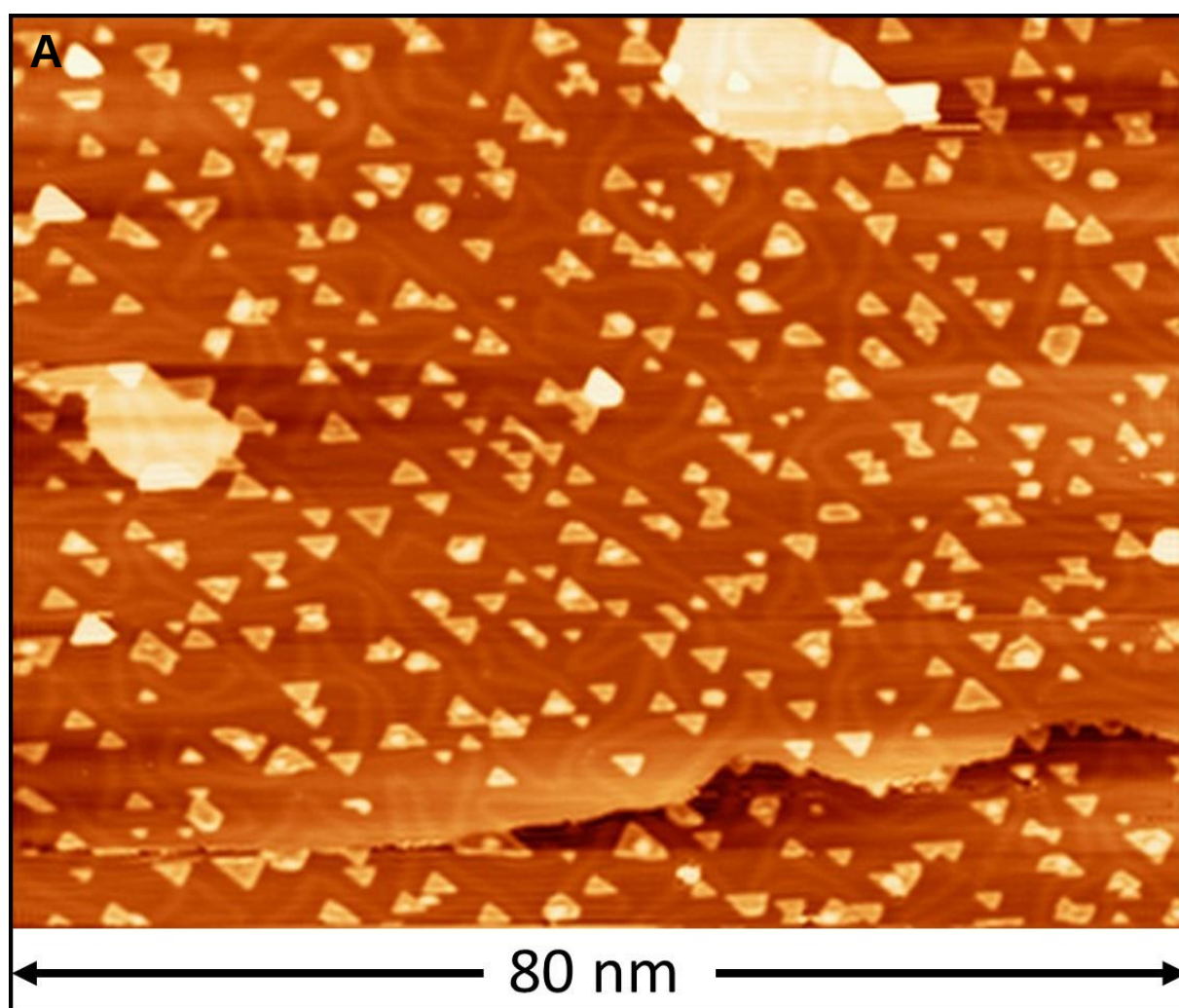


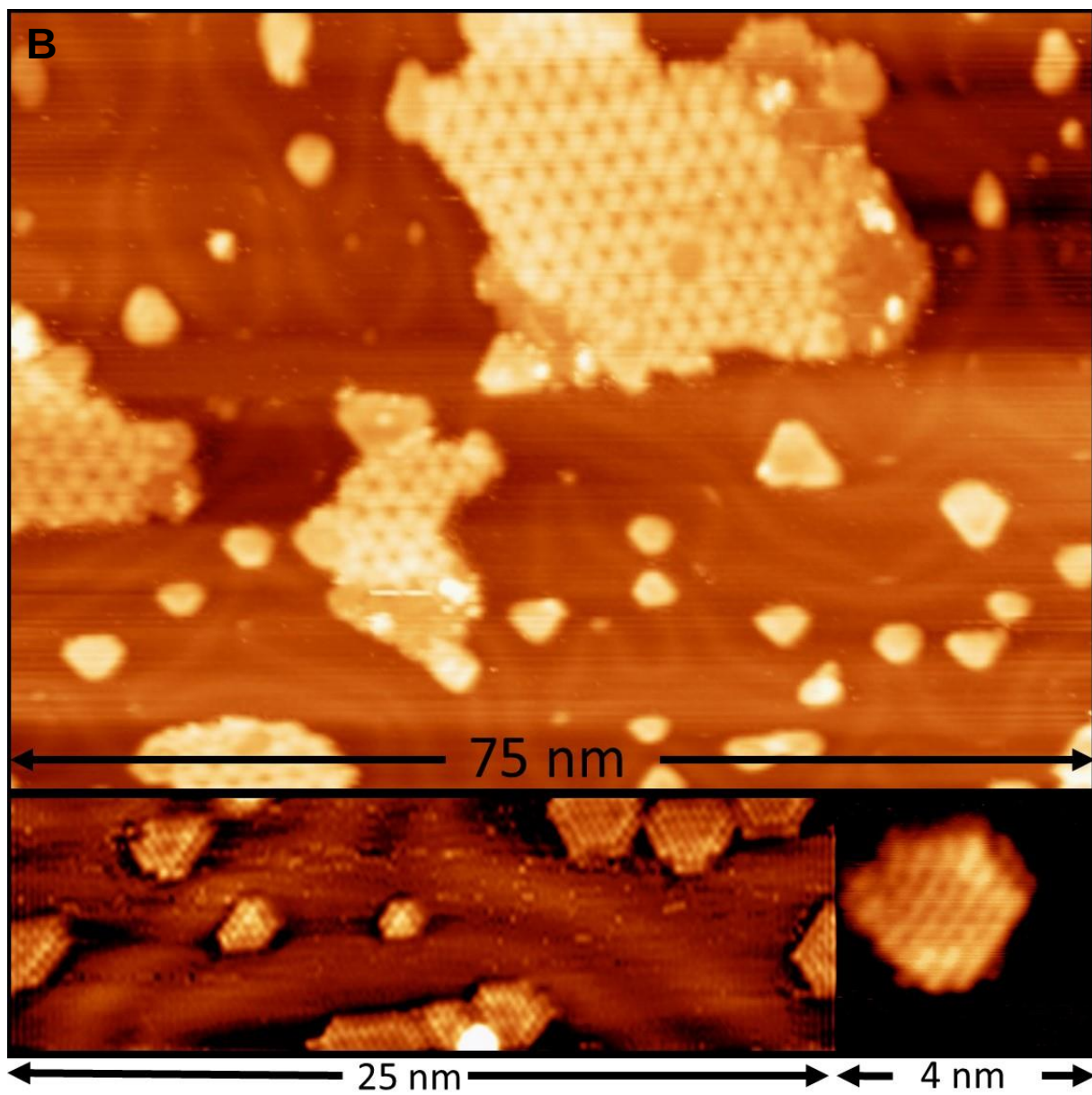
Figure S2: **Atomic modelling with DFT.** A) Ball model of the unit cell of the 1D CoMoS stripe model used for DFT calculations. Two gold layers are also considered for simulating STM images. B) Model of structure (4) from Figure 8c relaxed without and with the gold slab. Blue atoms are those of Co, white-grey atoms are of H, lavender atoms are those of Mo, yellow are those of S, and orange are of Au, and brown atoms are those of C.

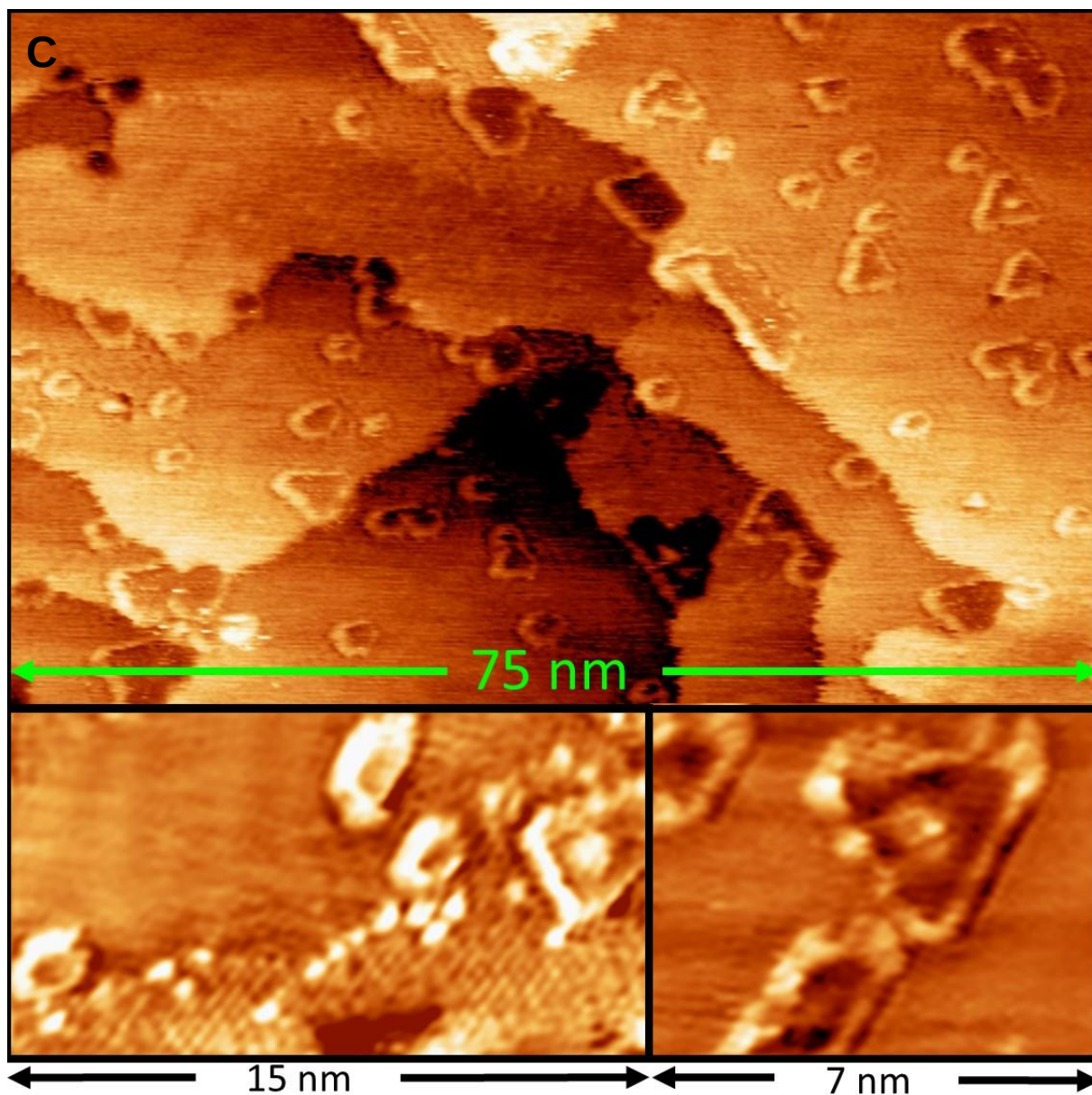
For the 1D gold slab, a stripe consisting of two layers, each comprised of 9 rows of 13 Au atoms (totaling 234 Au atoms), was created. Based on the experimental crystal structure of Au at room temperature (RT), it was observed that a row of 12 Au atoms measured 37.492 angstroms long. This measurement closely approximated the main axis length of 37.527 angstroms used in all calculations for the stripe model, accounting for 99.91% of it. A slight compression was noted, likely attributed to the PBE Density Functional, which tends to provide lattice constants approximately 1% longer than experimental values. Additionally, thermal expansion at 510 K could also contribute to the minor deviation.

For simulating STM images, the CoMoS structure (including C and H) was positioned on the Au stripe, and a geometry optimization was conducted with all 234 Au atoms immobilized in space. A sufficiently large unit cell was employed to ensure there was more than 10 angstroms of vacuum surrounding the stripes. For example, the effect of the Au slab is shown for structure (4) of Figure 8c following  $\text{CH}_3\text{SH}$  adsorption (see Fig. S2B). The edge sulfur atoms tend to sink closer to the Au support along with slight tilting of the  $\text{CH}_3$  group.

S3 Co-promoted MoS<sub>2</sub> and pristine MoS<sub>2</sub> slabs supported on Au(111)







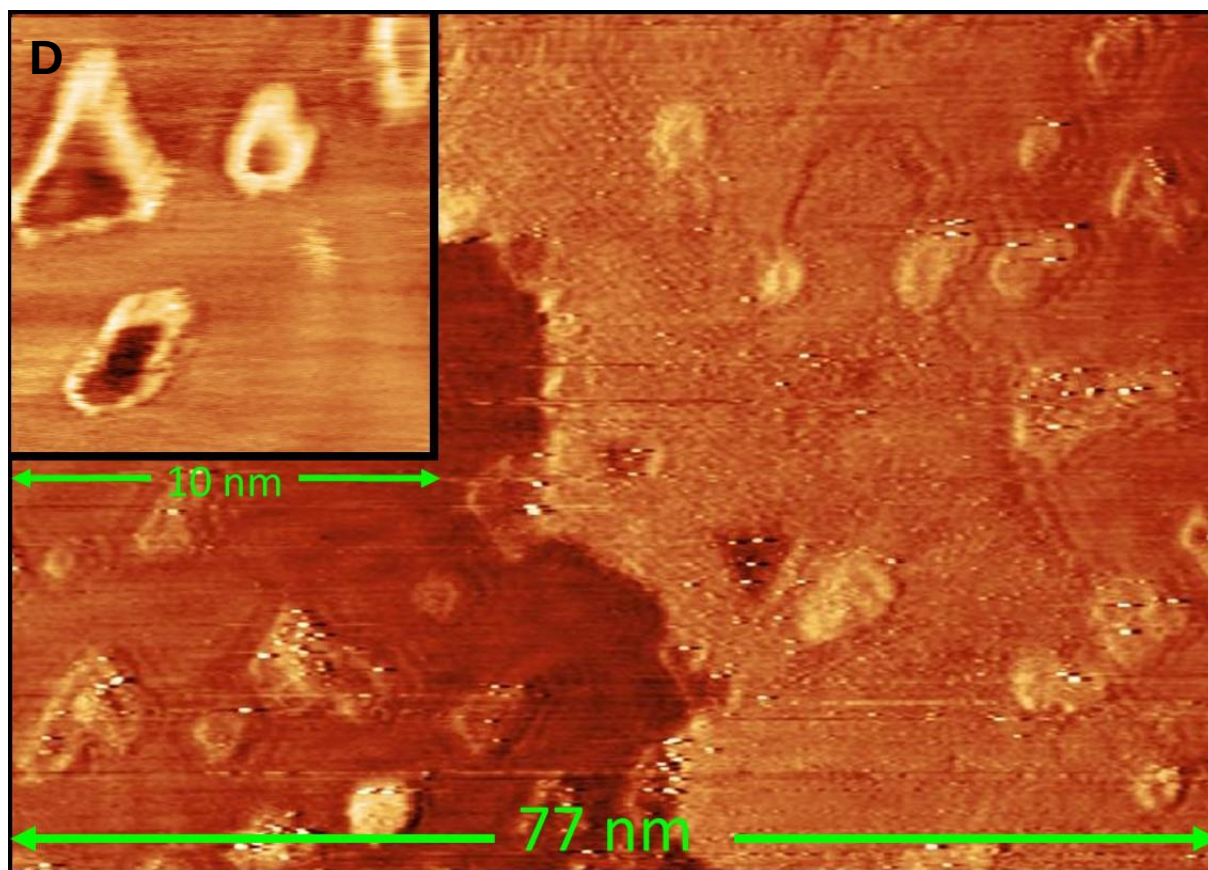


Figure S3: **UHV and high-pressure STM imaging.** A) STM image of single-layer MoS<sub>2</sub> slabs on Au(111). STM image acquired with sample voltage = -1.5 V and tunneling current = 100 pA. B) Large-scale STM image of single-layer Co-promoted MoS<sub>2</sub> slabs on Au(111) measured at room temperature in UHV prior to reduction in H<sub>2</sub>. The insets show atom-resolved STM images of CoMoS slabs that are not interacting with CoS<sub>2</sub> sheets. STM images are acquired with a sample voltage of -1.0 V and 200 pA tunneling current. (For the insets, sample voltage = -0.3 V, tunneling current = 100 pA). C) Large-scale *in situ* STM image of single-layer Co-promoted MoS<sub>2</sub> slabs on Au(111) measured at 510 K under 1 bar H<sub>2</sub> after 180 minutes of reduction; the insets show zoomed in images of truncated hexagonal CoMoS slabs. STM images are acquired with a sample voltage of -1.0 V and 400 pA tunneling current. (For the insets, sample voltage = -0.3 V, tunneling current = 400 pA). D) Large-scale *in situ* STM image of single-layer Co-promoted MoS<sub>2</sub> slabs on Au(111) measured at 510 K under 1 bar H<sub>2</sub> after 90 minutes of reduction; the insets show a zoomed in image of truncated hexagonal CoMoS slabs. STM images are acquired with a sample voltage of -1.0 V and 400 pA tunneling current. (For the insets, sample voltage = -0.4 V, tunneling current = 350 pA)

The STM images in Figures S3A and S3B are of the model catalyst before the H<sub>2</sub> reduction. The in situ STM images in Figures 2a and S3C are of the same model catalyst after 180 minutes of H<sub>2</sub> reduction. Between the two images, clearly the truncated-hexagonal slab shapes are retained. An additional image with a zoomed-in inset acquired under 1 bar H<sub>2</sub> at 510 K after 90 minutes of reduction is provided as S3D.

Imaging the catalyst up to ~90 minutes of reaching the operating temperature is not possible due to large thermal drifts from the heating up of the sample, seals, and STM components which leads to tip crashes. Furthermore, it takes an additional several tens of minutes for all the gas-solid and gas-tip interaction processes to reach steady state and better quality STM images can be acquired. Any potential slab shape change is expected to occur within this window, as the shape-change kinetics are fast [9].

We image the model catalyst up to 180 minutes to check for any previously unknown slow kinetic processes at work. We did not find evidence of any.

#### S4 DFT modelling of the 100% S Co edge

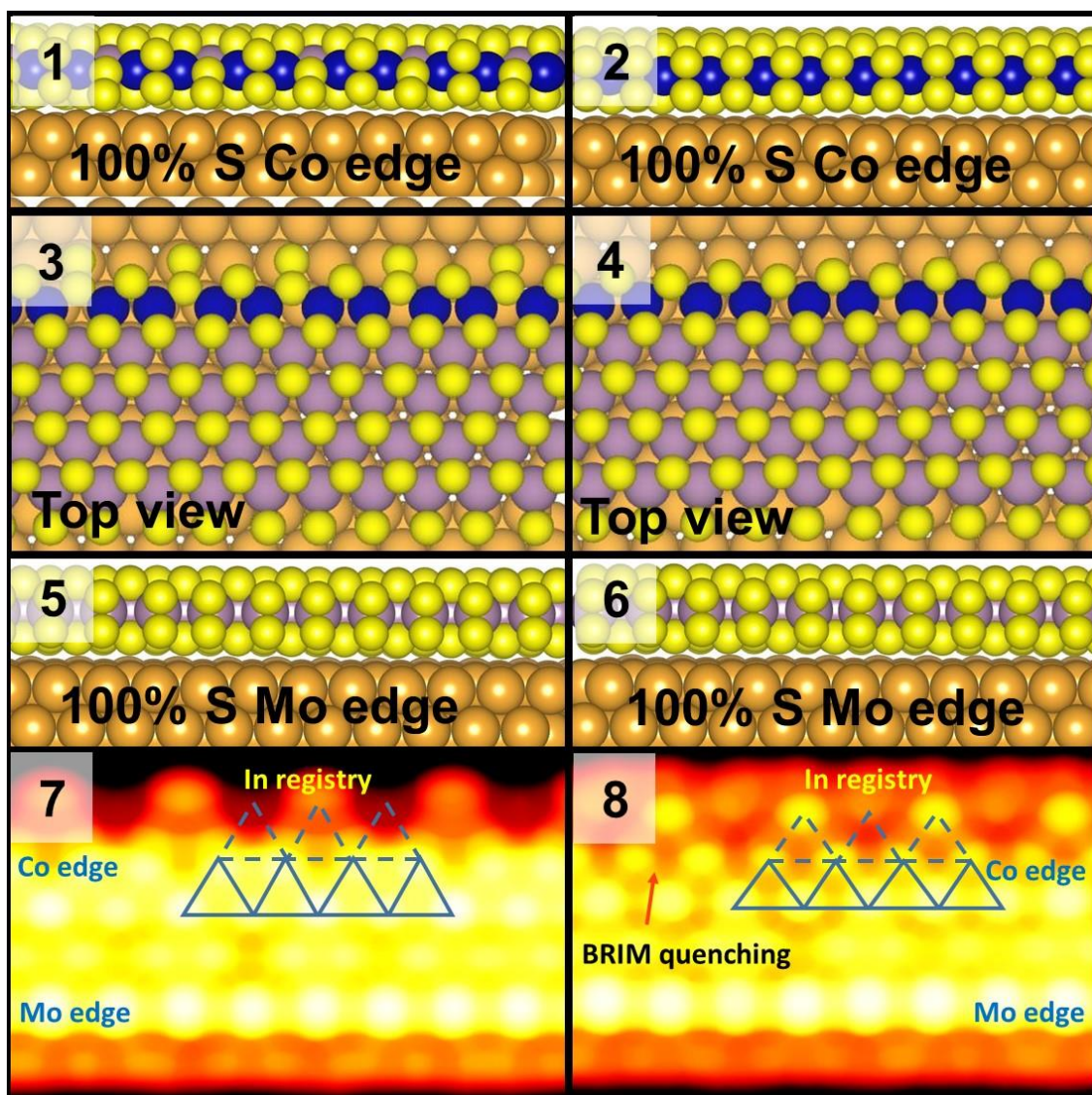
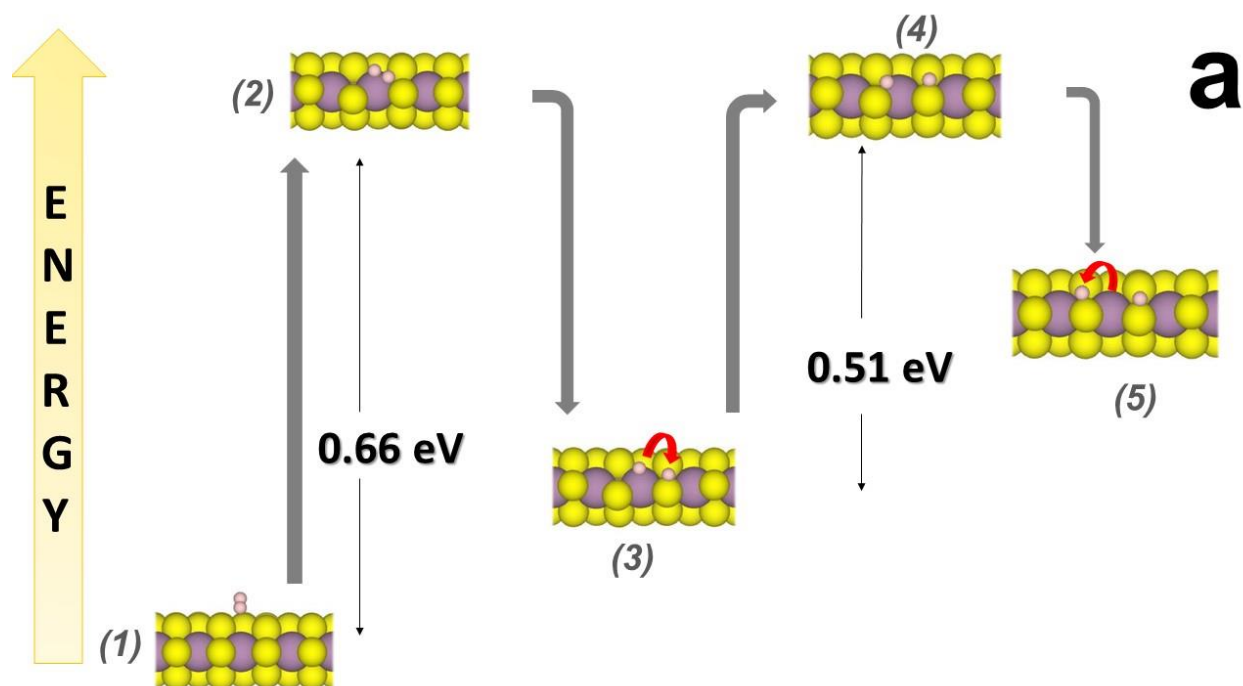


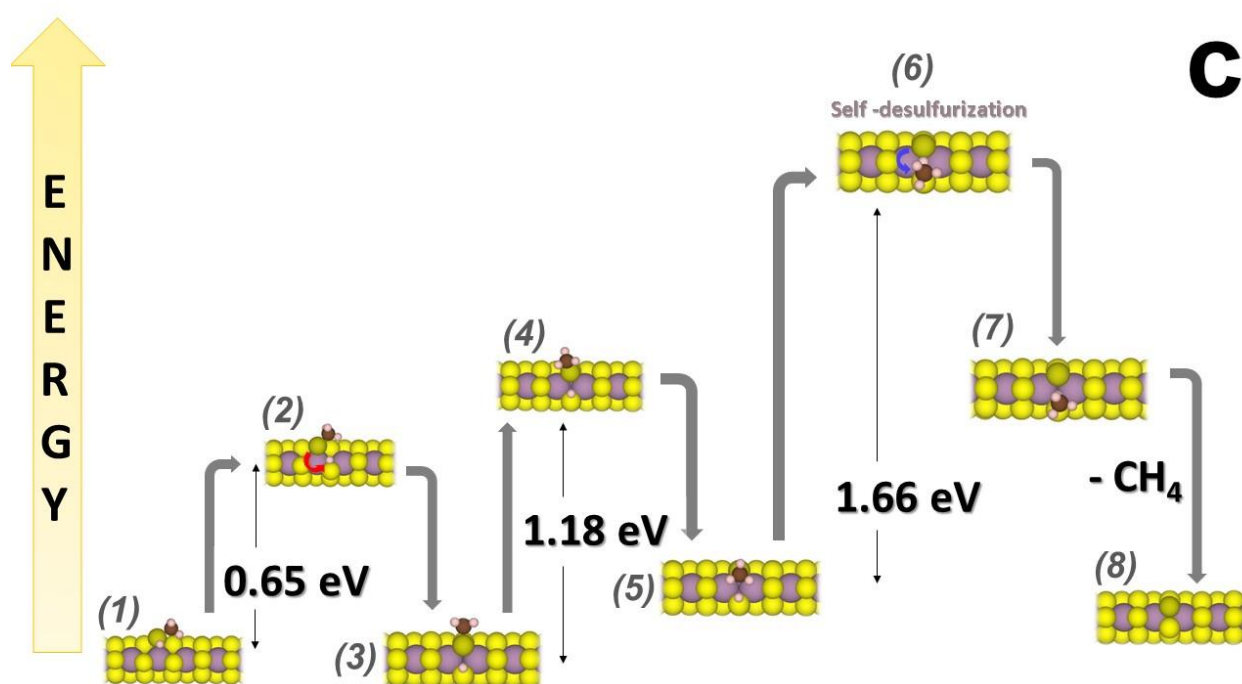
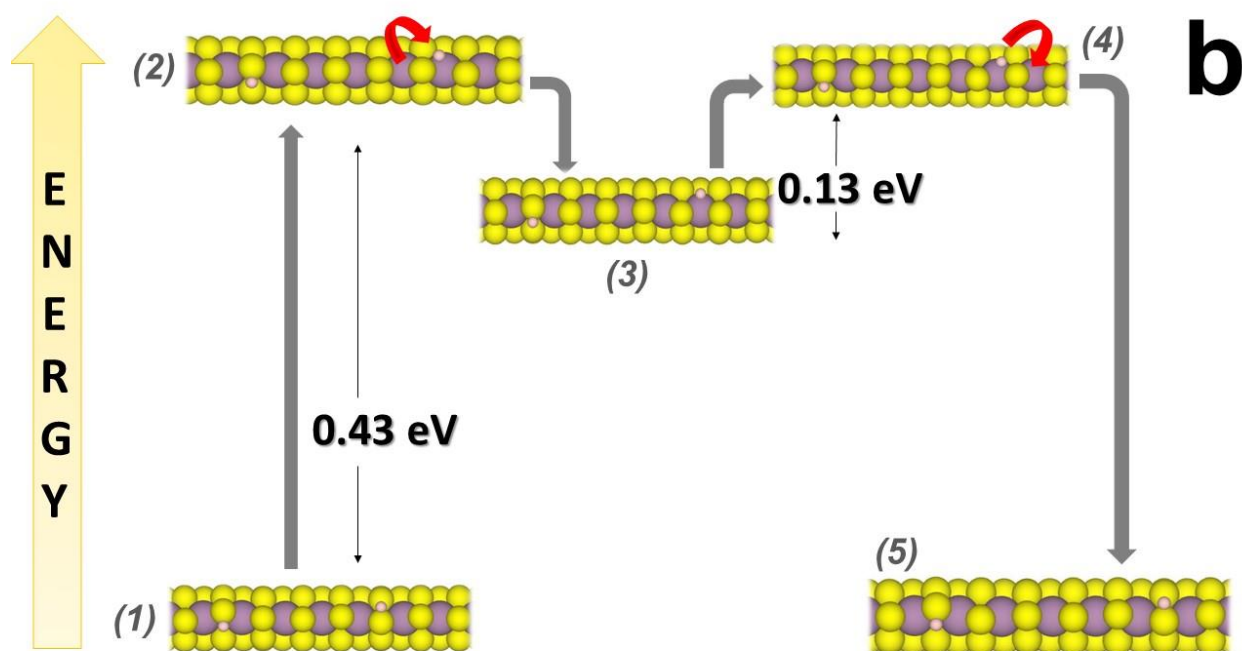
Figure S4: **Atomic models of CoMoS edges.** DFT-relaxed atomic models of the Co- and Mo-terminated edges with 100% S coverage. In the atomic models, blue atoms are those of Co, lavender atoms are those of Mo, yellow are those of S, brown are of C and orange are of Au. (1) 100% S Co edge where alternating double S units are linked to Au, (2) 100% S Co edge without direct linkages to Au, (3, 4) Top view of the semi-infinite CoMoS slab, (5, 6) 100% S Mo-terminated edge, (7) Simulated STM image of the model in (3), (8) Simulated STM image of the model in (4).

For the Co-substituted edge, however, Grønberg et al.<sup>si9</sup> did not simulate the STM image for their atomic model of a 100% S saturated Co edge to verify their assignment. Their work also demonstrates that the Co-substituted S edge brim sites are more susceptible to quenching than those of the Mo edge due to interactions with the Au substrate. It is possible that a 100% S Co edge also interacts with the Au substrate, which could potentially lead to brim quenching

contrary to what is observed in the experimental STM images. To investigate this possibility, we make use of DFT calculations to model a 1D periodic CoMoS stripe with a two-atom thick Au support as described in the theoretical methods section. The Mo and Co edges are taken as 100% S saturated. The stripe is fully relaxed on the gold and the corresponding STM image is calculated. For a 100% S Co edge, two kinds of structures are possible. First, where the double S atoms are both attached to the Co atoms, a structure that is considered in the work of Grønberg;<sup>17</sup> and second, where at least some of the double S units act as linkages to the Au substrate. The second possibility has not been considered in any prior work. For the sake of simplicity, we model a situation where every other edge sulfur dimer is bound to the gold. We have modeled both possibilities and the result is shown in Figure S4. The panels 1, 3 and 5 show the top view and side views of the relaxed atomic model of a CoMoS stripe that has every other S dimer linked to gold (see panel 1, Figure S4). The Figure S4 panels 2, 4 and 6 show the relaxed model where all the double S units on the Co edge are exclusively linked to Co atoms. The respective simulated STM images are shown in panels 7 and 8. In both panels 7 and 8 of Figure S4, the resulting registry protrusions are found to be in registry with the basal plane, but have alternating bright and dark protrusions on the edge, which is more severe in panel 7. For the case of double S linkages to Au, the disulfide sites linked to Au are imaged darker in the simulated STM image. For the case of all the double S units linked to Co only, a slight corrugation of the edge sulfur atoms forms (panel 2) which results in the less severe corrugations in the simulated STM image in panel 8. It can also be clearly seen that BRIM quenching occurs in both cases. We note that none of these features match with the experimentally obtained STM images of the Co edge, see Figure 1b. A possible solution to this discrepancy lies in consideration of additional residual H atoms on the double S atoms which can be the result of using H<sub>2</sub>S as a sulfiding agent instead of elemental sulfur, as H<sub>2</sub>S dissociation can result in the formation of an active H atom on the edge. Even slightly hydrogenated Co edges have been observed to have considerably higher BRIM contrasts as the added active H also weakens the edge S interaction with Au.<sup>si9</sup> Yet another possibility is that the corrugation of the Co edge is time-averaged at room temperature.

S5 HDS reaction pathways for the Mo edge





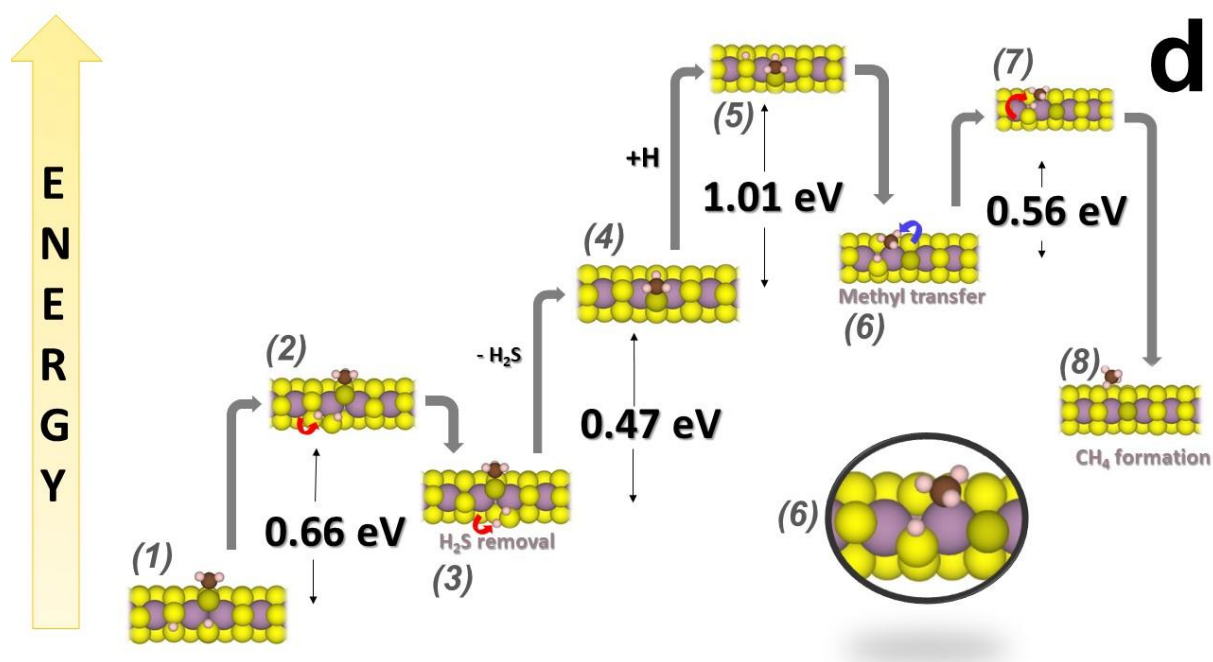


Figure S5: **HDS reaction pathways on Mo edge.** a) DFT-modeled reaction pathway for the  $\text{H}_2$  dissociation on a 50% S Mo edge; b) DFT-modeled reaction pathway for atomic H hopping on a 50% S Mo edge. The red arrows indicate the movement of H atoms; c) DFT-modeled reaction pathway for self-desulfurization of chemisorbed  $\text{CH}_3\text{SH}$  on a 50% S Mo edge; d) DFT-modeled reaction pathway for hydrodesulfurization of chemisorbed  $\text{CH}_3\text{SH}$  on a 50% S Mo edge. The inset shows an enlarged version of state 6 after 'methyl transfer'. In all the structures, grey atoms are those of H, brown are of C, lavender atoms are those of Mo, yellow are those of S and dark yellow are those of S from adsorbed  $\text{CH}_3\text{SH}$ . The red and blue arrows indicate the hopping of  $\text{H}^\cdot$  and  $\text{CH}_3^\cdot$ , respectively.

## S6 Transition state search algorithms

The CP2K program was modified for more effective transition state searches. The algorithms are based on the Rational Function Optimization method proposed by Banerjee [1]: Let, at any given point,  $\mathbf{H}$  be the hessian for a system with  $N$  atoms with eigenvectors  $\mathbf{v}_i$  and eigenvalues  $\epsilon_i$  ( $i=1, \dots, 3N$ ) and  $\mathbf{g}$  the gradient vector. The step vector  $\Delta\mathbf{x}$  is given by:

$$\Delta x_i = -\frac{g_i}{s_i}$$

$$s_i = \frac{\text{sign}}{2} \left( |\epsilon_i| + \sqrt{\epsilon_i^2 + 4g_i^2} \right)$$

where  $\Delta x_i$  and  $g_i$  are the components of  $\Delta\mathbf{x}$  and  $\mathbf{g}$  in the hessian eigenvector basis and *sign* equals -1 for the eigenvector with lowest eigenvalue (or, more general, for the eigenvector that is supposed to correspond to the reaction pathway) and +1 otherwise. This takes care of proper scaling of the step in all directions. The hessian does not necessarily have to be exact and can be updated during the transition state search by using information gained by the change in gradient at each step, either by the Murtagh-Sargent update [2]:

$$\mathbf{H}^{\text{new}} = \mathbf{H}^{\text{old}} + \Delta\mathbf{H}^{\text{MS}} = \mathbf{H}^{\text{old}} + \frac{(\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x}) \cdot (\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x})^{\text{T}}}{(\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x})^{\text{T}} \cdot \Delta\mathbf{x}}$$

where  $\Delta\mathbf{x}$  is the step taken and  $\Delta\mathbf{g}$  is the difference in gradients after and before the step; or by the Powell update formula [3].

$$\mathbf{H}^{\text{new}} = \mathbf{H}^{\text{old}} + \Delta\mathbf{H}^{\text{Powell}} = \mathbf{H}^{\text{old}} + \frac{(\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x}) \cdot \Delta\mathbf{x}^{\text{T}} + \Delta\mathbf{x} \cdot (\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x})^{\text{T}}}{\Delta\mathbf{x}^{\text{T}} \cdot \Delta\mathbf{x}} - \left[ (\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x})^{\text{T}} \cdot \Delta\mathbf{x} \right] \cdot \frac{\Delta\mathbf{x} \cdot \Delta\mathbf{x}^{\text{T}}}{(\Delta\mathbf{x}^{\text{T}} \cdot \Delta\mathbf{x})^2}$$

While usually superior to the Murtagh-Sargent update, the Powell expression can suffer from numerical instability when the step size becomes small. Bofill has proposed a combination of the two approaches using a switching parameter  $\phi$  [4].

$$\mathbf{H}^{\text{new}} = \mathbf{H}^{\text{old}} + \phi\Delta\mathbf{H}^{\text{MS}} + (1 - \phi)\Delta\mathbf{H}^{\text{Powell}}$$

$$\phi = \frac{\left[ (\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x})^{\text{T}} \cdot \Delta\mathbf{x} \right]^2}{\left[ (\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x})^{\text{T}} \cdot (\Delta\mathbf{g} - \mathbf{H}^{\text{old}} \cdot \Delta\mathbf{x}) \right] \cdot (\Delta\mathbf{x}^{\text{T}} \cdot \Delta\mathbf{x})}$$

In a study of 25 test cases Baker and Chan found that the Bofill update method worked not necessarily much better than using Powell updating, but never worse [5]. Both are superior to using Murtagh-Sargent updating and Bofill updating is therefore the best general choice.

In CP2K the standard dimer method [6] [7] is implemented for transition state searches. The method essentially involves three points: the current approximation  $\mathbf{x}$  to the TS and two points displaced from  $\mathbf{x}$  by a small vector  $\mathbf{d}$  (in  $3N$  dimensional space) and its opposite (the pair of points  $\mathbf{x}+\mathbf{d}$  and  $\mathbf{x}-\mathbf{d}$  are called a dimer, hence the name of the method). The vector  $\mathbf{d}$  is rotated such that the sum of energies of the dimer points is minimal. This implies that the

vector  $\mathbf{d}$  is the direction of lowest curvature around  $\mathbf{x}$ . The component of the gradient vector parallel to  $\mathbf{d}$  is inverted and the modified gradient is followed.

Since in this standard implementation there is no Hessian, the step length is determined by the Conjugate Gradient method using two-point interpolation for the optimal step along the (negative of) the modified gradient. There is no scaling of the step in different directions as in the Hessian-based method.

However, it is possible to integrate the dimer method into a Hessian-based search.

### *The modified dimer method*

Let  $\mathbf{d}$  be the normalized dimer vector at any step in the transition state search. We introduce matrix  $\mathbf{P} = \mathbf{d} \cdot \mathbf{d}^T$ ; this is a projection matrix since

$$\mathbf{P} \cdot \mathbf{d} = \mathbf{d} \cdot (\mathbf{d}^T \cdot \mathbf{d}) = \mathbf{d} \cdot 1 = \mathbf{d}$$

While for every vector  $\mathbf{v}$  orthogonal to  $\mathbf{d}$  we have:

$$\mathbf{P} \cdot \mathbf{v} = \mathbf{d} \cdot (\mathbf{d}^T \cdot \mathbf{v}) = \mathbf{d} \cdot 0 = \mathbf{0}$$

We use the projection matrix to modify the current Hessian (updated by means of the Bofill method) in the following manner:

$$\mathbf{H}^{\text{mod}} = (\mathbf{I} - \mathbf{P}) \cdot \mathbf{H} \cdot (\mathbf{I} - \mathbf{P}) + \epsilon \mathbf{P}$$

In which  $\epsilon$  is the curvature along the dimer vector and  $\mathbf{I}$  is the identity matrix. It is easy to verify that:

- $\mathbf{H}^{\text{mod}}$  is a symmetric matrix (as the Hessian should be), so its eigenvalues are real numbers.
- The dimer vector is an eigenvector and all other eigenvectors are therefore perpendicular to it.
- The eigenvalue of the dimer vector is the curvature along the direction of the dimer vector. If the other eigenvalues are reasonable approximations of the curvature along the corresponding eigenvectors, then the step size in all directions can be properly scaled by the RFO approach.

This then yields the following algorithm, which is started from a first guess at the TS structure.

1. Initiate the approximate Hessian. This can be done by setting it to the identity matrix but it was decided to use the method of Lindh [8] (in the slightly simplified version implemented in CP2K) to create a model Hessian at negligible expenditure of computer time.
2. From an initial guess (either given or made up from random numbers) rotate the dimer vector to the direction of smallest curvature.

3. Modify the Hessian to make the dimer vector a true eigenvector.
4. Determine the step with the RFO method. Move to the new point in 3N dimensional space.
5. Check for convergence. If yes, then the work is done. (However, also check that the curvature along the dimer vector is negative, otherwise this is not a TS.) If no, proceed with step 6.
6. Update the Hessian using the Bofill method.
7. Optimize the direction of the dimer vector.
8. Go to 3 (the modification step).

This procedure was programmed into CP2K. In a test over the 25 test cases from Baker and Chan [5], the modified method uses much fewer function evaluations (i.e. full SCF calculations), mostly because it is generally more effective but additionally because we avoid having to do two function evaluations for every Conjugate Gradient step.

### ***The use of a partial Hessian***

As stated before, the use of the Rational Function Optimization method with Bofill updating does not necessarily require starting from a fully exact hessian. A hessian may be used that is initialized as the identity matrix, followed by substitution of the computed elements over the hessian of only a subset of the atoms in the system. Such a subset can be selected in several ways; a very effective one is to do a limited calculation with the (modified) dimer method and establish the usually quite limited subset of atoms that are responsible for ~80% of the movement corresponding to the dimer vector. Using this procedure, the very costly calculation of the full hessian is avoided, while the approximate hessian obtained can be very effective in converging to the transition state.

This procedure was also implemented in the CP2K program.

S7 DFT-modelled reaction pathway for tetrahydrothiophene (THT) on a Co-substituted S edge

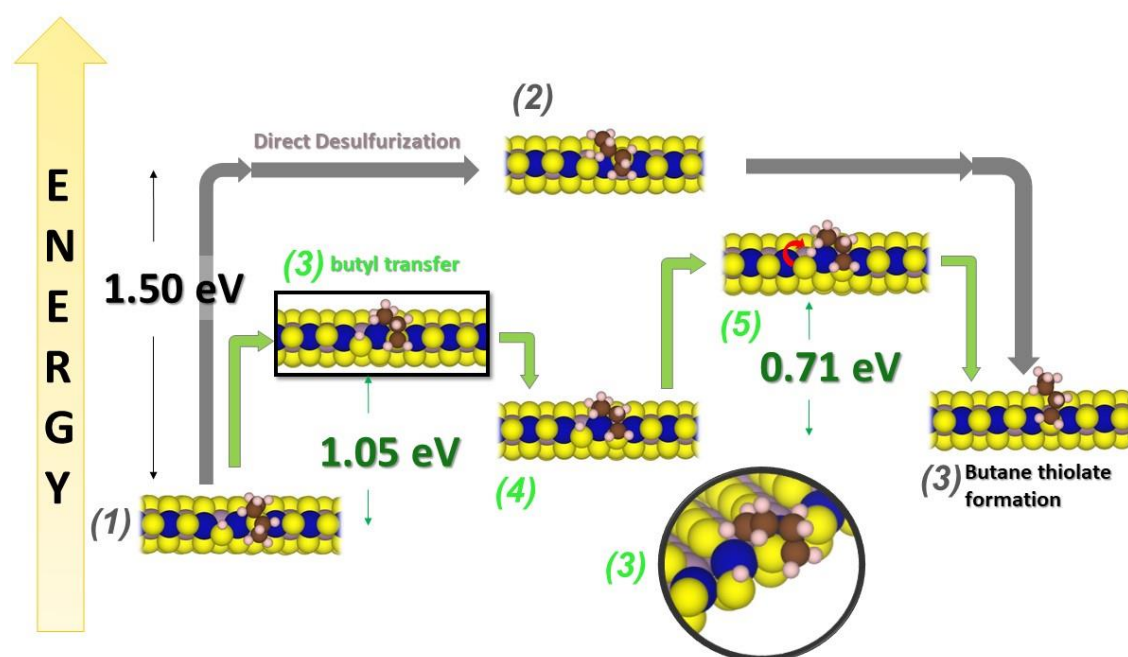


Figure S6: **HDS reaction of cyclic sulfides**. DFT-modeled reaction pathway for hydrodesulfurization of chemisorbed tetrahydrothiophene on a 50% S Co edge. The inset shows enlarged version of state 3 after 'butyl transfer'. In all of the structures, grey atoms are those of H, blue are of Co, brown are of C, lavender atoms are those of Mo, yellow are those of S.

## S8 Tables of DFT energies of the reaction models

Supplementary Table 1. Table of energies for H<sub>2</sub> dissociation on the S edge for the pathway in Figure 7a in the main text.

| Structure  | DFT Energy (eV) | dG (eV) |
|------------|-----------------|---------|
| <b>1</b>   | -6252.266       |         |
| <b>1→2</b> | -6253.435       | -0.062  |
| <b>2→3</b> | -6253.419       | 0.434   |
| <b>2→4</b> | -6253.420       | 0.401   |
| <b>4→5</b> | -6253.409       | 0.290   |
| <b>4→6</b> | -6253.435       | -0.412  |
| <b>6→7</b> | -6253.430       | 0.144   |
| <b>6→8</b> | -6253.449       | -0.378  |

Supplementary Table 2. Table of energies for H hopping on the S edge for the pathway in Figure 7b in the main text.

| Structure  | DFT Energy (eV) | dG (eV) |
|------------|-----------------|---------|
| <b>1</b>   | -6253.451       |         |
| <b>1→2</b> | -6253.427       | 0.665   |
| <b>1→3</b> | -6253.428       | 0.615   |
| <b>3→4</b> | -6253.426       | 0.054   |
| <b>3→5</b> | -6253.451       | -0.604  |

Supplementary Table 3. Table of energies self-desulfurization of CH<sub>3</sub>SH on the S edge for the pathway in Figure 8a in the main text.

| Structure                         | DFT Energy (eV) | dG (eV) |
|-----------------------------------|-----------------|---------|
| <b>1</b>                          | -6252.266       |         |
| <b>1→2</b>                        | -6270.548       | -0.310  |
| <b>2→3</b>                        | -6270.540       | 0.216   |
| <b>2→4</b>                        | -6270.588       | -1.084  |
| <b>4→5</b>                        | -6270.542       | 1.232   |
| <b>4→6</b>                        | -6270.583       | 0.111   |
| <b>6→7</b>                        | -6270.514       | 1.890   |
| <b>6→CH<sub>4</sub> formation</b> | -6270.542       | 1.122   |

Supplementary Table 4. Table of energies for HDS of CH<sub>3</sub>SH on the S edge for the pathways in Figure 8b in the main text.

| Structure                          | DFT Energy (eV) | dG (eV) |
|------------------------------------|-----------------|---------|
| <b>1</b>                           | -6271.772       |         |
| <b>1→2</b>                         | -6271.733       | 1.078   |
| <b>1→3</b>                         | -6271.748       | 0.658   |
| <b>3→4</b>                         | -6260.343       | 0.447   |
| <b>4→5</b>                         | -6260.339       | 0.087   |
| <b>5→6</b>                         | -6260.261       | 2.140   |
| <b>5→CH<sub>4</sub> formation</b>  |                 | -0.235  |
| <b>H - migration</b>               |                 |         |
| <b>5→11</b>                        | -6260.321       | 0.504   |
| <b>5→12</b>                        | -6260.326       | 0.372   |
| <b>12→13</b>                       | -6260.263       | 1.717   |
| <b>12→CH<sub>4</sub> formation</b> |                 | -0.608  |
| <b>Methyl transfer</b>             |                 |         |
| <b>5→8</b>                         | -6260.302       | 1.008   |
| <b>5→9</b>                         | -6260.314       | 0.696   |
| <b>9→10</b>                        | -6260.287       | 0.732   |
| <b>9→CH<sub>4</sub> formation</b>  |                 | -0.932  |

Supplementary Table 5. Table of energies for HDS of CH<sub>3</sub>SH on the S edge without prior H<sub>2</sub>S removal for the pathway in Figure 8c in the main text.

| Structure                         | DFT Energy (eV) | dG (eV) |
|-----------------------------------|-----------------|---------|
| <b>1</b>                          | -6270.556       |         |
| <b>1→2</b>                        | -6270.564       | 0.867   |
| <b>1→3</b>                        | -6270.543       | 0.652   |
| <b>3→4</b>                        | -6270.568       | 0.558   |
| <b>3→5</b>                        | -6271.747       | -0.120  |
| <b>5→6</b>                        | -6271.707       | 1.086   |
| <b>5→7</b>                        | -6271.715       | 0.864   |
| <b>7→8</b>                        | -6271.684       | 0.838   |
| <b>7→CH<sub>4</sub> formation</b> |                 | -1.010  |

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