

## SUPPLEMENTARY INFORMATION

### **Hydrogenolysis and $\beta$ -elimination mechanisms for C-S bond scission of dibenzothiophene on CoMoS edge sites**

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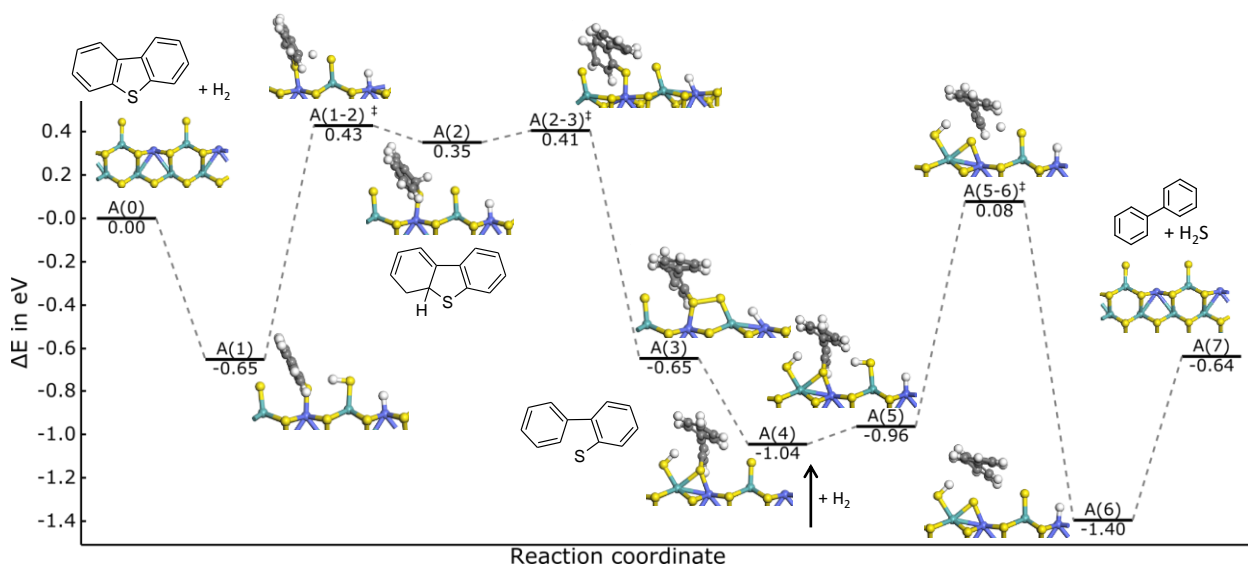
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## SI.1 Hydrogenolysis pathways on the M-edge alternated

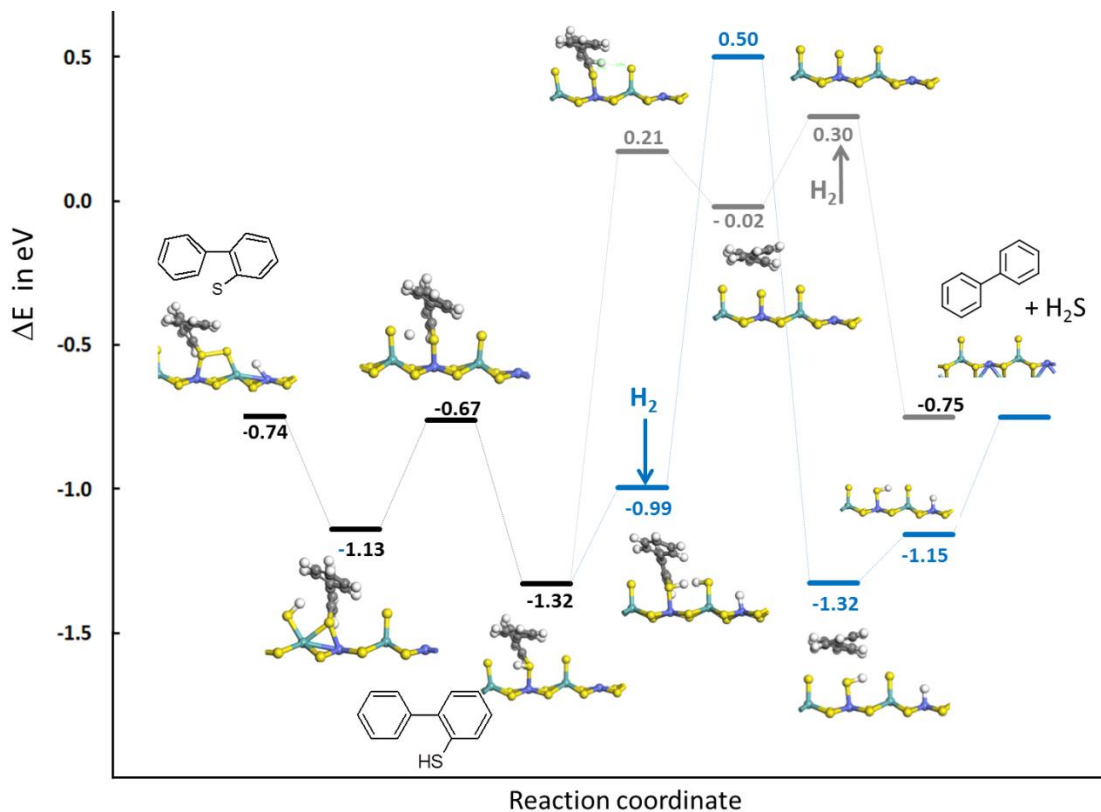
Preliminary statement: all energy profiles reported in this supplementary material, are electronic energies at 0K without ZPE and thermal corrections. This is justified by the fact that impact of thermal corrections on all adsorbed states reported in the main, was observed to remain modest. **Fig. S1** illustrates the electronic energy profile calculated for DBT hydrogenolysis on the M-edge alternated involving the 2-phenyl-thiophenolate intermediate (corresponding to the free energy profile given in the main text). This profile may be useful for a systematic comparison with the other electronic energy profiles reported in the present SI.



**Fig. S1.** Electronic energy profile of the hydrogenolysis pathway of DBT into biphenyl (BP) on the M-edge alternated involving the 2-phenyl-thiophenolate intermediate.

Here, we consider the formation of 2-phenyl-thiophenol which is slightly activated (+0.46 eV) with an exothermic reaction energy of -0.19 eV. The second hydrogenolysis can be performed either from an intramolecular H-transfer from the thiophenol to the  $C_\alpha$  or by involving a second adsorbed  $H_2$  molecule to hydrogenate the  $C_\alpha$  atom. The energy profiles of the two 2-phenyl-thiophenol based pathways are shown in **Fig. S2**. The formation of the thiophenol intermediate from thiolphenolate (after breaking of the S-S bond discussed before) is a weakly activated

process (+0.46). The thiophenol is now stabilized on top of the cobalt site, whereas the thiophenolate was located in a bridging Co-Mo position as explained in the main text.



**Fig. S2.** Electronic energy profiles of the second C-S bond scission leading to biphenyl (BP) and involving the 2-phenyl-thiophenol intermediate on the M-edge alternated: intramolecular H-transfer (gray) and H-transfer from -SH group (blue).

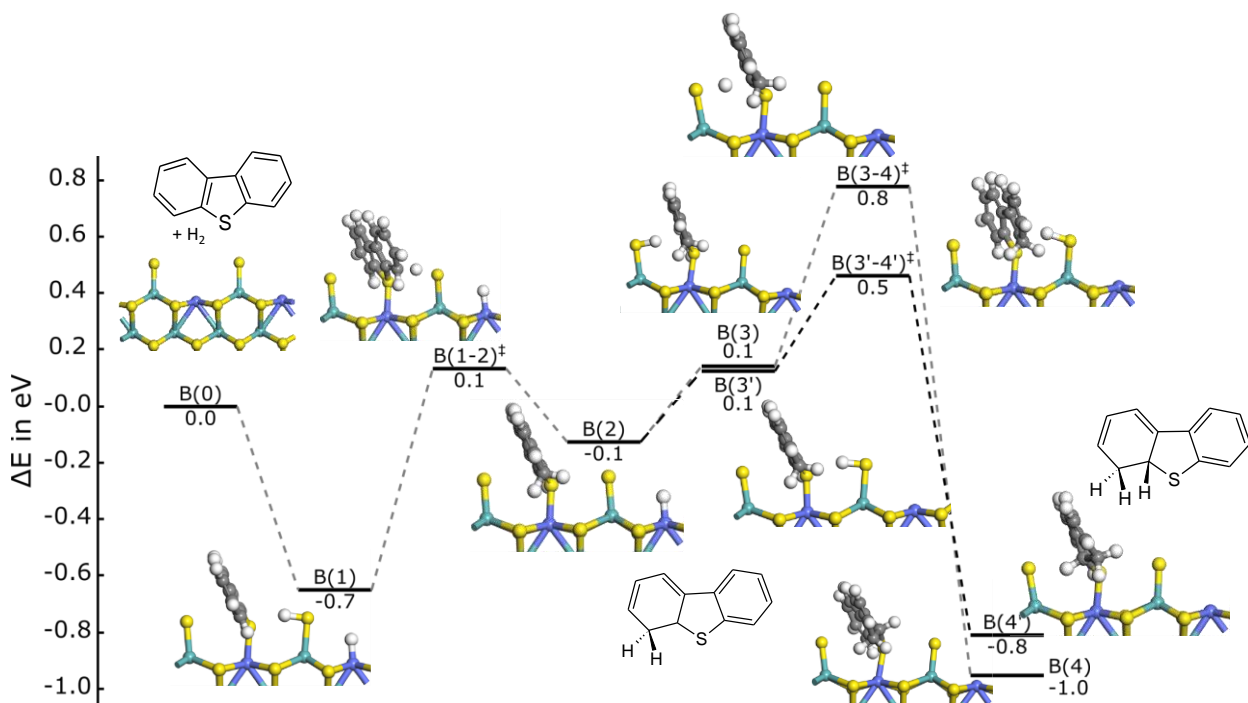
The subsequent intramolecular hydrogen transfer leads to a physisorbed BP on the edge covered by 3 sulfur atoms, which leads to the removal of one S linked to Co with an exothermic process (as already found in previous study [1]).

If one assumes that the second  $C_{\alpha}$  hydrogenation occurs through the addition of a second  $H_2$  molecule, the pathway leads to a physisorbed BP on the edge covered with 2 S atoms and one -SH group (0.00 eV, which is more thermodynamically favorable), but then requires the diffusion of the remaining surface H atoms in order to desorb  $H_2S$ .

These two paths display slightly different effective barriers. The intramolecular pathway with +1.62 eV (including the BP desorption step), is slightly less favorable than the 2-phenylthiophenolate path, while the H transfer from Mo-SH exhibits a higher effective barrier of +1.82 eV, rendering it the least competitive one.

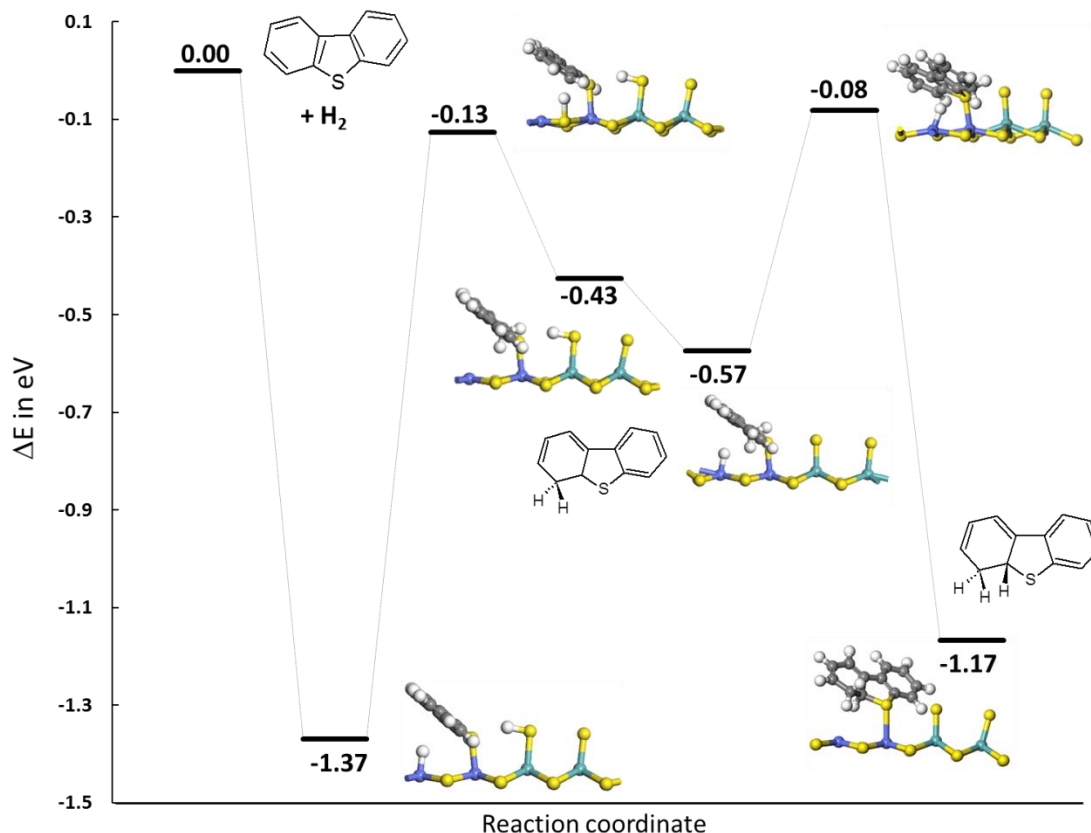
## SI.2 Dihydrogenation mechanisms

### SI.2.1 Reaction on Co-Mo-Co-Mo alternated sites



**Fig. S3.** Electronic energy profile of the C<sub>β</sub> followed by C<sub>α</sub> hydrogenation steps of DBT leading to the β,α-dihydrogenated DHDBT intermediate.

## SI.2.2 Reaction on Co-Co-Mo-Mo paired sites

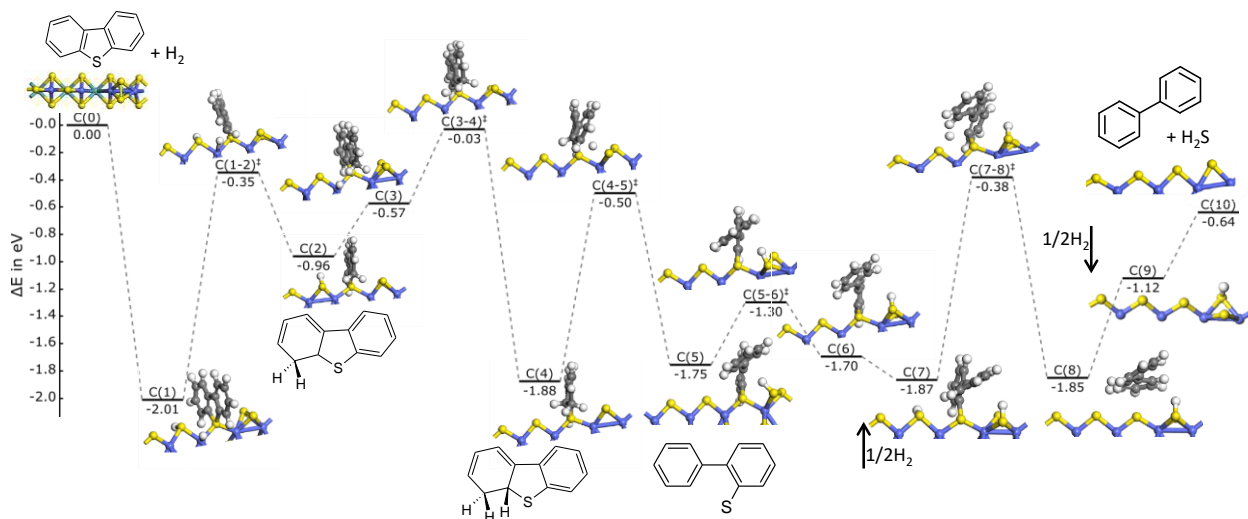


**Fig. S4.** Electronic energy profile for the  $\beta,\alpha$ -dihydrogenation of DBT on the M-edge paired.

For the first hydrogenation (**Fig. S4**), the H atom diffuses from Co to a S atom of the basal plane and connected to one Mo and two Co atoms at a relatively high energy (+1.24 eV) which is then transferred to DBT forming the  $\beta$ -HDBT. The second monohydrogenation originates now directly from the Co-H group to form the  $\beta,\alpha$ -DHDBT. The activation energy to hydrogenate first the  $\beta$  position is higher than on the M-edge alternated (+1.24 eV vs +0.78 eV), as well as the second hydrogenation in the  $\alpha$  position (+0.49 eV vs +0.34 eV).

Nevertheless, the overall activation energy (+1.29 eV) is competitive with the one involved for the direct hydrogenolysis on the M-edge alternated. Moreover, the DHDBT is slightly more stabilized on this paired Co promoted edge (-1.17 eV vs -0.95 eV on the alternated edge).

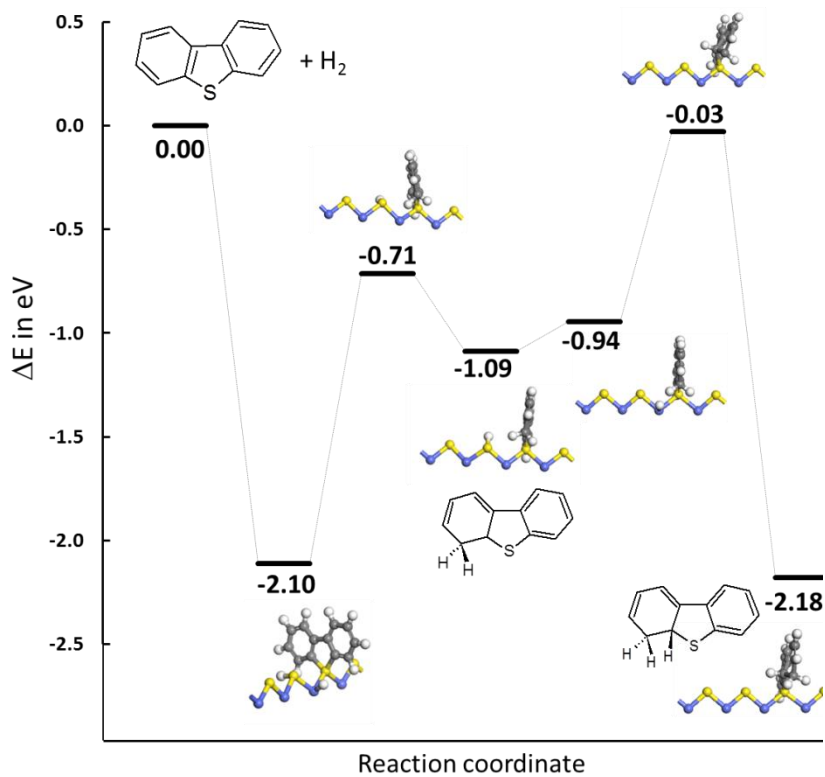
### SI.2.3 Reaction on S-edge with one S-vacancy obtained by S-diffusion



**Fig. S5.** Electronic energy profile of the total DDS of DBT on the S-edge with preliminary S-diffusion leading to the formation of one S-vacancy and one neighboring S<sub>2</sub> dimer.

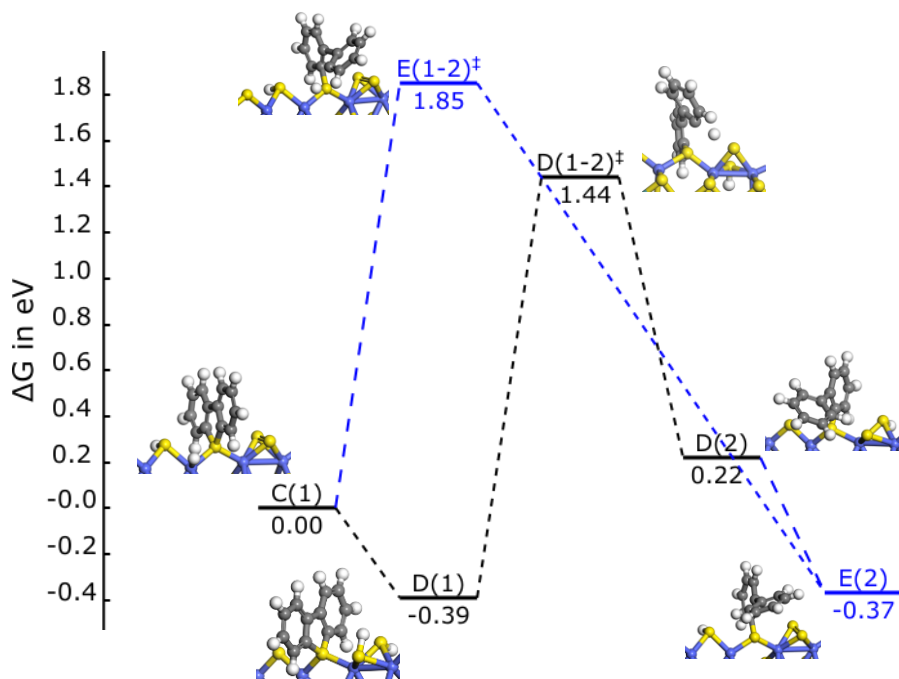
### SI.2.4 Reaction on S-edge with one S-vacancy obtained by S-removal

We start here from the configuration reported in **Fig. 3c** which assumes that one vacancy (energy cost of +1.66 eV) already exists on the S-edge. Once the H<sub>2</sub> molecule is dissociated on one S atom and on a close Co site, the hydrogenation proceeds through H-transfer on β position. As reported in **Fig. S7**, the activation energies to hydrogenate the β position and then the α one are higher than on the M-edge alternated (1.40 eV for the first one vs 0.80 eV, 0.91 eV vs 0.15 eV for the second). Even if they seem to remain individually acceptable, the combination of the two successive hydrogenation steps lead to an overall activation energy of +2.07 eV which is significantly higher than the previous mechanisms found on the M-edge.



**Fig. S6.** Energy profile for the  $\beta,\alpha$ -dihydrogenation of DBT on the S-edge with one S-vacancy formed by H<sub>2</sub>/H<sub>2</sub>S exchange.

### SI.3 Hydrogenolysis mechanism on the S-edge



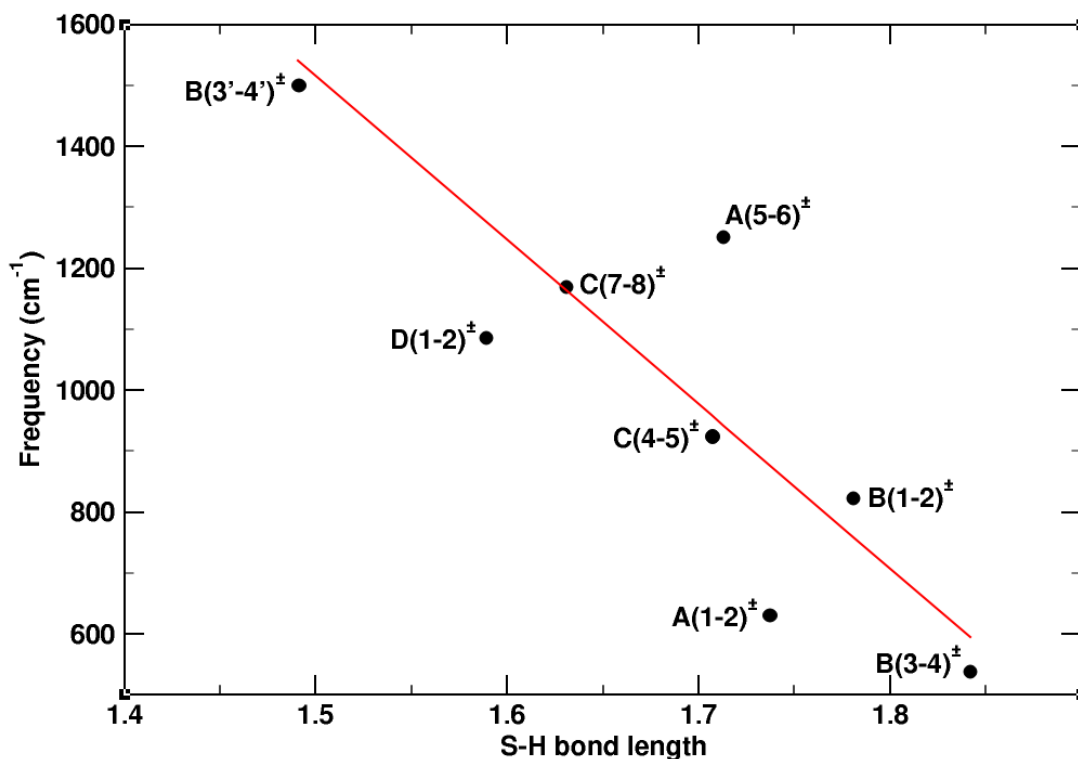
**Figure S7.** Free energy profiles of the hydrogenolysis mechanism of the first C-S bond scission on the S-edge with preliminary S-diffusion leading to the formation of one S-vacancy and one neighboring S<sub>2</sub> dimer. Black profiles: H-transfer from one -SH group formed on the S<sub>2</sub> dimer, Blue profile: H-transfer from Co-H.



#### SI.4 Vibrational frequencies analysis of transition states

**Table S1: Various TS modes and their respective imaginary frequencies. Spurious low imaginary frequencies are indicate in parenthesis.**

<b>TS Mode</b>	<b>Imaginary frequencies</b>
A(1-2)‡	630 (40)
A(2-3)‡	168
A(5-6)‡	1251 (16, 4)
B(1-2)‡	823
B(3-4)‡ / B(3'-4')‡	538, (47, 10) / 1500 (23)
C(1-2)‡	913
C(3-4)‡	1330 (19)
C(4-5)‡	925
C(5-6)‡	123 (30)
C(7-8)‡	1169
D(1-2)‡	1086
E(1-2)‡	1398



**Fig. S8:** S-H bond length of various transition states and corresponding frequencies.

Fig. S8 illustrates the correlation between the imaginary frequencies and their S-H bond length. Shorter S-H bond have higher frequency which is more close to the actual S-H vibrational frequency. Moreover as the S-H bond increases, frequency becomes closer to C-H bond vibration. A(1-2)<sup>‡</sup> and A(5-6)<sup>‡</sup> modes deviate slightly from this correlation. A(1-2)<sup>‡</sup> is a complex TS and involves of a stronger C-H-S hydrogen bonding which might explain this deviation. For A(5-6)<sup>‡</sup> involves the second C-S bond breaking along with the proton transfer to C, which affects the vibrational frequency.

## References

- [1] E. Krebs, B. Silvi, P. Raybaud, *Catal. Today* 130 (2008) 160.