Supplementary material for “Searching for the rate determining step of the H2S reaction on Fe(110) surface

**Effect of coverage on the H2S reactions**

By using larger simulation cell, we probe the effect of coverage on the key energetics of adsorption. We looked at the role coverage plays in determining how the orientation of H2S affect the adsorption energies. Here we make comparison between two different coverage; 0.25 ML and 0.0625 ML, by considering the best adsorption geometries from our earlier analysis. Generally, the trend obtained for molecular

adsorption of H2S as a function of adsorption site remain unchanged irrespective of the coverage, see (Figure S1), where the most favorable molecular adsorption angle on OT, SB, LB and TF are compared. Stronger adsorption is observed as we move from the higher to lower coverage. While the coverage is found to has insignificant role on the adsorption energies calculated for OT, SB and TF, the LB shows some sensitivity. Indeed, while the difference in adsorption energy for OT site (0.25 vs 0.0625) is negligible, a 70-90 meV difference was calculated for SB and TF. Interestingly, this difference becomes larger for the LB site, themost stable site for H$\_2$S adsorption. The role of coverage can be further elucidated by comparing the diffusion across the bridge, from R45@LB to R00, two energetically degenerate sites, as a function of coverage. This barrier is dependent on coverage, as the calculated barrier is reduced by 3meV upon reducing the coverage to 0.0625ML (see Figure S2). Analysis of the bonding at the initial, transition state and final state shows that at low coverage suggests that the difference can be related to the somehow distinct bonding in the two systems. We find that the Fe-S bond at the transition state for the case of the lower coverage stretch by 2.5% and for the higher coverage it elongates by only 1.6 % with respect to the free molecule.

A screenshot of a cell phone

Description automatically generated

Figure S1:Adsorption energy profile for the best molecular orientation for each site as a function of coverage



Figure S2:Minimum energy path for the diffusion of H2S across two bridge sites for 0.25ML and 0.00625ML

Adsorption energies and geometrical parameters such as bond length and angles for molecular H2S adsorption for 0.0625ML

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Configuration | EAds (eV) | H-S (Ang) | Fe-S (Ang) | H-S-H (degree) |
| F90@OT | -0.41 | 1.34 | 2.21 | 92.10 |
| F45@OT | -0.57 | 1.34 | 2.20 | 91.90 |
| R00@LB | -0.62 | 1.36 | 2.20 | 90.72 |
| R00@SB | -0.65 | 1.35 | 2.19 | 91.80 |
| R45@LB | -0.75 | 1.36 | 2.19 | 91.20 |