Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Theoretical insight into the sulfur atoms rearrangement on the Ni and Cu doped MoS_2 S-edge induced by hydrogen adsorption under HDS reaction conditions

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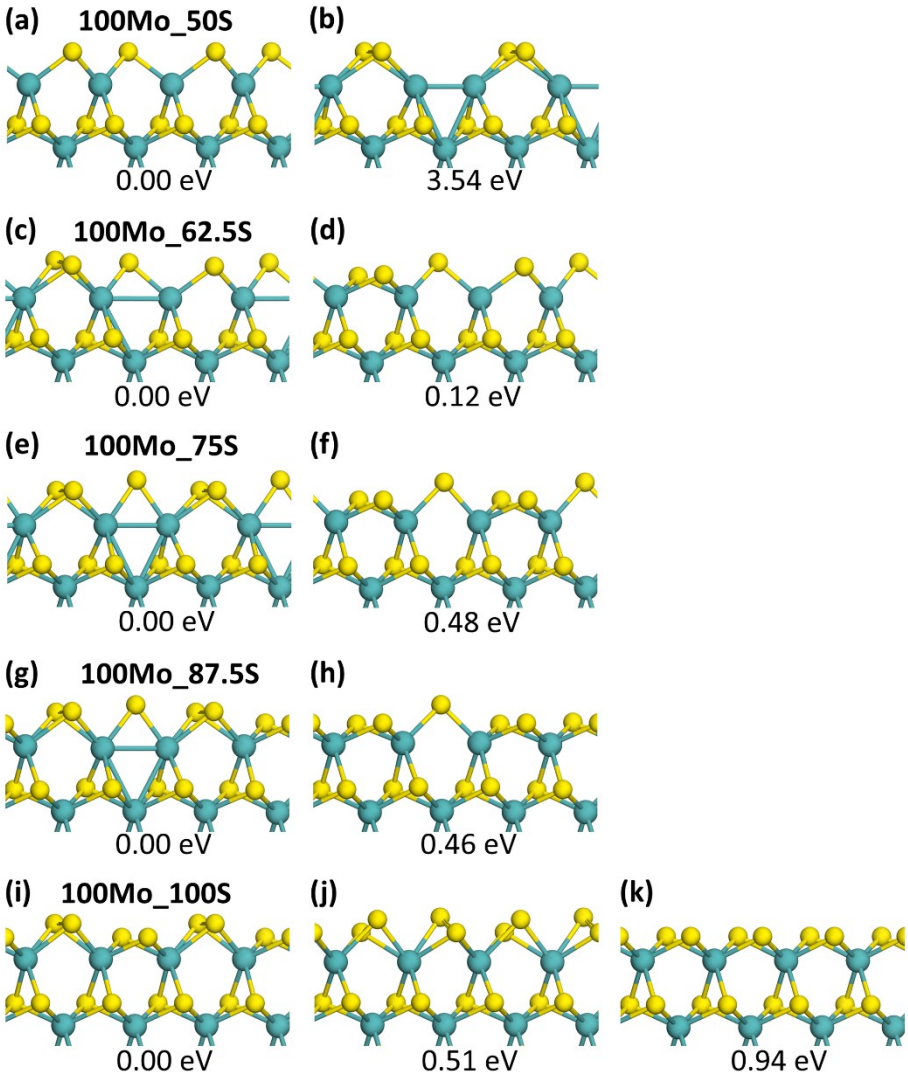

Figure S1. Optimized structures for different configurations of the undoped S-edge for sulfur coverages between 50% and 100%. For a given sulfur coverage, the configurations are shown in order of decreasing stability. The green and yellow spheres are the molybdenum and sulfur atoms, respectively.

Figure S1 summarizes all the tested configurations and relative energies for sulfur adsorption on the undoped S-edge for sulfur coverages between 50% and 100%. The most favorable configuration for each adsorption structure is taken as the reference. For the 50% sulfur coverage, the most favorable configuration is that in which sulfur atoms are bridged between two molybdenum atoms forming a zigzag pattern (Figure S1a), as has been widely reported in the literature.[1–4] The formation of S_2 dimers is less favorable by 3.54 eV. On the other hand, it is observed that the S atoms tend to dimerize for sulfur coverages between

62.5% and 100%. For the 100 % sulfur coverage, three configurations were calculated, one with two S_2 dimers alternating between S atoms in the bridging position (Figure S1i), another configuration with four S_2 dimers alternately bent to one side or the other (Figure S1j), and the other with the sulfur atoms occupying almost perfect lattice positions (Figure S1k). The configuration with two alternating S_2 dimers is the most favorable and is in agreement with previous DFT studies.[5,6] The alternating dimerization of the S atoms stabilizes the structure by 0. 94 eV compared to the nondimerized structure. On the other hand, the proximity of the S_2 dimers in the configuration of Figure S1j leads to a deformation of the structure that becomes less favorable (by 0.51 eV), as mentioned by Prodhomme et al.[6]

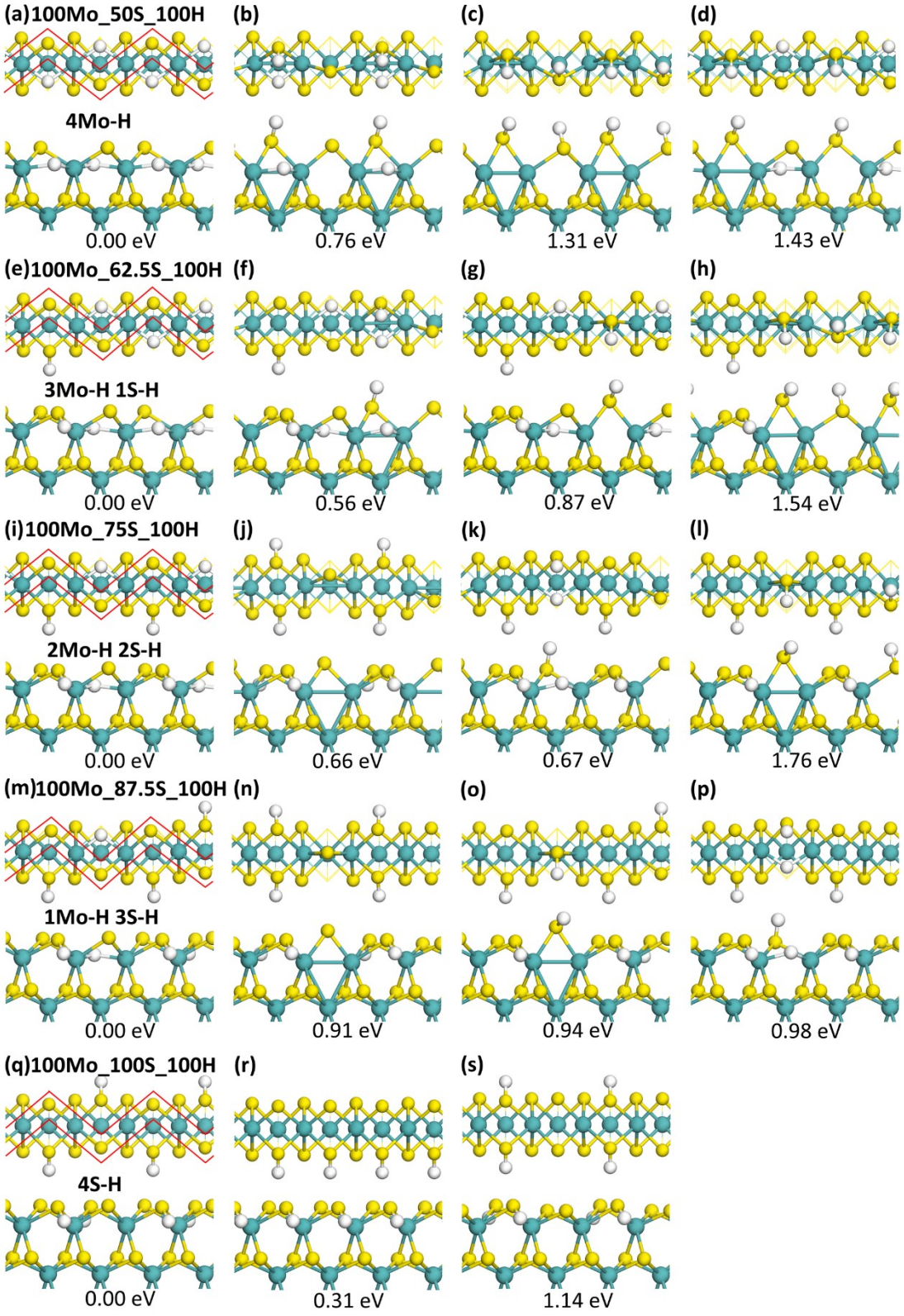

Figure S2. (a)-(s) Top and side views of the optimized structures for different configurations of the hydrogenated undoped S-edge for sulfur coverages between 50% and 100%. For a

given sulfur coverage, the configurations of hydrogen adsorption are shown in order of decreasing stability. The green, yellow, and white spheres are the molybdenum, sulfur, and hydrogen atoms, respectively. S atoms in a zigzag arrangement are marked by red lines.

Figure S2 summarizes all the tested configurations and relative energies for hydrogen adsorption on the undoped S-edge for sulfur coverages between 50% and 100%. Among all the configurations tested, adsorbed H atoms are always more favorable as Mo-H groups on the coordinatively unsaturated Mo atoms than when directly bound to sulfur atoms as S-H groups. For the 50% sulfur coverage, the most favorable configuration corresponds to four Mo-H groups, where the H atoms are bound in a bridging site between two molybdenum atoms (Figure S2a). The formation of four S-H groups is less favorable by 1.31 eV (Figure S2c). There are also two possible configurations that give rise to two bridging Mo-H and two S-H groups. (Figures S2b and S2d). In the configuration in Figure S2b, the bridging Mo-H and the S-H groups share two Mo atoms, whereas, in the configuration in Figure S2d, the bridging Mo-H and the S-H groups are side by side in an alternating arrangement. These configurations are less favorable by 0.73 eV and 1.43 eV, respectively. For sulfur coverages between 62.5% and 100%, the S_2 dimers split upon hydrogen adsorption. For the hydrogen adsorption on 100% sulfur coverage, three configurations were calculated. One configuration with the S-H groups alternated (Figure S2q), another configuration with the S-H groups side by side (Figure S2r), and the other one with the S-H groups located in the position of the S_2 dimers. The configuration with alternating S-H groups is the most favorable and is in agreement with previous DFT studies.[6–9] A preference for a zigzag arrangement of sulfur atoms without hydrogen adsorption is observed (marked with red lines). This can be attributed to the fact that the S atoms experience minimal steric hindrance in the zigzag arrangement.

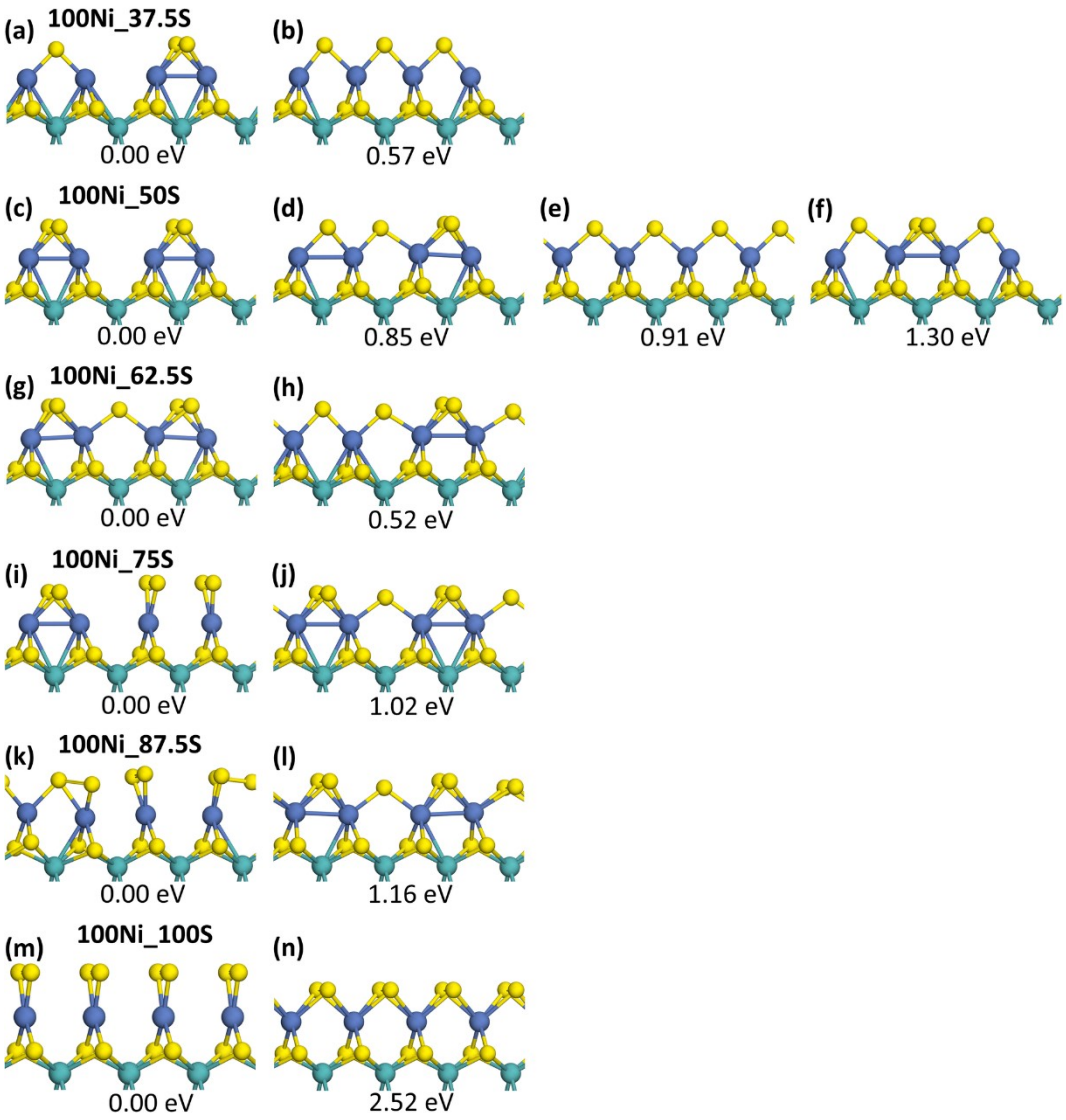

Figure S3. Optimized structures for different configurations of the Ni-doped S-edge for sulfur coverages between 37.5% and 100%. For a given sulfur coverage, the configurations are shown in order of decreasing stability. The green, blue, and yellow spheres are the molybdenum, nickel, and sulfur atoms, respectively.

Figure S3 summarizes all the tested configurations and relative energies for sulfur adsorption on the Ni-doped S-edge for sulfur coverages between 37.5% and 100%. Among all the configurations tested, adsorbed S atoms are always more favorable as S_2 dimers bonded between the Ni-Ni dimers or on top of the Ni atom. For example, at 50% sulfur coverage, the adsorption of S atoms in a bridging position (Figure S3e) is less favorable by 0.91 eV compared to the configuration where the S atoms are adsorbed as S_2 dimers between Ni-Ni dimers. (Figure S3c). For 100% sulfur coverage, the difference between the

adsorption of S_2 dimers on a single Ni atom and the adsorption of S atoms between two Ni atoms is 2.52 eV.

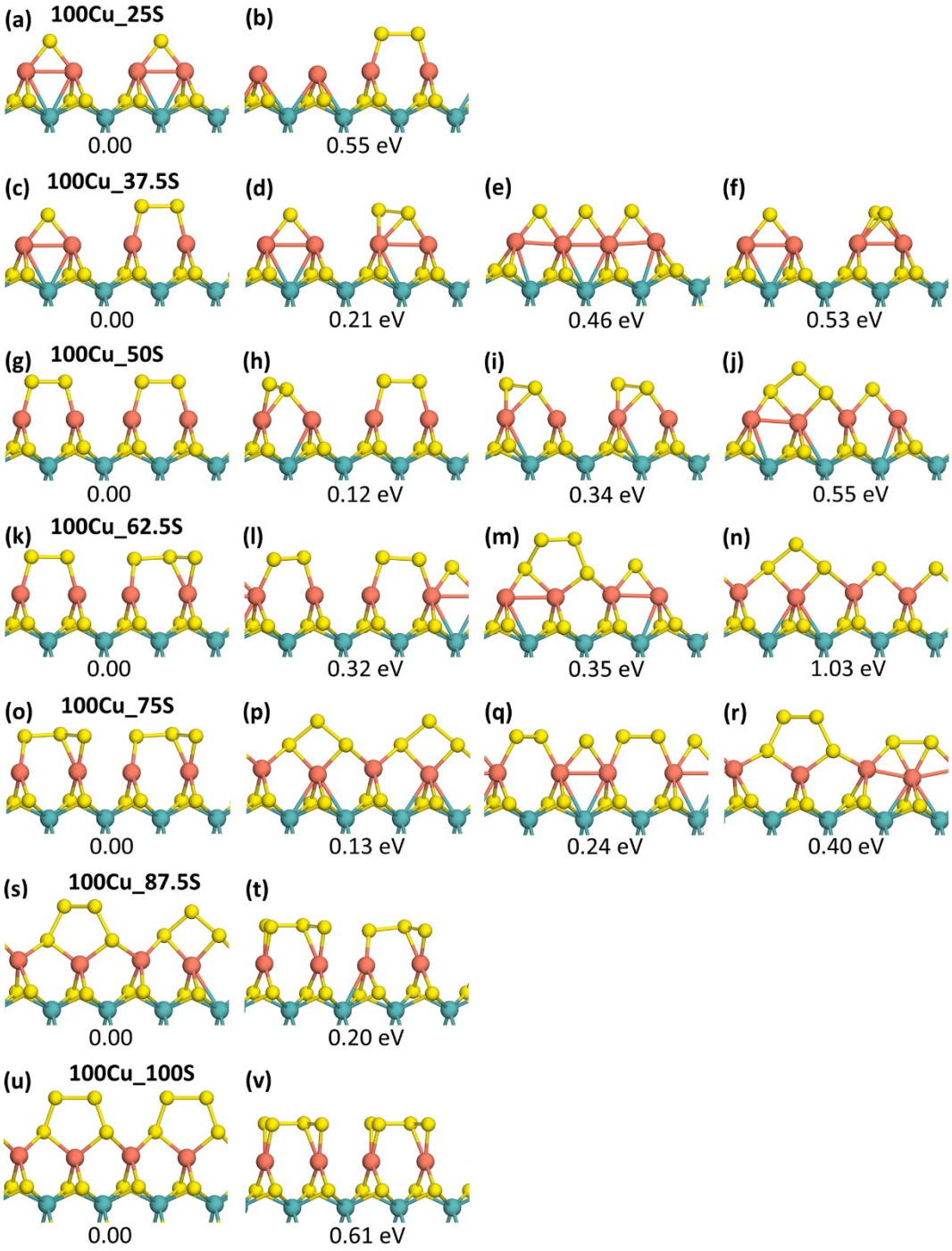

Figure S4. Optimized structures for different configurations of the Cu-doped S-edge for sulfur coverages between 25% and 100%. For a given sulfur coverage, the configurations

are shown in order of decreasing stability. The green, orange, and yellow spheres are the molybdenum, copper, and sulfur atoms, respectively.

Figure S4 summarizes all the tested configurations and relative energies for sulfur adsorption on the Cu-doped S-edge for sulfur coverages between 25% and 100%. For example, at 50% sulfur coverage, the most favorable configuration corresponds to the adsorption of S_2 dimers between two Cu atoms, where each S atom is bound to a single Cu atom (Figure S4g). In this edge structure, the coordination number of the Cu atoms is 3. This adsorption behavior is also observed at higher sulfur coverages, where the dimers are arranged in such a way that the Cu atoms maintain a low coordination number. For 100% sulfur coverage, the difference between the adsorption of S_2 dimers on the edge S atoms and the adsorption on the Cu atoms is 0.61 eV.

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