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

Supplementary Information

Oxidative Etching of S-Vacancy Defective MoS_2 Monolayer Upon Reaction with O_2

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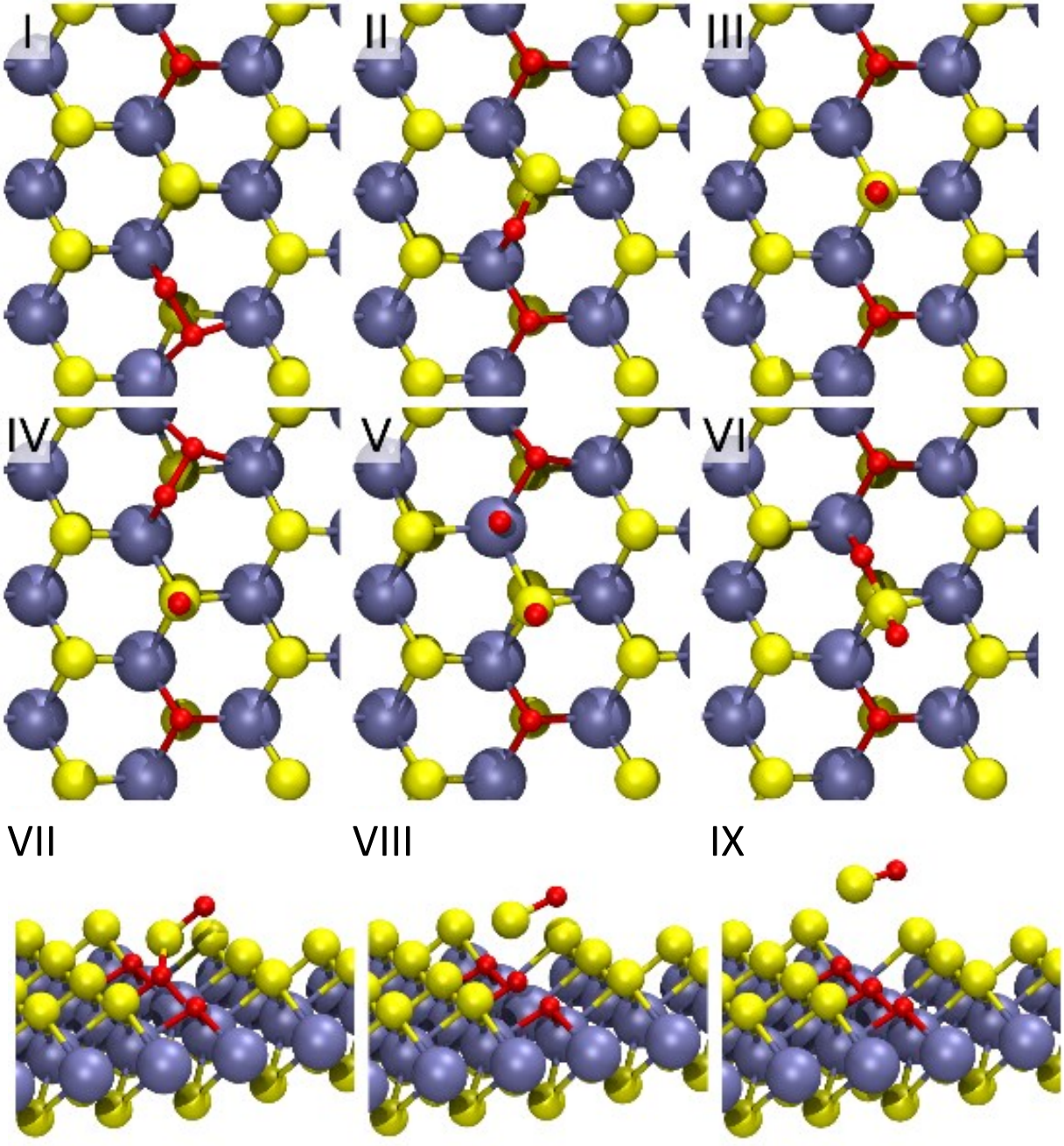

Figure S1. Intermediates obtained from CI-NEB calculations corresponding to the energy pathway in Figure 7 in the manuscript. **I)** Initial structure having upright and lying-down O_2 molecules adsorbed on S vacancy sites separated by a sulfur atom. **II)** Breakage of O–O bond of lying-down O_2 molecule, the formation of Mo–O–S–Mo intermediate and adsorption of O atom on hollow site between three Mo atoms. **III)** Breakage of Mo–O bond and formation of SO group. **IV)** Upper O_2 molecule switches from upright to lying-down configuration. **V)** Breakage of O–O bond yielding an O atom in the hollow site and an O atom ontop of Mo. **VI)** Formation of new O–S bond yielding SO_2 moiety bonded to the surface via S–O and Mo–S bonds. **VII)** Reorientation of SO_2 moiety after breakage of Mo–S bonds. **VIII)** Intermediate with enlarged O–S bond. **IX)** Desorption of SO molecule leaving three O atoms located on Mo hollow sites.

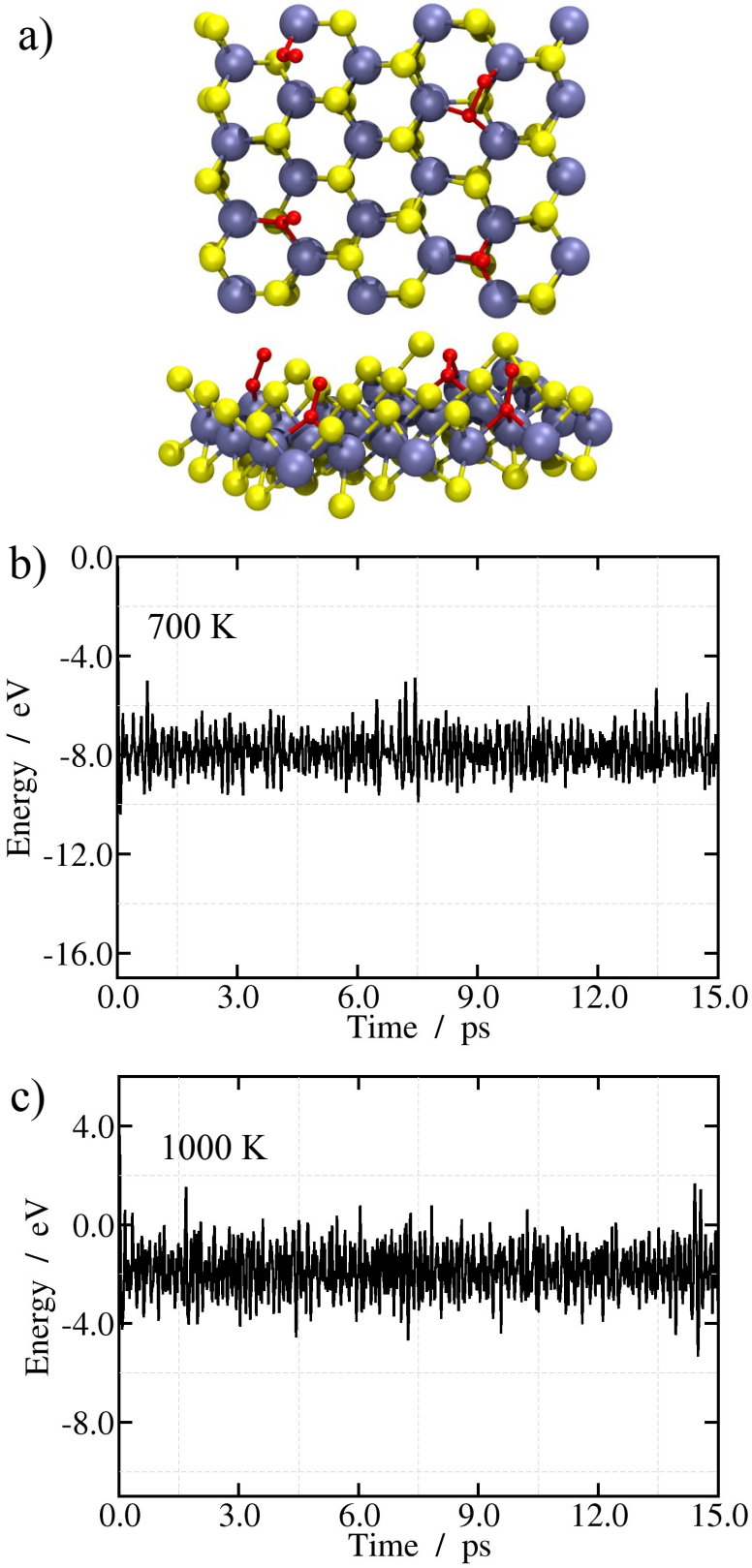

Figure S2. a) Supercell employed in AIMD simulations having two pairs of O_2 molecules adsorbed on S-vacancy sites. Each pair is separated by an S atom. Total energy profiles during AIMD simulations at **b)** 700 K and **c)** 1000 K. O_2 molecules remained adsorbed on the vacancy sites without further reactions.

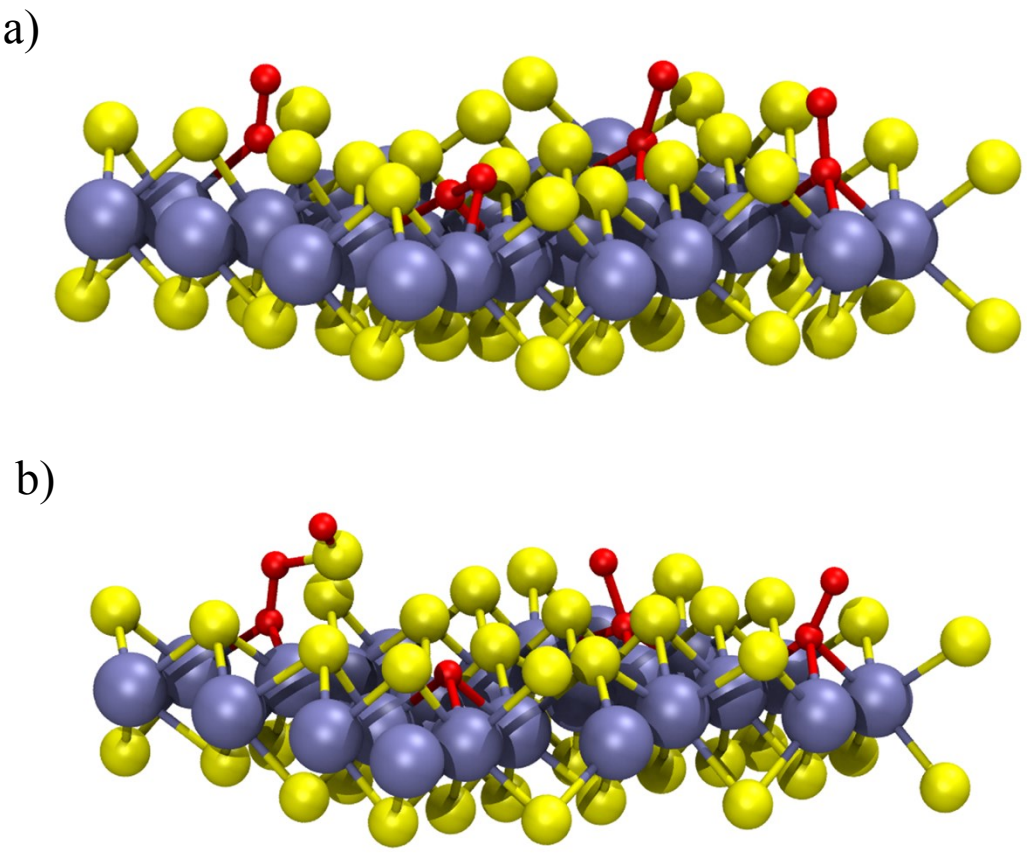

Figure S3. a) Snapshot of initial supercell structure at 0.147 ps having two pairs of O_2 molecules adsorbed on S-vacancy sites. Three of them are in the upright configuration and one of them in the lying-down configuration. **b)** Snapshot at 2.747 ps (before the desorption of SO_2) showing the abstraction of an O atom of O_2 by an SO group formed before. AIMD simulations performed at 1500 K.