

## Composition, structure, and stability of the rutile $\text{TiO}_2(110)$ surface: Oxygen depletion, hydroxylation, hydrogen migration, and water adsorption

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A comprehensive phase diagram of lowest-energy structures and compositions of the rutile  $\text{TiO}_2(110)$  surface in equilibrium with a surrounding gas phase at finite temperatures and pressures has been determined using density-functional theory in combination with a thermodynamic formalism. The exchange of oxygen, hydrogen, and water molecules with the gas phase is considered. Particular attention is given to the convergence of all calculations with respect to lateral system size and slab thickness. In addition, the reliability of semilocal density functionals in describing the energetics of the reduced surfaces is critically evaluated. For ambient conditions the surface is found to be fully covered by molecularly adsorbed water. At low coverages, in the limit of single isolated water molecules, molecular and dissociative adsorption modes become energetically degenerate. Oxygen vacancies form in strongly reducing, oxygen-poor environments. However, already at slightly more moderate conditions it is shown that removing full  $\text{TiO}_2$  units from the surface is thermodynamically preferred. In agreement with recent experimental observations it is furthermore confirmed that even under extremely hydrogen-rich environments the surface cannot be fully hydroxylated, but only a maximum coverage with hydrogen of about 0.6–0.7 monolayer can be reached. Finally, calculations of migration paths strongly suggest that hydrogen prefers diffusing into the bulk over desorbing from the surface into the gas phase.