Interaction of Hydrogen with the ZnO(10-10) Surface.

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The chemisorption of gases on ZnO surfaces has been studied extensively for more than 40 years. This interest is based on the application of zinc oxide in heterogeneous catalysis for hydrogenation and dehydrogenation reactions. Hydrogen adsorption on ZnO is one of the steps in methanol production from syngas. Therefore the understanding of the interaction of hydrogen with ZnO is of major importance.

In the current study we have focused on the mixed terminated nonpolar (10-10) surface of ZnO, which is the natural cleavage plane of ZnO crystals. Experimentally it was observed that upon hydrogen exposure at low temperatures an ordered adsorbate structure with a (1x1) periodicity is formed where both, zinc and oxygen dangling bonds are saturated by H atoms [1]. With increasing temperature, however, the Zn sites loose their H atom and the surface transforms into a reduced state which shows a metallic behavior [1,2]. No significant desorption of H_2 molecules was observed during this transformation process, which led to the speculation that the H atoms diffuse into the bulk. Furthermore, water may play a key role in the stability of different surface structures. Water adsorbs as a partially dissociated monolayer [3, 4], but can also lead to a full hydroxylation of the surface.

The aim of our calculations is to study the hydrogen adsorption and migration at different coverages of the ZnO(10-10) surface. The calculations are based on density functional theory (DFT) with a Hubbard-U correction using the PBE exchange-correlation functional and a pseudopotential/plane wave approach as implemented in the PWSCF code. The coverage dependence of the hydrogen adsorption was investigated by using different supercell sizes representing (1x1), (1x2), (2x1), (2x2) and (4x2) unit cells of the ZnO(10-10) surface. Hydrogen adsorption on the O as well as the Zn sites was taken into account. From the adsorption energies a phase diagram of the lowest-energy adsorbate structures for a ZnO(10-10) surface in thermodynamic equilibrium with a hydrogen gas phase at finite temperatures and pressures is constructed. In addition, zinc hydroxide formation via dissociative water adsorption was taken into account. The stability of these structures is analyzed in terms of a 2-dimensional phase diagram representing the admissible range of hydrogen and water chemical potential. For two limiting cases of a high and a low hydrogen coverage (using a (4×2) supercell) we determined the most stable configurations of H atoms in deeper surface layers, and energy barriers for the H atom migration along different diffusion paths were calculated with the help of the nudge elastic band (NEB) method.

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