

Methanol synthesis on ZnO(000 $\bar{1}$). I. Hydrogen coverage, charge state of oxygen vacancies, and chemical reactivity

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Oxygen vacancies on ZnO(000 $\bar{1}$) have been proposed to be the catalytically active sites for methanol synthesis on pure ZnO. The charge state and thus the chemical reactivity of such vacancies on this polar O-terminated basal plane of ZnO is expected to be intimately connected to the degree of its hydroxylation in view of its Tasker type(3) unstable character. Here, the interplay between hydrogen adsorption and the thermodynamic stability of O vacancies in various charge states, corresponding formally to F⁺⁺, F⁺, F⁰, F⁻, and F⁻⁻ centers, is investigated using electronic structure calculations. Assuming thermodynamic equilibrium of the defective surface with a hydrogen containing gas phase the thermodynamically most stable O vacancy type is determined as a function of temperature and pressure. For the adsorption of H₂ molecules at O vacancy sites it is found that the homolytic process leads to energetically more favorable structures than heterolytic adsorption and hydride formation. By homolytic adsorption and desorption one can switch between F⁺⁺, F⁰, and F⁻⁻ or between F⁺ and F⁻, a process which is believed to occur during methanol synthesis. However, the barrier for heterolytic dissociation of H₂ at O vacancies is significantly lower compared to homolytic cleavage. Furthermore, the barrier for transforming hydridic hydrogen, i.e., ZnH species, to protonic hydrogen, i.e., OH species together with a reduction of ZnO itself, is quite high. This implies that hydridic H⁻ species created as a result of heterolytic dissociation might have a long enough lifetime at O vacancies that they will be available for methanol synthesis. ZnH and OH vibrational frequencies have been computed in order to assist future experimental assignments. © 2009 American Institute of Physics. [DOI: [10.1063/1.3126682](https://doi.org/10.1063/1.3126682)]