

Ab initio cluster calculations on the electronic structure of oxygen vacancies at the polar ZnO(000-1) surface and on the adsorption of H₂, CO, and CO₂ at these sites*

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Oxygen vacancies at the polar O terminated (000-1) surface of ZnO are of particular interest, because they are discussed as active sites in the methanol synthesis. In general, the polar ZnO surfaces are stabilized by OH groups, therefore O vacancies can be generated by removing either O atoms or OH or H₂O groups from the surface. These defects differ in the number of electrons in the vacancy and the number of OH groups in the neighborhood. In the present study, the electronic structure and the adsorption properties of four different types of oxygen vacancies have been investigated by means of embedded cluster calculations. We performed ab initio calculations on F⁺ like surface excitations for the different defect types and found that the transition energies are above the optical band-gap, while F⁺ centers in bulk ZnO show a characteristic optical excitation at 3.19 eV. Furthermore, we studied the adsorption of CO₂ and CO at the different defect sites by DFT calculations. We found that CO₂ dissociates at electron rich vacancies into CO and an O atom which remains in the vacancy. At the OH vacancy which contains an unpaired electron CO₂ adsorbed in the form of CO₂⁻, while it adsorbed as a linear neutral molecule at the H₂O defect. CO adsorbed preferentially at the H₂O defect and the OH defect, both with a binding energy of 0.3 eV.

*Dedicated to Professor Volker Staemmler on the occasion of his 65th birthday