A density functional study of the methanol synthesis at an oxygen vacancy at the polar ZnO $(000\bar{1})$ surface

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Abstract

The elementary steps of the methanol synthesis reaction at oxygen vacancies on the polar $ZnO(000\bar{1})$ surface have been studied with density functional theory. We report results for reaction and activation energies for the most important elementary steps of the methanol synthesis reaction on this surface. At these oxygen vacancies the barriers for heterolytic cleavage of H_2 into protons, bound in surface OH groups, and hydrides, trapped in the vacancies, is low. The stabilized hydride facilitates the reduction of CO to formyl (stabilized in the vacancy) with a low barrier $\lessapprox$ 100 kJ/mol. After a fast rearrangement to formaldehyde and hydroxymethylene species a second reduction step leads probably to a surface bound methoxide which at reducing conditions desorbs from the surface under regeneration of an oxygen vacancy. Beside formate, which appears as a side product, and formyl species, oxygen bound hydroxymethylene might be another observable intermediate of the methanol synthesis reaction at oxygen vacancy sites on the $ZnO(000\bar{1})$ surface.