

## Prediction of vibrational frequencies of possible intermediates and side products of the methanol synthesis on ZnO(000 $\bar{1}$ ) by *ab initio* calculations

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We used *ab initio* density functional theory in combination with an embedded cluster approach to calculate vibrational spectra and formation enthalpies of possible intermediates and side products (spectator species) in the synthesis of methanol out of syngas on the ZnO(000 $\bar{1}$ ) surface. Our investigations are based upon our previous work on possible reaction pathways and activation barriers for this reaction at oxygen vacancies on ZnO(000 $\bar{1}$ ). We present and discuss calculated vibrational frequencies of short-living formyl, hydroxymethylene, formaldehyde, acetale, and hydroxymethyl intermediates and compare the calculated frequencies of formate and methoxy species as well as CO and CO<sub>2</sub> species, at the defect free surface and at oxygen vacancies, with recent experimental findings. All investigated species show characteristic features in their spectra. Therefore, the analysis of their vibrational frequencies is a suitable mean to distinguish them and gain new insights in this reaction which is of recent experimental interest. We are able to identify the structure and characteristics of different surface species, such as monodentate and polydentate carbonate and formate species, in agreement with experimental results. © 2012 American Institute of Physics. [doi:10.1063/1.3671450]