Methanol synthesis on ZnO(000$\bar{1}$). III. Free energy landscapes, reaction pathways, and mechanistic insights

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The interplay of physical and chemical processes in the heterogeneous catalytic synthesis of methanol on the ZnO(000$\bar{1}$) surface with oxygen vacancies is expected to give rise to a complex free energy landscape. A manifold of intermediate species and reaction pathways has been proposed over the years for the reduction of CO on this catalyst at high temperature and pressure conditions as required in the industrial process. In the present study, the underlying complex reaction network from CO to methanol is generated in the first place by using *ab initio* metadynamics for computational heterogeneous catalysis. After having "synthesized" the previously discussed intermediates in addition to finding novel species, mechanistic insights into this network of surface chemical reactions are obtained based on exploring the global free energy landscape, which is refined by investigating individual reaction pathways. Furthermore, the impact of homolytic adsorption and desorption of hydrogen at the required reducing gas phase conditions is probed by studying such processes using different charge states of the F–center. [doi:10.1063/1.3541826]