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Methanol Desorption from ZnO Surfaces: Key Factors and Catalytic Insights

The catalytic hydrogenation of CO_2 to methanol is a pivotal reaction in emerging carbon-capture-and-utilisation schemes,[1] yet its overall rate can be limited by how efficiently methanol can disengage from the oxide support. Although ZnO is the industrially preferred promoter for Cu-based catalysts, the atomistic factors that control methanol binding, surface diffusion, and final desorption on different ZnO facets—and in the presence of water or oxygen vacancies—remain poorly quantified in-operando conditions. A predictive picture is hampered by the wide disparity of relevant timescales, ranging from sub-picosecond bond vibrations to second-long rare events.

Here we combine ab-initio molecular dynamics with active-learning neural-network potentials and enhanced-sampling simulations to quantify dissociation, diffusion, and desorption of CH_3OH on the four most stable ZnO facets—(100), (110), (111), and $(00\bar{1})$.[2]

The $(00\bar{1})$ surface proves the least retentive: methanol adsorbs weakly and departs rapidly. Both (110) and (100) facets stabilise adsorbed methanol through a cooperative Zn–O–H hydrogen-bond network, leading to slower release and hindered surface diffusion. The (111) facet behaves differently again, undergoing spontaneous reconstruction that favours methanol dissociation into methoxy and hydrogen, effectively locking the fragment to the surface and suppressing molecular desorption. From these models we then inquired the dissociation/recombination of the methanol to/from methoxy, the diffusion on each surface of the molecules, (see Figure 1) and the effect provided by the presence of water molecules on each surface-type.

These facet-resolved free-energy landscapes and rate constants provide a microscopic rationale for the activity on ZnO-based catalysts and offer quantitative targets for tailoring ZnO morphology, defect density, and reaction environment to optimize methanol synthesis.

References: [1] A. Beck, M. A. Newton, L. G. A. van de Water, et al., Chem. Rev., 2024, 124, 4543-4678.

[2] O. Unke, S. Chmiela, H. E. Sauceda, et. al., Chem. Rev., 2021, 121, 10142–10186.

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