56a Experimental and Computational Probing of the Transition States to Surface Reactions

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Transition states determine the rates of surface catalyzed reactions, however, direct characterization of surface transition states is challenging. Previous work has probed the nature of the transition state to β-hydride elimination in fluorine substituted ethoxy groups on the Cu(111) using experimental determination of the reaction barriers, ΔE_{act}.

$RCH_2O_{(ad)}$ -> $RCH{=}O_{(ad)} + H_{(ad)}$ R = H, CH_3, CH_2F, CHF_2, and CF_3

Here we describe the structures of the ethoxy reactants and the transition states determined using plane wave Density Functional Theory (DFT). Our results allow us to assess characterization of these transition states based on previous experiments. These analyses rely on making a connection between substituent effects on reaction activation energies, ΔE_{act}, and characterization of transition states as reactant-like or product-like. More importantly, our results allow us to test the recently advanced proposition that surface reactions with reactant-like (product-like) transition states are relatively sensitive (insensitive) to the nature of the catalyst surface.

Numerous measurements have shown that methoxy groups are bound to the Cu(111) surface through the oxygen atoms bound in the threefold fcc hollow site. The DFT calculations show that this is also the case for the ethoxy groups. Our previous FT-IRAS measurements predicted that the ethoxy groups are bonded with the C-O bond tilted slightly away from the surface normal and that the plane of the O-C-C structure is also tilted slightly away from the surface normal. The DFT calculations reveal the same structure and are in extremely good quantitative agreement with the predictions of the FT-IRAS measurements.

The TPRS measurements of the kinetics of β-hydride elimination in fluorine substituted ethoxy groups have shown that the barrier to the reaction increases significantly as a result of fluorine substitution. This is ascribed to a transition state in which the β-carbon atom is cationic with respect to the initial state ethoxy group. DFT calculations make the same prediction. The comparison of the experimental values of ΔE_{act} and the predictions of DFT shows impressive agreement and verifies the predictions based on previous experimental measurements.