

## Model Studies On Ligand-Assisted Heterogeneous Catalysis

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Identifying the surface processes governing the selectivity in hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds on late transition metals is crucial for the rational design of new catalytic materials with the desired selectivity towards C=O vs. C=C bond hydrogenation. In the present talk it will be shown that the selectivity of these reactions can crucially depend on the presence of specific ligand-like surface co-adsorbates. Specifically, I will present a mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) surface and Pd nanoparticles supported on a model oxide support.<sup>1</sup> We show for the first time that selective hydrogenation of the C=O bond in acrolein to form the desired reaction product – an unsaturated alcohol propenol – is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface highly selective towards propenol formation. By applying pulsed multi-molecular beam experiments and *in operando* IRAS we identified the chemical nature of the spectator and the reactive surface intermediate as oxopropyl and propenoxy species, respectively. The evolution of the surface concentration of the propenoxy intermediate monitored spectroscopically was found to closely follow the propenol formation rate detected in the gas phase.

In the second part, the catalytic surfaces modified with chiral adsorbates will be discussed. In heterogeneous catalysis, such chiral modification of the non-chiral metal surfaces allows to turn the catalytic processes asymmetric and produce enantiopure compounds. We will discuss the atomistic details of the chiral modification as well as the interaction between the chiral modifiers and the prochiral adsorbates on well-defined Pt(111) surface.

### References:

1. Dostert, K.-H. et al, *J. Amer. Chem. Soc.* **2015**, *137*, 13496-13502.