# Understanding Ligand-Directed Heterogeneous Catalysis: When the Dynamically Changing Nature of the Ligand Layer Controls the Hydrogenation Selectivity

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One of the major challenges in chemistry is imparting selectivity to a multi-pathway reaction. Slight differences in the activation barriers often result in kinetic control over a chemical reaction. A strategy to overcome this issue is the development of selective catalysts that promote the reaction toward the desired product by functionalizing the surface with organic ligands. Previous works on the hydrogenation reaction of acrolein on Pd (111) single crystal show an almost 100% selectivity on the formation of the unsaturated propenol. This selectivity arises from a surface oxopropyl-species formed by acrolein during the initial stage of the reaction [1]. In our recent study [2], we demonstrated that Pd(111) can be functionalized with an acrolein-derived ligand, allyl cyanide, that promotes chemoselectivity toward propenol without being dependent on the spontaneous formation of the oxopropyl-species by acrolein itself. This was identified by the change in the kinetic of the reaction and the spectroscopic identification of both a new reaction intermediate and a stable ligand species [2].
In this contribution, a systematic study on hydrogenation of acrolein over ligand-functionalized Pd(111) is presented. We employ a combination of surface-sensitive tools along with the molecular beam techniques to obtain detailed information on the mechanisms and kinetics of acrolein partial hydrogenation to propenol. Specifically, infrared reflection absorption spectroscopy (IRAS) is employed to identify and study the evolution of the surface species, including the pre-adsorbed ligands and the reaction intermediates, under the reaction conditions. Complementary, their spatial distribution on the catalytic surface is monitored by scanning tunneling microscopy (STM). We present the results of the hydrogenation of acrolein over three different ligand-functionalized surfaces using spectroscopic and microscopic tools. We examine the effect of both geometric and electronic effects on the selective hydrogenation of acrolein by inserting different functional groups onto the same acrolein backbone [3]. Additionally, we performed experiments on the tunable ligand acetophenone that, depending on the adsorption geometry, has a positive (reduction of the induction period) or negative (retardation of the induction period) impact on the kinetics of the reaction.

[1] Dostert *et al.*, J. Am. Chem. Soc., **137**, 13496−13502 (2015).
[2] Schröder *et al.*, Angew. Chem. Int. Ed. Engl., **60**, 16349−16354 (2021).
[3] Schröder *et al.*, J. Phys. Chem. C, **126**, 4907−4920 (2022).