

Probing Enantioselective Processes on Chirally-Modified Model Systems

Smadar Attia, Evan J. Spadafora, Marvin C. Schmidt, Carsten Schröder and Swetlana Schauerma

Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Kiel, Germany
attia@fhi-berlin.mpg.de

Producing enantiopure chemicals is a topic of immense practical importance arising from the fact that the majority of biologically important molecules are chiral. The simplest and so far most promising strategy to induce enantioselectivity to heterogeneous metal catalysts is their modification by chiral organic compounds. While significant progress has been made in developing effective asymmetric powdered heterogeneous catalysts, the atomistic-level mechanisms of the underlying surface processes on chirally-modified metal catalysts are still only purely understood for the most of the known systems. At this stage, a molecular-level understanding of catalysis by the chirally-modified surfaces strongly gains importance in order to further advance this field and to achieve rational design of new chiral catalytic processes from first principles.

Towards this goal, we have recently setup a new UHV apparatus consisting of three independent vacuum systems for preparation and characterization of chirally-modified model catalysts as well as investigation of their reactivity behavior. This apparatus comprises three molecular beam, infrared reflection absorption spectroscopy (IRAS), as well as a number of standard tools for preparation and characterization of model surfaces, both single crystals and nanostructured surfaces consisting of metal nanoparticles supported on thin oxide films. This setup enables detailed kinetic measurements carried out under the isothermal reaction conditions and simultaneous monitoring of the surface species formed on the catalyst turning over by IRAS. The apparatus is additionally equipped with a high pressure cell, which provides an experimental possibility to study the enantioselective reactions under the ambient pressure conditions on the same well-defined model catalysts with gas-chromatograph detection of the gas phase products.

Specifically, we investigated the adsorption and reactivity behavior of a chiral modifier (*R*)-(+)-1-(1-Naphthyl)ethylamine (NEA) and a prochiral molecule acetophenone over Pt(111) over a broad range of coverage and temperature conditions by a combination of molecular beam techniques and IRAS. Additionally, the distribution of both molecules over the surface was characterized by scanning tunneling microscopy (STM) in the temperature range 90-300 K.

For acetophenone adsorption on Pt(111), simultaneous formation of mono- and dimer surface species was observed by STM. This observation was found to be in an excellent agreement with the spectroscopic data showing consecutive evolution of two different carbonyl bands, which are most likely related to mono- and dimer acetophenone species. Based on the frequency shift of the carbonyl bands in the adsorbates with respect to the gas phase value, it can be concluded that one of the adsorbed acetophenone species is strongly perturbed by the interaction with the metal substrate, while the second species interacts with Pt(111) significantly weaker. STM results suggest that acetophenone molecules in a dimer interact via formation of hydrogen bonds involving carbonyl group, such as e.g. C–H···O=C bond.

NEA was observed to homogeneously distribute over Pt(111) surface at room temperature, and to build self-assembled structures, mostly one-dimensional chains, at 180 K. Spectroscopically, NEA was found to adopt a tilted geometry even at sub-monolayer coverages. Currently, co-adsorption of NEA with acetophenone is investigated with STM and IRAS to follow the formation of NEA-

acetophenon complexes on the chirally-modified surface. Complementary, experiments in the high-pressure regime are carried out in an attempt to bridge the pressure gap between the reactivity behavior under UHV and ambient pressure conditions.

The obtained results provide new atomistic-level insights into the surface processes related to asymmetric heterogeneous catalysis and hold a great potential to provide important inputs for controlling enantioselectivity on surfaces.