Surface Science studies of strong metal-support interactions in heterogenous catalysts

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The strong metal-support interaction (SMSI) is among the best-known classes of metal-oxide interfacial interactions in heterogeneous catalysis, which is defined by the migration of oxide support onto metal nanoparticles, forming an ultrathin oxide overlayer. However, there is limited insight in the atomic scale understanding of the structure of the SMSI oxide. In this work, surface science techniques including scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), and low energy electron diffraction (LEED) were employed to investigate interfacial interactions in multiple catalytic systems, including ZnO-Pd and ZnO-Pt. To utilize the capabilities of the surface science techniques and to mimic a catalytic metal nanoparticle in SMSI state, ultrathin oxide films were prepared on metal single crystals as inverse model catalysts.

In the first project, the structural and chemical transformations of ultrathin zinc (hydroxy)oxide films on Pd(111) were studied under varying gas phase conditions. Sequential treatments of the submonolayer ZnO_xH_y films in a D_2/O_2 mixture evoked structural transformations from bilayer to monolayer and to a PdZn near-surface alloy, in accompany with the reduction of Zn, as evidenced by STM, HREELS and XPS. Theoretical calculations bridged the gap between ultrahigh vacuum experiments and high-pressure reaction conditions and predicted that under real SMSI conditions zinc oxide films on Pd nanoparticles would be stabilized by hydroxylation. Based on the experimental and theoretical observations, we propose that the mechanism of metal nanoparticle encapsulation involves both surface (hydroxy)oxide formation as well as alloy formation, depending on the environmental conditions.

In the second project, metal-oxide and metal-hydroxide interactions were compared in ZnO_xH_y/Pt(111) systems. Two distinct monolayer structures, graphite-like ZnO and honeycomb-like $Zn_6O_5H_5$, were prepared on Pt(111) surfaces and investigated by XPS, STM, and HREELS. Graphite-like ZnO is a compact structure and barely influence the surface chemistry of Pt. In contrast, the open $Zn_6O_5H_5$ structure divides infinite Pt surface atoms into small ensembles and donates negative charges to the surface Pt, changing its adsorption properties. This study demonstrated a unique metal-hydroxide interaction, which serves as a novel approach for the modification of metal catalysts.

Overall, through atomic-level characterization of inverse model catalysts, we provided insights into the nature of metal-(hydroxy)oxide interactions in multiple systems. These findings emphasize the necessity of understanding the real structure of catalytic surfaces under different reaction conditions and shed light on rational design of oxide supported metal nanoparticle catalysts.