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Title: Fundamental Insights on Model and Supported Catalysts

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A fundamental understanding of heterogeneous catalysis can be facilitated by the synthesis of catalytic surfaces that are a simplification of the technical catalysts to allow for better characterization but still captures the essence of the interactions. This work was divided in two areas, 1- preparation and characterization of model surfaces synthesized by vapor deposition techniques, 2- characterization and kinetic evaluation of technical catalysts for the water gas shift reaction.

In the first project, model surfaces were prepared using a chemical vapor deposition technique where diethyl zinc (DEZ) was exposed to Pd(111) and Pd(100) single crystals. The appropriate deposition conditions (temperature and exposure) required to ensure complete decomposition of DEZ was identified using a combination of x-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS). A significant chemical shift in the Pd 3d_{5/2} peak was seen by XPS indicating alloy formation with zinc. Using a combination of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) it was shown that the surface structure of the obtained alloy films were dependent on the substrate temperature during deposition. In total five structurally distinct PdZn alloy films were obtained and identified using this method.

To probe reactivity changes of these surfaces, adsorption experiments using probe molecules of CO and propylene were carried out using HREELS. A change in the adsorption phenomena of CO was observed on all surfaces, showing a destabilization of bridge bound CO in favor of linear bound. Some surfaces with Pd atoms exposed in the outer layer were now unable to bind CO, corresponding to a strong electronic change in the Pd atoms in the PdZn alloy. Similarly propylene was shown to be unable to adsorb on all but one of these PdZn surfaces at temperatures as low as 140K. This destabilization of propylene can help explain the enhanced selectivity of this catalyst as the desired product is propylene. If propylene adsorption is suppressed than further reaction of the desired product is also suppressed.

In the second project, Au/Fe₃O₄ heterodimer catalysts were characterized for their thermal stability. In-situ TEM and XPS characterization demonstrates that the gold nanoparticles transform into gold thin films that wet the Fe₃O₄ surface as the reduction of the oxide proceeds. It is shown that this reduction is partially mediated by the presence of gold, and that the reduction only occurs on nano-Fe₃O₄. Theoretical calculations show that the adhesion energy between the Au film is increased on a partially reduced Fe₃O₄ surface. This shows that the size and morphology of the metal oxide support plays an important role in the nature of the metal-support interaction.