A Study of Metal-Support Interactions in Ni, Pd, and Pt Catalysts

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Research Scope and Objectives

We are trying to determine the extent of SMSI behavior in different catalyst systems, examine its effect on adsorption and catalytic properties, and better understand the chemistry responsible for its formation. These studies involve the use of a variety of techniques including differential scanning calorimetry (DSC), IR spectroscopy, thermal gravimetric analysis (TGA), chemisorption of various gases, x-ray diffraction (XRD), STEM and probe reactions such as CO and benzene hydrogenation.

Description of Research Effort

The three listed metals have been dispersed on a variety of supports, including SiO_2, Al_2O_3, SiO_2-Al_2O_3, carbon and TiO_2, and characterized by chemisorption, XRD and TEM to determine crystallite size. The influence of reduction temperature on SMSI behavior is being examined by determining chemisorption and catalytic properties as a function of this parameter. DSC measurements are being used to observe the influence of support material and crystallite size on integral heats of adsorption and to see if correlations exist between these thermodynamic properties and kinetic behavior. The support can have a significant effect on catalytic behavior. For example, the specific activity for methanation on TiO_2-supported Pt is over 100 times higher than that on Pt/SiO_2 and 10 times higher than on Pt/Al_2O_3 catalysts. Reduction temperatures of only 200°C or higher are needed for this high activity of Pt on TiO_2. In contrast, the specific activity for benzene hydrogenation over Pd is higher on Pd/TiO_2 than Pd/SiO_2, Pd/Al_2O_3, and other Pd catalysts reported in the literature; however, this occurs only after low reduction tempera-

tures below 200°C. Increasingly high reduction temperatures result in a sharp, continuous decrease in specific activity on TiO_2-supported Pd, in agreement with studies on other metals, and this is currently attributed to an SMSI effect. DSC measurements on supported Pt catalysts show that the support has a much greater effect on $\Delta H_{(a)}$ values for H_2 than for CO, with values for H_2 varying from 35 kcal/mole on Pt/SiO_2 to 3 kcal/mole on Pt/TiO_2 in the SMSI state. The CO heats of adsorption ranged between 32 and 20 kcal/mole, with the highest value again on the Pt/SiO_2 catalyst.

Future Research

A thorough kinetic study of benzene hydrogenation on Pd will be completed and these supported Pd catalysts will then be characterized by DSC to measure ΔH_a values for H_2, CO and possibly C_6H_6. A similar study is planned for Ni catalysts. Characterization of the total catalyst system, i.e., the state of TiO_2 as well as the metal, is of principal importance, and a TGA system is being assembled to allow simultaneous DSC-TGA measurements. A new STEM on campus will also be utilized. The application of EPR spectroscopy is also planned to acquire additional information about the state of TiO_2. Finally, the hydrogenation of more complex aromatic molecules is planned.