

THE ROLE OF d-ELECTRONS IN CHEMISORPTION AND METAL-SUPPORT
INTERACTIONS STUDIED BY ELECTRON SPECTROSCOPY

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Research Scope and Objectives

The objective of this research program is to investigate the nature of strong metal-support interactions (SMSI) on model Rh/TiO₂ catalysts and the role that d-electrons of the support play in the process. Surface-sensitive electron-spectroscopic techniques are being used to characterize model catalysts fabricated on single-crystal TiO₂ supports in order to eliminate many of the problems inherent with powder supported catalysts.

Description of Research Effort

Our approach to the question of the origin of SMSI and the role of d-electrons in those interactions is to study model catalysts using surface-sensitive electron-spectroscopic techniques such as ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS), Auger and electron-energy loss (ELS) spectroscopies, low-energy-electron diffraction (LEED), etc. Rh/TiO₂ model catalysts are prepared in an ultrahigh vacuum (UHV) surface analysis system by deposition of various amounts of Rh onto well characterized, single-crystal TiO₂(110) surfaces whose geometric and electronic structures are known. It is possible to prepare TiO₂(110) surfaces that are either stoichiometric [i.e., having all Ti⁴⁺(3d⁰) surface cations] or that have a high density of Ti³⁺ ions on the surface. Metallic Rh is then deposited on the support by thermal evaporation, the amount being determined by XPS and Auger spectroscopy. The interaction between the valence and conduction bands of the TiO₂ [or the O(2p) and Ti(3d) orbitals in a localized picture] and the conduction band (or outer orbitals) of the Rh are studied by means of UPS, and the changes in valence or oxidation state of the Ti and Rh atoms are monitored by XPS.

UPS (and to a lesser extent XPS) is also used to study the chemisorption properties of the Rh/TiO₂ model catalysts. By taking difference spectra for catalyst surfaces before and after chemisorption, the molecular orbitals of the adsorbed species can be determined. This is important in assuring that our model catalysts in fact behave in the same manner as do "real" powder supported catalysts.

In order to determine the nature of the changes that occur when a catalyst transforms to an SMSI state, model catalysts are reduced and oxidized in situ in the surface analysis system using the same procedures as those used for high area supported catalysts. The suppression of CO

chemisorption is used as an indication of SMSI. The electronic changes that accompany SMSI are studied by means of UPS, XPS and ELS (the last technique giving information about the empty surface electronic states above the Fermi level), and information on the catalyst morphology is obtained from Auger spectroscopy coupled with inert gas sputter profiling.

We have found that when Rh/TiO₂ model catalysts are reduced at 673 K in H₂ or UHV, CO chemisorption is suppressed and the amount of surface exposed Rh decreases. Subsequent Auger sputter profiling of the catalysts gives strong evidence for migration of a sub-oxide of Ti over the Rh particles during high temperature reduction, thus physically blocking the Rh sites for chemisorption. When such SMSI catalysts are sputtered just enough to remove the Ti oxide layer, normal CO chemisorption is restored.

In a more theoretical vein, the calculations by Horsley on the charge transfer model of SMSI have been shown to be inapplicable to metal atom adsorption on real TiO₂ surfaces. The proper types of calculations that must be performed in order to realistically treat reduced, defect TiO₂ surfaces have been outlined.

Future Research

We are beginning to investigate the effects of high temperature oxidation and low temperature reduction following the initial high temperature reduction of our model catalysts in order to establish the reversibility of the SMSI transition. In addition to changes in catalyst morphology and surface composition, the electronic effects that accompany SMSI and their changes upon subsequent low temperature reduction will be carefully analyzed. Since changes in charge state, substrate screening and core hole relaxation of surface atoms can all contribute to changes in the core level binding energies measured by XPS, experiments using both TiO₂ and Ti₂O₃ supports will be performed in order to separate some of those effects. Model catalyst studies of this type are an important complement to catalytic experiments being performed on powder supported catalysts by other research groups.