

"Structure and Reactivity of Chemisorbed Species and Reaction Intermediates"

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Objectives

The overall objective of this program is to characterize the structure and reactivity of adsorbed molecules on both single-crystal surfaces and high-area catalysts. Specific goals include (a) understanding the influence of surface "additives" (e.g., promoters and poisons) on the structure and reaction chemistry of molecules on surfaces, (b) characterizing the kinetics and mechanisms of model catalytic reactions over well-characterized crystalline and high-area metal surfaces, and (c) determining the identity and structure of stable surface intermediates under catalytic reaction conditions.

Description of Research Effort: Recent Results

This program involves two areas of research which have a common theme - the investigation of surface processes related to catalytic chemistry.

A. Molecular Structure and Reactivity in Chemisorption and Catalysis.

A major activity has been to characterize the role of surface "additives" (e.g., promoters and poisons) on the structure and reactivity of adsorbed species. Our approach has been to use a combination of ultrahigh vacuum techniques including ESDIAD (electron stimulated desorption ion angular distributions), EELS (high resolution electron energy loss spectroscopy), LEED (low energy electron diffraction) and TDS (thermal desorption spectroscopy). Our goal is a microscopic understanding of the influence of both electropositive and electronegative adsorbed atoms on the geometric and electronic structure of adsorbed molecules, as well as on reaction pathways. In a variety of experiments involving the adsorption of H₂O and NH₃ on single crystal surfaces of Ni, Ru, Ag and Al, we have established that surface additive atoms (Na, O) can induce short-range structures in adsorbed molecules--structures which do not form on the clean surface. For example, NH₃ and H₂O are found to undergo major molecular reorientations in the presence of Na and O on a Ru(001) surface, and detailed molecular models have been developed. These observations may have implications for understanding the mechanisms by which promoters and poisons function.

B. Identity and Structure of Surface Intermediates, and Mechanisms and Kinetics of Catalytic Reactions

An important experimental challenge in catalysis is the characterization of surface species in their working environments, e.g., high temperature and high pressure. To this end, we have developed neutron inelastic scattering (NIS) at the NBS 10 MW Reactor as a tool for determining the vibrational spectra of hydrogen-containing molecules on the surfaces of high-area transition metal catalysts. We have used NIS in an in situ study of CO hydrogenation over Raney

Ni, and have seen evidence for a high surface concentration of hydrocarbon fragments, with a concentration of atomic H less than 1/3 of the saturation coverage. We have also studied the adsorption of H₂, C₂H₂ and C₂H₄ on Raney Ni and Pt black. Under comparable experimental conditions, there is often remarkable agreement between NIS data on high-area samples and high-resolution EELS data for single crystal samples; this agreement indicates that the dominant surface species are similar on both types of surfaces.

We have developed and used high-pressure reactors attached to uhv surface analysis instrumentation to measure CO hydrogenation rates and determine reaction mechanisms over single-crystal catalyst surfaces (Ni, Ru, Fe, W). In all cases where data exist for comparison, we have found excellent agreement between turnover numbers, activation energies and product distributions measured over single-crystal catalysts and high area catalysts; this indicates that single-crystal surfaces are excellent model catalysts for studying reaction mechanisms using uhv surface analysis techniques. Recent studies have included the influence of low levels of Fe on the catalytic activity of Ni, the rate of carbon deposition by the reaction of CO with Fe surfaces, and the hydrogenation of CO over Fe. We are currently characterizing the activity for W as a methanation catalyst, in an effort to settle a recent controversy.

Future Plans

A. Molecular Structure and Reactivity

We will examine how different additive atoms from electropositive to electronegative species (K, Na, S, O, Br, Cl) influence the local structure and surface chemistry of such molecules as H₂O, NH₃, CO, CH₃OH, C₂H₄ adsorbed on metal surfaces having different substrate symmetry (4-fold and 2-fold, in addition to the previously-studied 3-fold surfaces). We will also examine the structure and reactivity of small molecules adsorbed on the surfaces of well-characterized oxides of varying stoichiometry (e.g., Ti₂O₃, TiO₂). There are few uhv studies of crystalline inorganic compound surfaces, and virtually none using EELS or ESDIAD; we regard this as a potentially exciting area.

B. Surface Intermediates and Reaction Mechanisms

We will use NIS as an in situ probe of surface vibrational spectra during hydrogenation reactions (catalytic methanation, ethylene hydrogenation) over high-area Ni and Pt catalysts. We hope to measure directly the surface hydrogen concentration during reaction, and to identify the stable surface intermediates leading to product formation.

NIS studies will be extended to measurements of hydrogen chemisorption on high-area zeolite and sulfide substrates. We will also use a newly-constructed time-of-flight neutron spectrometer to study low-frequency torsional modes of adsorbed molecules and their decomposition fragments (e.g., the ethylidyne intermediate which is believed to be formed on a Pt surface when C₂H₄ is adsorbed at 300K).

Using the high-pressure reactor/uhv analysis system, we will initiate studies of catalysis by single-crystal alloy surfaces in an effort to quantify the relationship between catalytic activity and surface composition. A new high-pressure reaction chamber is under construction which will be interfaced with our EELS/ESDIAD system; this will enable us to measure vibrational spectra of stable surface species on single-crystal catalysts immediately following reactions. Studies will focus on hydrogenation and hydrogenolysis reactions, and on model supported catalysts.