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STRUCTURE AND KINETICS OF SURFACE SPECIES. (U)

JAN 79 T E MADEY, D W GOODMAN, G B FISHER

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STRUCTURE AND KINETICS OF SURFACE SPECIES

BY

T. E. Madey, D. W. Goodman, G. B. Fisher, J. T. Yates, Jr.

Surface Science Division

National Bureau of Standards

Washington, DC 20234

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Structure and Kinetics of Surface Species

T. E. Madey, D. W. Goodman, G. B. Fisher, J. T. Yates, Jr.
Surface Science Division
National Bureau of Standards
Washington, DC 20234

The ONR-supported research in the Surface Science Division at the National Bureau of Standards has been concentrated in two areas: (a) the characterization of the structure of adsorbed species using the Electron Stimulated Desorption Ion Angular Distribution (ESDIAD) method, and (b) kinetic and spectroscopic studies of surface species, with particular emphasis on molecular species of catalytic interest. Recent examples from each of these efforts are summarized below.

I. Use of ESDIAD in Studies of the Structure of Adsorbed Species

A continuing need in studies of molecules and atoms adsorbed on surfaces concerns the location of surface bonding sites and the geometrical structure of molecules and molecular fragments on surfaces. That is, where are adsorbed species bonded, what are the directions of the bonding orbitals between the atom (molecule) and surface, and what are the bonding directions of ligands in adsorbed molecular complexes? In a continuing series of experiments,^{1,2)} we have established that the ESDIAD method has clear potential for providing direct information regarding the site location and geometrical structure of molecules adsorbed on surfaces. The method is based on the fact that the angular distributions of ions liberated by ESD during electron bombardment of adsorbed gases on single crystal metal surfaces exhibit symmetrical patterns due to directed ion beams which are correlated with both adsorbate and substrate symmetry. A major thrust of our effort has been to examine the relationship between surface bond angles and ion desorption angles by studying the ESD of adsorbed molecules having known internal structure.

In one test of the utility of the ESDIAD method in studies of the geometry of adsorbed molecules, the chemisorption of CO on Ru(001) has been examined.⁽³⁾ Data previously reported using UPS (ultraviolet photoemission spectroscopy) and EELS (electron energy loss spectroscopy) have indicated that CO is terminally bonded to the Ru surface through the C atom, with the CO axis perpendicular to the surface. The ESDIAD results for CO confirm this orientation: for all

CO coverages in the temperature range 90 K to > 350 K, the angular distributions of O^+ and CO^+ ESD ions are centered about the surface normal. The widths of the ion beams are temperature dependent; for both O^+ and CO^+ , the half widths at half maximum, α , of the ion cones are $\sim 16^\circ$ at 300 K, and $\sim 12^\circ$ at 90 K. This temperature dependence, coupled with a simple model calculation, indicates that the dominant factors contributing to the width of ESD ion beams are initial state effects, i.e., CO surface bending vibrations of the type



Thus, the data suggest that both the directions and widths of ESDIAD beams are determined largely by the structure and dynamics of the initial adsorbed state.

Similar studies indicate that the ESDIAD-revealed structures of H_2O , NH_3 and C_6H_{12} on Ru(001) are all in agreement with predicted and/or known surface molecular configurations.^(2,4) Theoretical predictions of the structures of H on W(100) and W-O and W₂O structures on W(100) and W(111) are also consistent with ESDIAD results.⁽¹⁾

The above results demonstrate that ESDIAD studies of adsorbed molecules indicate structures consistent with known molecular geometry. However, in the case of strong, dissociative chemisorption (e.g., oxygen on tungsten), ESDIAD is sensitive to specific sites on metal surfaces. For oxygen on W, it appears that almost all of the ESD activity is due to adsorption of oxygen at low coordination sites; for the close packed W(110) surface, such sites exist at defects, steps, etc.

The role of surface steps in ESDIAD processes has been examined in an ESDIAD/LEED study of oxygen adsorption on a multifaceted tungsten monocrystal.⁽⁵⁾ The 7 mm diam. crystal was cut to expose 5 separate facets and was similar to one used in studies of adsorption on stepped W surfaces.⁽⁶⁾ The central facet was oriented within $1/2^\circ$ of the (110) plane, and the four surrounding facets were stepped surfaces of different step densities (6° and 10° off the (110) plane), and with step orientations perpendicular to [100] and [110] directions. ESD of chemisorbed oxygen and the oxidized surfaces revealed the following: (a) The only positive ESD ion observed was O^+ ; (b) The O^+ ESDIAD patterns from the faceted surfaces contain a number of ion beams which depend on step orientation (see Figure 1 for an example of the patterns observed); (c) The O^+ ESDIAD patterns from the faceted surfaces are dominated by beams perpendicular to the flats, as well as beams with azimuthal orientation in the "downstairs" directions; (d) A very weak O^+ ESDIAD signal is seen for oxygen adsorbed on the (110) plane. The results are consistent with an earlier observation of ESD from a

stepped surface, (1) and suggest that the "ESD-active" sites for oxygen on tungsten are low coordination sites which are absent on a perfect (110) surface, but present on the stepped surfaces.

II. Kinetic and Spectroscopic Studies of Adsorbed Species

A major theme of our kinetic and spectroscopic studies has been the chemistry of adsorbed molecules related to CO hydrogenation reactions on single crystal Ru and Ni surfaces. (Ru is regarded as one of the most active catalysts for the catalytic methanation reaction, $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, and Ni is widely used as a practical methanation catalyst). The activities range from studies of the adsorption and decomposition^(7,8) of small hydrocarbons on Ru and Ni using ultraviolet photoemission spectroscopy (UPS) and temperature programmed desorption (TPD), to kinetic studies of the methanation reaction over single crystal Ni in a specially-designed uhv catalytic reactor.⁽⁹⁾

We are addressing such topics as the nature of the possible intermediates in the methanation reaction ("carbide", CH, CH₂, HCO,?), the mechanisms of promotion of catalytic activity by alkali adsorbates, and the mechanisms of catalyst poisoning (by impurities such as Fe, S). In addition to the UPS, TPD and kinetic methods, we are also characterizing adsorbed layers using Auger spectroscopy, LEED, and reflection-absorption infrared spectroscopy.

Examples of the adsorption and kinetic studies include the following:

The adsorption of formaldehyde (H₂CO), hydrogen, and carbon monoxide on Ru(110) has been studied using UPS and TPD. The UPS spectra for low exposures of H₂CO at 80 K indicate that H₂CO dissociates to a substantial degree. These spectra are compared with UPS spectra for the sequential adsorption of hydrogen and CO. Whereas there are similarities between these spectra, the differences in the UPS, work function change, and TPD results are sufficient to suggest that a portion of the dissociated H₂CO may exist as a surface molecular complex containing H and CO. This is apparently the first reported example, based on a UPS study, of an oxygen-containing organic molecule which dissociates upon adsorption on a metal surface at 80 K. For high exposures at 80 K, adsorption of a condensed layer of molecular H₂CO is observed. Methanol (CH₃OH) and its initial decomposition products adsorbed on Ru(110) have also been studied. At 80 K, UPS spectra and work function change data show that methanol is molecularly adsorbed. After subsequent heating to near 200 K, the UPS spectra indicate that most of the chemisorbed methanol has already dissociated before any hydrogen desorbs. The UPS spectra, coupled with TPD evidence, suggest the existence of an intermediate surface complex involving H and CO during the decomposition of methanol. The relationship between these complexes and possible intermediates present during the catalytic methanation reaction is suggested.

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The kinetics of the catalytic methanation reaction are being studied in a specially designed ultrahigh vacuum system in which the effects of surface composition of a single crystal catalyst can be assessed.⁽⁹⁾ Surface cleanliness is characterized using Auger Electron Spectroscopy in an ultrahigh vacuum chamber, and reaction kinetics are determined following an in vacuo transfer of the sample to a catalytic reactor contiguous to the AES chamber. This apparatus has allowed us to "bridge the gap" between surface science and practical catalysis in that the specific reaction rate, its temperature dependence, and the product distribution for CO hydrogenation over a Ni(100) single crystal sample (H_2/CO ratio of 4:1, 120 Torr total pressure, $450\text{ K} < T < 750\text{ K}$) are virtually the same as those measured over high area, supported catalysts. This suggests that the Ni single crystal is a good model catalyst for studies of reaction mechanisms, as well as of deactivation (poisoning) and catalyst promoters. Spectroscopic and kinetic evidence for a "carbide" intermediate, and the mechanisms of poisoning by Fe and S are under investigation. Plans for further surface characterization using LEED and UPS, as well as studies of promoters, are being implemented.

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ESDIAD PATTERNS FOR OXIDIZED, FACETED
W (110) CRYSTAL

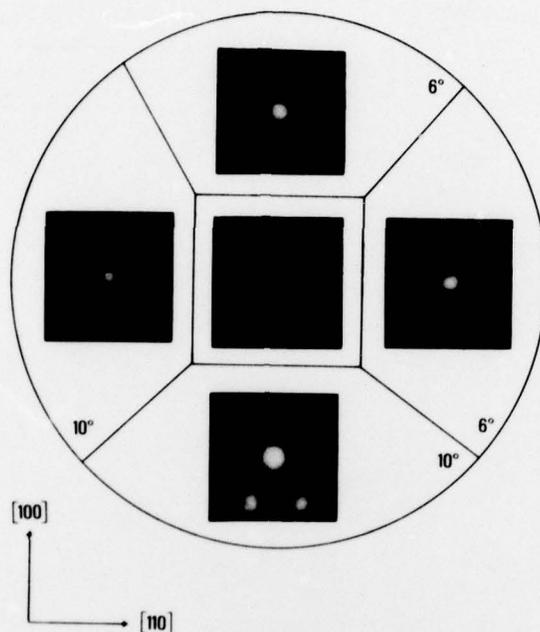


Figure 1. ESDIAD patterns for desorption of O^+ ions from the oxidized multifaceted W crystal described in the text. The central facet is oriented with its surface parallel to the (110) plane; the outer facets are inclined 6° and 10° away from the (110) plane in the directions indicated. The terrace widths on the 6° and 10° stepped surfaces are 13 \AA and 22 \AA , respectively. In all of the patterns above, the spot in the center of the picture corresponds to an O^+ beam desorbing normal to the surface. The O^+ beam from the central (110) facet is much less intense than the beams from the stepped surfaces.