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**MECHANISMS AND CONTROLLING CHARACTERISTICS OF THE
CATALYTIC OXIDATION OF METHANE**

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ABSTRACT

Methane dissociation and oxygen activation have been found to be structure sensitive on different single crystal palladium surfaces. We have formed geometrically restricted surface ensembles on palladium single crystal and polycrystalline surfaces using tetrachloroethylene and pentamethylcyclopentasiloxane and have compared the observed surface structures with those previously obtained using dichloromethane and chlorine. We have also investigated the adsorption and activation of oxygen, carbon monoxide, and water on clean palladium surfaces and those containing the surface ensembles. To interpret high resolution angle-resolved X-ray photoelectron spectra (HR AR-XPS), a new *self-modelling method* of resolving HR-XPS spectra has been developed and applied to the experimental spectra. We have also investigated the effects of electron-accepting chlorine, oxygen, and water adsorbates on Cs-covered MoS₂ by both HR AR-XPS and theoretical analyses. These studies are summarized in this report and described in detail in the following publications:

"Structure Sensitivity of Methane Dissociation on Palladium Single Crystal Surfaces," Klier, K., Hess, J. S., and Herman, R. G., J. Chem. Phys., **107**, 4033-4043 (1997).

"Interaction of Tetrachloro-ethylene with Pd(100) Studied by High Resolution X-Ray Photoemission Spectroscopy," Park, K. T., Klier, K., Wang, C. B., and Zhang, W. X., J. Phys. Chem., **101**, 5420-5428 (1997).

"Ensemble Effects in the Oxygen/Chlorine/Pd(100) System," Klier, K., Simmons, G. W., Park, K. T., Wang, Y.-N., Hess, J. S., and Herman, R. G., Langmuir, **14**, 1384-1391 (1998).

"Adsorption of Pentamethyl-cyclopentasiloxane on the Pd(100) Surface Studied by High Resolution X-Ray Photoemission Spectroscopy," Park, K. T., Herman, R. G., and Klier, K., Surface Sci., **417**, L1125-L1132 (1998).

"Electron Transfer Reactions on Cs/MoS₂(0002) with Chlorine, Oxygen, and Water: High Resolution X-Ray Photoelectron Spectroscopy and Theoretical Study," Park, K. T., Hess, J. S., and Klier, K., J. Chem. Phys., **111**, 1636-1649 (1999).

"A Self-Modeling Approach to the Resolution of XPS Spectra into Surface and Bulk Components," Simmons, G. W., Angst, D. L., and Klier, K., J. Electron Spectrosc. Relat. Phenom. (1999); in press.

"Dissociative Chemisorption of Pentamethylcyclopentasiloxane on a Palladium Foil," Hunsicker, R. A., Klier, K., and Herman, R. G.; under revision and to be submitted.

"XPS Resolution of Bulk and Surface Palladium Species by Self-Modeling of Angle Resolved Spectra of Palladium Foil after Pentamethylcyclopentasiloxane Adsorption," Hunsicker, R. A., Klier, K., and Simmons, G. W.; under revision and to be submitted.

"Electron Transfer and Redox Reactions on Li/MoS₂(0002) with Chlorine, Oxygen, and Water: High Resolution X-Ray Photoelectron Spectroscopy and Theoretical Study," Park, K. T., Klier, K., et al.; under revision and to be submitted.

Palladium Surfaces:

Different Pd crystal faces have exhibited a significant *structural anisotropy toward methane dissociation*, and very large anisotropy to *oxygen activation*. This has significance for understanding oxidative conversions of methane. Potential energy surfaces (PES) have been constructed for *methane dissociation* on Pd crystals with the result that on Pd(111) the dissociation is nearly thermoneutral with a classical activation barrier 74 kJ/mol that is penetrated by hydrogen to yield an effective activation energy of 56 kJ/mol [1]. On defect planes [Pd(679) and (311)], the reaction is exoenergetic, with thermodynamic driving force lowering the classical barrier, consistent with the Marcus Rule [1,2]. A quantitative model has been provided for structure sensitivity of CH₄ dissociation not only on Pd but also on Ni [2], with the result that classical barriers are higher but tunneling effects are more pronounced on Pd than on Ni.

The formation of *geometrically restricted surface ensembles* and the concomitant electronic effects have been studied by a combination of dissociative chemisorption of chlorohydrocarbons, high resolution angle-resolved X-ray photoelectron spectroscopy (HR AR-XPS) in the core level and valence band regions, and theory. The adsorption and reaction of tetrachloroethylene (C₂Cl₄) on a clean Pd(100) surface have been investigated at room and cryogenic temperatures [3]. Saturation of Pd(100) with C₂Cl₄ gas gave rise to a well-ordered p(2 x 2) overlayer structure. HRXPS established that the C-Cl bonds in the p(2 x 2) C₂Cl₄ overlayer were dissociated while retaining the stoichiometry 2C:4Cl, and the amounts of carbon and chlorine on the surface were 0.125 and 0.25 monolayer (ML), respectively. At 131 K, the exposure of the clean Pd(100) surface to C₂Cl₄ resulted in predominantly molecular adsorption, evidenced by the binding energies (BEs) of the Cl2p and Cl1s core levels. A detailed core level scan in the Cl2p region revealed two satellite Cl peaks: one shifted from the molecular C₂Cl₄ peak by $\Delta BE = -2.7$ eV and the other by $\Delta BE = -1.4$ eV, corresponding to atomic Cl and partially dissociated C₂Cl₄ species, respectively. As the temperature increased, the partially dissociated C₂Cl₄ gradually converted to adsorbed Cl atoms until 291K, at which temperature all Cl on the surface formed atomic Cl of 0.25 ML coverage. The carbon species, while present in stoichiometric amounts, did not give rise to additional structural features, but they indirectly affected the Cl ordering in forcing the p(2 x 2) structure, which does not form upon dissociative adsorption of elemental chlorine [3].

A further ensemble-controlling adsorbate was used in the form of *adsorbed siloxane rings*, initially five-membered pentamethyl pentamethylcyclopentasiloxane (PMPS). A new approach to ensemble control with a limiting aperture for access of molecules to the Pd surface has been demonstrated by chemisorption of the siloxane rings. On Pd(100), PMPS is strongly anchored through the formation of a Si-Pd bond but *the (-Si-O-)5 rings retain their integrity* [4]. Quantitative HRXPS analysis showed that the Si coverage corresponded to 0.74 ML. AR-XPS revealed a flat geometry of the siloxane ring and carbon from the methyl groups dissociated onto the Pd surface. Subsequent exposure of the PMPS-covered

Pd surface to CO and O₂ showed no adsorption of these molecules, demonstrating that the adsorbed PMPS completely blocked the metal surface. However, exposure to Cl₂ gave rise to two distinct Cl2p peaks in the HRXPS spectrum: a main component at 199.73 eV and a much smaller peak shifted from the main peak by $\Delta BE = -2.11$ eV, corresponding to Cl atoms covalently bonded to PMPS and atomic Cl bonded to the Pd metal, respectively. Thus, Cl₂ reacts with PMPS and the Cl atoms gain access to the Pd surface by rearranging the Cl/PMPS overlayer [4].

Chemisorption of PMPS has also been investigated on polycrystalline Pd foil [5]. The PMPS molecules dissociate upon adsorption onto the Pd foil and that a portion of the *Si-O-Si bonds are cleaved*, thereby destroying the cyclic nature of the compound. This resulted in the presence of three chemically different states of silicon at the Pd foil interface: Pd silicide, silicon carbide, and silicon oxide. Dramatic differences are found in the location of the Si and C species by using AR-XPS. The angular dependence of the photoemissions from the Pd foil revealed that dissociated Si atoms had diffused into the Pd foil and reacted to form a diluted Pd silicide layer estimated to be 12 ± 2 Å in thickness. This Pd silicide layer is located below a screening layer of approximately 8 Å. The screening layer is composed of a near-surface layer of silicon carbide, elemental carbon, and single-bonded silicon oxide species, and a surface layer of intact PMPS estimated to be 2.2 Å in thickness. These results [5] show that the Pd foil reacts with PMPS in a significantly more complex manner than does single crystal Pd(100), which was shown to result in PMPS chemisorption retaining the integrity of the siloxane rings [4].

A new *self-modelling method* of resolving HR-XPS spectra for cases in which core level emissions are composed of multiple unresolved components has been developed [6]. This method has now been applied to resolving the AR-XPS spectra of PMPS on polycrystalline Pd foil [7], where non-linear screening factors were imbedded in the theory. The spectra were successfully resolved into angular dependent bulk and surface components without making assumptions about their line shapes. It was shown that the spectral components corresponded to a surface palladium silicide surface layer and the bulk Pd metal component, with the Pd3d_{3/2} and 3d_{5/2} peaks for the former being shifted 0.45 eV to higher BEs relative to the latter bulk metal. Using an inelastic mean electron free path of $\lambda = 32.53$ Å (for inorganic materials), a surface component thickness of 26.68 Å was calculated [7]. This thickness for the surface component layer is consistent with an estimated thickness of ≈ 20 Å determined previously [5].

In our previous work with Pd(100), chemisorption of CH₂Cl₂ [8] and C₂Cl₄ [3] was found to be dissociative at room temperature and higher, forming very stable Cl overlayers. In the case of CH₂Cl₂, the dissociated chlorohydrocarbon overlayer was partially disordered, leaving enough space on the metal surface for oxygen chemisorption, and the surface carbon could be removed by reaction with the surface oxygen [8]. In contrast, the C₂Cl₄ molecules dissociated on Pd(100) into an ordered, fully saturated p(2 x 2) surface structure that contained Cl atoms and two-carbon residues, with no metal sites accessible to oxygen and

from which the carbon fragments could not be removed by oxidation [3]. The presence of small surface concentrations of Cl from CH_2Cl_2 caused the oxygen to desorb at lower temperatures, indicating a weakening of the O-Pd bond by lateral repulsion between the Cl and oxygen adatoms, and the range of this repulsion was over several Pd-Pd interatomic distances [8]. In separate experiments, photoelectron diffraction of surface core-level shifted Pd3d emission indicated that the O-Pd interaction extended over several Pd-Pd distances along the surface inward normal direction [9,10]. Those experiments suggested that the range of adsorbate interactions involving oxygen on Pd extends both laterally and into the metal beyond the nearest metal neighbors.

We subsequently examined the *lateral interactions of reactive oxygen adatoms* due to the presence of Cl on the surface of Pd(100), as well as the effect of the mobility or the lack thereof of both the O and Cl adsorbates on the behavior of the system [11]. The observed ensemble control of oxygen reactivity by immobile, partially ordered low coverage Cl overlayers has been cast into a statistical-mechanical model that quantitatively accounts for thermal programmed desorption (TPD) behavior with surface phase equilibria between a dense and a rare atomic oxygen phase [11]. It was shown that the Cl surface dopant exerts significant effects on the behavior of oxygen on the Pd metal surface at coverages (Θ_{Cl}) as low as $\Theta_{\text{Cl}} = 0.05$. The range of lateral Cl-O interactions is estimated to be some two Pd-Pd distances beyond and above the blocking of the fourfold holes and its nearest diagonal neighbors. This effect is attributed to the compression of the wanderer oxygen atom rare phase by restricting the free area for the oxygen atom mobility. The oxygen rare phase is in rapid equilibrium with the dense phase ($\Theta_{\text{Cl}} = 0.8$), and compression of the rare phase by $\text{Cl}_{(\text{ads})}$ forces an adjustment of the relative concentrations of the two oxygen phases, thereby also indirectly affecting the low temperature sharp desorption from the dense phase. The surface analyses for Cl and O, the O TPD, and the LEED patterns demonstrate that the Cl overlayer retains its coverage, distribution, and structure after cycling the system with oxygen up to 1000K. Thus, the Cl overlayers from CH_2Cl_2 display memory effects upon repeated oxygen adsorption-desorption cycles, showing that the ensemble control involves a permanent, partially ordered Cl structure [11].

A separate theoretical study of oxygen adsorption on Pd surfaces and its influence on XPS surface core-level peak shifts was carried out [12]. Theoretical calculations of surface core-level shifts of Pd3d induced by adsorbed oxygen were completed using the full-potential linearized augmented plane wave density functional theory (FLAPW-DFT) method for periodic slab structures, involving both initial and final states [12], yielding results in agreement with experiment [10] to within 0.2 eV.

MoS₂ Surfaces:

Single electron transfer and reactivity were previously examined in the Cs/MoS₂ system by high resolution angle-resolved (AR) core-level [13] and valence band [14] XPS. Photoelectron diffraction features were separated from initial orbital shape effects, which have shown spatial anisotropy for emissions from the frontier valence orbitals that agree with theory [14]. The Cs6s electron was found to be located to >90% in the Mo layer and was anisotropically screened in the photoemission process. A fundamental difference between ARXPS and ARUPS was found in observing signals averaged over many points of the surface Brillouin Zone in ARXPS while energy dispersion was observed in ARUPS. This feature assists significantly in the separation of diffraction phenomena from orbital shape effects.

That work has now been extended to the effects of *electron-accepting adsorbates* (Cl, O, H₂O) on Cs/MoS₂(0002) [15]. In particular, supra-valence electron transfer from surface Cs-doped MoS₂(0002) to electron acceptor adsorbates was investigated by high resolution X-ray photoelectron spectroscopy (HRXPS) in the valence band region and above the valence band maximum (VBM). Deposition of a sub-monolayer amount of Cs onto the basal plane of MoS₂ introduced a new electron density of state of *ca.* 1.25 eV about the VBM. Angle-resolved HRXPS and theoretical analysis located this electron density in the MoS₂ layer. Upon the reaction with Cl₂, this Cs-induced photoelectron almost completely disappeared and the Cs3d and Cl2p core levels indicated the formation of a surface Cs-chloride species.

The Cs-covered MoS₂(0002) surface also reacted at room temperature with O₂ to form *surface peroxides and superoxides*, as evidenced by two distinct binding energies of the O1s core level peaks. In contrast, the reaction with water proved to be more difficult. Exposure of the Cs-covered MoS₂(0002) surface to H₂O at 10⁻⁵ Torr did not result in electron transfer reaction. However, the Cs/MoS₂(0002) surface exposed to water at 1 Torr showed a substantial decrease in the density of states above the VBM, as well as formation of a surface hydroxide, indicated by the O1s core level position.

Theoretical calculations using a full-potential linearized augmented plane wave density functional theory (FLAPW-DFT) confirmed the conclusion based on experimental intensity anisotropy of the new peak that the Cs6s electron transfers into the MoS₂ substrate, forming the Cs/MoS₂ electron-acceptor complex with Cs^{δ+}. The FLAPW-DFT calculations also showed the subsequent capture of the electron from MoS₂ by surface Cl, forming a two-dimensional dispersed Cs-Cl layer. The theory and experiment are in excellent quantitative agreement in predicting and observing the electron transfer from the MoS₂ sheet to the electronegative molecular and atomic species [15].

The study of doped MoS₂ has been continued with Li/MoS₂. This system is much more complex than is Cs/MoS₂. HR AR-XPS investigation indicates that Li diffuses into the interlayers of MoS₂ and reduces part of the Mo [16].

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Junior Personnel Working on this Project:

Kenneth T. Park was the post-doctoral research associate working on this project. He is now an Assistant Professor of physics at Baylor University in Waco, TX.

James S. Hess was a graduate student working on this project. He received his Ph.D. in Chemistry in May 1998 and is now a post-doctoral research associate in the Department of Chemistry at the University of Delaware in Newark, DE.

Robert A. Hunsicker was a graduate student working on this project. He will receive the M.S. degree in Chemical Engineering in October 1999.

Andrew P. Butler was an undergraduate student who assisted in the computational modeling and theoretical analyses that were carried out. He received the B.S. degree in Chemistry in May 1999.