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MECHANISMS AND CONTROLLING CHARACTERISTICS OF THE CATALYTIC OXIDATION OF METHANE

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A PROGRESS REPORT TO THE
BASIC ENERGY SCIENCE DIVISION OF THE U.S. DEPARTMENT OF ENERGY

MASTER

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PROGRESS REPORT

Progress during the first 18 months of this three-year research project has included (i) construction and installation of an ultraviolet photoelectron spectrometer (UPS) with power supply and pumping system that has been added as an attachment to the SCIENTA ESCA-300 instrument, (ii) modification of the high resolution electron energy loss spectrometer (HREELS) to produce a stable ultra high vacuum (UHV) environment for initial experiments with a Pd(311) single crystal, (iii) construction of a separate high vacuum system for preparation of surface doped model catalysts by chemical vapor deposition and pretreatment of a Pd(100) single crystal in this system, (iv) carried out detailed experiments of methane activation and oxidation on Pd(679) using a high pressure reaction cell contained in a third ultra high vacuum system, (v) completion of adsorption/desorption studies of H_2, CO, and O_2 on Pd(679), (vi) utilized angle-resolved XPS to probe the diffraction characteristics and structure of the Pd(100) surface, (vii) determination of the electronic surface structure of Pd(100) using angle-resolved UPS, and (viii) computational analysis of oxygen overlayers on the Pd(100) surface. Each of these is discussed in further detail below.

With funding provided by DOE-BES and cost sharing by Lehigh University, an angle resolved ultraviolet photoelectron spectroscopy (ARUPS) system has been constructed to assist in carrying out the Year 2 and 3 studies, and it has been installed in the SCIENTA HR-ESCA-300 instrument earlier this year. The ARUPS system provides enhanced capability to investigate the valence band spectral region of the Pd single crystal catalysts and the Pd/M (M = Si, Sn, Au, Ag, etc.) alloys that will be prepared by special chemical vapor deposition techniques. In particular, ARUPS is being utilized and will be combined with the SCIENTA HR-ESCA for the determination of valence band energy dispersion ($E(\vec{k})$) spectra of Pd, Pd/M, and Pd/MO_x surfaces. The $E(\vec{k})$ spectra are essential for learning whether (i) band structure of an alloy or metal/oxide overlayer is developed, (ii) segregation of electronic states into those of islands of alloy components and the ensuing oxides occurs, (iii) there is island and atomic interdispersion, (iv) the different substructures are located at the surface or in the bulk, and (v) theory employed is correct.

The UV source consists of a VG MICROTECH gas discharge source that is designed to operate with gases such as He, Ne, Ar, and Xe. This provides for the flexibility of utilizing UV radiation in the range of 10-40 eV. Initially, the source will be operated with He since a He discharge lamp is remarkably free from other radiation. The He I (21.22 eV) and He II (40.80 eV) UV lines are both available with this source. The complete UV system also contains a differential pumping unit that removes He from the source while maintaining an ultra high vacuum in the sample chamber.

The high resolution electron energy loss spectrometer (HREELS) system has been renovated so that an ultra high vacuum of 10^{-10} torr is maintained. A Pd(100) single crystal is being used for vibrational spectra studies with this system, which has been extensively studied by LEED, TPD, and phase diagram determination methodology. Cleaning was carried out using argon sputtering and oxygen annealling at 800°C. The electron loss spectra due to impurities initially present, e.g. Pd-S, Pd-C, and Pd-H, have been used to tune the instrument. An initial oxygen adsorption on the Pd(100) surface was consistent with the Pd_4O bonding geometry that gives rise to an oxygen p(2x2) surface structure.

A separate UHV system has been constructed, and this is being used to clean the various Pd single crystals, e.g. new Pd(110) and Pd(111) crystals have been obtained, and will be used for the preparation of the Pd/M surface alloy model catalysts. This system consists of a large bell jar and accompanying pumping system, an Auger spectrometer with a single-pass cylindrical mirror analyzer, an ion gun for surface bombardment, and a doser for surface deposition. This system was first used to clean a Pd(311) single crystal.

A Pd(679) single crystal was placed in a third ultra high vacuum system that has low energy electron diffraction (LEED), temperature programmed desorption (TPD), Auger electron spectroscopy (AES), quadrupole mass spectrometry (MS), and dosing capabilities, as described elsewhere (2,3,10). This system also contains a high temperature, high pressure, including super- atmospheric pressure, reaction cell that can be used in a flowing reactant mode or a pulsed reactant mode (11). The Pd(679) single crystal was meticulously cleaned using an ion bombardment/thermal oxidation treatment procedure.

The reaction of H_2, CO, and O_2 with Pd(679), also designated as Pd(S)-[7(111)x(310)], was studied with objective of investigating the effect of surface morphology on the adsorption and desorption properties of these gases (1). The combined AES and TPD results indicated that the room temperature adsorption of these three gases was primarily at the (111) terrace sites with the estimated saturation surface coverages of 0.86, 0.28, and 0.20 monolayer (ML), respectively. No ordered new LEED structure arising from the adsorption of these three gases was observed. Thermal desorption spectra of H_2 and CO resemble that on the low-index Pd single crystals, and the observed activation energies were 15 and 32 kcal/mol, respectively, for the adsorbed phases. The absorption of hydrogen into the bulk of the Pd crystal was distinguishable by a second broad desorption peak at higher temperature. While O_2 desorption from the Pd(679) was observed at ≈700K, 80% of the surface oxygen was retained on the surface up to 900K, which then completely disappeared at 1050K. This suggests that the oxygen atoms adsorbed in the vicinity of the (310) edges thermally desorb at 600-800K with the rest of the oxygen atoms at the (111) terrace sites diffusing into the bulk of the crystal at 900-1050K. The results of this study indicate that the step and kink sites of the Pd surface play a role in influencing the adsorption states for oxygen.

In a separate experiment, the clean Pd(679) surface was exposed to methane at 650K and an elevated pressure of 35 psig (2.4 atm) for 2 min in the high pressure reaction cell (12). After cooling to 300K and evacuating the reaction cell, the Pd(670) crystal was moved out of the cell and into the ultra high vacuum environment and exposed to 90 L O_2 *via* the gas doser. After evacuating the system, TPD was carried out by increasing the temperature from 300K to 1100K in 90 sec. Products desorbed from the Pd(679) consisted of very large amounts of H_2 and much smaller quantities of CO, CO_2, and H_2O. In contrast to the lack of reactivity of methane on the Pd(100) surface under high vacuum conditions (13), the methane in the present case was observed to be activated and dissociated on Pd(679). It is further of interest now to carry out these studies with Pd(111) and Pd(311).

The atomic and electronic surface sturcture of Pd(100) is being probed by both ARXPS and ARUPS using a clean, well-characterized Pd(100) single crystal, which in some cases has been modified by surface dopants such as chlorine (2,3,10,14). The surface sensitive technique of ARXPS has been recently developed (15-19) and involves strong forward scattering that takes +place when X-ray photoelectrons or Auger electrons emitted by near-surface atoms are scattered and focused by the overlying surface atoms. This scattering process gives rise to intensity enhancements at certain polar (emission, θ) and azimuthal (ϕ) angles corresponding to the directions that connect the emitter atoms with the overlying nearest or next nearest neighbor surface atoms that scatter and focus the emitted photoelectrons. This is illustrated in Figure 1. Since XPS core levels are element specific, observations of the directions in which the photoelectron intensities are enhanced gives information of the local surface structure and short range ordering of the surface atoms. Thus, XPS forward focusing yields photoelectron diffraction data having direct surface structural information.

With the clean Pd(100) single crystal, the surface structure is already known and can be used to illustrate the quality of the data obtained. Because of the geometry of the surface, forward focusing is expected to produce enhanced diffracted photoelectron intensities at emission angles of 0, 35.3, and 54.7°, corresponding to third, fourth, and first nearest

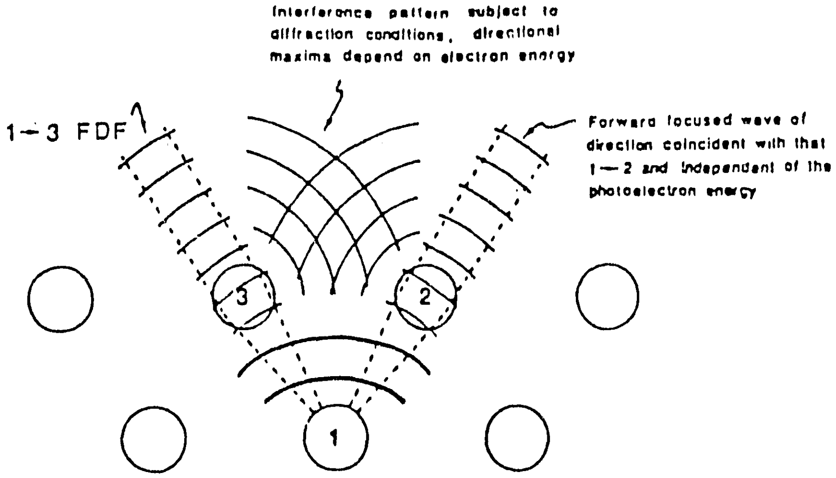


FIGURE 1. A schematic representation of high intensity forward directed focused photoelectrons emitted from Atom 1 along interatomic (1 → 2 and 1 → 3) axial directions and of low intensity diffracted waves in off-axial directions.

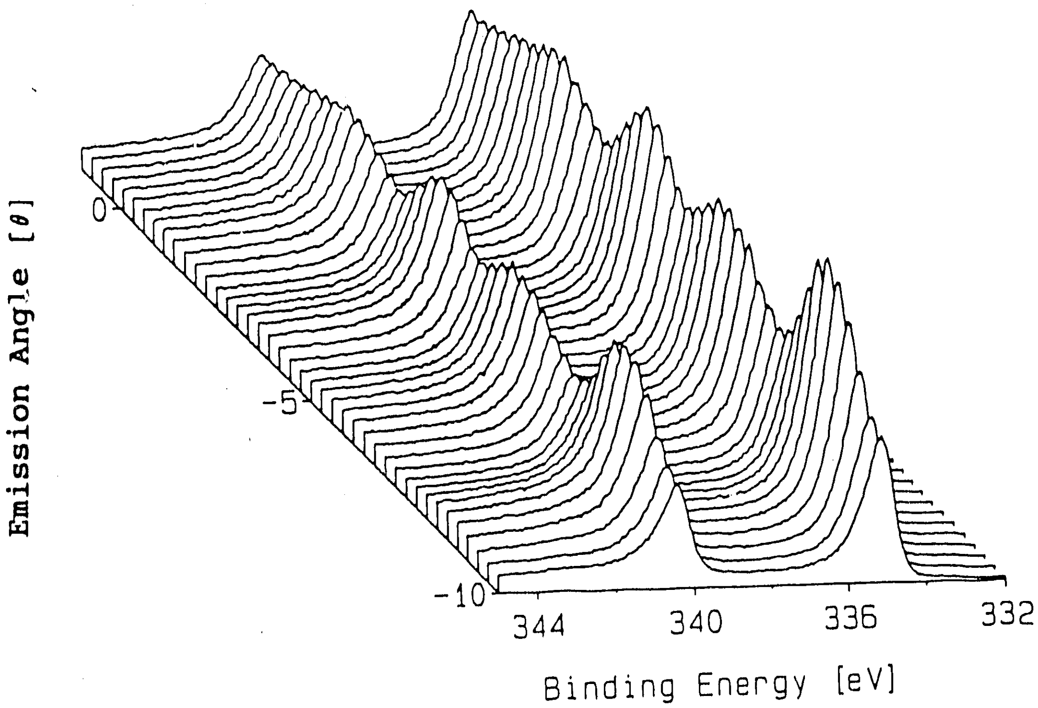


FIGURE 2. Angle resolved XPS spectral data obtained with Pd(100) for the Pd $3d_{3/2}$ (≈340.5 eV) and Pd $3d_{5/2}$ (≈335 eV) peaks by scanning the emission angle θ from -10^{o} to 70^{o} in 2^{o} increments (at an azimuthal angle ϕ of 45^{o} and with the analyzer axis along the [110] direction).

neighbor scattering, respectively, when using an azimuthal angle of 45^{o}. Figure 2 shows the spectral data obtained (20) by the 3-dimensional scanning procedure, and it can be noted that enhanced photoelectron intensities are observed at the predicted emission angles. Figure 3 shows this more clearly as the photoelectron intensity of the Pd $3d_{5/2}$ line as a function of the tilt (emission, θ) angle along the [110] azimuth. For comparison, a theoretical "pattern" calculated for the Pd(100) surface from the single scattering theory of Poon and Tong (9) is also shown in Figure 3. Note that the major experimental maxima are in agreement with theory, indicating that forward focusing of emitted photoelectron from 1 or 2 layers below the surface by overlying Pd atoms is dominant over simple diffraction effects in this case. A more complete description of XPS diffraction should, however, include dynamical effects.

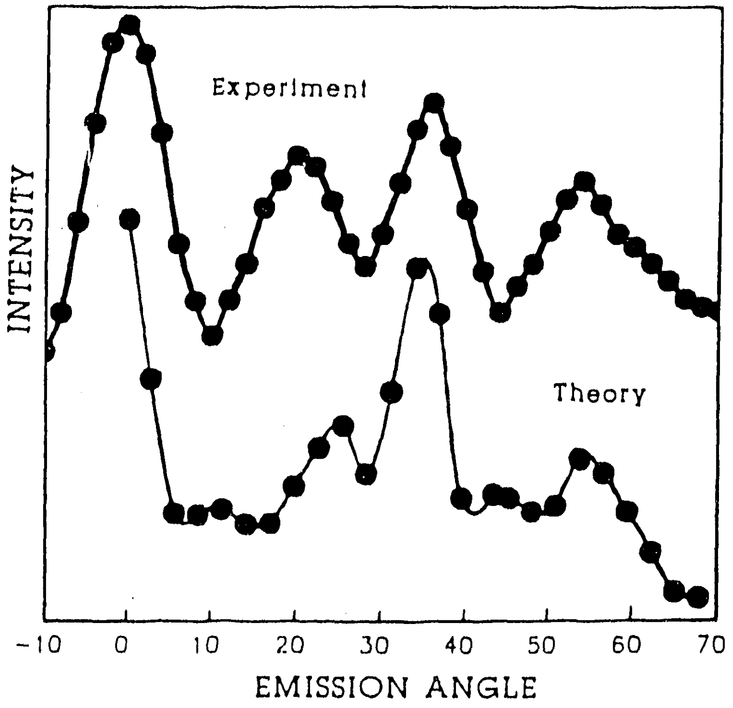


FIGURE 3. Photoelectron diffraction intensities of the Pd $3d_{5/2}$ peaks at ≈335 eV as a function of the emission angle θ from a Pd(100) single crystal with the analyzer axis along the [110] direction.

UPS is used for the study of the valence electrons of atoms and has three major advantages over XPS for the study of surfaces. Photon capture cross-sections of valence electrons are larger at UPS excitation energies of 10 eV < $\hbar\omega$ < 50 eV than XPS energies of $\hbar\omega$ > 1 keV. Second, due to the low excitation energy, the escape depth of the photoelectrons is only a few monolayers deep, and this makes the UPS technique to be very surface sensitive. Finally, the natural line widths of the typical UV vacuum line sources, e.g. He I and II UV lines, are about three orders of magnitude smaller than laboratory X-ray sources. These properties make UPS a very good technique to study surfaces, adsorbates, and epitaxial layers.

ARUPS has been used for mapping the electronic structure of the Pd(100) surface. The principal high symmetry directions in the two dimensional Brillouin zone are selected by setting the azimuthal angle according to the pre-oriented single crystal. In a typical ARUPS experiment, the kinetic energy and the direction of emission of the photoelectrons are measured. The kinetic energy, E, that is determined from the spectrum is used to calculate the only conserved component, the parallel component $k_{\|}$, of the photoelectron wavevector. Using the free electron model, the relation betweeen E and $k_{\|}$ is given by the following equation,

$$k_{\|} = (2mE/h^2)^{1/2} \sin \theta,$$

where θ is the photoelectron emission angle measured from the surface normal. Therefore, each peak gives rise to a point on the dispersion diagram.

Figure 4 shows the ARUPS spectra of the valence band of Pd(100), which allows the electronic structure of the surface along the high symmetry Γ-M direction in the surface Brillouin zone to be investigated. Smoothing and 2nd derivative analysis of the data in Figure 4 resolved 5 distinct bands,

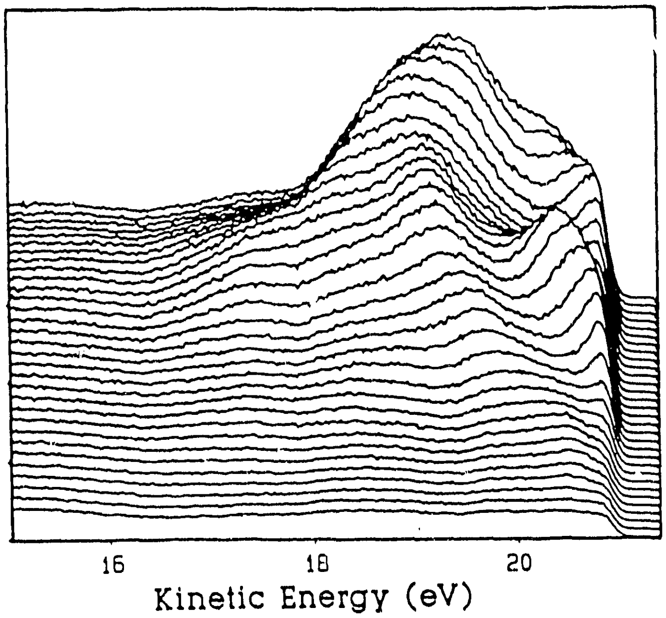


Figure 4. A 3-D representation of the ARUPS spectra of Pd(100) recorded with azimuthal angle $\phi = 45^o$ using the He I excitation at 21.22 eV. Shifts in the peak positions with emission angle θ (k vector) is the result of a band dispersion.

which have been used to obtain the experimental surface band structure along the Γ-M direction. The top of the valence bands is reasonably flat, while the band ≈1.5 eV below the Fermi edge shows a very large 10.7 eV dispersion, suggesting a strong bonding inside the valence band. Quantum mechanical calculations that are being performed will identify the atomic orbitals responsible for the observed electronic band structure.

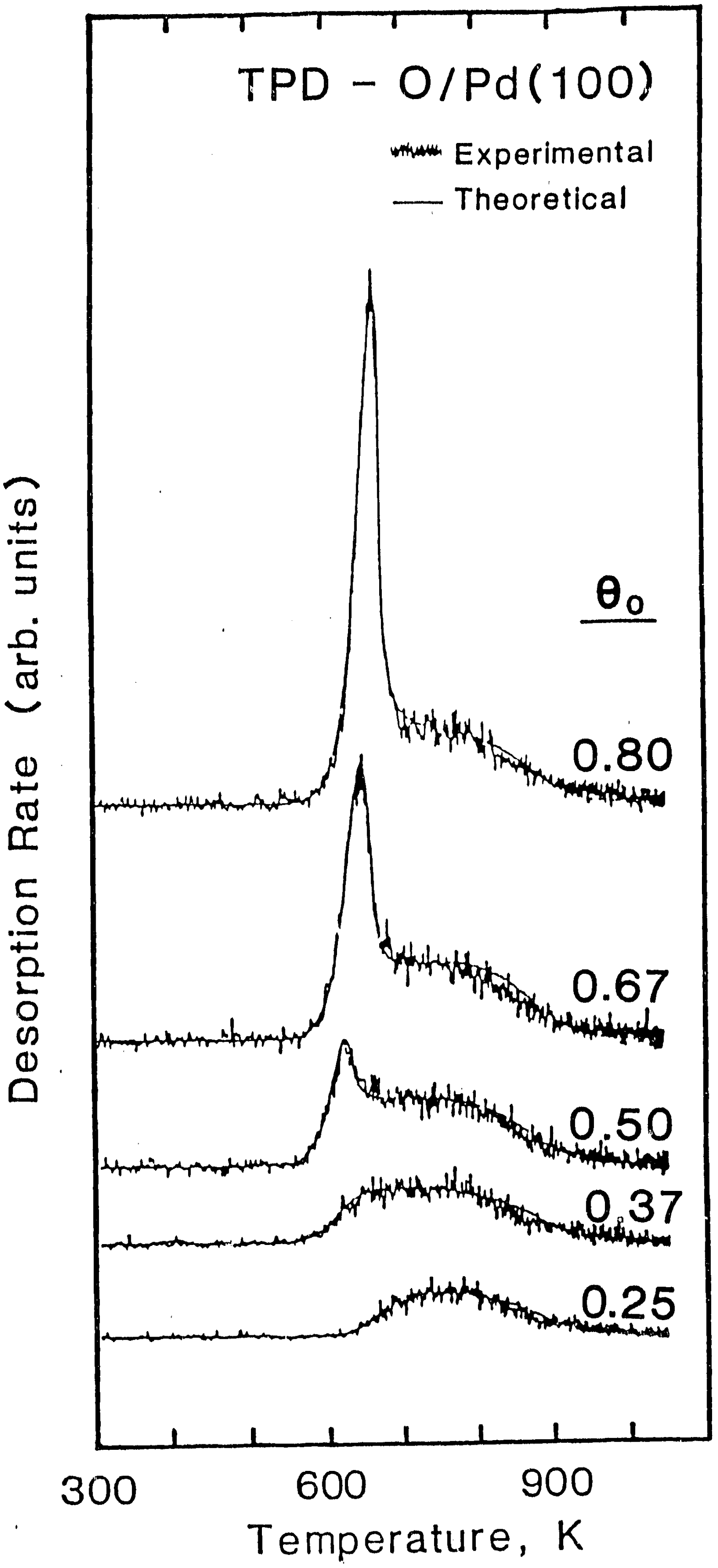
Computational modelling of oxygen and ensemble-controlling surface species has been carried out. The effective Pd-O bond strength was found to strongly depend on the surface concentration of adsorbed oxygen and of ensemble controlling agents such as adsorbed Cl due to strong lateral repulsive dipole-dipole interactions. The surface dipole of the Pd-O adsorbate is -2.6 Debye per oxygen atom, which is comparable to that of acetone, acetyl chloride, and formamide. Lateral repulsion energies of 5.3 kcal/mol between oxygen atoms are estimated to exist in the half-monolayer c(2x2) surface structure, and they strongly influence the desorption temperature, as well as the pressure/temperature regime at which the Pd surface is rendered bare, partially covered, or fully covered by oxygen.

A full statistical mechanical theory based on a wanderer molecule cell model was developed that quantitatively accounts for the TPD behavior of the Pd-O overlayers. This rare-phase, mobile adsorbate theory was coupled with that for the surface phase transformation of the c(2x2) → R27°($\sqrt{5}$x$\sqrt{5}$) + p(2x2) transition, and it was found to fully account for the thermal desorption rates in the bi-phase overlayers. The kinetic treatment was simplified for very rare adsorbates ($\theta < 0.25$) with the account for effective mean free path of the adsorbed oxygen atoms to travel and to recombine to O_2 molecules prior to desorption. The effective collision cross-section was determined by the condition that the pairwise lateral dipole repulsion energy was equal to kT. The mean free path so determined was used in evaluating the translational entropy of the O ad-atoms and the O_2 ad-molecules, resulting in the estimate of entropy stabilization of the adsorbate. As the ensemble site decreased due to the presence of adsorbed Cl, the adsorbate entropy stabilization decreased correspondingly, and the free energy of the Pd-O was reduced.

A semi-quantitative account of this ensemble entropy restriction has been developed, and experimental thermal desorption rates in the Pd-O-Cl overlayers interpreted. An example of the experimental (line with noise) and the theoretical (continuous smooth line) TPD spectra for O_2 desorption from Pd(100)-O overlayers with different initial densities is shown in Figure 5.

The proposed research to be carried out during Year 3 follows the program detailed in our original approved proposal, "Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane," to the U. S. Department of Energy, Basic Energy Sciences Division. No major changes in approaches are anticipated.

FIGURE 5


TPD - O/Pd(100)
Experimental
Theoretical
Desorption Rate (arb. units)
θ_o
0.80
0.67
0.50
0.37
0.25
300
600
900
Temperature, K

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