

# Abstract: Interaction of H<sub>2</sub> and O<sub>2</sub> on platinum (111)

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The interaction of O<sub>2</sub> and H<sub>2</sub> on Pt(111) surfaces has been examined using atomic- and molecular-beam scattering, AES, LEED, and thermal-desorption mass spectrometry. The surfaces are prepared *in situ* by thermal annealing in oxygen. Careful scanning of the LEED to reveal the possible existence of ordered steps and the Debye-Waller extrapolation of elastic helium scattering<sup>1</sup> has been used to establish that the surface contains approximately 10% defects, most of which appear to be disordered.

Molecular oxygen was adsorbed onto such surfaces from a thermal-energy molecular beam. Sticking coefficients were found to be  $\sim 10^{-2}$  with an activation energy for adsorption of  $\sim 2$  kcal/mole.<sup>2</sup> Note that adsorption on the defects only with such an activation energy would rationalize the absolute value of the sticking probability. Adsorption of O<sub>2</sub> from an isotropic source at 300 K shows similar values for the sticking coefficient, first order desorption kinetics, and produces a  $2 \times 2$  LEED pattern often observed by others.<sup>3</sup> At an elevated surface temperature (above 700 K), an epitaxial oxide is formed which has a  $(\sqrt{3} \times \sqrt{3})R-30^\circ$  structure superposed on a weak  $(3 \times 15)$  pattern. On Pt(110) the (100) face of PtO rationalizes a  $(6 \times 12)$  coincidence lattice which has been found for the high-temperature oxidation.<sup>4</sup> The work function of the epitaxial oxide is 1 V less than the clean surface, while Spicer<sup>5</sup> has shown that chemisorbed oxygen increases the work function by 0.8 V.

Hydrogen adsorbs on this surface through a precursor state<sup>6</sup> evidenced by a decrease in the sticking coefficient from 0.1 to 0.01 as the surface temperature increases from 300 to 400 K. There is evidence of two adsorbed states, one with a binding energy of 15–20 kcal/mole, and one with a binding energy of 30–32 kcal/mole. There is strong kinetic mixing between these two states during the flash desorption, and so a detailed interpretation is not possible. The gross features of

the adsorption-desorption and inter-state transfer are reproduced in both the flash-desorption experiments and constant-temperature desorption experiments using elastic helium scattering to measure the amount of hydrogen adsorbed. Using CSFO-BEBO model calculations,<sup>7</sup> the low-energy binding state is tentatively identified as molecular hydrogen and the more strongly bound state as atomic hydrogen.

The reaction of hydrogen with chemisorbed oxygen, assumed to be dissociated, proceeds with a cross section of  $35 \text{ \AA}^2$  up to a coverage of  $2.9 \times 10^{14} \text{ cm}^{-2}$ , above which it is independent of oxygen with a reaction probability of unity. These kinetics are consistent with neither the Langmuir-Hinshelwood (surface-surface) nor the simple Rideal-Eley (gas-surface) mechanism, but suggest a kinetic precursor which is different from the precursor associated with H<sub>2</sub> chemisorption. These results are compared with previously published CFSO-BEBO calculations<sup>7,8</sup> which predicted the following: (1) a small activation energy (2–4 kcal/mole) for O<sub>2</sub> adsorption; (2) an activation energy for the Rideal-Eley mechanism which is less than that for the Langmuir-Hinshelwood mechanism; and (3) the correct adsorption energies for both the molecular and atomic adsorption states.

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<sup>3</sup>H. P. Bonzel and R. Ku, *Surf. Sci.* **40**, 85 (1973).

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<sup>5</sup>D. M. Collins, J. B. Lee, and W. E. Spicer, *Surf. Sci.* **55**, 389 (1976).

<sup>6</sup>V. Lampton (V. Weinberg), M.S. thesis (Department of Chemical Engineering, University of California at Berkeley, 1971) (unpublished).

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