

Summary Abstract: Chemisorption of water on Rh(111)

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The chemisorption of H₂O on the (111) surface of Rh has been studied by thermal desorption mass spectrometry and low-energy electron diffraction. In addition to the clean surface, the chemisorptive behavior of H₂O has been examined when various coverages of oxygen, hydrogen, or carbon monoxide have been pre-adsorbed on the surface in the form of atomic oxygen, atomic hydrogen and molecular CO.

At coverages of less than 10% of saturation on the clean surface, only one feature appears in the thermal desorption spectra of H₂O, with a peak temperature of approximately 191 K. This feature is attributed to the weakly chemisorbed first monolayer of water on the surface. As the coverage is increased, a broadening of the first monolayer feature is observed and a low temperature shoulder appears in the thermal desorption spectra which develops into a second feature with a peak temperature of approximately 165 K. This second feature, observed near 70% of saturation of the first monolayer, corresponds to the formation of multilayers of H₂O on the Rh(111) surface.

The adsorption kinetics of the first monolayer of H₂O on the clean Rh(111) surface are shown in Fig. 1. The data indicate a dependence of coverage on exposure which appears approximately linear suggesting a mobile precursor model of adsorption. The constant sticking probability of $S_0 = 0.58$ is calculated from a least squares fit to the data weighted by the standard deviation in the coverage values. In addition, theoretical results for first-, second- and half-order Langmuir adsorption kinetics are presented in Fig. 1. Clearly, the adsorption of water on Rh(111) does not correspond to first- or second-order Langmuir kinetics. However, it would be incorrect to preclude half-order adsorption kinetics entirely in favor of the precursor model. It is possible that half-order adsorption kinetics corresponds to the formation of islands of H₂O on the surface. The formation of islands of H₂O may also explain why the multilayer feature appears in the thermal desorption spectra before the first monolayer is completely saturated. A conclusive assignment of the adsorption kinetics cannot be made on the basis of these data alone.

Using the method of Chan *et al.*,¹ the activation energy of desorption of H₂O from the clean surface was calculated as 17 kcal/mol with an unusually high pre-exponential factor of $9.2 \times 10^{19} \text{ s}^{-1}$ in the limit of zero coverage. Alternatively, assuming a pre-exponential factor of 10^{13} s^{-1} fixes the energy of desorption at 7.5 kcal/mol. This value seems unreasonably low with respect to the heat of sublimation of normal ice, 12.1 kcal/mol, corresponding to the desorption energy of the multilayer from the surface. Further experiments to measure isosteres are proposed to attempt to clarify the desorption kinetics.

A $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is observed for the first

monolayer of H₂O on the surface. After saturation of the first monolayer, additional exposure of the surface to H₂O causes formation of multilayers of H₂O which obscure the LEED pattern. This observation indicates that the multilayer itself is not ordered.

Three different oxygen overlayers were prepared on the Rh(111) surface to act as substrates for the chemisorption of H₂O. An ordered $[(2 \times 2)]$ unsaturated oxygen overlayer corresponding to approximately 30% of saturation, a saturated unordered oxygen overlayer and a saturated ordered $[2 \times 2]$ oxygen overlayer were all prepared using results of a previous investigation of the chemisorption of O₂ on Rh(111).²

Three features are observed in the thermal desorption spectra of H₂O from each oxygen covered Rh(111) surface which differ in their rates of saturation, but not in peak temperature, from surface to surface. At the lowest exposures, a peak near 220 K is observed for all three oxygen covered Rh surfaces which may result from hydrogen bonding of water to surface oxygen. A second feature, with peak temperature near that of the first monolayer on the clean surface, begins to appear after an exposure of 1.1 L (1 L = 1 Langmuir = 10^{-6} Torr s) on the unsaturated ordered oxygen/Rh(111) surface, an exposure of 0.44 L on the saturated unordered oxygen/Rh(111) surface, and is already present at the lowest exposure of 0.22 L on the saturated ordered oxygen/Rh(111) surface.

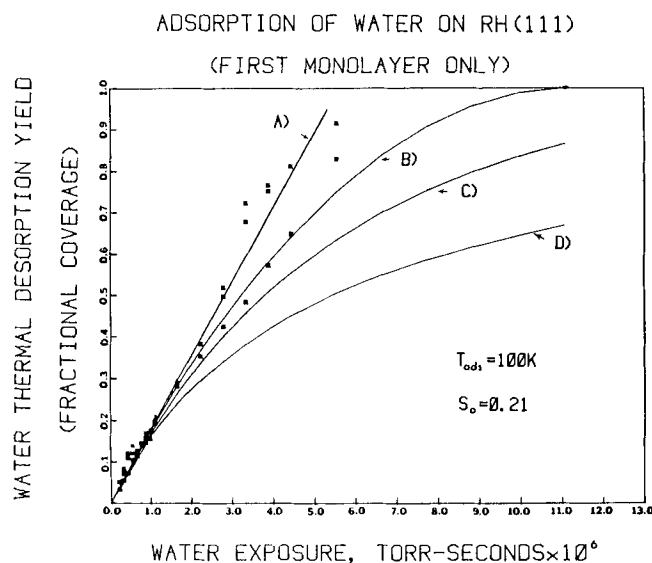


FIG. 1. Adsorption kinetics of the first monolayer of H₂O on the clean Rh(111) surface: (a) Least squares fit to the data weighted by the standard deviation in the coverage values; (b) Theoretical plot of half-order Langmuir adsorption kinetics, $S_0 = 0.58$; (c) Theoretical plot of first-order Langmuir adsorption kinetics, $S_0 = 0.58$; (d) Theoretical plot of second-order Langmuir adsorption kinetics, $S_0 = 0.58$.

The third feature, identified as desorption of the multilayer, appears at an exposure of 3.33, 1.5, and 0.8 L on the unsaturated ordered oxygen/Rh(111), saturated unordered oxygen/Rh(111) and saturated ordered oxygen/Rh(111) surfaces, respectively. The multilayer initially appears at a peak temperature almost 10 K higher than the clean surface for all the oxygen/Rh(111) surface, suggesting that low concentrations of multilayer on the surface are still influenced by surface oxygen. The peak temperature of the multilayer drops rapidly to the clean surface value as the amount of multilayer on the surface is increased past several monolayers.

An unsaturated hydrogen overlayer, corresponding to approximately 40% of saturation, and a saturated hydrogen overlayer were prepared as described previously³ and were used as substrates for the chemisorption of H₂O.

The thermal desorption spectra of H₂O from the unsaturated hydrogen/Rh(111) surface resemble those obtained on the clean surface with respect to features observed and peak temperatures. A saturation coverage of hydrogen on Rh(111) essentially prohibits formation of any feature but the multilayer. However, a small high temperature shoulder is observed, suggesting the presence of a small amount of weakly chemisorbed H₂O. The multilayer peak temperature corresponds to that found on the clean surface. It appears that although the presence of oxygen on the surface distinctly affects the chemisorption of H₂O, no such effect is observed due to the presence of hydrogen on the surface.

An unsaturated CO overlayer, corresponding to a coverage of 45% of saturation and chosen to produce the maximum intensity in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO LEED pattern as reported previously and corresponding to 1/3 monolayer,⁴ and a saturation coverage of CO on Rh(111) were also prepared and used as substrates for the chemisorption of H₂O.

As in the case of unsaturated hydrogen/Rh(111), the thermal desorption spectra of H₂O from the unsaturated CO/Rh(111) surface closely resemble those of the clean surface in spectral features and peak temperatures. Only the multilayer feature accompanied by a small high temperature shoulder is observed in the thermal desorption spectra of H₂O from a saturated CO/Rh(111) surface. A saturation coverage of CO blocks almost all the chemisorption of H₂O as observed with the saturated hydrogen/Rh(111) surface.

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¹C.-M. Chan, R. Aris and W. H. Weinberg, *Appl. Surf. Sci.* **1**, 360 (1978).

²P. A. Thiel, J. T. Yates, Jr., and W. H. Weinberg, *Surf. Sci.* **82**, 22 (1979).

³J. T. Yates, Jr., P. A. Thiel, and W. H. Weinberg, *Surf. Sci.* **84**, 427 (1979).

⁴P. A. Thiel, E. D. Williams, Y. T. Yates, Jr., and W. H. Weinberg, *Surf. Sci.* **84**, 54 (1979).