Water formation on Pd(111) by reaction of oxygen with atomic and molecular hydrogen

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In this work we have studied the steady-state reaction of molecular and atomic hydrogen with oxygen on a Pd(111) surface at a low total pressure (<10⁻⁷ mbar) and at sample temperatures ranging from 100 to 1100 K. Characteristic features of the water formation rate Φ(PH₂; PO₂; TPd) are presented and discussed, including effects that are due to the use of gas-phase atomic hydrogen for exposure. Optimum impingement ratios (OIR) for hydrogen and oxygen for water formation and their dependence on the sample temperature have been determined. The occurring shift in the OIR could be ascribed to the temperature dependence of the sticking coefficients for hydrogen (S_H₂) and oxygen (S_O₂) on Pd(111). Using gas-phase atomic hydrogen for water formation leads to an increase of the OIR, suggesting that hydrogen abstraction via hot-atom reactions competes with H₂O formation. The velocity distributions of the desorbing water molecules formed on the Pd(111) surface have been measured by time-of-flight spectroscopy under various conditions, using either gas-phase H atoms or molecular H₂ as reactants. In all cases, the desorbing water flux could be represented by a Maxwellian distribution corresponding to the surface temperature, thus giving direct evidence for a Langmuir–Hinshelwood mechanism for water formation on Pd(111). © 2004 American Institute of Physics. [DOI: 10.1063/1.1643352]

I. INTRODUCTION

Due to its technological importance, water formation on catalytically active crystalline surfaces, such as palladium and platinum, has been studied extensively over a large pressure and temperature range, using a variety of experimental techniques. For the investigation of the reaction H₂ + O₂ → H₂O on palladium under UHV conditions the applied techniques comprised coadsorption, thermal desorption spectroscopy (TDS), molecular-beam relaxation and scanning tunneling microscopy (STM). The reactive surfaces studied were either Pd single crystals or polycrystalline palladium metal-oxide-semiconductor devices (Pd-MOS). For studies in the high pressure regime (1.0–10⁵ Pa), mostly Pd foils or membranes have been used. Directly related to the water formation itself, numerous investigations also dealt with the interaction of the two single reactants hydrogen and oxygen with Pd surfaces, including the determination of corresponding sticking coefficients, diffusion barriers, desorption energies and their dependence on surface temperature and coverage. It is well known that water formation is a thermally activated process with an activation barrier of 0.3–0.42 eV (Refs. 3 and 4) for OH formation on Pd(111). Due to this barrier, a minimum surface temperature of about 200 K is needed for H₂O formation. Recently, also the interaction of gas-phase hydrogen atoms with adsorbed oxygen on Pt(111) has been investigated, suggesting a new reaction channel for H₂O formation at low surface temperatures (85 K) via hot atoms. In this work we have focused on differences in the kinetics of water formation on a Pd(111) single crystal surface, by using either molecular or gas-phase H atoms to react with oxygen. The experiments have been performed mostly under steady-state conditions, thus also offering the possibility of high resolution time-of-flight (TOF) measurements on desorbing H₂O, formed at the sample surface.

II. EXPERIMENTAL DETAILS

The experiments have been carried out in an ultrahigh vacuum chamber with a base pressure of 10⁻¹⁰ mbar, equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), a multiplexed quadrupole mass spectrometer (QMS), and an extractor ion gauge. For dosing with atomic hydrogen, a highly efficient capillary doser, designed after the concept of Bischler and Bértel has been used. A detailed characterization of this doser was performed by Eibl et al., which allows the calculation of the number of incident atoms on the sample surface during exposure. For the water formation experiments, oxygen has always been dosed isotropically, whereas hydrogen could be dosed either isotropically (H₂) or via the atomic source (H, H₂) with a variable angle of incidence between 45°–90° and a distance of about 2.5 cm from the capillary. The UHV system also offers the possibility to measure the kinetic energy of desorbing species by a time-of-flight (TOF) unit attached to the main chamber. It consists of two differentially pumped chambers (turbo- and Ti-sublimation-pumps), the first containing a motor driven chopper-disk and the second the detector quadrupole mass spectrometer. These chambers are connected via a system of carefully aligned apertures, integrated into specifically constructed liquid nitrogen cooled cryo panels. The pressure in the TOF-detector chamber thus always stayed below 3×10⁻¹¹ mbar, provid-