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Partial dissociation of water on Ru(0001) at low temperatures – Adsorption, structure formation and hydrogen passivation effects

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This paper is dedicated to Professor P.A. Thiel, on the occasion of her 65th birthday and in recognition of more than 30 years searching for the truth in science.

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ABSTRACT

Aiming at an improved molecular scale understanding of the interaction of water with Ru surfaces and electrodes, in particular with respect to thermally induced water dissociation, we have performed a systematic study of the low temperature adsorption and structure formation behavior of water on Ru(0001) by scanning tunneling microscopy (STM). Typical structures formed upon adsorption at below 100 K indicate the presence of molecularly adsorbed water. For adsorption at 120 K, in contrast, the resulting structures are identical to phases which have been associated with partially dissociated adsorbed water, indicating that for continuous adsorption under these conditions thermally induced water dissociation is activated. This assignment is supported by the strongly hindered activity for further adsorption of H_2O or CO (at 100 K) on surfaces where only half of the surface is covered by structures related to an adsorbed H_2O/OH phase. This is attributed to passivation by a H adlayer on the remaining, apparently bare surface areas, which results from H_2O dissociation. Consequences of these findings on the understanding of water interaction with Ru(0001) are discussed.

1. Introduction

The adsorption of water on single crystal metal surfaces under ultrahigh vacuum (UHV) conditions has often been considered as a model system for the interaction of water with electrodes in an aqueous electrochemical environment and has therefore been investigated extensively during the last decades [1–4]. Interaction of water with Ru (0001) has found particular interest. Early water adsorption experiments on Ru(0001), employing low energy electron diffraction (LEED), electron stimulated desorption – ion angular detection (ESDIAD) and high resolution electron energy loss spectroscopy (HREELS) revealed a rather poorly ordered adlayer after exposure at 95 K and a well ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure after adsorption at 165 K [5,6]. Based on LEED structure determination, the oxygen atoms in the water adlayer were found to be almost coplanar [7], in contrast to the so-called bilayer model proposed by Doering et al. [6], which was commonly accepted at that time and which also exhibits a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, but with a relatively large difference in the vertical position of the oxygen atoms. Other experiments indicated that this adsorption system is more complex than initially anticipated, indicating that adsorbed water dissociates partly on Ru(0001) at temperatures below desorption. First experimental evidence for this came from temperature programmed desorption (TPD) studies on the desorption behavior of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structured water adlayer [8,9]. A first theoretical model for a partially dissociated water monolayer on Ru(0001) with almost coplanar oxygen atoms was subsequently presented by Feibelman [10]. Since then, dissociation of water on Ru(0001) has been reported in various experiments [3,11–17]. Nevertheless, there are significant discrepancies about onset temperature and physical origin for the dissociation of adsorbed water, with dissociation being reported already at 105 K [11], while on the other hand molecularly adsorbed water was claimed to remain intact up to 145 K [13], as measured by X-ray photoelectron spectroscopy (XPS) in both cases. This will be discussed in detail later. Relevant in particular for comparison with the electrochemistry of Ru electrodes is the question in how far partly dissociated water on Ru (0001) affects the further adsorption of water and its interactions with coadsorbed species such as CO. The latter appears, *e.g.*, either as a contamination or as a side product in low temperature fuel cells, where PtRu electrodes have been demonstrated to be most CO tolerant [18–20].

These questions are topic of the present work. They were investigated systematically by scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions. We first explored the structure formation of water adlayers at different adsorption temperatures in the range of 97 – 150 K and evaluated the dissociation state, using characteristic structures, which had been identified previously for molecularly adsorbed and partly dissociated water adlayers, respectively, as indicator. Furthermore, we investigated the interaction

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between pre-adsorbed water phases and subsequently adsorbed species, specifically possible changes in structurally well-defined partially dissociated stripe-like water adlayer structures upon subsequent adsorption of water of water or CO below the temperatures at which we had observed dissociation. This provides insights on the molecular segregation behavior of the different species (H_2O, OH, H, CO) on the surface and possible effects of the pre-adsorbed adlayer towards further water adsorption or towards subsequent CO adsorption.

Before discussing and presenting our experiments, we will briefly summarize previous results and findings, in addition to those mentioned above, which are relevant for the present work. TPD experiments clearly revealed two different desorption states in H_2O desorption from Ru(0001) [8,9,14], which were attributed to desorption of molecularly adsorbed water (at 150 K) and recombinative desorption of (partly) dissociated water [9]. For annealing at 130 K, after adsorption at 40 K, non-dissociated water adlayers were reported to be metastable [15], while for annealing above 140 K, there was clear evidence for dissociation [15,21].

Spectroscopy studies reported intact water adsorbates up to 145 K, as measured by reflection–absorption infrared spectroscopy (RAIRS) [21] and by XPS [13]. On the other hand, partial dissociation was claimed already at 105 K based on XPS [11]. This apparent discrepancy was, tentatively explained by electron stimulated dissociation [14]. Alternatively, the above discrepancies may be related also to different monolayer preparation procedures, either by slow adsorption of (sub-) monolayer coverages at 105 K, which resulted in partial dissociation [11]. Interestingly, adsorbing a multilayer water film and subsequent thermal removal of the multilayers led to an almost intact molecular adlayer, which led those authors [13,14] to suggest electron beam damage effects as responsible for the dissociation observed previously [11].

Structurally, the previous studies agree that for water adsorption on Ru(0001) both, molecularly intact water and the partly dissociated water adlayer, result in the formation of ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures [5,9,10,15,22–24]. For dissociated water on Ru(0001), previous STM studies revealed the formation of stripe structures oriented along the $\langle 1\ -100 \rangle$ directions, which exhibit a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, at least in their inner part [15]. Stripe formation was also observed for adsorption of intact water, but in that case, the stripes were oriented along the $\langle 1000 \rangle$ directions [17,25]. In this study we will use the stripe structures oriented along the $\langle 1{-}100 \rangle$ direction as indication for partial dissociation of adsorbed water.

2. Experimental

The experiments were performed in an UHV system with a base pressure of 1×10^{-10} mbar, which was equipped with standard facilities for sample preparation and characterization, an X-ray photoelectron spectroscopy (XPS) system with a Mg/Al X-ray source (X-ray gun: *VG-Microtech* XR3E2) and a hemispherical electron analyzer (*VG Clam 2*), and a commercial variable temperature STM (*Specs-Aarhus,* STM 150). Cleaning and preparing the Ru(0001) surface was performed as it has been described previously [26,27]: Before each experiment, the Ru (0001) single crystal (*Mateck*), which was oriented to better than 0.1° (roughness < 10 nm), was cleaned by Ar^+ ion sputtering at 300 K (ion current of 3–4 μA, kinetic energy of 0.5 keV) for 2 × 20 - 2 × 45 min, depending on the initial cleanness), followed by 7 cycles of oxygen adsorption (2×10^{-6} mbar, 10 s below 550 K) and flash annealing to 1620 K. The cleanness and structural perfection of the resulting surfaces were characterized by STM, which revealed atomically smooth surfaces with terrace widths typically between 25 and 150 nm, and residual impurities far below the detection limit of XPS (1% of a monolayer).

For water and CO dosing the sample was placed in the STM, which was cooled to 120 K or 100 K, depending on the experiment (see figure captions for details). Ultrapure water vapor (MilliQ, 18.2 MΩ cm) was dosed into the UHV chamber *via* a leak valve connected to a glass vessel at room temperature (RT) where a liquid phase was in equilibrium and with water vapor. During exposure, the pressure in the main chamber was 1×10^{-8} mbar. To clean the water from residual dissolved gases, the vessel was evacuated three times before each water dosing by a turbomolecular pump for *ca.* 1 min until the water started to freeze. For the initial cleaning after filling water into the vessel, it was pumped three times for *ca.* 5 min, at which the water in the flask was completely frozen. CO (Linde AG, purity 99.97%) was also dosed *via* a leak valve directly into the UHV chamber at a pressure of 1×10^{-8} mbar. During exposure, the STM tip was retracted from the surface and the STM electronics were switched off in order to avoid influencing the adsorption conditions, *e.g.*, by electric fields from the piezo ceramics. STM imaging of the adsorbate structure was carried out at 95 – 115 K (specified in the respective experiments in the results section) using a W tip. During the STM measurements, the cooling was disconnected, resulting in a slow warm-up of STM and sample. This means that for water adsorption below 100 K, the STM acquisition temperature can be slightly higher, and therefore the STM temperature given for the respective images is also the maximum ‘annealing’ temperature of the adsorbate dosed at 100 K or below. In contrast, for water dosing at 120 K, the temperature during STM imaging was below the dosing temperature. Overall, the procedure for water and CO dosing is identical to that used previously [27], making experimental results and parameters directly comparable.

In order to minimize tip-induced modifications of the water adlayer during STM imaging, we applied tunneling currents and bias voltages not higher than 1 V (with the sample at negative potential) and 30 pA. The sample temperature was measured by a thermocouple spot-welded to the clamps of the STM sample-holder. Analysis and processing of the STM images was done by using the WSXM software (see [28]). For precise determination of the adsorbate structures, the STM was calibrated using the atomic structure of the bare Ru(0001) surface.

3. Results and discussion

3.1. *Temperature dependent structure formation of water adsorbing on Ru (0001)*

In this section, we present STM results of water adsorbate structures formed on Ru(0001) after adsorption at different sample temperatures. A representative STM image recorded after water adsorption at 97 K (nominal exposure 4.5 L) on an extended Ru(0001) terrace (acquisition temperature 102 K) is presented in Fig. 1a. It shows an adsorbate layer with coexistent well-ordered domains and disordered areas in between with different apparent heights, close to a Ru step. In this image, the contrast was optimized to resolve the small height variations in the adlayer, therefore the range of the color scale is limited to display the height variations only on the upper Ru terrace. On this terrace, three different topographic main levels are resolved, with apparent heights of around 0 Å, 0.2 Å and 0.4 Å, as shown in the height profile displayed in Fig. 1b (main levels indicated by dashed lines). A large fraction of the higher domains shows a well-ordered hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (see the higher resolution image in Fig. 1c). However, there are also disordered areas at the same apparent height. The smooth dark areas (0 Å) refer to bare Ru(0001) areas. The intermediate height domains show a disordered surface with no molecular ordering. One possible reason for the different height levels would be multilayer growth, with the presence of monolayer (0.2 Å) and two layer (0.4 Å) covered areas in addition to bare Ru(0001) areas (0 Å). Such multilayer formation has been proposed for very similar water adlayers, observed in STM images measured at 77 K on Ru(0001), after directed dosing with a capillary array doser pointing to the sample at 140 K [24]. Another reason for the two topographic levels could be different apparent heights due to different rotational orientations of the hexagons (difference of 30°), leading to different apparent heights for the symmetrically non-equivalent phases, as it was reported in ref. [16,17]

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