

Kinetics of H₂O Adsorption on Clean and Potassium Precovered Ni(111) Surfaces

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The interaction of water with clean and potassium precovered Ni(111) was studied by X-ray photoelectron spectroscopy (XPS) in combination with an H₂O particle beam for K submonolayer coverages. Equilibrium measurements of the kinetic parameters of the water desorption were performed in the H₂O partial pressure range up to $2 \cdot 10^{-3}$ Pa. At temperatures between 155 K and 175 K the coverage dependent apparent Arrhenius parameters can be obtained. On the clean surface water adsorbs in a bilayer structure and no dissociation of the water molecules was observed, whereas for potassium covered surfaces a dissociation of approximately one water molecule per potassium atom and a more complex adsorption behaviour was observed. The apparent Arrhenius parameters for the water desorption on the clean surface and for various potassium precoverages are presented. The different H₂O layers are discussed and qualitatively compared with temperature programmed desorption (TPD) measurements.

Introduction

The important reaction steps of electrocatalytic processes take place at the solid-liquid interface between a metal electrode and an electrolytic solution. Due to the difficulties of in situ investigation only few data are available to electrochemists. In recent years simulation experiments in ultrahigh vacuum (UHV) have been performed in order to obtain reliable information about the binding properties at these interfaces [1–4]. Generally, the adsorption of water with single crystal surfaces as model catalysts is studied [1,4–6]; in a further step ionic species are coadsorbed to simulate the charging of the interface in the electrochemical double layer [1–3,7].

In the present investigation the adsorption of water on clean and potassium precovered Ni(111) is studied, using XPS as a surface science technique in combination with a water particle beam device which allows exposure of the sample during the acquisition of an XP spectrum.

TPD and UPS experiments on the system H₂O/K/Ni(111) show that the adsorption of potassium prior to water adsorption leads to a dissociation of the water molecules when the potassium precoverage exceeds 0.14 and to a strengthening of the water-substrate bonding of the molecularly adsorbed water [8]. Possible symmetries of the adsorbed layer were derived from UPS spectra [8].

However, difficulties in the interpretation of TPD spectra complicate the availability of coverage dependent kinetic parameters [9]. To overcome this difficulty and to obtain reliable kinetic data, equilibrium measurements of the water desorption were performed in the present work. If the water coverage in a dynamic equilibrium of adsorption and desorption is determined with XPS, direct measurement of the coverage dependence of the kinetic parameters of the water desorption is possible. Further insight into the binding properties of water on pure and potassium precovered Ni(111) is achieved.

Experiment

Experiments were carried out in a standard UHV chamber equipped with a spherical electron analyzer ($r = 127$ mm), an X-ray source with Mg and Al anodes, a LEED system and devices for sample preparation. The analyzer acceptance area on the sample was set to approximately 3×4 mm² by means of electrostatic lenses in the entrance path of the analyzer. The overall resolution in the spectra shown in this paper was 1.4 eV.

Potassium was evaporated from a commercial SAES-Getters filament, which was carefully degassed prior to operation. The potassium layers were prepared by evaporating higher coverages at 180 K and subsequent heating to certain temperatures.

The sample was prepared using standard techniques, and the quality of the surface checked routinely by XPS and LEED.

Ultrapure water (Merck) was used, which was further purified by cycles of freezing, pumping and thawing. Water vapour in the pressure range of 0–4000 Pa is expanded through a heated aperture of 70 μ m diameter positioned approximately 25 mm from the sample surface. The part of the beam not directed onto the sample is cut off by a second aperture of 1 mm diameter and subsequently pumped by a liquid nitrogen cooling trap and a turbomolecular pump. The incident angle of the water beam on the sample was 55° to the surface normal; the distance between the two apertures and the distance to the sample are adjustable and were set to give an area of constant water exposure of approximately 6×5 mm² on the sample. A water partial pressure up to $2 \cdot 10^{-3}$ Pa at the sample surface is reached whilst running an XPS acquisition, during which the overall pressure in the analysis vacuum chamber does not exceed 10^{-7} Pa.

Absolute coverage determination was performed using the O1s and K2p peak areas calibrated with respect to the LEED O-p(2×2) and K-p(2×2) structures, respectively. Coverages are given normalized to the surface atom number. For the equilibrium measurements the analyzer is fixed to a binding energy of 533.2 eV, and the count rate at that energy for different water coverages calibrated versus the O1s peak area.

The H₂O beam intensity was calibrated with respect to the water pressure before expansion by time dependent water uptake curves at 100 K sample temperature, assuming a sticking coefficient of 1.

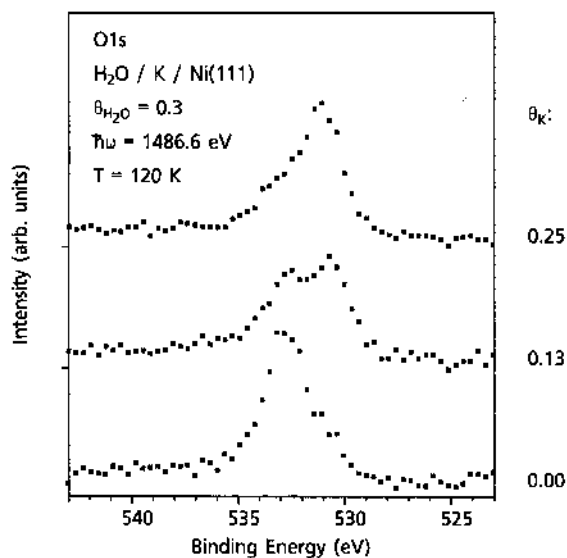


Fig. 1
O1s spectra of 0.3 ML water adsorbed at 120 K on a clean (bottom curve) and on potassium precovered Ni(111) surfaces with potassium coverages of 0.13 (middle curve) and 0.25 (upper curve)

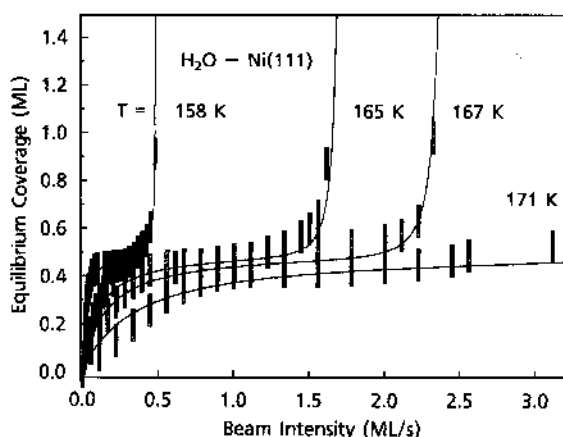


Fig. 2
Equilibrium curves of the water coverage of H₂O/Ni(111) over the H₂O beam intensity at temperatures of 158 K, 165 K, 167 K and 171 K

Results

O1s spectra for a water coverage of 0.3 are shown in Fig. 1 for the clean Ni(111) surface and for potassium precoverages of 0.13 and 0.25. Without preadsorbed potassium only one peak at a binding energy of 533.2 eV is observed. With increasing potassium precoverage, initial water adsorption leads to a peak at 531.0 eV binding energy, which saturates at a coverage approximately equal to the potassium coverage. A second peak at the same binding energy of 533.2 eV as on the clean Ni(111) surface develops when the water coverage is increased. For even higher water coverages, no saturation of this peak can be observed.

In Fig. 2 equilibrium curves are shown for the clean Ni(111) surface at four different temperatures. For a given H₂O flux onto the sample a certain equilibrium coverage adjusts itself, provided that the desorption rate depends upon coverage. The abrupt increase of the curves indicates the onset of zeroth order desorption, which causes a continuous multilayer growth at H₂O fluxes exceeding the coverage-independent desorption rate.

All available evidence indicates that the adsorption of H₂O on metals is not activated and that the sticking coefficient is close to unity and independent of temperature and coverage [5]. Assuming thus an adsorption probability of 1, an Arrhenius plot can be constructed, using the H₂O beam intensities at a fixed water coverage at various temperatures. Coverage dependent kinetic parameters for the H₂O desorption are obtainable this way.

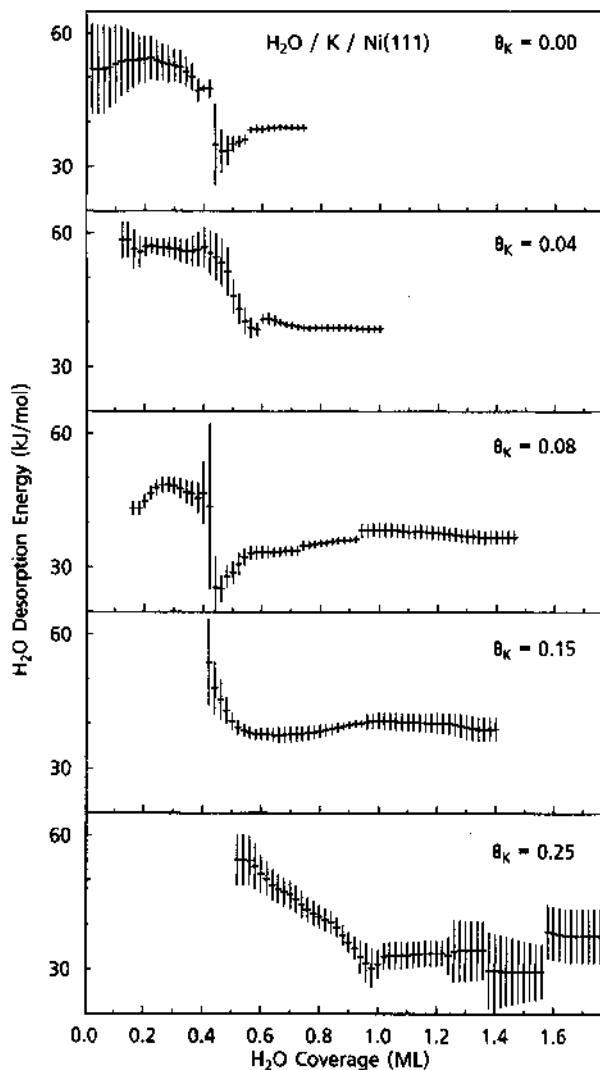


Fig. 3
Apparent H₂O desorption energy for clean and potassium precovered Ni(111) surfaces with potassium coverages of 0.04, 0.08, 0.15 and 0.25, obtained from equilibrium measurements

Results for the desorption energy on the clean Ni(111) surface and for four different potassium precoverages are depicted in Fig. 3. On the clean Ni(111) surface for H₂O coverages up to 0.42 a nearly constant desorption energy of (52 ± 3) kJ/mol was found, which falls abruptly to a value of (38.6 ± 0.3) kJ/mol at water coverages up to $\theta_{\text{H}_2\text{O}} = 0.75$, where zeroth order desorption starts. At potassium coverages of 0.04, 0.08 and 0.15, the same break in the curves at $\theta_{\text{H}_2\text{O}} = 0.42$ is observed as on the clean surface. Similar values as those for the clean surface are found for the desorption energy at $\theta_{\text{H}_2\text{O}} < 0.42$. However, there is an increasing amount of water which does not significantly desorb at the temperatures at which the equilibrium measurements were performed. This amount can be derived from the onset of the energy curves in Fig. 3.

The same desorption energy as on the clean surface is found for all potassium coverages before the onset of zeroth order desorption, which increases to 1.0, 1.5 and 1.4 for $\Theta_K = 0.04, 0.08$ and 0.15, respectively.

At $\Theta_K = 0.25$, the amount of more strongly adsorbed water exceeds 0.42, and the energy curve starts at $\Theta_{H_2O} = 0.5$ with (55 ± 6) kJ/mol, decreases continuously up to $\Theta_{H_2O} = 0.95$ and reaches the same value as at the other K coverages until at $\Theta_{H_2O} = 2.2$ zeroth order desorption starts.

The preexponential factor exhibits without exception a behaviour satisfying the compensation effect with values of $10^{16 \pm 1} \text{ s}^{-1}$ for the initial H₂O layer at the clean surface and $8 \cdot 10^{12 \pm 0.1} \text{ s}^{-1}$ before the onset of zeroth order desorption.

Discussion

The peak at 533.2 eV binding energy in Fig. 1, which does not saturate, can be attributed to molecularly adsorbed water. A binding energy of 531.0 eV is usually assigned to an adsorbed OH species [5, 10, 11]. The peak at that binding energy is visible even at low potassium coverages like 0.04. From that it can be concluded that water adsorbs molecularly on the clean Ni(111) surface, whereas preadsorbed potassium induces a dissociation of approximately one water molecule per potassium atom, which agrees with other studies in which alkali-induced dissociation is observed [7, 8, 12]. The H either desorbs as H₂ or is adsorbed separately. In contradiction to results from TPD and UPS investigations [8], the critical potassium coverage, above which dissociation starts, has to be fixed to be less than 0.04.

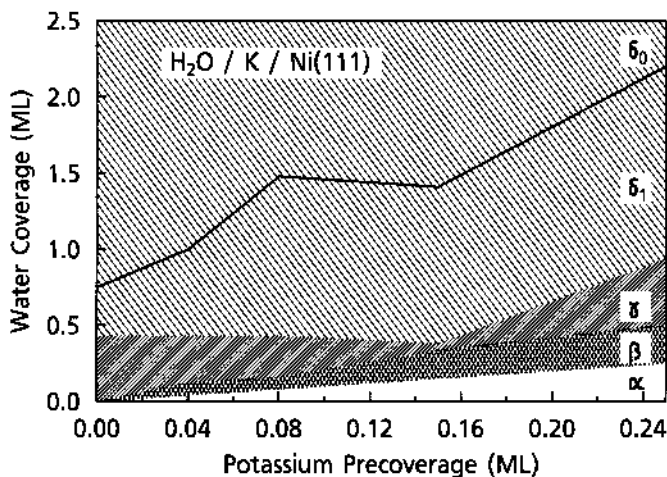


Fig. 4

Portions of adsorbed water of H₂O/K/Ni(111). α : water dissociated to OH upon adsorption, β : more strongly bound molecular water, γ : monolayer water, δ : water exhibiting multilayer desorption parameters, desorbing with first order (δ_1) and zeroth order (δ_0) desorption characteristic

The break at a water coverage of 0.42 is the same for potassium coverages up to 0.15, whereas the onset of the energy curves in Fig. 3 shifts towards higher coverages with increasing potassium coverage: as discussed above, an amount equal to the potassium precoverage is dissociated and stable up to temperatures over 350 K. It will from now

on be called α . An additional amount, which is bound more strongly to the surface than on clean Ni(111), is found on the potassium precovered surface and is denoted by β . The coverages of α and β together manifest themselves in the energy curves of Fig. 3 as a delayed onset, which is caused by a water coverage not desorbing at zero beam intensity at the temperatures at which the equilibrium measurements were performed. Calling the next H₂O layer γ , one can see that the total coverage of α , β and γ is 0.42 and constant up to a potassium coverage of 0.15, where the coverages of α and β alone reach 0.42.

In Fig. 4 the different components of adsorbed water are depicted over the potassium precoverage at five different Θ_K . δ denotes the adsorbed water with a desorption energy of (38.6 ± 0.3) kJ/mol, where δ_1 and δ_0 are the portions with a first and zeroth order desorption characteristic, respectively.

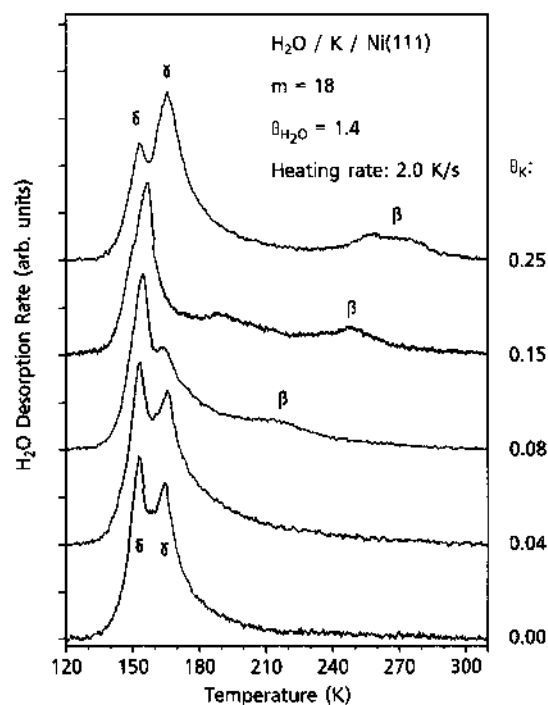


Fig. 5

Thermal desorption spectra of 1.4 ML water adsorbed on the clean Ni(111) surface and for potassium precoverages of 0.04, 0.08, 0.15 and 0.25. The indices β , γ and δ correspond to the nomenclature used in Fig. 4

For potassium precoverages lower than 0.15 the desorption energy of the γ species was found to be (52 ± 3) kJ/mol with a preexponential factor of $10^{16 \pm 1} \text{ s}^{-1}$, independent of potassium coverage. This agrees with values of (57 ± 5) kJ/mol and $10^{17 \pm 1} \text{ s}^{-1}$, as found by Pache et al. from TPD measurements for H₂O/Ni(111) [13]. The values of 38.6 kJ/mol and $8 \cdot 10^{12} \text{ s}^{-1}$ for the multilayer are somewhat lower than the 42–48 kJ/mol and $1 \cdot 10^{13} \text{ s}^{-1}$ generally found in the Literature [5, 14], but agree well with 38 kJ/mol found by He and Norton employing isothermal desorption [15]. An enhanced roughness of the ice-layers produced under

equilibrium conditions may be an explanation for the deviation from the sublimation enthalpy of water (47 kJ/mol).

For a potassium precoverage of 0.25 a new layer develops with desorption parameters similar to the γ layer for lower Θ_K . It is also called γ , though it must not necessarily be the same species. In contrast to the other potassium coverages, the desorption energy shows a decrease with increasing water coverage, indicating lateral interactions or different types of adsorption sites.

Comparing these results with thermal desorption spectra shown in Fig. 5 for a fixed H₂O coverage of 1.4 and identifying the peaks at 153 K and 165 K with δ and γ , respectively, the decrease of the γ -peak up to $\Theta_K = 0.15$ is easily observed and explained by the reduction of the γ layer in favour of α and β . The desorption peak at 165 K reappears at $\Theta_K = 0.25$, indicating the formation of the "new" γ layer at higher potassium coverages.

Species β can be observed as a high temperature desorption state, as indicated in Fig. 5, shifting towards higher temperatures with increasing K coverage. This strong shift and the large width of this peak indicate a complex adsorption behaviour, which complicates the access to the desorption parameters.

As has been demonstrated, combining surface science techniques with a UHV compatible permanent operating water supply provides a method for investigating the kinetic properties of water adsorption. Using this method, different adsorption states of water in H₂O/K/Ni(111) could be distinguished according to their desorption energy. The desorption parameters of the ice multilayer and the preceding water layer could be determined individually and are con-

stant for different Θ_K . A dissociation of H₂O to OH, induced by precovered potassium, was derived from XP spectra.

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