The interaction of water and hydrogen with nickel surfaces
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Summary

As nickel and platinum are in the same group of the periodic table, the Ni(111) and Pt(111) surfaces may be expected to show similar interaction with water and hydrogen. However in this thesis, we show these interactions for Ni(111) are quite different from those of Pt(111). Moreover, our results show that the Ni(111) surface is a unique surface with regards to its chemistry of water and hydrogen.

The experiments described in this thesis were carried out under ultra-high vacuum (UHV) conditions. We used a nickel single crystal surface, Ni(111), as a substrate in our experiments. Two main techniques employed in our study are temperature-programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS).

The interaction of H_2O and D_2O with a bare and hydrogen-saturated Ni(111) surface is studied and compared to Pt(111) in chapter 3. We reported that hydrogen, atomically bound to Ni(111), affects the interaction between this metal surface and water significantly. Whereas a hydrogen-bonded network of water multilayers shows isotopic scrambling without water dissociation at 85 K on the surface, the H-Ni bond is too strong to allow isotope exchange with co-adsorbed water. We expect that the same H-Ni bond strength prevents formation of H_3O^+ or similar species, which have been suggested for Pt(111). In contrast, our data actually suggest that saturating the Ni(111) surface with hydrogen makes the surface hydrophobic, and that multilayered islands of water molecules form at submonolayer coverages.

In chapter 4 we described the surface coverage dependence of the co-adsorption of D and D_2O on the Ni(111) surface. This co-adsorption behavior on Ni(111) shows big differences compared to Pt(111). We show how pre-covering the surface with various amounts of D under UHV conditions affects adsorption and desorption of D_2O. We suggest that the effects of co-adsorption are strongly dependent on D-coverage. In the deuterium pre-coverage range of 0 - 0.3 ML, adsorption of deuterium leaves a fraction of the available surface area bare for D_2O adsorption, which shows no significant changes compared to adsorption on the bare surface. Our data indicates phase segregation of hydrogen and water into islands. At low post-coverages, D_2O forms a two-phase system on the remaining bare surface that shows zero-order desorption kinetics. This two phase system likely consists of

a two-dimensional (2D) solid phase of extended islands of hexamer rings and a 2D water gas phase. Increasing the water post-dose leads at first to 'freezing' of the 2D gas and is followed by formation of ordered, multilayered water islands in between the deuterium islands. For deuterium pre-coverages between 0.3 and 0.5 ML, our data may be interpreted that the water hexamer ring structure, $(D_2O)_6$, required for formation of an ordered multilayer, no longer forms. Instead, more disordered linear and branched chains of water molecules grow in between the extended, hydrophobic deuterium islands. These deuterium islands have a D-atom density in agreement with a (2x2)-2D structure. The disordered water structures adsorbed in between form nucleation sites for growth of 3D water structures, which (partially) spill over the deuterium islands. Loss of regular lateral hydrogen bonding and weakened interaction with the substrate reduces the binding energy of water significantly in this regime and results in lowering of the desorption temperature. At deuterium pre-coverages greater than 0.5 ML, the saturated (2x2)-2D structure mixes with (1x1)-1D patches. The mixed structures are also hydrophobic. On such surfaces, submonolayer doses of water lead to formation of 3D water structures well before wetting the entire hydrogen-covered surface. From the literatures, we find that the Pt(111) surface has not been studied in the same detail for co-adsorption of hydrogen and water. However, the few studies that have investigated this system show no evidence for such complex behavior as we observe on Ni(111).

The identification and characterization of hydroxyl (OH) on the Ni(111) surface is described in chapter 5. We find clear evidence of stretching, bending and translational modes in HREEL spectra that differ significantly from modes observed for H_2O and O on Ni(111). Hydroxyl may be produced from water using two different methods. Annealing of water co-adsorbed with atomic oxygen at 85 K to above 170 K leads to creation of OH with simultaneous desorption of excess water. Pure water layers treated in the same fashion show no dissociation. However, exposure of pure water to 20 eV electrons below 120 K produces OH in the presence of adsorbed H_2O. In combination with temperature-programmed desorption studies, we show that OH groups recombine between 180 and 240 K to form O and immediately desorbing H_2O. The lack of influence of co-adsorbed H_2O at 85 K on hydroxyl's O-H stretching mode indicates that OH does not participate in a

hydrogen-bond network. This is in agreement with the theoretical prediction of an almost vertically bound OH on Ni(111). In comparison to Pt(111), again we observe very different behavior as OH, formed by similar methods, is incorporated in hydrogen-bonded networks of OH and H_2O on Pt(111).

The second part of this thesis starts in chapter 6 with the investigation of the interaction of atomic hydrogen with bare Ni(111). We have demonstrated that dosing atomic hydrogen on Ni(111) at a surface temperature below 90 K leads to molecular hydrogen bound to an ultrathin nickel hydride layer. We suggest that the adsorption of molecular hydrogen is due to reversible roughening associated with formation of the NiH_x layer. However, the roughening is modest and likely consists only of relaxation of nickel atoms normal to the surface. The newly found molecular state of hydrogen persists to 125 K and may present an interesting case to study H_2 reaction and scattering dynamics. Atomic adsorption of hydrogen finds no undisputed equivalent for Pt(111), and the absorption behavior on Pd is also quite different due its exothermicity. For Pd however, the molecularly-bound state and upward surface relaxation have been observed.

In the last chapter of this thesis, chapter 7, the interaction of atomic hydrogen and deuterium with D or H-pre-covered Ni(111) is studied. Our results show a large isotopic effect when reversing the order of the isotopes used in preparing a thin nickel hydride (deuteride) layer, capped by a (nearly-)saturated surface hydrogen (deuterium) layer. Our results also show that atomic D atoms can "hammer" surface-bound H into the subsurface sites, whereas atomic H does not "hammer" surface-bound D into the subsurface sites. The large difference in CIA cross-section for the two isotopes has various consequences. CO desorption traces and surface roughness probed using the elastically scattered intensity of an electron beam suggest that that NiH_x patches bulge upward relative to the remaining flat hydrogen or deuterium-covered Ni(111) surface. Decomposition of the NiH_x patches releases enough energy to desorb co-adsorbed CO.

Summary