The interaction of water and hydrogen with nickel surfaces
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Chapter 1

Introduction

1.1 Water on surfaces

Water is life! It is a precondition for the survival of all known forms of life as well as an indispensable resource for the vast majority of industries and the global economy. It can appear in three states: the liquid state, the solid state (also called ice), and gaseous state (also called water vapor). As a chemical substance, water has a rather simple molecular structure. A single water molecule consists of two hydrogen atoms covalently bonded to an oxygen atom with a chemical formula of H_2O. The angle between the two O-H bonds is 104.45° with a distance of 0.9584 Å between the oxygen and hydrogen atoms. The oxygen atom has a slightly negative charge while the two hydrogen atoms have a slightly positive charge, which makes the water molecule a polar molecule. The different dipoles of each molecule yield an attractive interaction, which makes water molecules mutually attractive.

The hydrogen bond between water molecules is also an important factor that causes them to stick one another. The hydrogen bond is a bond between one electronegative atom and a hydrogen atom covalently bonded to another electronegative atom. A single water molecule has two hydrogen atoms covalently bonded to an oxygen atom (the electronegative atom). Therefore two water molecules can form a hydrogen bond between them. When more molecules are present, more hydrogen bonds are possible. This is because one oxygen atom of a single water molecule has two lone pairs of electrons, each of which can form a hydrogen bond with hydrogen atoms on two other water molecules. This can repeat so that each water molecule is H-bonded with up to four other molecules.

In physics and chemistry, the fundamental understanding of the properties of water has attracted considerable attention. Due to its relevance to industry, scientists in many physical or chemical fields often investigate basic questions concerning the interaction of water with solid surfaces. However, despite extensive studies of water on solid surfaces, our understanding of how water adsorbs on a solid surface, how water desorbs, and how coadsorbates influence water adsorption or desorption still remains limited [1,2].

Depending on the precise physical circumstances, two types of adsorbed water ice exist, amorphous solid water and crystalline ice. Both types are present in nature [3]. Amorphous solid water can be obtained by vapor deposition at a substrate temperature below ~ 130 K under ultra-high vacuum (UHV) conditions [4]. Crystalline ice can be formed by direct vapor deposition above ~130 K or by crystallization of amorphous solid water [5,6]. Investigations of both types formed under UHV conditions contribute to the understanding of the properties of amorphous solid water and crystalline ice in nature.

Many investigations of water adsorbed on solid surfaces are carried out in UHV conditions. In these studies, a single metal crystal is often applied as the substrate. In his recent review, Henderson concluded that these studies generally focus on five broad categories; the electronic structure of adsorbed water, the vibrational properties, the tendency to form local or long-range order, the dynamical properties, and the water-water and water-surface interactions [2]. Research described in this thesis, falls under three of these categories. There are the vibrational properties, the tendency to form local or long-range order, and the water-water and the water-surface interactions.

1.2 Hydrogen on surfaces

Hydrogen is the most abundant chemical element in the universe, constituting roughly 75% of the normal mass. Hydrogen gas is highly flammable and it burns according to the following reaction equation: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) + 572$ kJ (286 kJ/mol). Since the only reaction product is water, hydrogen is considered as a clean energy carrier for the future, especially for mobile applications.

Significant challenges for the use of hydrogen in mobile applications are on-board storage or production of hydrogen. There are many ways to store hydrogen, for example as liquid hydrogen [7]. The method of using metal hydrides is one of the most exciting potential solutions for on-board hydrogen storage. While many metal hydrides can be formed by interaction of hydrogen with pure metals, only few may be applicable for reasons such as the required storage capacity and weight. Thus, studies of metal-hydrogen system are crucial in hydrogen storage research.

Hydrogenation reactions play a very important role in modern industrial processes. Since hydrogenation reactions are catalyzed by metal surfaces, understanding how hydrogen interacts with metals is essential. Also for some metal catalysts, for example Raney Nickel, it is not clear that why they are such good hydrogenation catalysts.

When hydrogen is situated far from a metal surface, the H_2 molecule is considered to be in the gas phase, and there is no interaction between hydrogen and the metal surface. When the hydrogen molecule approaches the metal surface, the molecule can bounce back into the gas phase; or dissociate and a**d**sorb as atomic hydrogen on the metal surface. Dissociation and adsorption on metal surfaces has been studied using theoretical and experimental methods [see e.g. 8-10]. Hydrogen atoms can also be present in the bulk of many metals and diffuse in between interstitial sites. Hydrogen a**b**sorption and diffusion is also a well-studied topic, for example due to its importance in hydrogen embitterment [11-13].

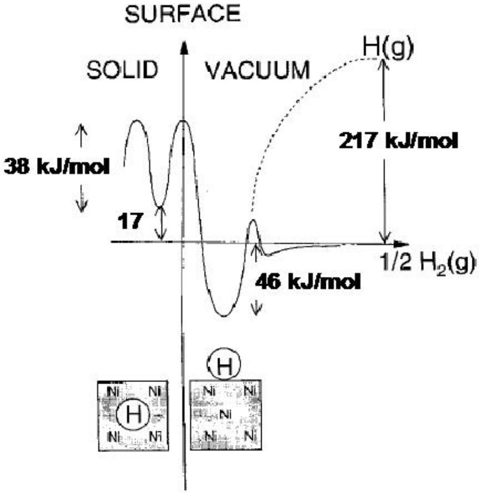

Figure 1.1 Potential energy diagram for the hydrogen-Ni(111) system. Left part of the surface represents a H atom beneath the surface. Right part of the surface represents a H atom or a H_2 molecule at or away from the surface. The figure is adopted from Ref 14.

In this thesis, we will focus on the interaction of hydrogen with the nickel surface. The potential energy diagram for the hydrogen-Ni(111) system is shown in figure 1.1. As can be seen in this diagram, a gas-phase H_2 molecule can dissociate and a**d**sorb on the nickel surface. The diagram also shows a large energy barrier, ~101kJ/mol, to continue from surface sites to subsurface sites. This large energy barrier does not allow H_2 molecules to dissociatively a**b**sorb into subsurface sites under vacuum conditions. However, as shown in figure 1.1, the initial energy level of atomic hydrogen is high enough to overcome the energy barrier to subsurface a**b**sorption. Experiments performed by Ceyer and co-workers show that subsurface hydrogen can be created under UHV conditions by impinging atomic hydrogen onto Ni(111) [14,15]. Interestingly, subsurface hydrogen has been reported to be extremely active in the hydrogenation of simple hydrocarbons [14,16].

1.3 Nickel metal surface

Nickel is a silvery-white metal with atomic number 28. It is hard, ductile, and corrosion-resistant. Nickel belongs to the transition metals and is widely used in many industrial and consumer products, such as magnets, special alloys, and stainless steel. In the laboratory or industrial catalysis, nickel based catalysts are frequently used in hydrogenation reactions.

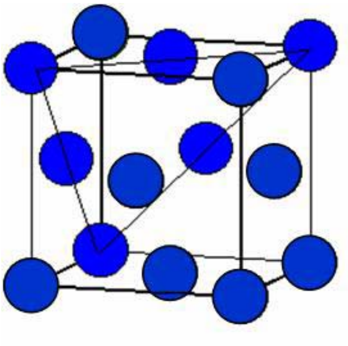

Figure 1.2 The fcc unit cell of nickel.

Nickel has a face-centered cubic (fcc) unit cell, as shown in figure 1.2. The lattice constant of the unit cell is 3.52 Å. In the laboratory, nickel single crystals, such as Ni(111), Ni(110), and Ni(100) are often used to mimic real catalyst surfaces. The most stable nickel single crystal is Ni(111). Figure 1.3 shows the conventional birds-eye view of the Ni(111) surface. The blue circles are the first layer of nickel atoms, while the green circles represent second layer atoms. The common adsorption sites are top sites, bridge sites, and three-fold hollow sites. It is worth to note that there are two types of the three-fold hollow sites, fcc hollow sites and hcp hollows sites. The difference between these two types is that below fcc hollow site there is no second layer nickel atom, while there is a second layer nickel atom below a hcp site. In figure 1.3, sites marked with 1 are fcc hollow sites, whereas sites marked with 2 are hcp hollow sites. The octahedral subsurface sites are located just beneath the fcc hollow sites. Beneath the hcp hollow sites, the hollows are tetrahedral subsurface sites.

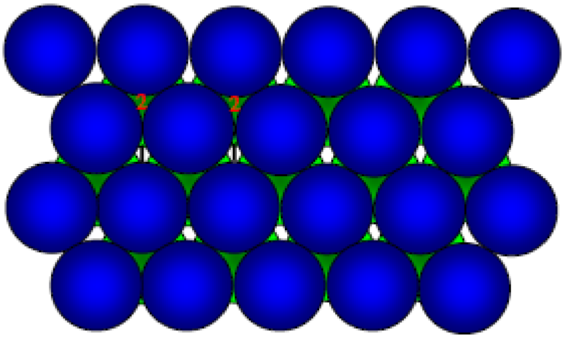

Figure 1.3 Schematic of Ni(111) .

1.4 Structure of this thesis

This thesis *"The interaction of water and hydrogen with nickel surfaces"* investigates two main areas of interest. First, the interaction of water with the bare Ni(111) surface is investigated as well as its co-adsorption behavior with hydrogen and oxygen. Second, we investigate formation and decomposition of nickel hydride (NiH_x) as an extremely thin layer formed on a Ni(111) surface.

The understanding of the interaction of water with the nickel surface is quite important for industry, due to the wide application of nickel as electrode material. However such interactions as well as co-adsorption behaviors of water with hydrogen or oxygen on nickel surfaces remain poorly understand. On the other hand, nickel hydride has found widespread application in hydrogenation processes as Raney nickel and also as a hydrogen storage material in batteries. However, at the atomic level, the formation of nickel hydride from the pure metal and hydrogen is poorly understood. In this thesis we investigate these two areas and describe our results in following chapters.

This thesis is structured as follows: Chapter 2 describes the UHV apparatus and provides some background on the analysis techniques employed including temperature-programmed desorption, high resolution electron energy loss spectroscopy, and Auger electron spectroscopy. The first main area of interest, the interaction of water with the bare Ni(111) surface as well as its co-adsorption behaviour with hydrogen and oxygen, encompasses chapters 3, 4 and 5. Chapter 3 discusses the interaction of H_2O and D_2O with a bare and hydrogen-saturated Ni(111) surface. Surface-coverage dependencies for co-adsorption are explored in Chapter 4 and in chapter 5 we identify and characterize hydroxyl (OH) on the Ni(111) surface. The second main area of interest, formation and decomposition of nickel hydride (NiH_x) on a Ni(111) surface, encompasses chapters 6 and 7. In Chapter 6 we show that molecular hydrogen may bind to a thin film of nickel hydride prepared by impact of atomic hydrogen on the Ni(111) surface. Chapter 7 explores formation and decomposition of the film using isotopic labeling experiments. Here, we show that large isotope effects result from combined abstraction and collision-induced absorption processes when atomic H and D atoms impact on the surface.

1.5 References

[1] P. A. Thiel, and T. E. Madey, *Surf. Sci. Rep.,* 1987, **7**, 211.

[2] M. A. Henderson, *Surf. Sci. Rep.,* 2002, **46**, 5.

[3] P. Ehrenfreund, H. J. Fraser, J. Blum, J. H. E. Cartwright, J. M. Garcia-Ruiz, E. Hadamcik, A. C. Levasseur-Regourd, S. Price, F. Prodi, and A. Sarkissian, *Planet. Space Sci.,* 2003, **51**, 473.

[4] K. P. Stevenson, G. A. Kimmel, Z. Dohnálek, R. S. Smith, and B. D. Kay, *Science,* 1999, **283**, 1505.

[5] D. Chakarov, and B. Kasemo, *Phys. Rev. Lett.,* 1998, **81**, 5181.

[6] E. H. G. Backus, M. L. Grecea, A. W. Kleyn, and M. Bonn, *Phys. Rev. Lett.,* 2004, **92**, 236101.

[7] L. Schlapbach, and A. Züttel, *Nature*, 2001,**414**, 353.

[8] P. Nieto, E. Pijper, D. Barredo, G. Laurent, R. A. Olsen, E. J. Baerends, G. J. Kroes, and D. Farias, *Science*, 2006, **312**, 86.

[9] J. Q. Dai, J. Sheng, and J. Z. H. Zhang, *J. Chem. Phys.,* 1994, **101**, 1555.

[10] I. M. N. Groot, H. Ueta, M. J. T. C. Van der Niet, A. W. Kleyn, and L. B. F. Juurlink, *J. Chem. Phys.,* 2007, **127**, 244701.

[11] G. Alefeld, and J. Völkl, *Hydrogen in Metals 7-Application-Oriented Properties*, 1978, Springer-Verlag, Berlin.

[12] M. V. C. Sastri, B. Viswanathan, and S. S. Murthy, *Metal Hydrides-Fundamentals and Applications*, 1998, Narosa Publishing House, New Delhi.

[13] Y. Fukai, The metal-hydrogen system, 1993, Springer-Verlag, Berlin.

[14] S. T. Ceyer, *Acc. Chem. Res.,* 2001, **34**, 737.

[15] A. D. Johnson, K. J. Maynard, S. P. Daley, Q. Y. Yang, and S. T. Ceyer, *Phys. Rev. Lett.,* 1991, 67, 927.

[16] A. D. Johnson, S. P. Daley, A. L. Utz, and S. T. Ceyer, *Science,* 1992, **257**, 223.

Chapter one