INTERACTIONS OF ENERGETIC HYDROGEN AND DEUTERIUM
WITH LITHIUM FILMS AND NICKEL (110)

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Abstract

Interactions of incident energetic hydrogen (H) and deuterium (D) species (ions and atoms) with surfaces plays a crucial role in a wide range of fields, including plasma-surface interactions in nuclear fusion experiments, plasma-enhanced catalysis, plasma processing of semiconductors, dangling bond passivation, and interstellar molecular hydrogen production. This dissertation presents fundamental surface science studies examining the interactions of energetic H/D species with surfaces related to two applications: plasma-surface interactions of lithium films utilized in nuclear fusion experiments and plasma-enhanced catalysis of dry reforming.

Interactions of energetic H/D species with lithium (Li) films, of interest as coatings for plasma-facing components in nuclear fusion experiments, was investigated. The ability of Li and lithium oxide (Li-O) films to retain H (from irradiation using 500 eV H$_2^+$) was examined over a temperature range of 90-520 K. For both types of films, the total H retention dropped with increasing surface temperature, from 95% at 90 K to 35% at 520 K. The sputtering yields of D ions (from irradiation using 400-1600 eV D$_2^+$) on Li, Li-O and composite Li-C-O films were measured to be ~0.1-0.3, in good agreement with previous simulations and bulk erosion measurements. The time dependence of D retention in pure Li, Li-O and Li-C-O films was also studied after these films were irradiated by 450 eV D$_2^+$ ions. The amount of D retained in both Li and Li-O films at 300 K decreased at the same rate, i.e. by 45% after 16 hours, while the amount of D retained in the Li-C-O film was found to be independent of time for up to three days.

The unique chemistry at metal surfaces of energetic H/D species that are present in plasma-enhanced catalysis was investigated. The D uptake and subsequent thermal
desorption of D$_2$ from a Ni(110) single crystal surface were measured using incident gaseous D$_2$ molecules, D atoms, and D$_2^+$ ions. Molecular D$_2$ exposures on Ni(110) at 90 K formed D adatoms at the surface, and did not populate subsurface D binding states under ultrahigh vacuum (UHV) conditions. In contrast, such subsurface states of Ni(110) are readily populated at 90 K by incident D atoms and D$_2^+$ ions. The reactivity of these various sorbed D states was also studied for the hydrogenation of subsequently adsorbed carbon monoxide (CO) on Ni(110) over the temperature range of 100 – 600 K under UHV conditions using preadsorbed surface D and subsurface D. Related experiments were conducted using D atoms and D$_2^+$ ions incident on preadsorbed CO. Surface-bound D adatoms did not react with coadsorbed CO in temperature programmed desorption (TPD) measurements. In contrast, subsurface D formed by incident D atoms or D$_2^+$ ions can hydrogenate post-adsorbed CO in subsequent TPD measurements to form formaldehyde (CD$_2$O) and methanol (CD$_3$OD). D atoms and D$_2^+$ ions incident on preadsorbed CO were less reactive than subsurface D for the hydrogenation of CO on the Ni(110) surface.
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Chapter 1. Introduction

The interaction of hydrogen with metal surfaces is an important topic within the field of surface science. A significant number of earlier studies [1] were motivated by the fundamental role of hydrogen’s interactions with metal surfaces in various heterogeneous catalytic reactions, such as ammonia synthesis and Fischer-Tropsch reactions. More recently, studies have been motivated by hydrogen’s promising potential as a clean energy source, and as such, its interactions with metals is important in technologies including fuel cells and electrolysis. Consequently, surface science studies of the interactions of molecular hydrogen, H₂, with metal surfaces are numerous.

Energetic hydrogen species, namely ions and atoms, present another interesting perspective. The high energy nature of these species allows them to access unique physical and chemical processes that molecular hydrogen cannot. The interaction of incident energetic hydrogen (H) and deuterium (D) species with surfaces play a crucial role in a wide range of fields, including plasma-surface interactions in nuclear fusion experiments [2][3], plasma-catalytic dry reforming [4][5], plasma processing of semiconductors [6]-[8], dangling bond passivation [9] and interstellar molecular hydrogen production [10][11]. These applications provide strong motivation for studies of energetic H/D species at many surfaces.

This dissertation presents fundamental surface science studies examining the interaction of energetic H/D species with surfaces related to two of the aforementioned applications: plasma-surface interactions in nuclear fusion experiments and plasma-catalytic dry reforming.
1.1. Plasma-surface interactions in tokamaks

1.1.1. Tokamaks and fusion

A tokamak is a type of magnetic plasma confinement device designed to produce thermal energy by controlled nuclear fusion reactions [12]. In nuclear fusion, hydrogen isotopes deuterium (D) and tritium (T) react to produce an alpha particle (3.5 MeV) and a neutron (14.1 keV) [13]. In order for this reaction to occur, D and T must be heated to the 10-100 keV range, where the reaction cross section becomes significant as the kinetic energy overcomes the repulsive electrostatic force between the nuclei.

Figure 1.1: Schematic drawing of a tokamak showing a simplified view of the magnetic coils and a cutaway view of the plasma chamber. Adapted from [12].

At such high temperatures, D and T exist in the form of plasma, an ionized gas consisting of positive ions and free electrons. No material container can withstand such high temperatures, and instead, magnetic confinement devices, known as tokamaks, are
typically employed. Inside a tokamak, plasma ions and electrons are confined within a torus-shaped vacuum chamber by the magnetic field generated from the magnetic coils, as depicted schematically in Figure 1.1. This configuration isolates the very hot plasma from the relatively cold chamber walls.

1.1.2. Plasma-surface interactions

However, the current magnetic field confinement technology is not perfect [2] and some energetic ions escape magnetic confinement and along with energetic atoms interact with the surfaces surrounding the plasma. The materials of these surfaces are referred to as plasma facing components (PFCs) and the processes that occur between PFCs and the plasma are collectively called plasma-surface interactions (PSI) or plasma-materials interactions (PMI). A schematic summary of the PSI processes is presented in Figure 1.2. As can be seen, PSI is very complicated due to many processes occurring simultaneously [15]. Two important processes shall be discussed in more detail.

First, as an incident ion collides with a surface, momentum transfer can lead to the ejection of a surface atom. This is known as physical sputtering, which causes a large source of impurities in the plasma. The presence of impurities drains energy from the plasma through a process known as line radiation, which increases with increasing atomic number Z of the impurities [1][16]. This leads to a cooling effect on the plasma, which lowers plasma performance.
Second, energetic fusion fuel ions (D/T) can implant within PFCs and recycle back into the plasma through recombinative desorption. Recycling effectively replaces hot D/T ions with cold D/T molecules at the plasma-wall interface. This causes a temperature gradient from the core to edge plasma, which cools the plasma and induces plasma instabilities [17]. The effect of recycling on plasma temperature is demonstrated in Figure 1.3, in which the electron temperature is plotted as a proxy for plasma temperature against radial distance from the tokamak wall with different wall recycling coefficients $R_w$. Figure 1.3 shows that reducing the recycling coefficient increases the electron temperature at the wall, thus minimizing the temperature gradient from core to edge plasma.
1.1.3. Lithium conditioning of plasma-facing components

Lithium is a strong candidate for PFC coatings. A lithium coating on key PFCs (historically typically carbon but moving to tungsten or other high melting point materials) may mitigate high Z PFC sputtering into the plasma. As the solid element with lowest Z at room temperature, lithium does not contribute significantly to line radiation even when sputtered into the plasma. Furthermore, since lithium is highly reactive, it is also a good pump for D/T, so D/T is trapped in the lithiated wall and not recycled back into the plasma, thus reducing wall recycling.

Lithium conditioning of PFCs has been tested in major magnetic confinement fusion devices, such as the National Spherical Torus Experiment (NSTX) [20], tokamak T-11M [21], Frascati Tokamak Upgrade (FTU) [22], Experimental Advanced
Superconducting Tokamak (EAST) [23], Tokamak Fusion Test Reactor (TFTR) [24] and Lithium Tokamak Experiment (LTX) [25]. Results showed marked improvement on plasma performance including enhanced confinement, increased stability, lower recycling and impurity suppression [26]-[30].

An example of improved plasma performance with lithium conditioning of PFCs is shown in Figure 1.4, in which the plasma current is plotted against time for two separate plasma shots in LTX, one with and the other without lithium conditioning of the stainless steel (SS) reactor wall. With lithium conditioning, both the maximum plasma current and the duration for which the plasma is sustained increased.

![Figure 1.4](image.png)

Figure 1.4: Effect of lithium conditioning of PFCs on plasma current. Taken from [31].

Some of the critical questions that arise from more than a decade of work on lithium conditioning of PFCs are as follows. What is the key mechanism(s) for H/D/T retention in lithium [32]? How do impurities affect H/D/T retention in lithium [33]-[35]? What
happens to H/D/T retained in lithium over time [36][37]? What is the temperature range for viable lithium-based PFCs [38]? This dissertation research addresses these questions.

1.2. Plasma-catalytic dry reforming

In this section, another application in which energetic hydrogen species may play a crucial role, plasma-catalysis and specifically plasma-catalytic dry reforming, will be discussed.

1.2.1. Dry reforming of methane

A reaction of great current interest for alternative fuels is the dry reforming of methane (CH\textsubscript{4}) (DRM) with carbon dioxide (CO\textsubscript{2}) through the following highly endothermic reaction requiring 247 kJ/mol [39]:

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2
\]  

(1)

DRM is traditionally carried out at high temperature in the presence of heterogeneous catalysts [40]-[45]. Unfortunately, this process is plagued with carbon deposition on catalyst surfaces, which leads to catalyst deactivation [46]-[49]. Furthermore, due to the high pressure and temperature conditions, the reactor is large and expensive, adding to capital costs.

Since the early 1990s, applications of plasma technology to hydrocarbon reforming has attracted increasing attention due to the fast on/off time performance and compatibility for a broad range of hydrocarbons [50]. Adding to the appeal of plasma is
the recent investigations into non-equilibrium plasma, in which the electrons are at much higher energy than the ions in the plasma. In such cases, while the overall gas kinetic temperature remains low, the electrons can achieve very high electron temperatures of 10,000–100,000 K (1–10 eV), which is sufficient to breakdown inert molecules to produce reactive species such as radicals and ionic fragments. These reactive species in such plasma could overcome kinetic barriers in DRM reactions and enable kinetically unfavorable reactions to occur at low temperature and atmospheric pressure [51]-[53]. However, due to the presence of energetic ions and a variety of chemically active species, the reaction selectivity obtained with plasma technologies is generally lower than that achieved with the traditional catalytic reforming processes. This is one of the most important bottlenecks needed to be resolved for further industrial application [50].

1.2.2. Plasma-catalytic dry reforming of methane with nickel catalysts

Since the traditional catalytic dry reforming approach suffers from the requirement of high temperature and pressure, and the plasma approach suffers from a lack of selectivity, it is of interest to integrate these two approaches and capitalize on the strengths of both approaches. The concept is to use plasma to produce reactive species on the surface of the catalyst, thus allowing the reaction to proceed at milder conditions.

Hammer et al. observed that the selectivity to CO increased when plasma is integrated into the methane-steam-reforming reaction with a commercial Ni catalyst over 700 K [54]. Cheng et al. reported that by placing a Ni/Al₂O₃ catalyst within the discharge zone of a plasma, the resulting DRM conversion was greater than the summed
conversions of only using plasma and only using catalyst, especially when the temperature was above 673 K. The selectivity to CO and H\textsubscript{2} reached nearly 95\% at 573 K. However, a temperature of 773 K was needed to achieve the same selectivity if using only catalyst [55]. Tu and Whitehead showed that conversion, selectivity, and energy efficiency of the DRM reaction increased when a Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was added to pure plasma reforming [56]. Importantly, there exists an optimal temperature for the synergistic effect between plasma and catalyst [54]-[59].

Traditionally, DRM has been studied with a number of catalysts – Ni, Co, Rh, Ru, Pt, Pd, etc., in their metal or oxide form, with and without a support. Among them, Ni, with the advantage of low cost, high abundance, and high resistance to carbon deposition, shows much potential.

In this dissertation research, the Ni(110) surface was chosen as a model catalyst. The Ni(110) facet is selected because it has the highest sticking coefficient, 1x10\textsuperscript{-7} at 500 K, for methane, compared to Ni(100) and (111) surfaces, with sticking coefficients of 6x10\textsuperscript{-8} and 1x10\textsuperscript{-8} at 500 K, respectively [60]. Furthermore, it has the unique ability for CO\textsubscript{2} activation. CO\textsubscript{2} weakly chemisorbs on Ni(110) at 90 K and undergoes a geometrical distortion, triggered by electron transfer from the substrate to the molecule. This leads to the formation of a partially negatively charged, bent CO\textsubscript{2}\textsuperscript{5-} adsorbate, which is more reactive [61].
1.2.3. Reaction mechanisms of hydrogen at metal surfaces

Understanding the reason for plasma and catalyst synergism is important for improving plasma catalysis. To do so, one essential step is to investigate the reaction mechanism between energetic species in the plasma and their interactions with the catalyst surface (as well as adsorbed species on the surface). Despite a good understanding of the overall thermodynamics of plasma catalytic DRM, little is known about the fundamental reaction mechanisms involved in this process [62][63].

Surface reactions are usually classified into three major mechanisms: Langmuir-Hinshelwood (LH) mechanism, Eley-Rideal (ER) mechanism, and the Hot Atom (HA) mechanism.

The most common mechanism, the LH mechanism, requires that both reactants are adsorbed on the surface prior to collision and subsequent formation of products [64][65]. This mechanism is considered indirect as the chemisorbed reactants must come to thermal equilibrium with the surface [66]. A classic example of this is the catalytic oxidation of CO to CO$_2$ on Pd(111), in which a chemisorbed CO molecule combines with an oxygen adatom from dissociative O$_2$ adsorption to produce CO$_2$ [67].

The ER reaction involves the direct impingement of a gas phase species on an adsorbed species, resulting in the immediate formation of the product, which can either remain adsorbed on the surface or escape into the gas phase [68][69]. In the ER mechanism, since the incident reactant does not accommodate with the surface, it does not give up completely its incident energy, and consequently, the products of an ER reaction can be out of equilibrium with the surface temperature [70]. Molecules do not
readily undergo ER reactions. However, energetic species such as ions and atoms are much more likely to undergo ER or HA reaction mechanisms [64].

In the HA mechanism, the incident species approaching the metal surface becomes trapped in a deep adsorption potential well, but are not energetically accommodated and therefore can transfer part of their kinetic energy normal to the surface into motion parallel to the surface, and so moves along the surface as a “hot” atom [71]. The hot atom travels across the surface until it either (i) dissipates enough of its energy so that it sticks on an empty site, or (ii) reacts with an adsorbed species.

Energetic hydrogen ions and atoms present in plasma can access a fourth reaction pathway that is less well-known than the three mechanisms discussed above: the subsurface reaction pathway. The ability to form subsurface hydrogen, hydrogen absorbed in the bulk instead of adsorbed on the surface, has been demonstrated on a number of surfaces [72]-[79] It is speculated that subsurface hydrogen has a higher reactivity than surface hydrogen [80]. This is because subsurface hydrogen has high potential energy compared to surface bound hydrogen [81], as can be seen in Figure 1.5.
1.3. Research objectives

In this dissertation, I shall present fundamental surface science studies of interactions of highly energetic hydrogen species with lithium films and model catalyst surfaces in order to address outstanding research questions raised in several applications that are organized into the following chapters.
In chapter 3, I address the effect of oxygen impurities and temperature on hydrogen retention cross sections in lithium films. The objective is to first check whether oxygen-contaminated lithium coatings of PFCs will have a lower hydrogen retention cross section compared to pure lithium, and secondly to determine a suitable temperature range for the application of lithium on PFCs.

In chapter 4, I look at the sputtering cross section of lithium and lithium compounds by energetic hydrogen and helium ions. The objective is to develop an understanding of the robustness of lithium under ion bombardment. The result can provide guidance to how long a lithium coating on PFCs can last under fusion experiment conditions.

In chapter 5, I examine the time-dependent hydrogen retention capabilities of lithium and lithium compound films. The objective is to understand for how long the hydrogen will be trapped within lithium-conditioned PFCs. This information is crucial for future long-pulse plasma conditions because of nuclear safety regulations related to tritium inventory in tokamaks.

In chapter 6, the formation of subsurface hydrogen in Ni(110) is examined. The objective of this work is to first study how subsurface hydrogen can be generated in Ni(110) and secondly to compare the behavior of subsurface hydrogen in Ni(110) compared to other metal surfaces.

In chapter 7, I expand the work in chapter 6 and investigate the hydrogenation of adsorbed CO on Ni(110) by subsurface hydrogen. The aim is to establish the subsurface
reaction pathway as a viable (or even primary) reaction mechanism for the reaction between energetic hydrogen species and adsorbed molecules.

1.4. References


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Chapter 2. Experimental methods

2.1. Description of UHV chamber

The experiments in this thesis were performed in a three-level, stainless-steel ultrahigh vacuum (UHV) chamber located in the Surface Science and Technology Laboratory (SSTL) at the Princeton Plasma Physics Laboratory (PPPL). A schematic of the chamber is shown in Figure 2.1. The chamber was pumped primarily by using two 220 L/s Perkin Elmer (Differential/Noble Diode) ion pumps and a titanium sublimation pump (TSP) to maintain a base pressure of $2 \times 10^{-10}$ Torr. A 170 L/s turbomolecular pump (Pfeiffer Balzers, Model TPU 170), backed up by a rotary vane mechanical pump (CTI Alcatel 2008A), was also attached to the chamber and used primarily for pumping down the system after venting to atmosphere. A gas handling system, consisting of a manifold of stainless steel tubing and Nupro valves connected by VCR fittings, and pumped by a rotary vane vacuum pump (CTI Alcatel 2012A), was used to introduce high purity gases, supplied by lecture bottles, into the UHV chamber through precision variable leak valves.

The chamber is equipped with optics and instrumentation for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). LEED was performed with a PHI 15-120 LEED optics. AES was performed with a PHI 15-255G double-pass cylindrical mirror analyzer (CMA). XPS was performed using the CMA with a dual anode PHI 04-548 X-ray source. TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer (QMS) with the shield nozzle located 1 mm from the sample. Ions were produced with a PHI 04-303A differentially pumped ion gun with an adjustable ion
energy from 0-5 keV. The ion gun was pumped by a turbomolecular pump (Pfeiffer Balzers, Model TPU 170) and was equipped with two leak valves. Atoms were produced from a custom-built atom doser, similar to a design described by Engel and Rieder [1].

Figure 2.1: A schematic of the UHV chamber used for experiments described in this dissertation. An X-ray source and ion gun are installed at the back of the chamber. Image courtesy of B.E. Koel.

2.2. Temperature programmed desorption

Temperature programmed desorption (TPD) is a common method used to investigate the chemical composition of desorbed molecules, surface adsorbate coverage, and desorption activation energies. In a typical TPD experiment, molecules are exposed to a cooled sample surface for them to physisorb or chemisorb onto the surface. Subsequently, the sample temperature is increased linearly with time and the partial
pressures of the desorbing species are monitored by a QMS. The resulting QMS signals, which are proportional to the desorption rates of the monitored species, are usually plotted against temperature.

The desorption rate can be expressed in a general form by the Polanyi-Wigner equation:

\[-\frac{d\Theta}{dt} = v_n \Theta^n \exp\left(-\frac{E_d}{RT}\right)\]  

(2.1)

where \(\Theta\) is the adsorbate coverage, \(v\) is the pre-exponential factor, \(n\) is the kinetic order of desorption, \(E_d\) is the desorption activation energy, \(R\) is the ideal gas constant and \(T\) is the temperature of the sample [2]. The coverage and desorption rate of the adsorbed molecules as well as the surface temperature as a function of time in a typical TPD experiment are shown in Figure 2.2.

A set of TPD spectra plotting MS signal against temperature for increasing exposure can be used to obtain desorption kinetics data, as shown in Figure 2.3. A zeroth order desorption is usually associated with multilayer desorption. A first order desorption is usually associated with atomic or simple molecular desorption. A second order desorption is usually associated with recombinative desorption.
Figure 2.2: In a typical TPD experiment, the surface temperature is ramped linearly with time. This causes the adsorbed species to desorb as molecules from the surface as described by the desorption rate equation. As the molecules desorb, the surface coverage of the surface species decreases. Image courtesy of L. Buzi.

Figure 2.3: TPD spectra showing zeroth, first, and second order desorption kinetics.

Adapted from [3].
2.3. Auger electron spectroscopy

Auger electron spectroscopy (AES) is a practical and straightforward characterization technique for probing the elemental composition at the surface of a solid material [4]. It is a sensitive technique able to evaluate the surface composition over the probe depth of a few nanometers with a sensitivity of 0.1 atomic %. High energy (typically 3 or 5 keV) electron bombardment of atoms cause ionization to create a core hole, that eventually decays via a 2-electron non-radiative internal rearrangement by filling of the hole with an electron from a higher energy level simultaneously releasing this energy by emission of a second electron. This emitted electron, the Auger electron, from the sample has a kinetic energy characteristic of the parent atom. The Auger process is illustrated in Figure 2.4. The Auger electrons are detected using a double-pass CMA in our chamber, but a simpler single-pass CMA is shown in Figure 2.5. Due to the unique core level energies of each element, elemental identification of the sample surface can be achieved.

An AES spectrum can be represented as a plot of the number of electrons detected, \( N(E) \), as a function of electron kinetic energy, \( E \). However, due to the large background arising from secondary and backscattered electrons, the differentiated signal, \( \frac{dN(E)}{dE} \), is usually plotted as a function of \( E \) [5].
Figure 2.4: The Auger process. a) An incident electron (shown in red) causes the ejection of a core electron (shown in black), creating a core hole. b) An outer shell electron (shown in red) fills the core hole and the excess energy generated ejects another outer shell electron (shown in black). The ejected electron is known as an Auger electron. Taken from [3].

Figure 2.5: Schematic of a single pass CMA.
2.4. Low energy electron diffraction

Low energy electron diffraction (LEED) is a technique used for the determination of surface structures [3]. In LEED, a beam of electrons with a well-defined low energy (typically in the range 20-200 eV) is incident normal to the sample. The sample itself must be a single crystal with a well-ordered surface structure in order to generate a back-scattered electron diffraction pattern as spots on a phosphorescent screen. Only the elastically-scattered electrons contribute to the diffraction pattern. The lower energy (secondary) electrons are removed by energy-filtering grids placed in front of a phosphorescent screen. The relative position of the spots on the screen can be used to determine the surface crystallographic structure.

Figure 2.6: LEED pattern of Ni(110).
2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative surface-sensitive spectroscopic technique that measures the elemental composition and oxidation state of the elements that exist within the top 10 nm of the material being analyzed. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of ejected core electrons that escape from the material surface. The basic principle is represented by the following equation [4]:

\[ E_B = E_{hv} - E_K - \Phi_{sp} \]  

(2.2)

where \( E_B \) is the binding energy of the electron, \( E_{hv} \) is the energy of the incident X-ray, \( E_K \) is the kinetic energy of the ejected photoelectron, and \( \Phi_{sp} \) is the work function of the spectrometer.

Since the binding energy of the electron is characteristic of the ionized atom, XPS allows for identification of the elements in the near surface region. Small chemical shifts of core-level binding energies reflect the oxidation state and chemical bonding of the specific element.

2.6. References


Chapter 3. Hydrogen retention in lithium and lithium oxide films

This chapter is an adaptation of a published article.


This chapter describes the outcome of a collaborative study involving experimental work conducted in Princeton University and simulation performed in Northwestern University. I performed all the experiments described in this chapter while the simulations were done by Wei Lin at Northwestern University. This chapter includes both my experimental work and the simulations done to facilitate presentation of concrete results.

In this chapter, studies of the hydrogen retention capabilities of lithium and lithium oxide thin films at different temperatures are presented. This work addresses two important questions:

(1) Is oxidized lithium still capable of retaining hydrogen?

(2) What is a suitable temperature range for using lithium as a plasma facing material in fusion experiments?

3.1. Introduction

Li conditioning of plasma-facing components (PFCs) has improved plasma performance with energy confinement and lowered H recycling in magnetic fusion devices [1-4] and suppressed edge-localized modes (ELMs) in NSTX [5,6]. Li
conditioning of the NSTX divertor resulted in significant reduction (50%) of the heat load due to enhanced radiation [7,8]. These effects may be due in part to lithium's efficiency in binding H isotopes, thereby increasing the H retention and lowering the recycling of these species.

Accordingly, an understanding of H retention mechanisms and parameterization of H uptake in Li is needed for future applications of Li in high heat-flux and long-pulse duration machines, as well as for H storage applications [9-11]. Such information is also needed for Li2O because at typical base pressures of 1x10^8 Torr, which is not uncommon in tokamaks, Li2O can form rapidly (2Li + H2O → Li2O + H2 [12]). For instance, in NSTX the walls were exposed to 100-600 L (1 L = 1x10^6 Torr•sec) of water vapor in between the plasma shots, during which the Li oxidation occurred. According to the residual gas analysis, the gas consisted of 77% of hydrogenic species (mass 2, 3, 4) and 18% of water vapor (mass 17, 18, 19, 20) [13]. Li oxidation has also been observed in in-vacuo measurements of Li-coated samples of PFCs in LTX using the Materials Analysis Particle Probe (MAPP) [14-16]. The problem will continue to be important for the high-Z PFC phase of operation in NSTX-U in which Li2O is also quickly formed, during Li evaporation, under typical water partial pressure conditions in the 1x10^9 Torr range.

Several studies have addressed the mechanisms of H retention in Li. Baldwin et al. [17] measured deuterium (D) retention in Li as a function of ion fluence and reported full uptake of D until volumetric conversion to LiD. Ion fluences beyond saturation led to a switch from the low to the high recycling regime (i.e. high retention to low retention), independent of the Li temperature (523-673 K). Taylor et al. [18,19], after analyzing NSTX tiles and performing ex-situ experiments on ATJ graphite samples, reported D
bonding with Li after Li interacted with carbon and oxygen. Krstic et al. demonstrated that O concentrations could increase up to 40 at% with significant D fluence, which was later reconfirmed by experiments by Taylor et al. [20]. Using quantum classical molecular dynamics calculations (QCMD) on lithiated graphite surfaces, Krstic et al. [21,22] showed that D is bound to O containing complexes rather than to Li, thus promoting oxygen as having a main role in D retention. MAPP results on LTX indicated that it is not crucial to have just elemental Li to bind H, and Li oxide could also act as a binding agent [16]. However, in order to gain a better understanding and evaluate Li oxide's ability to reduce recycling, the efficiency of Li oxide compared to elemental Li in retaining H needs further investigation.

This work is built upon previous experiments where an ultrathin (3 monolayer, ML) Li film was deposited on a polycrystalline TZM sample and irradiated with D ions [23]. Release of oxygen from TZM and subsequent oxidation of Li films during TPD, as well as the complex Li-TZM interface, introduced uncertainties into interpreting those experiments. In order to address these issues, we have conducted a systematic study in which five to seven times thicker Li films were deposited on a nickel (Ni) single crystal. The purity of the Li film was checked with auger electron spectroscopy (AES). Modeling of the results is done by Molecular Dynamics (MD) using REAXFF bond-order potentials [24,25], with correction for dynamical polarization effects due to difference in Li, H and O electronegativities by Electronegativity Equalization Method (EEM) [26,27].
3.2. Experimental methods

3.2.1. Experimental Setup

All experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a $2 \times 10^{10}$ Torr base pressure. Low energy electron diffraction (LEED) was performed by using PHI 15-120 LEED optics. AES was done using a PHI 15-255G double-pass cylindrical mirror analyzer (CMA). TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer (QMS), with the shield nozzle located 1 mm from the sample, using a heating rate of 4 K/s. A K-type thermocouple (chromel-alumel) was spot-welded directly on the sample to monitor the temperature.

The Ni(110) single crystal (8 mm square, $\pm 0.5^\circ$ orientation) sample was spot-welded onto tantalum (Ta) wires used for resistive heating. The crystal was cleaned using cycles of 1.5 keV Ar$^+$ ion sputtering and annealing in vacuum at 1100 K. Oxidation in $4 \times 10^8$ Torr O$_2$ with the sample at 1000 K was used to eliminate residual carbon, and reduction in $4 \times 10^8$ Torr H$_2$ with the sample at 1000 K was used to eliminate residual oxygen. Good surface order was confirmed with LEED. Surface purity was checked with AES to ensure carbon and oxygen concentrations were below 1%. The quality of the Ni(110) surface was also confirmed to be good using the position and shape of the H$_2$ desorption peaks in TPD [28]. In these experiments, we used a Ni (110) single crystal as a substrate to avoid effects due to grain boundaries, intrinsic defects, and impurities diffusing to the surface. Moreover, due to the low solubility of alkali metals in Ni, Li and Ni are immiscible, and thus do not form either bulk alloys or two-dimensional surface alloys [9,29].
Li dosing was performed with a commercial Li metal dispenser (Li/NF/7.3/17/FT, SAES Group) by thermal evaporation onto the Ni substrate. H$_2^+$ ions were produced in a differentially pumped ion gun (PHI 04-303 A) with adjustable ion energy from 0 to 5 keV, and a liquid nitrogen trap was used in the H$_2$ gas line to mitigate H$_2$O contamination. H$_2$ gas (Praxair, 99.999%) and O$_2$ gas (Praxair, 99.995%) was introduced into the chamber following a liquid nitrogen trap and using a high precision variable leak valve. Hydrogen, rather than deuterium, was used in these experiments for convenience and H has the same chemistry as D. After surface preparation, Li films were exposed to a 500 eV H$_2^+$ ion beam, which is nominally composed of 90% H$_2^+$ and 10% H$^+$ [30]. The H$_2^+$ flux was defocused over the surface and the current measured on the sample was 1.74 mA. The H$_2$ pressure in the chamber during H$_2^+$ irradiation was 4x10$^8$ Torr and the total exposure time was 120 s. These conditions provided a total fluence of 4x10$^{15}$ H$^+$cm$^{-2}$. The Li areal density was ~3x10$^{15}$ Li cm$^{-2}$, as discussed later.

3.2.2. Computational approach

We simulated these experiments by using Molecular Dynamics. Amorphous target surfaces of pure Li and Li$_2$O were prepared for a set of temperature values T (90, 300, 400, 500, and 600 K), following the procedure in Refs. [21,22] for each temperature. Computational cells of about 2000 atoms were used. These amorphous cells were created initially at 300 K, one with random distribution of lithium atoms, and another one with a predefined random distribution of 33% O and 67% of Li atoms. These cells were energy optimized in a succession of heating (1000 K max) and annealing processes, and finally thermalized to a desired temperature using a Langevin thermostat with time constant of
100 fs. The final numbers of atoms in the prepared cells at various temperatures are shown in Table 3.1.

Table 3.1. Atomic content for Li and Li$_2$O target surfaces at various temperatures after energy optimization and thermalization processes.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>90</th>
<th>305</th>
<th>400</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li atoms</td>
<td>1340</td>
<td>1340</td>
<td>1335</td>
<td>1329</td>
<td>1320</td>
</tr>
<tr>
<td>O atoms</td>
<td>660</td>
<td>660</td>
<td>658</td>
<td>656</td>
<td>658</td>
</tr>
</tbody>
</table>

Periodic boundary conditions were applied in the x-y directions to simulate an infinite surface slab, with D impact in the z-direction. The lateral dimensions of the cells were 3.6 nm in z direction and about 3.4 nm in x and y directions for both surfaces (Figure 3.1). The cell depth of 3.6 nm is sufficient to prevent penetration of the D atoms to the cell bottom boundary, thus avoiding artificial reflections.

The atomistic simulations were performed by MD, using Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [31] with Reactive Force Field (ReaxFF) Bond Order (BO) potential [24,25,32], and corrections for dynamic atom charge effects by semi-empirical EEM [26,27]. The classical ReaxFF potentials used for Li, O, D were verified in previous computations [33] of retention and sputtering of Li-C-O-D surfaces by Quantum-Classical Molecular Dynamics (QCMD), using Self Consistent Charge Tight Binding Density Functional Theory (SCC-DFTB) [34]. The ReaxFF potentials implemented in LAMMPS are able to model the dynamics of breaking and forming of chemical bonds [24,32], as well as to calculate the dynamic changes in
charges of the atoms in the system with the change of atomic coordinates using the Electronegativity Equalization Method [26,27]. The latter is important in the presence of mutually polarizable materials with very different electronegativities, such as Li (0.94) and O (3.4), while the H electronegativity (2.2) is in the middle.

Figure 3.1. a) Li system (2000 lithium atoms), b) Li2O system: 33% of O (660 atoms) and 67% of Li (1340 atoms). Green and red symbols represent Li and O, respectively.

The prepared computational cells, with various atomic contents and at various temperatures, were bombarded by $N = 5040$ independent 10 eV D atoms, with trajectories starting 1 nm at random location above the surface, in the direction orthogonal to the surface. This large number of trajectories led to the adequate statistics of H retention probability and was done at supercomputing facilities using “embarrassing parallelization”. If the number of D atoms retained in the surface is $N_D$, then the retention probability per D is calculated as $N_D/N$. The retention chemistry of D evolves at the end of the collision cascade when the impact particle is thermalized allowing comparison with the experimental results at higher impact energies [21]. We carry out the analysis of
the resulting chemistry after the final rest location of each D impact, by performing the nearest-neighbor (NN) estimation for each retained D (H) atom in the surface, defining the most-probable bonds [21]. While role of Li in bonding hydrogen is not challenged in the pure lithium surface, it is surprising that O-D and Li-D NNs are similarly represented. Although there is two times more Li than oxygen atoms in the surface, oxygen has coordination number 2, two times larger than coordination number of Li (1). This indicates approximate similar efficiency of H (D) retention in Li and Li$_2$O surfaces. We note that the O-D bond percentage is slightly bigger than Li-D one, and that effectiveness of O to bond D slightly increases with temperature.

3.3. Results and discussion

Auger electron spectroscopy (AES) analysis was done on the sample surface to determine the elemental composition. Electrons with energy 3 keV were used to irradiate the sample and the generated Auger electrons were analyzed with a double-pass cylindrical mirror analyzer (CMA). Fast AES scans were taken on the pure Li film to avoid oxidation and/or other impurity deposition. AES spectra of the Li metal films on Ni(110) showed a Li peak at 51 eV, which is characteristic of pure metallic Li, as shown in Figure 3.2. Carbon and oxygen impurity concentrations in the film, as detected by AES and carbon monoxide (CO) TPD, were less than 1%. When the Li film was oxidized by exposure to 10 L O$_2$ at fixed exposure temperatures in the range 90-520 K, the Li AES transitions split into two negative-going peaks at 36 and 42 eV, indicating the formation of Li$_2$O [9,35,36]. No metallic Li signal in AES remained. The estimated Li film
thickness was 5 nm; slightly below the AES probing depth (~10 nm) therefore the Ni peaks are still visible.

Figure 3.2. AES of (top) Li metal and (bottom) Li₂O films on Ni(110).

A total fluence of 4x10^{15} \text{ H}^+ \text{cm}^{-2} of 500 eV H₂⁺ ions was used to irradiate the Li and Li₂O films after deposition. TPD was performed within 2-5 min after ion irradiation, the time needed to move the manipulator and place the sample in front of the mass spectrometer. Li and H₂ TPD profiles are shown in Figure 3.3.

The initial Li coverage before irradiation was checked with TPD at room temperature and its reproducibility was within 1-2%. During the Li and H₂⁺ exposures, the Ni substrate was kept at a fixed exposure temperature, ranging from 90 to 520 K. Li and H₂ desorption curves are given in Figure 3.3 for each exposure temperature in order to illustrate this influence, however we will focus our discussion below on the two highlighted curves at 90 and 520 K.
Figure 3.3. (a) Li and (b) H₂ TPD curves after pure Li films at 90-520 K were irradiated with 500 eV H₂⁺. Panel (a1) shows data from panel (a) on an expanded y scale.
As seen in Figure 3.3 (a), the amount of Li desorbing in the multilayer peak near 600 K started to decrease when exposure temperatures above 450 K were used, since Li started evaporating significantly at temperatures above 450 K [37]. The higher temperature Li desorption (700-1000 K), as shown more clearly on an expanded y scale in Figure 3.3 (a1), corresponded to desorption from the Li monolayer [37]. H$_2^+$ irradiation caused the formation of LiH and a new Li desorption peak near 650 K due to LiH decomposition [9]. This Li peak was coincident with the H$_2$ desorption peak, shown in Figure 3.3 (b), demonstrating that Li and H$_2$ evolution in TPD was rate-limited by LiH decomposition in the films, as previously reported [9]. The H$_2$ TPD curves showed that the amount of H retained in the Li film at 90 K was higher than that at 520 K and only a slight decrease was observed from 300 K to 520 K. The amount was quantitatively analyzed in the next section. No LiH (8 amu) desorption was detected in these experiments.

To understand the H retention measurements, we need a determination of the absolute coverage (atoms/cm$^2$) for both Li and H in the films. The Li coverage was calibrated by determining the Li TPD area from a Li film that formed a saturation monolayer coverage (just prior to formation of a Li multilayer desorption feature) and assigning the integrated area under this Li TPD curve, after correction for the mass spectrometer sensitivity to the translational energy of the desorbed species [38], to a Li coverage corresponding to a hexagonal close packed structure of Li adatoms with their metallic atomic radii (3.02x10$^{15}$ atoms/cm$^2$) [37]. The surface coverage ($\theta$) is given in ML, where 1 ML corresponds to the surface Ni atom density of Ni(110) of 1.14x10$^{15}$ atoms/cm$^2$. This gives an absolute Li coverage, $\theta_{\text{Li}}$, of 2.56 ML referenced to the Ni(110)
surface atom density. The H coverage was determined in a similar method by
determining the integrated area under the H$_2$ TPD profiles. We assign a surface saturation
of $\theta_H = 1.5$ ML (1.71x10$^{15}$ atoms/cm$^2$) when produced from dissociative adsorption of H$_2$
on Ni(110) at 300 K [28][39].

Similar experiments to those described above were performed on Li$_2$O films.
These films were oxidized by the same exposure of 10 L O$_2$ at fixed exposure
temperatures in the range 90-520 K. After H$_2^+$ ion irradiation of Li$_2$O films, H$_2$ (m/z = 2),
Li (m/z = 7) and LiOH (m/z = 24) desorption was detected in TPD. TPD curves for these
desorbed products are provided in Figure 3.4 (a-c). No desorption of LiO, H$_2$O, or LiH
was observed. Figure 3.4 (a) shows that Li is retained at the Ni surface to higher
temperatures after oxidation, due to the increased thermal stability of Li$_2$O. In this case,
Li is only desorbed when Li$_2$O decomposes, which produces a Li TPD peak at 900 K.
The temperature was increased up to 1200 K during TPD due to the limitations with the
thermocouple operation therefore the highest temperature peak was not completely
captured.

For 300 K exposure case (Figure 3.4 (a)), 18% of the Li layer was not oxidized
since a Li metallic peak at 570 K was still present (2.2 ML) and about 10% of the Li layer
(1.2 ML) formed the LiH (Li peak at 630 K). The exposure at 400 K produced a Li peak
(LiH decomposition temperature) at 630 K (Figure 3.4 (a)), indicating that about 27% of
the Li film formed LiH (4.7 ML). H$_2$ TPD showed a low temperature peak at 630 K only
for 90 K and 300 K exposure temperature (Figure 3.4 (b)). When the temperature
increased beyond 300 K, only the high temperature peak remained at 900 K. It is not
understood why the H$_2$ peak is missing for the 400 K exposure, and presumably this is
related to another channel for the consumption of \( \text{H}_2 \) during or prior to TPD, but this requires further studies. \( \text{LiOH} (m/z = 24) \), \( \text{Li}_2\text{O} (m/z = 30) \) and \( \text{O}_2 (m/z = 32) \) were also monitored and desorbed at 900 K, although the calibration for these species is not provided in this work (see \( \text{LiOH} \) decomposition in Ref. [40]).

It is important to point out that no \( \text{H} \) was measured from TPD experiments after irradiation with 500 eV \( \text{H}_2^+ \) ions on Ni at room temperature, therefore the hydrogen retention in these experiments can be attributed solely to the \( \text{Li}/\text{Li}_2\text{O} \) layer. Energetic \( \text{H}_2^+ \) ions (500 eV) get implanted in the first few nm of the Ni substrate, but since Ni does not retain \( \text{H} \) at room temperature and above, \( \text{H} \) immediately diffuses out of Ni at these temperatures and reacts with the \( \text{Li}/\text{Li}_2\text{O} \) layer. In this case Ni serves as a reservoir (virtual source) of thermal \( \text{H} \), which interacts with \( \text{Li}/\text{Li}_2\text{O} \) and forms other compounds such as \( \text{LiH}, \text{LiOH} \) etc. From this point of view, the 10 eV impact energy used in the MD calculation (in which case the impact particles do not reach the bottom of the slab) is applicable to the experimental results. This is supported by the fact that the retention chemistry develops mainly when impact particles thermalize [21], irrespectively of their impact energy.
Figure 3.4: (a) Li, (b) H\textsubscript{2} and (c) LiOH TPD curves after Li\textsubscript{2}O films at 90-520 K were
irradiated with 500 eV H\textsubscript{2}\textsuperscript{+} ions.
AES spectra were obtained from all of these surfaces at fixed exposure temperatures in the range 90-520 K after H$_2^+$ irradiation and these are given in Figure 3.5. As a reference, AES spectra from the clean Ni(110) surface and pure Li on Ni(110) at 90 K is also provided in Figure 3.5 (a) and (a1). In addition, AES spectra from the oxidized Li film surface at 90 K prior to H$_2^+$ irradiation is provided in Figure 3.5 (b) and (b1).

The top panels of Figure 3.5 show AES spectra after H$_2^+$ irradiation of pure Li for the Li (a) and O (a1) regions. In Figure 3.5 (a), at 90 K, H$_2^+$ irradiation caused no shift in the metallic Li peak at 51 eV; 500 eV H$_2^+$ irradiation of the 5 nm Li film mostly resulted in H implanted in Ni, and at 90 K this H was not mobile, and remained primarily in the Ni substrate, and so the metallic Li signal in AES was maintained. The penetration depth in Ni for 500 eV H$_2^+$ ions, calculated by the SRIM code [41] was 6 nm and it scaled up to 10 nm for the Li/Ni system.

Li normally attenuated the Ni peak at 61 eV, except on the curve labeled “a”, where Li exposure occurred at 300 K. In the 300 K case, the Li layer may have been slightly thinner. Alternatively, the “as dosed Li” may have not formed a uniform layer at 300 K, exposing some Ni, whereas at higher temperatures Li diffused to form a more uniform layer covering the Ni surface. The O AES spectra shown in Figure 3.5 (a1) showed a small oxygen peak at 512 eV, which was still less than 2% in the film.

The bottom panels of Figure 3.5 provided AES spectra taken after H$_2^+$ irradiation of Li$_2$O films for (b) Li and (b1) O AES regions. Exposure of a 5 nm thick Li film to 10 L O$_2$ oxidized the Li to create a Li$_2$O film. As shown in Figure 3.5 (b), this caused the metallic Li AES peak at 51 eV to be eliminated and two peaks near 36 and 42 eV, characteristic of Li$_2$O, to appear. However, LiH also has peaks in the range 36-42 eV.
In order to understand whether the peak represented LiH or Li$_2$O (peak at 40±1 eV), we look at the shift in the O peak [3][42].

At temperatures up to 470 K, O peaks appeared at 508-509 eV (LiOH), and at higher temperatures it shifted to 512 eV (Li$_2$O). It was known that slow conversion of LiOH to Li$_2$O and H$_2$O occurred on the order of minutes [36]. In the present experiments, TPD was performed 2-5 min after H$_2^+$ irradiation, therefore, at temperatures higher than 470 K, it is believed that LiOH decomposed to form Li$_2$O and H$_2$O according to the reaction: $2\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$ (g). H$_2$(g) formation between H$_2^+$ exposure and TPD may be another cause of the H retention drop at elevated temperatures.

Figure 3.5. a) Li and a1) O AES signal after H$_2^+$ exposure of pure Li. b) Li and b1) O AES signal after H$_2^+$ exposure of Li$_2$O.
In Figure 3.6, the total amounts of Li and H$_2$ are plotted for both pure and oxidized Li experiments. The data points are connected with a spline fit to guide the eye and the dashed and dotted lines in the graph show the initial Li coverage in Li and Li$_2$O experiments before H$_2^+$ ion irradiation. We note no large effect of exposure temperatures on H retention exceeding the Li melting point. This was to be expected since the H retaining compounds, LiH and LiOH, decompose at much higher temperatures than pure Li (see Figure 3.3 and Figure 3.4). These measurements were carried out below the saturation H uptake level (Li:H = 1) to more clearly identify changes in retention in the films due to exposure temperature.

Figure 3.6. Concentrations of H and Li from TPD measurements after irradiation of Li films. The dashed and dotted lines show initial Li coverage in Li and Li$_2$O experiments respectively.
Results from both experiments and MD simulations are compared in Figure 3.7. In Figure 3.7, the retention fraction of H is plotted for pure and oxidized Li and compared with computed MD results for D. The total incident H was calculated by the TPD profile of H retained in Ni(110) at 90 K (8.2 ML/Ni). The retention for Li and Li$_2$O is similar. We note that retention in the case of oxidized Li may be higher than shown due to the release of LiOH, which was not calibrated and not accounted for in this plot. Noise/scattering in the data was attributed to the statistical error due to the integration of the TPD profiles, the inherent uncertainty of the measuring instruments and the reproducibility of H$_2^+$ dosing. At temperatures higher than 450 K, Li coverage starts to drop rapidly due to evaporation, which may also contribute to a larger scatter in the data for H retention.

For each computed data point, we report a standard error defined as $\sigma_S = \sigma N^{-1/2}$, where $s$ is the standard deviation of our sample of $N$ cases. In summary, the MD calculations demonstrated that the oxidation of the Li slab resulted in the formation of various Li oxides and the retained D atoms were located in the interstitial positions of Li or bonded to oxygen. We also calculated the retention of the same samples but with impact of H. The values obtained for the retention are 89 ± 2.5% at 90 K, 72 ± 3% at 300 K and 62 ± 3% at 500 K.

Experiments and calculations consistently showed retention by both pure Li and Li$_2$O, indicating that both pure and oxidized Li can bind H with similar efficiency. The same drop of retention with increasing $T_{\text{exp}}$ was observed for both Li and Li$_2$O. The exponential decay of retention with temperature may originate from diffusion, since it is a thermally activated process (i.e., higher $T_{\text{exp}}$ leads to higher H desorption from the Li...
An interesting observation was the comparison between H and D in terms of total retention in pure Li. From the calculations, one can see that H retention is slightly lower compared to D retention. Although H and D are chemically similar, their different mass could lead to different diffusion rates in Li.

![Graph showing H retention fraction as a function of exposure temperature.](image)

Figure 3.7. H retention fraction (H retention/H incident) in Li and Li$_2$O decreases as a function of exposure temperature, in good comparison with D and H retention from Classical Molecular Dynamics (CMD) calculations. Lines are drawn to guide the eyes.

### 3.4. Conclusion

H retention in pure Li and Li$_2$O films was calculated by molecular dynamics and measured experimentally as a function of surface temperature under UHV conditions. It was experimentally shown that upon oxidation, Li thermal stability increased. It was also shown that both pure Li and Li$_2$O are able to retain H in almost same amounts. In
addition, it was shown that H and D retention drops with surface temperature in the range 90-520 K from 95% to 35% due to outwards diffusion of H at high temperatures.

Results of the MD modeling with EEM corrections were qualitatively consistent with experimental results in terms of both retention fraction and the drop of retention with temperature, when using either H or D as impact particles. Similar trends and agreements were seen between the experimental results for Li₂O and the MD results for a mixture of Li and oxygen with atomic concentration ratio Li:O = 2:1.

In TPD measurements, the Li and H desorption peaks were observed at the same temperature (650 K) and this was interpreted as the decomposition of LiH. In addition to TPD analysis for Li₂O films irradiated with H ions, AES measurements were consistent with the formation of LiOH, which decomposed to Li₂O and H₂O at exposure temperatures higher than 470 K.

The results from experiment and MD modeling do not preclude the possibility that the hydrogen is retained through the formation of large LiₙHₙ molecules. Earlier DFT studies, for example, predicted the formation of a rock-salt structure for LiD under deuterium bombardment of lithium films [43]. The Li and H could then bind to form LiH at the surface, which would subsequently dissociate at the same temperature as observed experimentally.

The details of the chemistry underlying H retention and Li and Li₂O films may thus be complex. Nevertheless, both experiment and modeling support the possibility that low H recycling can be achieved if Li₂O is formed under fusion reactor conditions, as both Li and Li₂O have comparable efficiency for trapping H.
3.5. References


Chapter 4. Sputtering of Li, Li-O and Li-C-O thin films under deuterium and helium ion bombardment

This chapter is an adaptation of a paper submitted for publication and is currently under review.


This chapter describes the outcome of a collaborative work from multiple authors. I participated fully in performing all the experiments, analyzing the results and writing the papers.

In this chapter, studies of the sputtering yields of lithium and lithium-compound thin films under deuterium or helium ion irradiation are presented. This information is critical in determining the robustness of lithium as a plasma facing material in experimental fusion devices.

4.1. Introduction

Lithium (Li) coated plasma-facing components (PFCs) have been successfully utilized to enhance the operational plasma performance in the National Spherical Torus Experiment (NSTX) and the Lithium Tokamak Experiment (LTX) by exploiting the impurity gettering and deuterium (D) retention properties of Li [1,2]. Enhanced D retention from Li reduces D recycling and therefore leads to hotter plasma edge and reduced instabilities, which in turn improves overall plasma performance [3,4].
However, Li PFCs can also undergo significant erosion and sputtering by energetic ion bombardment, both limiting the material lifetime and contaminating the plasma [5]. An understanding of the complex dynamics of Li sputtering is thus valuable when characterizing Li as a potential PFC on fusion reactors. In current fusion experiments the presence of oxygen and carbon inevitably creates Li oxides and carbonates (Li-O and Li-C-O compounds) [6,7]. Investigating the mechanisms of D retention and sputtering for these Li compounds is crucial for the application of Li as a plasma-facing material. Additionally, Li-C-O compounds may be of interest as new fusion-relevant materials. For example, lithium carbide has recently been proposed as a prospective breeder material for fusion reactors [8].

It is difficult to study the details of Li PFC behavior in-situ since tokamaks inherently create a complex environment for plasma and material characterization. Sputtering and reflection rates of D and tritium (T) into Li, along with associated self-sputtering yields, were originally calculated with Monte Carlo simulations by László and Eckstein [9]. Measurements and modeling of solid phase bulk Li and of liquid Li showed that the Li sputtering yield decreases significantly upon D saturation of the surface due to preferential sputtering of D atoms [10,11]. Further first-principles molecular dynamics simulations have suggested that rock-salt like LiD precipitates quickly in liquid Li under D bombardment [12], and corresponding measurements have shown that surface erosion rates are reduced in the presence of LiD for low (20-40 eV) incident ion energies [13]. Additional in-situ [5] and laboratory studies [14-16] strengthened the case that the chemical state of Li in the surface has a strong effect on Li erosion rates. What remains is
to characterize this effect on thin Li films where chemical processes can be observed experimentally.

In this work, as a representation of Li PFCs in a tokamak [3], the D retention and sputtering characteristics of thin Li and Li compound (Li-O and Li-C-O) films on a nickel (Ni) substrate were studied in the well-controlled environment of a surface science apparatus. By working in an ultrahigh vacuum (UHV) chamber with a base pressure of $10^{-10}$ Torr, thin (~5 nm) Li films can be created and studied with minimal oxidation and contamination effects, and Li compounds can be formed under controlled conditions. Contaminates (C and O) can be added in controlled amounts to replicate surfaces likely to be found in a tokamak environment. The chemical state of these films was monitored with Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) as a function of $D_2^+$ and $He^+$ fluence and of incident ion energy to determine surface evolution properties and Li sputtering yields. The investigation of D retention and Li sputtering in thin Li films in a surface science apparatus elucidates the mechanisms involved in Li PFCs, strengthening their candidacy for application as a tokamak PFCs. The main questions addressed here are related to the sputtering of Li, Li-O, and Li-C-O films with $D_2^+/He^+$, D retention at a monolayer level, and the role of the Li-substrate (Ni) interface.

4.2. Experimental methods

All experiments were performed at 300 K in a UHV chamber with a $2\times10^{-10}$ Torr base pressure as described in detail in Ref. [16]. TPD and AES were used to measure D
retention and sputtering rates under various irradiation conditions. For TPD, the sample was positioned in line-of-sight of the ionizer of a Hiden UHV 301 mass spectrometer (QMS), with the nozzle located 10 mm from the sample, using a heating rate of 4 K/s. A K-type (chromel-alumel) thermocouple was spot-welded directly on the sample to monitor the temperature. The Ni (110) single crystal (8 mm square, ±0.5° orientation) sample was held with tantalum (Ta) wires used for resistive heating.

A Ni (110) single crystal was used as a substrate throughout these experiments to avoid possible effects due to grain boundaries, intrinsic defects, and impurities diffusing from the bulk to the surface. Additionally, Li and Ni are immiscible due to the low solubility of alkali metals in Ni, and thus do not form either bulk alloys or two-dimensional surface alloys [17,18]. The crystal was cleaned using cycles of 1.5-keV Ar\(^+\) ion sputtering and annealing in vacuum at 1100 K in oxygen and hydrogen backgrounds. While performing this work we discovered that an atomically clean Ni surface could be achieved by evaporating a thin Li layer on Ni and heating it to 1000 K. The desorbing Li binds with remaining C and O upon leaving the surface.

Li films were deposited on the Ni crystal surface using a commercial Li metal dispenser (Li/NF/7.3/17/FT, SAES Group) by thermal evaporation. Li-O and Li-C-O compounds were formed by dosing O\(_2\) and CO on pure Li films at room temperature. After surface preparation, Li films were exposed to a high-energy (450 to 1600 eV) ion beam composed of either D\(_2^+\) or He\(^+\) ions from a differentially pumped ion gun (PHI 04-303 A). The D\(_2^+\) beam is nominally composed of 90% D\(_2^+\) and 10% D\(^+\) [19]. D\(_2\)/He gas was introduced into the ion gun through a high precision variable leak valve, and a liquid nitrogen trap was used in the D\(_2\)/He gas line to mitigate H\(_2\)O contamination. The incident
ion flux was defocused over the sample surface to provide uniform irradiation at ~1 μA integrated current. The sputtering time and thus fluence was varied at these conditions to allow for measurements of the sputtering rate.

4.3. Results and discussion

Four sets of experiments were conducted to gain insight into Li sputtering rates and retention properties upon D$_2^+$/He$^+$ irradiation of pure Li and Li compound films. First, a thin Li film at 300 K was repeatedly exposed to a D$_2^+$ ion beam with 450-1200 eV/D$_2^+$ incident energy at various ion fluences. The initial Li coverage before D$_2^+$/He$^+$ irradiation was checked with TPD and was found to be reproducible within 5%. As it will be shown later, it was observed that D$_2^+$ irradiation led to LiD formation; a second set of experiments using He$^+$ was conducted to determine physical sputtering rates from pure Li films. The third and fourth sets of experiments were dedicated to sputtering of Li oxide (8 ML (monolayers) Li + 25 L (Langmuirs; 10$^{-6}$ Torr·s) O$_2$) and Li-C-O (8 ML Li + 45 L CO) films with D$_2^+$ ions in the energy range 1000-1600 eV/D$_2^+$ at room temperature. The D$_2^+$ ion flux was 3x10$^{17}$ D$^+$m$^{-2}$s$^{-1}$. In each case, Li was first evaporated on Ni at 300 K and then the chamber was backfilled with either O$_2$ or CO to form Li-O and Li-C-O respectively. Note that the Li-O nomenclature refers to the oxidized film, which may be Li$_2$O. The retention and sputtering results are presented below.
4.3.1. \textit{D}_2^+ \textit{irradiation of pure Li films}

Li films were irradiated with \textit{D}_2^+ ions at 450, 600, 800, 1000 and 1200 eV for 1-60 min to elucidate the sputtering and retention mechanisms. After each ion irradiation, the samples were analyzed with AES and TPD and an identical film was subsequently formed. As seen in Figure 4.1, where Li and \textit{D}_2 TPD signals for 450 eV \textit{D}_2^+ irradiations are compared, the Li metallic peak is transformed into LiD decomposition peak after about 5 min of irradiation. This is evidenced both by the shift of the Li TPD peak from the Li multilayer value of \textasciitilde560 K to a peak centered at \textasciitilde630 K, and by the simultaneous appearance of a \textasciitilde630 K peak in the \textit{D}_2 TPD signal \footnote{16}. Notably, LiD conversion occurs before an appreciable amount of Li is lost through sputtering. After 10 min of \textit{D}_2^+ irradiation, the LiD peak decreased due to Li sputtering. For longer sputtering periods where the film thickness was reduced to < 2 ML, a second \textit{D}_2 TPD peak appeared at \textasciitilde510 K. Finally, after the longest sputtering time of 60 min, we saw that the \textit{D}_2 TPD peak was almost fully shifted to a third location at \textasciitilde390 K. Neither the \textasciitilde510 K nor the \textasciitilde390 K \textit{D}_2 peaks were associated with any peaks in the Li TPD signal. Note that at long sputtering times, a Li-O compound was formed (Li peak at \textasciitilde850 K that indicates the presence of Li oxide) as shown in Figure 4.1 (b), from interaction with oxygen impurities in the background gas.

In order to determine the retention mechanisms behind the \textasciitilde510 K and \textasciitilde390 K \textit{D}_2 peaks, two additional experiments were performed. First, the clean Ni substrate was irradiated by a total fluence of \textasciitilde10^{15} \textit{D}^+ cm^{-2} of 1000 eV ions which were implanted into the Ni bulk. The resulting \textit{D}_2 TPD spectrum in Figure 4.1 (a) shows that the implanted D is released as \textit{D}_2 from the Ni at \textasciitilde370 K. Second, the same experiment was repeated on a
1 ML Li film on Ni that was prepared by heating the sample at 545 K to remove any Li in a multilayer film. Since the first monolayer of Li on Ni is assumed to not form LiD (due to the strong Li – Ni bonding), at monolayer Li coverage $\text{D}_2^+$ is retained at the Li-Ni interface and in the Ni subsurface region. $\text{D}_2$ TPD in Figure 4.1 (a) shows two distinct peaks at ~370 and ~500 K, which were interpreted to be indicative of implantation into subsurface Ni and trapping at the Ni-Li interface, respectively.
Figure 4.1. (a) D$_2$ and (b) Li TPD curves after 450 eV D$_2^+$ incident on a 3 ML Li film. As D$_2^+$ irradiation time was increased, Li was quickly converted to LiD before a substantial amount of Li was lost to sputtering.

Comparison of these two experiments with observations of D$_2^+$ sputtering on thin Li films suggests a three-stage mechanism for D retention in thin Li films. First, D is retained in Li, converting it to LiD. Second, as the LiD is sputtered, D is still retained at the Li/Ni interface. Third, upon additional sputtering, D is retained in the bulk Ni. Since the Li to LiD transition occurs faster than relevant sputtering timescales, the sputtering yield of D$_2^+$ into LiD was calculated. The sputtering yields for each incident ion energy are reported in Figure 4.3.
Note that in order to compare to literature values, where D$^+$ sputtering is reported, our measured incident D$_2^+$ ion energies and measured D$_2^+$ sputtering rates were both divided by a factor of 2.

4.3.2. He$^+$ irradiation of pure Li films

In order to determine the physical sputtering rate of D$_2^+$ into pure Li, He$^+$ was chosen as an inert substitute for D$_2^+$ due to its similar mass. He$^+$ sputtering rates were calculated for incident ion energies of 450, 600, 800, 1000 and 1200 eV. The results are compared with D$^+$ sputtering rates of LiD and with literature values in Figure 4.3. First, no He was retained in the Li films. Second, the measured sputtering rates of He$^+$ into Li are 2-3 times higher than the measured sputtering rates of D$_2^+$ into LiD, indicating that the Li sputtering yield decreases significantly upon D retention. This behavior has been previously reported for bulk and liquid Li films, and was attributed to the preferential sputtering of D atoms over Li atoms [10,11,13]. Another explanation was related to the formation of LiD bonds that are stronger than Li-Li bonds (2.5 vs. 1 eV) [20]. Therefore, the presence of accumulated D decreases the sputtering yield of Li.

4.3.3. D$_2^+$ irradiation of Li-O and Li-C-O films

H$_2$O and CO are the main gas-phase contaminants in fusion experiments leading to the formation of Li oxide and Li-C-O compounds. The next sets of experiments were
dedicated to the irradiation of Li oxide (8 ML Li + 25 L O₂) and Li-C-O (8 ML Li + 45 L CO) with D₂⁺ ions. TPD profiles of D₂ and Li after irradiation of Li-O and Li-C-O films by 1200 eV D₂⁺ at 300 K are plotted in Figure 4.2. As expected, the thermal stability of Li in Li-O is larger than that of pure Li. Heating the sample to high temperatures during TPD from the Li-O films revealed Li peaks at 1200 K. As seen in Figure 2(b), the high temperature peaks shift by ~50 K. Though the reason for this shift is not clear, it could be related to the layer morphology during irradiation. D is mainly implanted in Ni and D₂ desorbed at 400-500 K. This peak shifted to lower temperatures for higher D₂⁺ fluences indicating that after the Li-O layer and the Ni implantation region is saturated, D started recombining at the surface and desorbing. There was also a small amount of D retained to ~900 K, which coincides with a Li peak from the Li-O.

Not all the Li in the film was converted to Li-C-O when CO was exposed on Li. Upon D₂⁺ irradiation, the remaining metallic Li formed LiD, and in subsequent TPD Li desorbed in a peak at 630 K simultaneously to the corresponding D₂ peak. Li TPD peaks at 700-850 K coincided with CO desorption. Most of the D was desorbed as D₂ in multiple peaks from 390-630 K, which are attributed to arise from implanted D in Ni, D trapped at the Li-Ni interface, and LiD. The D₂ peak desorbing from LiD decreases with D₂⁺ fluence due to the sputtering of the Li film. In both cases (Li-O and Li-C-O), D retention saturated with increased incident D₂⁺ fluence.
Figure 4.2. TPD profiles of D$_2$ (a, c) and Li (b, d) after exposure of Li-O and Li-C-O to 1200 eV D$_2^+$. 

4.3.4. Li sputtering results

The Li sputtering yield results from pure Li and Li compound (Li-O and Li-C-O) films with D$_2^+/\text{He}^+$ irradiation are plotted in Figure 4.3 and compared with simulated and measured values from the literature [4,9,21]. Sputtering of Li-O with D$_2^+$ had the highest Li sputtering rate due to D$_2^+$ and it peaked at higher ion energies than for pure Li and Li-C-O (1600 eV/ D$_2^+$). While Li sputtering rate values of LiD and Li compare well with the literature, the sputtering rate values of He$^+$ on Li are 2-3 times higher indicating that hydride or hydroxide formation reduces physical sputtering of Li. MD simulations of sputtering of the Li-C-O
compounds showed a chemical sputtering reduction of more than a factor of four due to the presence of oxygen [22]. We note that when comparing the data of our measurements in this work with data on bulk Li, backscattering from the Ni substrate of the incident ions may increase the sputtering yield of these thin films.

The above sputtering results can be extrapolated to predict approximate surface lifetimes for Li-coated PFCs in LTX and future machines. LTX is a low aspect ratio tokamak that has shown significant increase in plasma performance for Li layers on the order of 50 nm [4,6]. Typical relevant parameters are edge electron temperatures of 200 eV and edge ion temperatures of 60 eV, but it is noted that the wall sheath potential accelerates the ion impact energy on the wall up to 1 keV [4]. Assuming uniform sputtering with an edge fluence of $1 \cdot 10^{21}$ m$^{-2}$ per shot and taking a measured sputtering yield of 0.1 ions/atom, we predict that the deposited Li film should be fully sputtered in approximately 50 shots, which is about as long as a typical run day. In practice, slightly longer lifetimes have been observed. The discrepancy could be a result of significant backscattering from Ni in measurements for the thinnest Li films used in this experiment, the nonuniformity of Li coatings in the tokamak, or the unconsidered redeposition of sputtered Li back onto the walls in LTX experiments. Furthermore, the sputtering yield decreases at higher edge incident ion energies, which increases the lifetime of Li films due to sputtering. The persistence of low-recycling wall conditions in LTX after an appropriate sputtering time suggests that these other effects must be considered.
Figure 4.3. Measured sputtering yields of Li and their dependence on incident ion energy are compared with simulated and measured values from the literature (a, b) [9] (c) [4] (d, e) [21].

4.4. Conclusion

Temperature programed desorption was used to study Li sputtering yields in pure Li, LiD, Li-O, and Li-C-O films at 300 K upon bombardment by energetic He\(^+\) and D\(_2^+\) ions. Pure Li films were observed to become LiD films upon D\(_2^+\) irradiation before significant sputtering occurred. He\(^+\) sputtering of pure Li yielded 2-3 times higher sputtering yields compared to D\(_2^+\) irradiation. This result indicates that the formation of LiD reduces the sputtering yield, in agreement with previous measurements on bulk and liquid Li.
The Li sputtering yield upon D$_2^+$ irradiation of Li-O film was lower than the Li-C-O sputtering yield and peaked at higher energy (1600 eV/ D$_2^+$). Based on the current studies, Li oxide formation in a fusion experiment may be advantageous due to the enhanced thermal stability of Li-O, lower sputtering yield of Li-O, and similar hydrogen retention properties of Li-O when compared with pure Li. However, the role of LiOD formation and its dissociation to Li$_2$O and H$_2$O in a fusion experiment should be further studied.

We make several additional conclusions from these experiments. Upon oxidation, the temperature for complete Li desorption (removal) was increased by 350 K, while CO exposures on a pure Li layer, which formed a Li-C-O compound surface increased this stability by 300 K. In addition, D retention saturates when irradiating Li and Li compound films with increasing incident D$_2^+$ fluences. TPD analysis showed that as the Li film was sputtered away, and the thickness was reduced to a monolayer level, D was retained at the Li-Ni interface and in the Ni substrate.

4.5. References


Chapter 5.  Post-exposure time dependence of deuterium retention in lithium and lithium compounds

This chapter is an adaptation of a paper submitted for publication and is currently under review.


Materials from this chapter have been presented at the 2018 International Conference on Plasma Surface Interactions in Controlled Fusion Devices and the 2018 Physical Electronics Conference.

This chapter describes the outcome of a collaborative work from multiple authors.
I took the leading role in performing all the experiments, analyzing the results and writing the papers.

In this chapter, investigations of the amount of deuterium retained in lithium and lithium compound thin films as a function of time are discussed. This information is important for planning and operating experimental fusion devices in which there are often long periods of time between plasma shots.

5.1. Introduction

Lithium (Li) coating of plasma-facing components (PFCs) has led to improved plasma performance such as longer discharge time and higher current density in fusion experiments [1]-[6]. These effects have been attributed to the effectiveness of Li in
reducing impurities in the plasma and retaining hydrogen (H) isotopes such as deuterium (D), thus reducing recycling [7]-[12]. Since Li readily reacts with background gases present in fusion devices, it is important to understand and parameterize D retention in both Li and Li compounds (Li-O and Li-C-O) for applications of Li under operating conditions. Furthermore, the evolution of D retention in the PFCs, i.e. the time dependent fuel retention property, is crucial under future long-pulse plasma conditions because of nuclear safety regulations related to tritium inventory in tokamaks [13],[14].

Several previous works have examined the effect of impurities on D retention in Li. Taylor et al. studied the effect of oxygen on D retention in lithiated graphite [33],[34]. Capece et al. examined the effects of both temperature and contamination on D retention in ultrathin Li films on TZM [35]. Similarly, a few studies have addressed the time dependent fuel retention in PFCs. Bisson et al. [13] and Wierenga [36] have separately examined the retention of D in tungsten as a function of time. Ohno et al. have studied the time evolution of D in graphite [37]. Presently, no time dependent retention study on Li exists in literature. This work extends existing literature on H retention by investigating D retention in Li and Li compounds (Li-O and Li-C-O) as a function of waiting time after exposure to 450 eV D$_2^+$ ions. This is a critical step in addressing what happens to D trapped in Li PFCs between plasma shots, e.g., whether it diffuses out of the Li, stays trapped or forms other compounds.
5.2. Experimental methods

All experiments were performed in a three-level, stainless-steel UHV chamber (2×10⁻¹⁰ Torr base pressure) equipped with Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) capabilities. AES was performed with a PHI 15-255G double-pass cylindrical mirror analyzer (CMA). TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer with the shield nozzle located 1 mm from the sample. The heating rate was 4 K/s. TPD was conducted monitoring these 12 masses: 2, 3, 4, 7, 9, 16, 18, 19, 20, 25, 28 and 32 amu. Surface coverages θ are given in monolayers (ML), where 1 ML corresponds to the surface Ni atom density of Ni(110) (1.14×10¹⁵ atoms/cm²).

A Ni(110) crystal (Princeton Scientific Corp, 8 mm square, 1 mm thick, ±0.5° orientation) was used as the substrate for all experiments to avoid effects due to grain boundaries, intrinsic defects, and impurities diffusing to the surface [20]. The Ni(110) crystal cleaned initially using 1.5 keV Ar⁺ ion sputtering and annealing cycles at 1100 K. Additional oxygen treatments for several minutes at p(O₂) = 4×10⁻⁸ Torr with the sample at 1000 K were used to eliminate residual carbon. Hydrogen treatments for several minutes at p(H₂) = 4×10⁻⁸ Torr with the sample at 1000 K were used to eliminate residual oxygen. Surface purity was determined with AES to ensure carbon and oxygen concentrations of less than 0.1%.

Li dosing was performed with a commercial Li metal dispenser (Li/NF/7.3/17/FT, SAES Group) by thermal evaporation onto the Ni substrate. D₂⁺ ions were produced in a PHI 04-303A differentially pumped ion gun with adjustable ion energy from 0-5 keV, and a liquid nitrogen trap was used in the D₂ gas line to reduce H₂O contamination. O₂
and CO (Praxair, 99.9%) was dosed through backfilling the chamber. Hydrogen impurities from background coadsorption in all deuterium experiments were less than 0.01 monolayers. All experiments were performed at 300 K unless otherwise noted.

5.3. Results and discussion

5.3.1. Time dependent D retention in Li

Three layers of Li were deposited onto a Ni substrate and subsequently irradiated with $4 \times 10^{15}$ D$_2^+$ cm$^{-2}$ at 450 eV. We confirmed that the entire Li film was converted to LiD by the disappearance of metallic multilayer Li peak in TPD (550 – 600 K) [38]. The LiD film was left undisturbed at 300 K for various amounts of time before being analyzed by AES and then by TPD.
Figure 5.1. TPD (left) and AES (right) of a 3-layer Li film irradiated with $4 \times 10^{15}$ D$_2^+$ cm$^{-2}$ at 450 eV for increasing amounts of waiting time at 300 K.

D$_2$ TPD curves and AES spectra of the LiD film after different amount of waiting time before analysis are shown in Figure 5.1. D$_2$ TPD curves show that D$_2$ desorbed from a LiD decomposition-limited peak at 630 K [38]. With increasing amounts of waiting time, the 630 K peak decreased and a shoulder at 520 K grew. The 520 K shoulder occurred at similar temperature to D$_2$ desorption temperature from oxidized Li film, discussed in Section 3.2, indicating that the LiD film could have been converted into Li oxide with increasing amounts of waiting time. The suggested conversion of Li to Li oxide was confirmed by the AES spectra, which showed a decrease in metallic Li signal (51 eV) and an increase in Li$_2$O signal (33 and 40 eV) and LiOD signal (45 eV) [22]-[25] over time.
5.3.2. Time dependent D retention in Li-O and Li-C-O

Li oxide film was formed by first depositing 3 layers of Li onto the Ni substrate followed by backfilling the chamber with 1x10⁻⁷ torr of O₂ for 5 min. Li oxide, which chemically could be Li₂O or Li₂O₂, shall be presented as Li-O in this work. We confirmed that the entire Li film was converted to Li-O by the disappearance of metallic Li peak in AES (51 eV) and by the disappearance of metallic multilayer Li peak in TPD (550 – 600 K) [38]. The Li-O film was subsequently irradiated with 4×10¹⁵ D₂⁺ cm⁻² at 450 eV. The D₂⁺ ion treated Li-O film was left undisturbed at 300 K for increasing amount of waiting time before being analyzed by AES and then by TPD.

D₂ TPD curves and AES spectra of the D₂⁺ ion irradiated Li-O film after different amounts of waiting time before analysis are shown in Figure 5.2. D₂ TPD curves show that D₂ desorbed from a single peak at 500 K. No LiD decomposition limited peak at 630 K was observed. With increasing waiting time, this 500 K peak decreased. No other TPD peaks were observed over time, indicating that the D₂⁺ ion treated Li-O film was chemically stable over time. This was confirmed by the AES spectra, which showed two peaks at 33 and 40 eV (Li₂O [23]) with no significant changes over time.
Twenty minutes of CO exposure at 1×10^{-7} torr to a 3-layer Li film led to the formation of a mixed Li-C-O composite surface. We confirmed that the entire Li film was converted to Li-C-O by the disappearance of metallic Li peak in AES (51 eV). The Li-C-O composite film was subsequently irradiated with 4×10^{15} D_2^+ cm^{-2} at 450 eV. The D_2^+ ion treated Li-C-O film was left undisturbed at 300 K for increasing amounts of time before being analyzed by AES and then by TPD.

D_2 TPD curves and AES spectra of the D_2^+ irradiated Li-C-O film after different amounts of waiting time before analysis are shown in Figure 5.3. D_2 TPD curves show that D_2 initially desorbed from two peaks at 500 K and 550 K. No LiD decomposition limited peak at 630 K was observed. With increasing waiting time, the 550 K peak
decreased and diminished while the 500 K peak grew. No other TPD peaks were observed. The AES spectra showed a small decrease in the LiOD signal (45 eV) but no significant changes in Li$_2$O signals (33 and 40 eV) over time.

Figure 5.3. TPD (left) and AES (right) of a 3-layer Li-C-O film irradiated with $4 \times 10^{15}$ D$_2^+$ cm$^{-2}$ at 450 eV for increasing amounts of waiting time at 300 K.
5.3.3. Summary and comparison to literature

The normalized amount of Li and D\textsubscript{2} retention as a function of time is plotted in Figure 5.4. The amount of Li is calculated by integrating the total area under a Li TPD curve, corrected for the mass spectrometer sensitivity to the translational energy of the desorbed species. This amount is normalized with respect to the amount of Li with 1 min waiting time before analysis. The retention fraction of D\textsubscript{2} is defined here as the integrated D\textsubscript{2} TPD area at various waiting time divided by the integrated D\textsubscript{2} TPD area at 1 min waiting time.

In addition to the results of the three experiments discussed in Section 3.1 and 3.2, the results of two more experiments are included in in Figure 5.4. First, labeled as Li (thick), 16 layers of Li were deposited onto a Ni substrate and subsequently irradiated with 8\times10^{15} \text{D}\textsubscript{2}+ \text{cm}^{-2} at 450 eV. This thicker Li film was left undisturbed at 300 K for increasing amounts of time before being analyzed by AES and then by TPD. Second, labeled as Li (High_T), 3 layers of Li were deposited onto a Ni substrate and subsequently irradiated with 4\times10^{15} \text{D}\textsubscript{2}+ \text{cm}^{-2} at 450 eV. This Li film was left undisturbed at 420 K for increasing amounts of time before being analyzed by AES and then by TPD.

Furthermore, the time dependent D\textsubscript{2} retention results at room temperature on tungsten by Bisson et al. [13] and Wierenga [36] and on graphite by Ohno et al. [37] are included for comparison.

From Figure 5.4, we can observe that the amount of Li is independent with respect to time. This is expected since Li does not evaporate below 420 K and Li does not intermix with or diffuse into the Ni substrate at less than 1 ML Li coverage on Ni [20].
As TPD is a destructive analysis technique, the Li or Li compounds had to be redeposited each time. The error in Li dosing led to the ±20% scatter in the amount of Li in Figure 5.4.

The D$_2$ retention fraction in the 3-layer Li film (black circle), 16-layer Li film (square) and 3-layer Li-O film (triangle) at 300 K decreased at similar rates to a final value of 0.5 – 0.6 after 1000 min. Li and Li-O films exhibit similar D$_2$ retention as a function of time likely due to the fact that Li is converted to Li oxide during waiting time, as discussed in Section 3.1. The D$_2$ retention fraction in the 3-layer Li film at 420 K (red circle) decreased at a faster rate to a final value of 0.32 after 730 min. This faster rate of decrease at higher temperature can be explained if the loss mechanism of D$_2$ from Li and Li-O films is physical diffusion.

The D$_2$ retention in the 3-layer Li-C-O film is found to be independent of time up to 4320 min (3 days). The D$_2$ retention fraction in the 3-layer Li-C-O film eventually decreased to 0.75 after 9360 min (6.5 days). Clearly, Li-C-O altered the loss mechanism for D$_2$ retained in Li compounds.

Comparing to D$_2$ retention in tungsten and graphite, it can be seen that at 300 K, the D$_2$ retention fraction decreased fastest in graphite over time, followed by Li and Li$_2$O, and then tungsten. The D$_2$ retention fraction decreased slowest in Li-C-O.
Figure 5.4. Amount of Li and retention fraction of D₂ as a function of time after exposure of D₂⁺ on Li, Li-O and Li-C-O films. Literature results of D₂ retention fraction on tungsten [13,18] and graphite [19] over time are also included for comparison. Lines are drawn to guide the eye.
5.4. Conclusion

D$_2$ retention in pure Li and Li compound (Li-O and Li-C-O) films has been studied as a function of time after these films are exposed to 450 eV D$_2^+$ ion irradiation. The amount of D$_2$ retained in both Li and Li$_2$O films at 300 K decreased at similar rates by 45% after 16 hours, likely due to Li being oxidized to Li oxide during the waiting time. The retention in Li-C-O film was found to be independent of time up to three days. Increasing the temperature of the Li film to 420 K increased this rate of decrease, which can be explained if the D$_2$ loss mechanism from Li film is physical diffusion. Comparing to literature results of D$_2$ retention in other materials at 300 K, the D$_2$ retention capability of Li and Li$_2$O over time falls between graphite (which loses D$_2$ faster) and tungsten (which loses D$_2$ slower).

5.5. References


[18] H. Wierenga, Modelling diffusion processes of deuterium in tungsten, Faculty of Science Theses, Utrecht University, 2013


Chapter 6. Formation and thermal stability of subsurface deuterium in Ni (110)

This chapter is an adaptation of a published article.


This chapter describes the outcome of a collaborative work from multiple authors.
I took the leading role in performing all the experiments, analyzing the results and writing the papers.

In this chapter, measurements of the uptake and subsequent D₂ thermal desorption from exposures of deuterium molecules, atoms and ions on a Ni(110) surface are discussed. This is relevant to plasma-enhanced catalysis, since the presence of reactive hydrogen atoms and ions in the gas phase above the catalyst surface in plasma-enhanced catalysis can potentially lead to different reaction mechanisms compared to typical thermal heterogeneous catalysis.

6.1. Introduction

Subsurface hydrogen has a unique chemistry, since it can hydrogenate adsorbed species that are otherwise unreactive with hydrogen adsorbed on the surface under ultrahigh vacuum (UHV) conditions. Ceyer and coworkers showed that emerging subsurface hydrogen (or deuterium) was the reactive species in the hydrogenation of adsorbed methyl [1], acetylene [2], and ethylene [3] on Ni(111) surfaces. Recently, Lin et al. also demonstrated using DFT calculations that subsurface hydrogen can either modify the energetics of reactions occurring on the surface or participate directly as a reactant for
hydrogenation reactions [4]. The capability to form subsurface hydrogen has been well established in previous studies of various metal surfaces, such as Ni(111) [5]-[8], Rh(100) [9], Cu(110) [10]-[12], Cu(111) [13]-[15], Ag(100) [16], and Pd(100) [17]-[20].

On Ni(110) at low temperature (100 K), exposures of H₂ in UHV does not result in the formation of subsurface hydrogen, but rather leads to a (2x1) LEED pattern at a coverage, \( \theta_H \), of H adatoms of 1.0 ML, referenced to the nickel surface atom density (1 ML = 1.14 x 10^{15} \text{ atoms/cm}^2) [21]. Increasing exposures to saturation, with \( \theta_H=1.5 \text{ ML} \), results in a surface reconstruction into a (1x2) phase. Heating the (1x2) phase above 220 K leads to a streaked (1x2) phase [22]-[24], which can also be formed by cooling the clean surface in an H₂ background [26]. The desorption of H₂ during temperature programmed desorption (TPD) measurements occurs in three states: an \( \alpha \) state with a peak at 220 K, associated with the transition from the (1x2) to the streaked (1x2) phase, and \( \beta_1 \) and \( \beta_2 \) states with peaks between 250 and 400 K that are associated with desorption from the (1x1) surface and the streaked (1x2) phase, respectively [22]-[24].

Hydrogen uptake past \( \theta_H=1.5 \text{ ML} \) following H atom exposures has been reported and attributed to the formation of subsurface hydrogen [25]. Additionally, cooling Ni(110) from temperatures greater than 350 K in a D₂ background results in additional uptake and a new desorption state (\( \beta_3 \)), with a desorption peak centered at 435 K that saturates with \( \theta_D=0.06 \text{ ML} \) [26]. This same feature has also been observed upon exposing CO to a hydrogen-saturated surface at temperatures greater than 375 K, and was attributed to hydrogen residing just below the surface [27].

We expand upon these studies and show evidence on Ni(110) for an additional low temperature, subsurface desorption state that can be populated using
incident D atoms or ions, and that does not saturate. In addition, we show that incident D ions are more efficient than D atoms at populating the subsurface-derived $\beta_3$ desorption state. Interestingly, as observed on Ni(111) [7], we observed that the thermal desorption temperature of subsurface D depends on the incident D energy used to create the subsurface species. Furthermore, we observed that although the desorption temperatures of surface-bound D on Ni(110) and Ni(111) are different, the thermal desorption behavior of subsurface D is nearly identical at these two surfaces [5].

6.2. Experimental methods

All experiments were performed in a stainless steel UHV chamber with a base pressure of $2 \times 10^{-10}$ Torr. Low energy electron diffraction (LEED) was performed with a PHI 15-120 LEED optics and Auger electron spectroscopy (AES) was performed with a PHI 15-255G double-pass cylindrical mirror analyzer (CMA). TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer (QMS) with the shield nozzle located 1 mm from the sample. The heating rate for TPD was 3 K/s.

The Ni(110) crystal (Princeton Scientific Corp; 8 mm square, 1 mm thick, $\pm 0.5^\circ$ orientation) was cleaned using 1.5 keV Ar$^+$ ion sputtering combined with annealing cycles to 1100 K. Oxygen treatments for several minutes at $p(O_2) = 4 \times 10^{-8}$ Torr with the sample at 1000 K were used to eliminate residual carbon. Finally, hydrogen treatments for several minutes at $p(H_2) = 4 \times 10^{-8}$ Torr with the sample at 1000 K were used to eliminate residual oxygen. Surface ordering was confirmed with LEED and surface purity
was determined with AES to ensure carbon and oxygen concentrations of less than 0.1%. A clean surface was also confirmed using the position and shape of the H$_2$ TPD peaks, which are sensitive to surface contamination.

D atoms were produced in a resistively heated, U-shaped Pt-tube, similar to a design described by Engel and Rieder [28]. The temperature of the Pt-tube source was monitored by an optical pyrometer (Omega OS3708) and was maintained at 1500±10 K. D$_2^+$ ions were produced in a PHI 04-303A differentially pumped ion gun with an adjustable ion energy of 0-5 keV. D$_2$ gas (Praxair, 99.999%) was introduced into the chamber after passing through a liquid nitrogen cooled trap on the gas inlet line using a precision leak valve and backfilling the UHV chamber. Exposures were performed with the Ni(110) crystal at 90 K. Hydrogen impurities from background coadsorption in all our deuterium experiments were less than 1%.

Surface coverages, θ, discussed herein are given in monolayers (ML), where 1.0 ML corresponds to the Ni(110) surface atom density of 1.14×10$^{15}$ atoms/cm$^2$. Deuterium coverages, θ$_D$, were determined using TPD. For calibration, we have assumed that the saturation coverage of D adsorbed at the surface is 1.5 ML when produced from dissociative adsorption of D$_2$ on Ni(110) below 130 K under UHV conditions [29][30].

6.3. Results and discussion

Figure 6.1a shows D$_2$ thermal desorption curves following increasing exposures of D$_2$ to Ni(110) at 90 K. D$_2$ desorption, denoted here as α, β$_1$, and β$_2$, occurred in three different peaks, as observed previously [21]-[24] and described in the Introduction above.
The $\beta_1$ (280 K) state was populated first at low coverage, followed by the $\beta_2$ (350 K) state. Further increases in $D_2$ exposures led to the saturation of the $\beta_1$ and $\beta_2$ peaks, and the emergence of the $\alpha$ state (220 K). The $\alpha$ state is associated with an ordered (1x2) to “streaked” phase transition of the Ni(110) surface during heating, and it is sensitive to the heating rate. The low $\beta_2$ to $\beta_1$ coverage ratio [23] indicates that oxygen contamination at the surface was minimal. The coverage of surface-bound deuterium saturates at 1.5 ML [29][30].

The $D_2$ TPD curves following exposures of 700 eV $D_2^+$ ions on Ni(110) at 90 K are shown in Figure 6.1b. We note that at these high energies, incident 700 eV $D_2^+$ ions are equivalent to incident 350 eV $D^+$ ions. The $D_2$ TPD curve following a saturation exposure of $D_2$ (from Figure 6.1a) is shown for comparison as the dashed curve. Following exposures of $D_2^+$ ions, $D_2$ desorption in TPD occurred in four states. The $\beta_3$ (435 K) state was populated first at low coverage, and this feature has been attributed to D atoms bonded just below the topmost surface Ni layer [26][27]. However, the $\beta_3$ (435 K) state in previous reports was not observed with a concentration above 0.06 ML [26][27]. Our observation of the $\beta_3$ state observed in Figure 1b with a concentration of $>0.5$ ML is attributed to the exceptionally high efficiency of $D^+$ ions at populating this state. Because the $\beta_3$ state was previously reported to be formed by coadsorbed CO-induced diffusion of surface D into the subsurface region [27], we performed a control experiment by coadsorbing 0.4 ML CO with pre-saturated surface D adlayer. We found that no more than 0.05 ML of subsurface D was formed using this method.

Increasing $D_2^+$ exposures led to the population of $\beta_1$ (280 K) and then $\beta_2$ (350 K) states. Further increases in $D_2^+$ exposures led to the formation of a desorption feature
denoted as $\gamma_1$ (260 K) that did not saturate in our experiments (resulting in a highest value that we explored of $\theta_0=20$, with no shift in peak temperatures or changes in desorption profile, and is not shown here), and therefore was attributed to the population of subsurface sites for D absorption. Incident D$^+$ ions at 350 eV are well understood to directly (physically) penetrate the Ni surface layer and come to rest in the subsurface region of the Ni(110) substrate, and then evidently are kinetically trapped there for the Ni(110) crystal at 90 K. We note that the $\alpha$ state associated with the (1x2) to “streaked” phase transition was not observed. Perhaps the presence of subsurface D altered the Ni(110) (1x2) phase transition.

The D$_2$ TPD curves following exposures of D atoms on Ni(110) at 90 K are shown in Figure 6.1c. Again, the D$_2$ TPD curve following a saturation exposure of D$_2$ gas (from Figure 6.1a) is shown for comparison as the dashed curve. Like D$_2^+$, exposures of D atoms populate the $\beta_2$ (350 K) and $\beta_1$ (280 K) states. D$_2$ desorption from the $\alpha$ state, associated with an ordered (1x2) to “streaked” phase transition of the Ni(110) surface during heating, was eliminated at high coverages, which is consistent with the role of subsurface D in altering the Ni(110) (1x2) phase transition. A comparison of the $\beta_3$ and $\beta_2$ peak areas following exposures of D atoms and D$_2^+$ ions shows that D atoms were less efficient at populating the $\beta_3$ and $\beta_2$ states than D$_2^+$. High exposures of D atoms lead to desorption from additional low temperature peaks, labeled as $\gamma_1$ (185 K) and $\gamma_2$ (195 K), that we attribute to desorption from D bound in subsurface sites. This common origin for $\gamma$ peaks following exposures of D atoms and D$_2^+$ ions will be addressed in more detail in Figure 6.3 below.
Premm et al. [5] previously performed similar experiments on Ni(111), exposing this surface at 130 K to both D$_2^+$ and D atoms, and we have adopted the nomenclature used in that report. Compared to the $\beta_1$ (280 K) and $\beta_2$ (350 K) peaks from chemisorbed deuterium adatoms at the Ni(110) surface, chemisorbed deuterium on the Ni(111) surface desorbed at higher temperatures in the $\beta_1$ (335 K) and $\beta_2$ (370 K) peaks (using the same heating rate in TPD in the two experiments). However, no $\beta_3$ (420 K) peak from subsurface deuterium was observed from the Ni(111) surface. Premm et al. did report the formation of a subsurface state that desorbed D$_2$ at 265 K (that they denoted as $\alpha$) following 500 eV D$_2^+$ exposures on Ni(111), which is at a temperature close to our observation of the $\gamma_1$ (260 K) state following 700 eV D$_2^+$ exposures on Ni(110). Premm et al. also reported that incident D atoms formed subsurface deuterium that desorbed on Ni(111) in $\gamma_1$ (185 K) and $\gamma_2$ (210 K) peaks, which are comparable to our $\gamma_1$ (185 K) and $\gamma_2$ (195 K) peaks following D atom exposures on Ni(110). In summary, chemisorbed surface-bound deuterium desorbs in TPD from Ni(111) at somewhat higher temperatures than from Ni(110), and without the phase-transition derived peak on Ni(110), but subsurface deuterium populated by both D atoms and ions desorbs at very comparable temperatures. The simplest explanation for this observation is that subsurface D atoms reside within interstitial sites in bulk nickel and subsequent D$_2$ desorption during TPD is rate-limited by bulk transport (diffusion) of D atoms to the surface.

Possible isotope effects between hydrogen and deuterium were measured in separate TPD experiments (not shown here) following exposures of 700 eV H$_2^+$ ions on Ni(110). The resulting H$_2$ TPD profiles were nearly identical to those for D$_2$ TPD shown in Figure 6.1b, except that the $\gamma_1$ (250 K) peak for H$_2$ was shifted to lower temperature by
15 K compared to that for D$_2$. This observation is consistent with the explanation above that D$_2$ desorption from subsurface D atoms is rate-limited by D diffusion to the surface, since the heavier D atoms have a slower diffusion rate from subsurface to surface sites compared to the lighter H atoms.
Figure 6.1. D\textsubscript{2} TPD curves following exposures of (a) D\textsubscript{2}, (b) 700 eV D\textsubscript{2}\textsuperscript{+}, and (c) D atoms to Ni(110) at 90 K under UHV conditions. For comparison, the D\textsubscript{2} TPD trace from a saturation coverage of surface deuterium, from panel (a) is shown as a dashed curve in panels (b) and (c). The γ peaks do not saturate at higher doses (not shown here) of D\textsubscript{2}\textsuperscript{+} ions and D atoms, and are assigned to D\textsubscript{2} desorption from D absorption in subsurface sites.

Uptake curves, in which the amount of D (coverage) that is retained by the Ni(110) crystal and that subsequently desorbs as D\textsubscript{2} in TPD for a given fluence (exposure) of D, is shown in Figure 6.2 for incident D\textsubscript{2} molecules, 700 eV D\textsubscript{2}\textsuperscript{+} ions, and D atoms on Ni(110) at 90 K. The initial sticking coefficient of D\textsubscript{2} was calculated to be 0.4 assuming that the saturation D coverage is 1.5 ML [29][30]. This value agrees well with the range (0.3-0.35) previously reported [23][25],[31]. The initial sticking coefficient of D\textsubscript{2}\textsuperscript{+} ions was calculated to be unity, as obtained by measurements of the ion current density, corrected for secondary electron emission, and using the D coverage calibration above. The initial sticking coefficient of D atoms was set to be unity up to $\theta_D = 1.5$ ML, and this resulted in a calculated sticking coefficient of 0.09 for $\theta_D > 1.5$ ML. Previous studies for Ni(110) have reported the initial sticking coefficient of D atoms to be 0.9 [25] and 0.01-0.04 past 1.5 ML [25][31]. This demonstrates that high energy D\textsubscript{2}\textsuperscript{+} ions are much more effective than low energy D atoms at penetrating a saturated layer of chemisorbed D at the Ni(110) surface and populating subsurface Ni sites.
Figure 6.2. Uptake curves for D$_2$ (♦), 700 eV D$_2^+$ ions (■), and D atoms (♦) on Ni(110) at 90 K. The initial sticking coefficients of D$_2$ gas and D$_2^+$ ions were measured to be 0.4 and 1. Setting the initial sticking coefficient of D atoms to be unity up to $\theta_D = 1.5$ ML leads to a sticking coefficient of 0.09 for $\theta_D > 1.5$ ML.

In the above discussion, we assigned the origin of the $\gamma$ peaks in D$_2$ TPD to subsurface D in both Figure 6.1b and Figure 6.1c, arising from both incident D$_2^+$ ions and D atoms, even though the D$_2$ TPD peak temperatures were quite different. Figure 6.3 shows that the desorption temperature of the $\gamma_1$ peak on Ni(110) increased with increasing incident D$_2^+$ ion energy up to 600 eV (above this energy, up to 1.5 keV, we did not observe any additional shift in temperature). This energy dependence is consistent with D diffusion to the surface from within the subsurface region of Ni as the limiting factor for D$_2$ desorption in TPD since D atoms from higher energy D$_2^+$ ion exposures are formed more deeply in the nickel substrate and thus take a longer time to diffuse back to the surface during heating in TPD to desorb as D$_2$. The same trend was observed
previously on Ni(111) [5],[7] and these data are plotted in Figure 6.3 for comparison. This data for Ni(110) and Ni(111) agree very well, indicating that once deuterium penetrates into the bulk, the surface orientation no longer influences the thermal stability of D in these samples.

Figure 6.3. D\(_2\) desorption temperature in TPD measurements of subsurface deuterium forming the \(\gamma_1\) feature from exposures to D\(_2^+\) ions (■) and D atoms (●) on Ni(110) and D\(_2^+\) ions (▲) on Ni(111) [5],[7] for increasing energy of the incident D used to create subsurface D. The \(\gamma_1\) D\(_2\) desorption temperature remains constant at 265 K for incident energies above 600 eV on both Ni(110) and Ni(111) surfaces.
6.4. Conclusion

Reactive hydrogen radicals and ions present in plasma-enhanced catalysis can form subsurface hydrogen, which has been previously demonstrated to have a unique ability to hydrogenate adsorbed species that are otherwise unreactive with adsorbed hydrogen at the surface. Therefore, accounting for the presence of subsurface hydrogen and its reactivity for hydrogenation is an important component for understanding plasma-enhanced catalysis over Ni-based catalysts. We have investigated the uptake and subsequent thermal desorption of deuterium on a Ni(110) surface using incident D$_2$, D atoms, and D$_2^+$ ions. Subsurface deuterium binding sites on Ni(110) are readily populated at 90 K by incident D atoms and D$_2^+$ ions, but not molecular D$_2$. Subsurface D atoms recombine to desorb as D$_2$ gas in TPD measurements to create characteristic subsurface-derived D$_2$ thermal desorption peaks. The temperature of these peaks increases linearly with increasing energy (up to 600 eV) of the incident deuterium atoms and ions. Furthermore, we report that D$_2^+$ ions are very efficient at populating a high temperature (435 K) D$_2$ desorption state from subsurface deuterium, which had been previously reported only from co-adsorbed CO or cooling in background hydrogen gas. A comparison of Ni(110) and Ni(111) surfaces shows that the thermal stability and D$_2$ TPD peaks from subsurface D atoms are nearly the same for these two substrates. A simple explanation for this behavior is that D$_2$ desorption during TPD is rate-limited by the diffusion of D to the surface from interstitial sites in the near-surface region of nickel. Overall, information on the uptake and thermal stability of subsurface hydrogen will be helpful for a fuller understanding of the role of subsurface hydrogen and its reactivity in
hydrogenation for plasma-enhanced catalysis over Ni-based catalysts, with implications for the broader class of metal-based catalysts.

6.5. References


Chapter 7. Hydrogenation of CO on Ni(110) by energetic deuterium

This chapter is an adaptation of a published article.


This chapter describes the outcome of a collaborative study involving experimental work conducted in Princeton University and simulation performed in Northwestern University. I performed all the experiments described in this chapter while the simulations were done by Wei Lin at Northwestern University. This chapter includes both my experimental work and the simulations done to facilitate presentation of concrete results.

In this chapter, the work from Chapter 6 is expanded upon and investigations of the unique chemistry of subsurface deuterium, i.e. the ability to hydrogenate adsorbed species that are otherwise unreactive with hydrogen adsorbed on the surface under ultrahigh vacuum (UHV) conditions, is expanded upon. The hydrogenation reactivity of subsurface deuterium to that of incident deuterium atoms and ions is also compared.

7.1. Introduction

The interaction between coadsorbed hydrogen and carbon monoxide (CO) has been widely studied on various metal surfaces due to its role in heterogeneous catalysis and hydrocarbon synthesis, such as the Fischer-Tropsch process and the CO methanation
reaction [1]-[10]. Comparatively few studies have focused on the interaction of energetic hydrogen species, such as H atoms and ions, with CO adsorbed on metal surfaces. For example, as a way to overcome the high activation barrier associated with dissociative adsorption of ground state H\(_2\) on Cu(110), H atoms were used to study the interaction of H and CO on Cu(110) and Ni/Cu(110) [11]. Similarly, on Ru(001) [12], H atoms were used as a method to simulate Fischer-Tropsch chemistry under UHV conditions by overcoming the thermodynamic and kinetic barriers that prevent this study using H\(_2\). More investigations are needed of energetic hydrogen interactions with CO because of the role that H atoms and ions could play in plasma enhanced catalysis [13]-[15].

Plasma enhanced catalysis combines a plasma with a catalyst to carry out catalytic processes, such as dry methane reforming, in which two greenhouse gases, methane (CH\(_4\)) and carbon dioxide (CO\(_2\)), are converted into syngas. In plasma catalytic dry reforming a synergistic effect has been observed in experimental studies that combined plasmas with catalysts [13]-[18], but the mechanism of this synergism is not understood. Investigating the interaction of energetic hydrogen species with adsorbates, such as CO, on metal surfaces is an important step towards developing this understanding. CO is of particular interest since it is a likely and stable adsorbate in plasma catalytic dry reforming, as well as an important reactant in the Fischer-Tropsch and CO methanation reactions.

Although surface reactions most commonly occur by a Langmuir-Hinshelwood mechanism (LH), in which both reactants are adsorbed on and thermally equilibrated with the surface prior to collision and subsequent formation of products, incident H atoms readily follow an Eley-Rideal (ER) or hot atom (HA) mechanism [19]. The ER reaction
involves the direct impingement of a gas phase atom on an adsorbed species, resulting in
the immediate formation of the product, which may either desorb or remain adsorbed on
the surface [20]. The abstraction of adsorbed H by incident H atoms on Si(100) and
Si(111) [21], as well as the reaction of incident H atoms with adsorbed H, CO, O, and
formate on Ru(001) [20] follow the ER mechanism. In the HA mechanism, the incident H
atom first strikes the metal surface, releasing the H adsorption energy into (mostly) H
atom translational energy. Subsequently the H atom undergoes several bounces between
metal atoms, before hitting a CO and reacting directly with it.

Another possibility is that incident energetic hydrogen species penetrate the
surface to form subsurface hydrogen. Experimentally, subsurface hydrogen has been
found to be the active species in the hydrogenation of methyl and acetylene on Ni(111)
[22][23], while theoretical work on Ni(110) has shown that subsurface hydrogen can
reduce adsorbed CO$_2$ to CO and H$_2$O [24], and hydrogenate adsorbed CO to CH$_2$O and
CH$_3$OH [25].

In this paper, we report on studies of H/D reacting with CO-covered Ni(110) that
expand on previously reported work [25], including exploration of the hydrogenation of
CO using both subsurface D, incident D atoms and D$_2^+$ ions. We also compare BOMD
simulations of H atoms impinging on a clean and CO-precovered Ni(110) surface.

7.2. Experimental methods

Experiments were conducted in a three-level, stainless-steel UHV chamber
(2×10$^{-10}$ Torr base pressure) equipped with low energy electron diffraction (LEED),
Auger electron spectroscopy (AES), and temperature programmed desorption (TPD) capabilities. LEED was performed with a PHI 15-120 LEED optics. AES was performed with a PHI 15-255G double-pass cylindrical mirror analyzer (CMA). TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer with the shield nozzle located 1 mm from the sample. The heating rate was 3 K/s. TPD was conducted monitoring these 14 masses: 2, 3, 4, 16, 17, 18, 19, 20, 28, 30, 32, 34, 40, and 44 amu. We assign 32 amu to CD$_2$O and 34 amu to CD$_3$OD based on matching cracking ratios in our experiments and NIST. CD$_2$O was monitored following 32 amu to differentiate from CD$_3$OD, which has a large cracking fraction at 30 amu.

The Ni(110) crystal (Princeton Scientific Corp, 8 mm square, 1 mm thick, ±0.5° orientation) was cleaned initially using 1.5 keV Ar$^+$ ion sputtering and annealing cycles at 1100 K. Additional oxygen treatments for several minutes at p(O$_2$) = 4×10$^{-8}$ Torr with the sample at 1000 K were used to eliminate residual carbon. Subsequent hydrogen treatments for several minutes at p(H$_2$) = 4×10$^{-8}$ Torr with the sample at 1000 K were used to eliminate residual oxygen. Ni(110) surface ordering was determined with LEED and purity was confirmed with AES to ensure carbon and oxygen concentrations of less than 0.1%. A clean surface was also confirmed using the position and shape of the D$_2$ TPD peaks, which are sensitive to surface contamination.

D atoms were produced in a resistively heated, U-shaped Pt-tube, similar to a design described by Engel and Rieder [26]. The temperature of the Pt-tube source was measured by an optical pyrometer (Omega OS 3708) and was maintained at 1473 K. D$_2^+$ ions were produced in a PHI 04-303A differentially pumped ion gun with adjustable ion
energy from 0-5 keV. The nickel sputtering yield for 100-400 eV D$_2^+$ ions is <0.04 (Ni atoms/incident ion) [27], and ion exposures were limited in our experiments to ≤ 2 monolayer equivalents. D$_2$ gas (Praxair, 99.999%) was introduced into the chamber after passing through a liquid nitrogen cooled trap on the gas inlet line using a precision leak valve and backfilling the UHV chamber. CO (Praxair, 99.9%) was dosed through backfilling the chamber. Exposures were performed with the Ni(110) crystal at 100 K. Hydrogen impurities from background coadsorption in all of the deuterium experiments were less than 0.01 monolayers.

Surface coverages θ are given in monolayers (ML), where 1 ML corresponds to the surface Ni atom density of Ni(110) (1.14×10$^{15}$ atoms/cm$^2$). D coverages, θ$_D$, were determined using TPD. We assumed a surface saturation coverage of D adatoms was θ$_D$ = 1.5 ML when produced from dissociative adsorption of D$_2$ on Ni(110) at 100 K under UHV conditions [28].

7.3. Computational methods

All Born-Oppenheimer molecular dynamics (BOMD) simulations in this study were performed with spin−polarized density functional theory (DFT) and periodic boundary conditions as implemented in VASP 5.3.5 [29][30]. The PBE functional [31] was used to model exchange and correlation interactions, while electron−ion interactions were modeled using projector-augmented wave (PAW) potentials. The Ni(110) surface used in this study was a 2 × 3 unit cell with 6 Ni atoms per layer and 7 layers in total, in which the top 4 layers were allowed to relax and the bottom 3 layers were constrained to
maintain the bulk Ni structure. The unit cell also contained about 12 Å of vacuum between the uppermost Ni layer and the upper boundary (in the positive z direction) to avoid electronic interactions between vertically neighboring cells. A 4 × 3 × 1 Monkhorst–Pack mesh was used for k-sampling of the Brillouin zone. The kinetic energy of the impinging H atoms was set to 1473 K to mimic the condition in the experiments herein and the rest of the system was set to 100 K. In total, 100 trajectories were run with the initial H atoms randomly distributed in a unit cell that is 5 Å above the Ni surface. The BOMD simulations were performed in a microcanonical (NVE) ensemble with a 0.5 fs time step. All trajectories were one picosecond in length, after which the hydrogen atoms were mostly thermalized on the surface or bulk. Note that electronic friction effects should not be important on this time scale so we have not included them.

7.4. Results and discussion

The various potential hydrogenation mechanisms for CO have been examined on the Ni(110) surface at 100 K under UHV using coadsorbed surface D, subsurface D, and incident D atoms and D$_2^+$ ions. The study of the interaction of surface D and CO, presented in Section 7.4.1, was designed to probe the LH mechanism. Next, the study of the interaction of subsurface D with CO, presented in Section 7.4.3, was designed to probe the subsurface D pathway. Finally, the study of the interaction of incident D species and preadsorbed CO, presented in Section 7.4.4, was designed to probe the ER and HA mechanism.
7.4.1. Interaction of surface D and CO on the Ni(110) surface

We first examined the interaction between CO and surface D, formed by the dissociative adsorption of D₂, to establish a baseline for later comparisons and calculations. Overall our results are consistent with those reported previously [32][33]. Uptake curves demonstrated that a 5 L exposure of CO on clean Ni(110) at 100 K resulted in a saturation coverage of CO, which has been reported to be θ_{CO} = 1 ML [34][35], and this CO exposure was used in all following experiments. The black dashed TPD curve in Figure 7.1a shows CO desorption following exposure of CO on Ni(110) at 100 K. CO desorbs from Ni(110) in two peaks: a higher temperature peak at 430 K attributed to CO adsorbed primarily at on-top sites and a lower temperature peak at 280 K attributed to tilted CO at bridge sites [34][35]. CO desorption below 200 K may arise from heated parts of the sample holder and was ignored.

Uptake curves also showed that 5 L D₂ exposures on clean Ni(110) at 100 K resulted in a saturation coverage, reported to be θ_{D} = 1.5 ML [28]. The black dashed TPD curve in Figure 7.1b shows D₂ desorption following this exposure of D₂ on Ni(110) at 100 K. Three D₂ TPD peaks denoted as α, β₁, and β₂, occurred as observed previously [28]. The α (220 K) peak accommodates 0.5 ML D and is associated with desorption from the (1 x 2) reconstructed phase and the transition to the streaked (1 x 2) phase, while the β₁ (280 K) and β₂ (350 K) peaks are due to desorption from the (1 x 1) surface and the streaked (1 x 2) phase, respectively [28]. The formation of subsurface D [36] was not observed at these or higher (10 L) exposures of D₂ on Ni(110) at 100 K.

CO and D₂ TPD curves obtained simultaneously following exposure of 5 L (4x10⁻⁸ torr, 120 s) of D₂ on a CO-saturated Ni(110) surface at 100 K are shown by the blue
curves in Figure 7.1a and b, respectively. D₂ did not adsorb on this surface, but rather displaced some CO from the on-top sites. No reaction products were observed in these TPD measurements, as discussed below in Section 7.4.4.
Figure 7.1. Comparisons of CO and D\textsubscript{2} TPD from Ni(110) after three different experiments: (a) CO TPD curves following exposing clean Ni(110) to 5 L CO (black dashed), exposing CO-saturated Ni(110) to 5 L D\textsubscript{2} (blue), and exposing D-saturated Ni(110) to 5 L CO (red); and (b) D\textsubscript{2} TPD curves following exposing clean Ni(110) to 5 L D\textsubscript{2} (black dashed), exposing CO-saturated Ni(110) to 5 L D\textsubscript{2} (blue); exposing D saturated Ni(110) to 5 L CO (red). T\textsubscript{s} = 100 K.

CO and D\textsubscript{2} TPD curves following exposure of 5 L CO on a D-saturated Ni(110) surface, reversing the order of CO and D\textsubscript{2} exposure from above, are shown by the red
curves in Figure 7.1a and b, respectively. Comparison of TPD areas of the red and black dashed curves in Figure 7.1a indicates that the D-saturated Ni(110) surface only accommodated 0.73 ML CO. Furthermore, comparison of the red and black dashed curves in Figure 7.1b shows that incident CO displaced 0.08 ML preadsorbed D and changed the D$_2$ desorption profile. The $\alpha$ peak split into two smaller peaks and the $\beta_2$ peak was removed completely. This is in accordance with previous studies that revealed a change in CO and H adsorption sites and a lifting of the (1x2) hydrogen-induced reconstruction [8],[37][38]. Again, no reaction products were observed in these TPD measurements, as discussed below in Section 7.4.3.

7.4.2. Formation of subsurface D with D atoms and D$_2^+$ ions on the Ni(110) surface

D$_2$ TPD curves following exposure of D$_2$ (black dashed), D atoms (1473 K, 0.13 eV) (green), and 400 eV D$_2^+$ ions (equivalent to 200 eV D$^+$ ions) (red) are shown in Figure 7.2. The TPD curve in Figure 7.2 following exposure of D$_2$ to give 1.5 ML D was reproduced from Figure 7.1b for comparison. Exposures of D atoms and 400 eV D$_2^+$ ions on Ni(110) at 100 K resulted in coverages of 3.6 and 4.1 ML D as shown by the green and red curves in Figure 7.2, respectively. These exposures of energetic deuterium were used in experiments discussed in Section 7.4.3. Incident D atoms populated the $\gamma_1$ (160 K) peak, attributed to D$_2$ desorption from subsurface “bulk” D [36]. Increasing exposures of D atoms revealed that the $\gamma_1$ peak did not saturate. Similarly, exposure of 400 eV D$_2^+$ ions populated the subsurface $\beta_3$ (380 K) and $\gamma_1$ (250 K) peaks. Note that the desorption temperature of the subsurface $\gamma_1$ peak is a function of the incident D energy [36].
Figure 7.2. Formation of subsurface D using incident D atoms and D$_2^+$ ions as probed by D$_2$ TPD. These curves following exposure of D$_2$ (black dashed), D atoms (green), and 400 eV D$_2^+$ ions (red) on Ni(110) correspond to $\theta_D = 1.5$, 3.6, and 4.1 ML D, respectively. $T_s = 100$ K.

7.4.3. Interaction of subsurface D with CO on the Ni(110) surface

All of the TPD curves shown in Figure 7.3 were obtained after deuterium pre-exposures were given on Ni(110) at 100 K followed by a subsequent 5 L CO exposure. Products from CO hydrogenation formed from pre-exposure of gaseous D$_2$ (blue), incident D atoms (green), or 400 eV D$_2^+$ ions (red), along with the accompanying D$_2$ desorption, are shown in Figure 7.3 for peaks at 32 amu (assigned to CD$_2$O) and 34 amu
(assigned to CD$_3$OD), respectively. The close correspondence of the low-temperature D$_2$
peaks with the product peaks in Figure 7.3 indicates reaction-rate limited desorption of
these two products. Subsurface D from either source was much more effective than D
adsorbed at the surface from D$_2$ exposure for hydrogenating adsorbed CO in these TPD
measurements, and the desorption peak temperatures depend on how the subsurface D
was formed: 170 K for incident D atoms and 240 K for incident D$_2^+$ ions.

Although the amount of CD$_2$O and CD$_3$OD formed in Figure 7.3 was not
quantified directly, the changes in the accompanying D$_2$ and CO TPD curves can be used
to estimate these yields. The D$_2$ TPD area following the exposure of D atoms on Ni(110)
with and without post-exposure of CO indicates that the amount of D desorbed decreased
from 3.6 to 3.3 ML, as shown in Figure 7.4b. As calculated in Section 7.4.1, 0.08 ML of
surface D adatoms was displaced by incident CO molecules during exposure, and
therefore 0.22 ML D reacted with the incident CO to form CD$_2$O and CD$_3$OD. We can
also calculate the amount of CO that appears in these hydrogenated products by
measuring the amount of CO desorbed (0.5 ML) in TPD in these experiments, as shown
by the green curve in Figure 7.4a for using incident D atoms. This amount of desorbed
CO is then compared to the amount of CO (0.73 ML) desorbed from the D-saturated
surface, in which no subsurface D is present, as shown by the blue curve in Figure 7.4a.
For reference, Figure 7.4a also shows CO TPD from clean Ni(110) where $\theta_{CO} = 1.0$ ML.
Therefore, in the case of incident D atoms, 0.23 ML CO, i.e. 30\% of the post-adsorbed
CO reacted with subsurface D to form CD$_2$O and CD$_3$OD. Note that this is an estimate of
the amount of CO and D that reacted, since CD$_2$O and CD$_3$OD partially decompose on
Ni(110) to evolve CO and D$_2$ in TPD measurements [39][40], and additionally, CO and
D₂ could have been consumed through another pathway that was not monitored in our TPD measurements.

Figure 7.3. TPD curves obtained after forming adsorbed D at the Ni(110) surface at 100 K using 5 L D₂ exposures (blue), and additionally forming subsurface D on Ni(110) using D atoms (green) and 400 eV D₂⁺ ions (red) and giving a post-exposure of 5 L CO. The desorption of CO hydrogenation products CD₂O and CD₃OD occurs in peaks coincident with D₂ desorption from D populated subsurface sites.
Figure 7.4. TPD curves for (a) CO and (b) D$_2$ that can be used to calculate the amounts of CO and D reacted to form CD$_2$O and CD$_3$OD. In (a) we show CO TPD for a saturation coverage of CO on: clean Ni(110) (black dashed); surface saturated with D adatoms from a 5 L D$_2$ predose (blue); and surface containing subsurface D from a D atom predose (green). In (b) we show D$_2$ TPD for: surface saturated with D adatoms from a 5 L D$_2$ exposure (black dashed); surface containing subsurface D from a D atom exposure (black); and surface containing subsurface D from a D atom predose followed by 5 L CO post-exposure (green). $T_s = 100$ K.
7.4.4. Interaction of incident D species on the CO saturated Ni(110) surface

Figure 7.5 shows TPD curves following the exposure of D\textsubscript{2} (blue), D atoms (green) or 100 eV D\textsuperscript{2+} ions (equivalent to 50 eV D\textsuperscript{+} ions) (red) on a CO-saturated Ni(110) surface at 100 K. This reverses the order of exposures of CO and D species from Section 7.4.3. Gaseous (5 L) D\textsubscript{2} did not react with preadsorbed CO or stick on the CO-saturated surface and no hydrogenated products or D\textsubscript{2} desorption was observed in TPD measurements. Incident D atoms were sorbed, forming subsurface D, and reacted with preadsorbed CO in subsequent TPD measurements to desorb trace amounts of CD\textsubscript{2}O in peaks at 140 and 220 K. No significant desorption of CD\textsubscript{3}OD was observed. The low temperature CD\textsubscript{2}O peak appears below the temperature for D\textsubscript{2} desorption from subsurface D, which indicates that this product was formed either during D atom exposure via an ER or HA mechanism directly involving incident D atoms or at or below 140 K from reactions of coadsorbed D and DCO or CO. Exposure of the CO-saturated surface to incident 100 eV D\textsuperscript{2+} ions resulted in sorption of D, with formation of subsurface D, and the desorption of D\textsubscript{2}, CD\textsubscript{2}O, and CD\textsubscript{3}OD at 200 K in TPD measurements. The D\textsubscript{2} TPD peak occurred at the same temperature at which subsurface D (formed from 100 eV D\textsuperscript{2+} ions) desorbed as D\textsubscript{2} from clean Ni(110). The appearance of all of the desorbed products in peaks at the same temperature is consistent with a mechanism in which subsequent heating in TPD causes subsurface D to emerge at the surface and react with adsorbed CO to form the CD\textsubscript{2}O and CD\textsubscript{3}OD products observed in TPD. This also demonstrates that higher energy D\textsuperscript{2+} ions are more effective than lower energy D atoms at penetrating a monolayer of chemisorbed CO on the Ni(110) surface.
and populating subsurface Ni sites, and therefore more extensively access a subsurface D reaction pathway for the hydrogenation of CO.

Figure 7.5. TPD curves for D₂, CD₂O, and CD₃OD following exposure of a CO-precovered Ni(110) surface to incident D₂ (blue), D atoms (green), and 100 eV D₂⁺ ions (red). Tₛ = 100 K. Coincident desorption of CD₂O and CD₃OD with D₂ arising from subsurface D indicates the important role of subsurface D species in hydrogenating adsorbed CO.
7.4.5. BOMD simulation of H impinging on clean and CO covered Ni(110) surface

The experiments presented above have been addressed from an energetics point of view in a previous paper [25], in which the lowest energy pathway for CO hydrogenation to CH$_3$OH for several metal surfaces has been compared. The Ni(110) surface itself has relatively high energy barriers, but if we take into account the electronic energy stored when a subsurface hydrogen atom emerges to the surface (0.6 eV per H$_{sub}$), the overall effective barriers for Ni(110) + H$_{sub}$ are much lower than those for clean Ni(110) and comparable to those for CO hydrogenation on clean Cu(111) and Cu(211), which are favorable for forming methanol. In that same paper [25], our BOMD simulations have shown that the direct impact of H atoms on a partially CO-covered Ni(110) surface could not hydrogenate CO via either an Eley-Rideal or hot-atom mechanism. To further investigate the possibility of subsurface hydrogen formation, BOMD simulations were performed for hydrogen impinging on the clean Ni(110) surface. The kinetic energy (temperature) of the impinging H was set to 2.9 kcal/mol (1473 K) and the temperature of Ni(110) was set to 100 K to mimic the conditions of the TPD experiments. As shown in Figure 7.6a and b, of the 100 trajectories that were studied, only 5 of them led to reflection of the hydrogen atom back to vacuum (denoted “Reflected H” in Figure 7.6b), and about half of the hydrogen atoms thermalized on the surface. Overall, 44% of the hydrogen atoms either reached the subsurface or bulk, with 25% and 13% of them resulting in subsurface hydrogen or bulk hydrogen, respectively, followed by diffusion back to the surface, and 6% resulting in thermalized bulk hydrogen. Although the overall ratio of bulk hydrogen is relatively low in our simulations, 44% of the simulated hydrogen can either reach subsurface or bulk. In our simulations, only one hydrogen
atom was used to impact the clean Ni(110), hence the interactions between the absorbed hydrogen and impinging hydrogen that can occur in the experiments were not taken into account. Furthermore, only four layers of relaxed Ni were used in the simulations. As shown in Figure 7.6a, some trajectories reach the bulk and then return to the surface. The force from the rigid Ni layers may therefore increase the possibility for bulk hydrogen emerging to surface.

Figure 7.6. (a) The z-axis of the impinging hydrogen atom and (b) the populations of hydrogen along the 100 trajectories of BOMD simulations on clean Ni(110).
7.4.6. Hydrogenation mechanisms for energetic D at the CO-saturated Ni(110) surface

We can combine the details about the reaction channels for CO hydrogenation on Ni(110) due to incident D, surface-bound D, and subsurface D with our experimental data to obtain insights into the importance of these various pathways. Incident D$_2^+$ ion exposure on a CO-precovered Ni(110) surface forms both CD$_2$O and CD$_3$OD, as discussed above for Figure 7.5. However, as can be seen by the direct comparison in Figure 7.7a and b, this situation (red curves) yielded 5 times less hydrogenation products than the reaction between pre-absorbed subsurface D formed by incident D$_2^+$ ion exposure on a clean Ni(110) surface followed by CO exposures (black curves). These observations demonstrate that the ER mechanism is not as efficient as a reaction pathway with subsurface D for CO hydrogenation by energetic D at these energies on Ni(110). This conclusion is valid extending all the way to low, thermal energies since a similar conclusion was reached for incident versus pre-exposed D atoms [25]. This is also supported by the BOMD simulations discussed above, which show that subsurface D plays the major role in the hydrogenation of CO on Ni(110) under these conditions.
Figure 7.7. Comparisons of the yields of CO hydrogenation from TPD curves for (a) CD$_2$O and (b) CD$_3$OD. Black curves: TPD curves following the formation of subsurface D using incident D$_2^+$ ions on a clean Ni(110) surface followed by post exposure of 5 L CO. Red curves: TPD curves following exposure of a CO-saturated Ni(110) surface to incident D$_2^+$ ions. $T_s = 100$ K.

7.5. Conclusion

We have investigated the hydrogenation of adsorbed CO molecules on a Ni(110) surface at 100 K under ultrahigh vacuum (UHV) conditions using coadsorbed surface deuterium (D), subsurface D, and incident D atoms and D$_2^+$ ions. Surface-bound D adatoms did not hydrogenate coadsorbed CO to form gas-phase products in TPD measurements. In contrast, subsurface D reacted with adsorbed CO to form the hydrogenated TPD products formaldehyde (CD$_2$O) and methanol (CD$_3$OD). The desorption peaks of CD$_2$O and CD$_3$OD in TPD were coincident with D$_2$ desorption from
D occupation of subsurface sites. A CO pre-saturated Ni(110) surface completely blocked
the adsorption of D from incident D$_2$ under these conditions. Energetic 100 eV D$_2^+$ ions
penetrate the adsorbed CO adlayer to populate D in subsurface sites that subsequently
lead to hydrogenation of adsorbed CO to form CD$_2$O and CD$_3$OD in TPD measurements.
Incident D atoms also form subsurface D but only forms the CD$_2$O product.

The experiments show that incident energetic D species are less reactive than
subsurface D for the hydrogenation of CO on the Ni(110) surface. Additionally, Born-
Oppenheimer molecular dynamics (BOMD) simulations show that the direct impact of H
atoms on a CO covered Ni(110) surface does not hydrogenate CO via an Eley-Rideal or
hot-atom mechanism. Therefore, in environments where energetic D species are incident
on adsorbate-covered surfaces, one needs to include the important, likely dominant role,
of subsurface D in reaction chemistry, as our BOMD simulations indicate the possibility
of subsurface H formation on Ni(110). Overall, these results will be helpful for a fuller
understanding of the synergistic effects observed in plasma-enhanced catalysis over Ni-
based catalysts. As demonstrated, incident hydrogen atoms and ions in hydrocarbon
reforming plasmas can carry out hydrogenation reactions more effectively than surface-
bound hydrogen.

7.6. References


Chapter 8. Conclusions

This dissertation examined the interaction of energetic hydrogen (H) and deuterium (D) species with surfaces related to two applications: plasma-surface interactions in nuclear fusion experiments and plasma-catalytic dry reforming.

The first application concerns energetic H/D species involved in plasma-surface interactions in nuclear fusion experiments. A lithium (Li) coating on PFCs prevents the high Z PFCs from being sputtered into the plasma. As the solid element with lowest Z at room temperature, Li does not contribute significantly to line radiation even when sputtered into the plasma. Furthermore, since Li is highly reactive, it is also a good pump for hydrogen isotopes, so these are trapped in the lithiated wall and not recycled back into the plasma, thus reducing wall recycling and this is also beneficial for plasma performance.

The ability of Li and lithium oxide (Li-O) films to retain H following 500 eV H$_2^+$ irradiation was examined at different temperatures (90-520 K) under UHV conditions. It was experimentally shown that upon oxidation, Li thermal stability increased. It was also shown that both pure Li and Li$_2$O are able to retain H at almost the same amounts. In addition, it was shown that H and D retention drops with surface temperature in the range 90-520 K from 95% to 35% due to outwards diffusion of H at high temperatures. Results of MD modeling with EEM corrections were qualitatively consistent with experimental results in terms of both retention fraction and the drop of retention with temperature, when using either H or D as impact particles. In TPD measurements, the Li and H desorption peaks were observed at the same temperature (650 K) and this was interpreted as the decomposition of LiH. In addition to TPD measurements from Li$_2$O films that
were irradiated with H$_2^+$ ions, AES measurements were consistent with the formation of LiOH, which decomposed to Li$_2$O and H$_2$O at exposure temperatures higher than 470 K. Overall, both experiments and modeling supports the possibility that low H recycling can be achieved if Li$_2$O is formed under fusion reactor conditions, as both Li and Li$_2$O have comparable efficiency for trapping H.

The sputtering yields for 400-1600 eV D$_2^+$ ions on Li, Li-O, and composite Li-C-O films were measured to be around 0.1-0.3, in good agreement with previous simulations and bulk erosion measurements. Pure Li films were observed to become LiD films upon D$_2^+$ irradiation before significant sputtering occurred. He$^+$ sputtering of pure Li yielded 2-3 times higher sputtering yields compared to D$_2^+$ irradiation. This result indicates that the formation of LiD reduces the D$_2^+$ sputtering yield, in agreement with previous measurements on bulk and liquid Li. The Li sputtering yield upon D$_2^+$ irradiation of Li-O films was lower than the Li sputtering yield and peaked at a higher energy (1600 eV/ D$_2^+$).

D retention in pure Li, Li-O, and Li-C-O films was also studied as a function of time after these films were exposed to 450 eV D$_2^+$ ion irradiation. The amount of D$_2$ retained in both Li and Li$_2$O films at 300 K decreased at similar rates by 45% after 16 hours, likely due to Li being oxidized to Li oxide during the waiting time. Increasing the temperature of the Li film to 420 K increased this rate of decrease, which can be explained if the D$_2$ loss mechanism from Li films is physical diffusion. The retention in Li-C-O films was found to be independent of time up to three days.
Based on these studies, Li oxide formation in a fusion experiment may be advantageous due to the enhanced thermal stability of Li-O, lower sputtering yield of Li-O, and similar hydrogen retention properties of Li-O when compared with pure Li.

The second application concerns energetic hydrogen species involved in plasma-catalytic dry reforming. Reactive hydrogen radicals and ions present in plasma-enhanced catalysis can form subsurface hydrogen, which has been previously demonstrated to have a unique ability to hydrogenate adsorbed species that are otherwise unreactive with adsorbed hydrogen at the surface. Therefore, accounting for the presence of subsurface hydrogen and its reactivity for hydrogenation is an important component for understanding plasma-enhanced catalysis over Ni-based catalysts.

We have investigated the uptake and subsequent thermal desorption of deuterium on a Ni(110) surface using incident D₂, D atoms, and D₂⁺ ions. Subsurface D binding sites on Ni(110) are readily populated at 90 K by incident D atoms and D₂⁺ ions, but not molecular D₂. Subsurface D atoms recombine to desorb as D₂ gas in TPD measurements to create characteristic subsurface-derived D₂ thermal desorption peaks. The temperature of these peaks increases linearly with increasing energy (up to 600 eV) of the incident D atoms and ions. Furthermore, we report that D₂⁺ ions are very efficient at populating a high temperature (435 K) D₂ desorption state from subsurface D, which had been previously reported only from co-adsorbed CO or cooling in background hydrogen gas. A comparison of Ni(110) and Ni(111) surfaces shows that the thermal stability and D₂ TPD peaks from subsurface D atoms are nearly the same for these two substrates. A simple explanation for this behavior is that D₂ desorption during TPD is rate-limited by the diffusion of D to the surface from interstitial sites in the near-surface region of nickel.
We have also investigated the hydrogenation of adsorbed CO molecules on a Ni(110) surface at 100 K under ultrahigh vacuum (UHV) conditions using coadsorbed surface D, subsurface D, and incident D atoms and D$_2^+$ ions. Surface-bound D adatoms did not hydrogenate coadsorbed CO to form gas-phase products in TPD measurements. In contrast, subsurface D reacted with adsorbed CO to form the hydrogenated TPD products formaldehyde (CD$_2$O) and methanol (CD$_3$OD). The desorption peaks of CD$_2$O and CD$_3$OD in TPD were coincident with D$_2$ desorption from D occupation of subsurface sites. A CO pre-saturated Ni(110) surface completely blocked the adsorption of D from incident D$_2$ under these conditions. Energetic 100 eV D$_2^+$ ions penetrate the adsorbed CO adlayer to populate D in subsurface sites that subsequently lead to hydrogenation of adsorbed CO to form CD$_2$O and CD$_3$OD in TPD measurements. The experiments show that incident energetic D species are less reactive than subsurface D for the hydrogenation of CO on the Ni(110) surface. Additionally, Born-Oppenheimer molecular dynamics (BOMD) simulations show that the direct impact of H atoms on a CO covered Ni(110) surface does not hydrogenate CO via an Eley-Rideal or hot-atom mechanism. Therefore, in environments where energetic D species are incident on adsorbate-covered surfaces, one needs to include the important, likely dominant role, of subsurface D in reaction chemistry. These results will be helpful for a fuller understanding of the synergistic effects observed in plasma-enhanced catalysis over Ni-based catalysts. As demonstrated, incident hydrogen atoms and ions in hydrocarbon reforming plasmas can carry out hydrogenation reactions more effectively than surface-bound hydrogen.
The information in these studies on the uptake and thermal stability of subsurface hydrogen and its reactivity in hydrogenation will be helpful for a fuller understanding of the role of subsurface hydrogen in plasma-enhanced catalysis over Ni-based catalysts, with additional implications for the broader class of metal-based catalysts.
Publications


