



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

Yuxin Yang^{a,1}, Michelle S. Hofman^{b,1}, Bruce E. Koel^{a,*}

^a Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA

^b Department of Chemistry, Princeton University, Princeton, NJ, USA



ARTICLE INFO

Keywords:

Subsurface deuterium
Temperature programmed desorption
Deuterium atom
Deuterium ion

ABSTRACT

A unique feature of plasma-enhanced catalysis compared to thermal catalysis is the presence of reactive hydrogen radicals and ions in the gas phase above the catalyst surface. The uptake and subsequent thermal desorption of deuterium on a Ni(110) surface have been measured using incident gaseous D₂ molecules, D atoms, and D₂⁺ ions. Molecular D₂ exposures on Ni(110) at 90 K form adsorbed D adatoms at the surface, but do not populate subsurface deuterium binding states under UHV conditions. In contrast, such subsurface states on Ni(110) are readily populated at 90 K by incident D atoms and D₂⁺ ions. Subsurface D atoms recombine to desorb as D₂ gas in temperature programmed desorption (TPD) measurements to create new characteristic subsurface-derived D₂ thermal desorption peaks near 175 K for incident D atoms and 190–260 K, depending on the energy of the incident D₂⁺ ions used, along with a new peak at 435 K for incident ions. While there are small differences for adsorbed D adatoms on Ni(110) and Ni(111) surfaces regarding their thermal stability and subsequent D₂ TPD curves, the thermal stability and D₂ TPD peaks from subsurface D atoms are nearly the same for these two substrates. This information 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.

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 co-workers 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 (2 × 1) LEED pattern at a coverage, θ_H, of H adatoms of 1.0 ML, referenced to the nickel surface atom density (1 ML = 1.14 × 10¹⁵ atoms/cm²) [21]. Increasing exposures to saturation, with θ_H = 1.5 ML, results in a surface reconstruction into a (1 × 2) phase. Heating the (1 × 2) phase above 220 K leads to a streaked (1 × 2) 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 α state with a peak at 220 K, associated with the transition from the (1 × 2) to the streaked (1 × 2) phase, and β₁ and β₂ states with peaks between 250 and 400 K that are associated with desorption from the (1 × 1) surface and the streaked (1 × 2) phase, respectively [22–24].

Hydrogen uptake past θ_H = 1.5 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 (β₃), with a desorption peak centered at 435 K that saturates with θ_D = 0.06 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 β₃ desorption state. Interestingly, as observed on Ni(111) [7], we observed that the thermal desorption

* Corresponding author.

E-mail address: bkoel@princeton.edu (B.E. Koel).

¹ These two authors contributed equally to this paper.

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].

2. Experimental procedure

All experiments were performed in a stainless steel UHV chamber with a base pressure of 2×10^{-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 15–255 G 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 $p(\text{O}_2) = 4 \times 10^{-8}$ Torr with the sample at 1000 K were used to eliminate residual carbon. Finally, hydrogen treatments for several minutes at $p(\text{H}_2) = 4 \times 10^{-8}$ 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 H₂ 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. D₂⁺ ions were produced in a PHI 04–303A differentially pumped ion gun with an adjustable ion energy of 0–5 keV. D₂ 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/cm². 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 D₂ on Ni(110) below 130 K under UHV conditions [29,30].

3. Results and discussion

Fig. 1a shows D₂ thermal desorption curves following increasing exposures of D₂ to Ni(110) at 90 K. D₂ 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 β_1 (280 K) state was populated first at low coverage, followed by the β_2 (350 K) state. Further increases in D₂ exposures led to the saturation of the β_1 and β_2 peaks, and the emergence of the α state (220 K). The α state is associated with an ordered (1 × 2) to “streaked” phase transition of the Ni(110) surface during heating, and it is sensitive to the heating rate. The low β_2 to β_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 D₂ TPD curves following exposures of 700 eV D₂⁺ ions on Ni(110) at 90 K are shown in Fig. 1b. We note that at these high energies, incident 700 eV D₂⁺ ions are equivalent to incident 350 eV D⁺ ions. The D₂ TPD curve following a saturation exposure of D₂ (from Figure 1a) is shown for comparison as the dashed curve. Following exposures of D₂⁺ ions, D₂ desorption in TPD occurred in four states. The

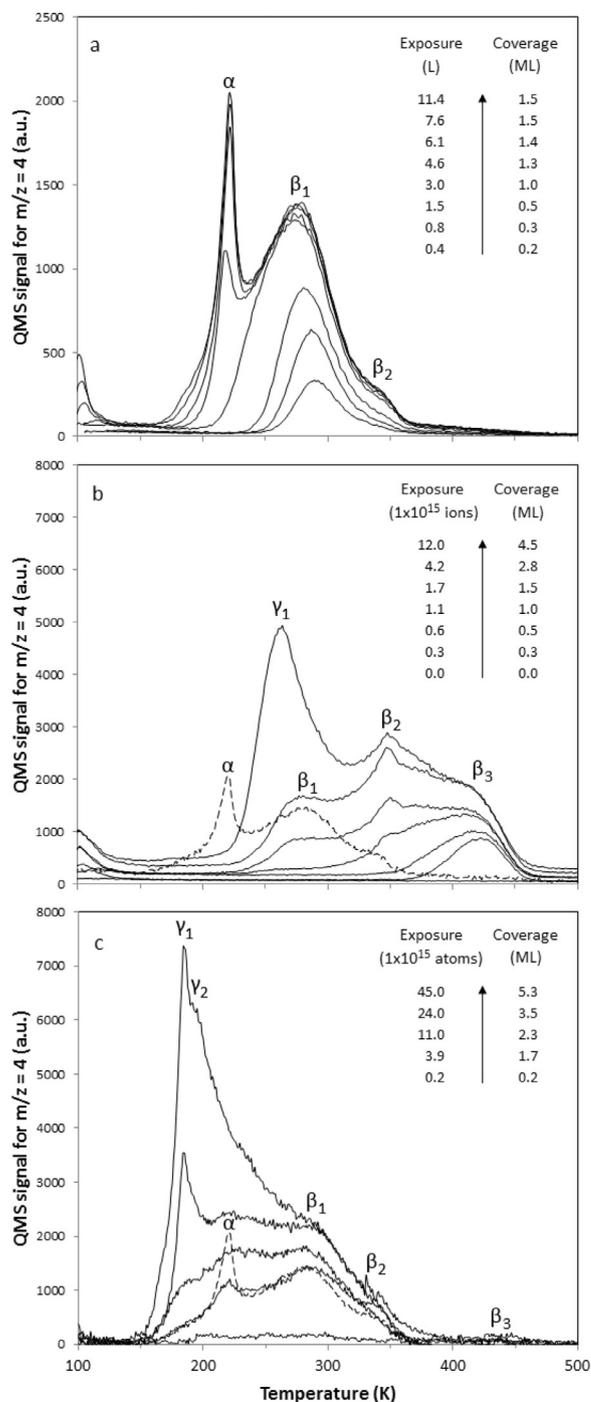


Fig. 1. D₂ TPD curves following exposures of (a) D₂, (b) 700 eV D₂⁺, and (c) D atoms to Ni(110) at 90 K under UHV conditions. For comparison, the D₂ TPD trace from a saturation coverage of surface deuterium, from panel (a) is shown as a dashed curve in panels (b) and (c). The γ peaks do not saturate at higher doses (not shown here) of D₂⁺ ions and D atoms, and are assigned to D₂ desorption from D absorption in subsurface sites.

β_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 β_3 (435 K) state in previous reports was not observed with a concentration above 0.06 ML [26,27]. Our observation of the β_3 state observed in Fig. 1b with a concentration of > 0.5 ML is attributed to the exceptionally high efficiency of D⁺ ions at populating this state. Because the β_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 β_1 (280 K) and then β_2 (350 K) states. Further increases in D_2^+ exposures led to the formation of a desorption feature denoted as γ_1 (260 K) that did not saturate in our experiments (resulting in a highest value that we explored of $\theta_D = 20$, 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 α state associated with the (1×2) to “streaked” phase transition was not observed. Perhaps the presence of subsurface D altered the Ni(110) (1×2) phase transition.

The D_2 TPD curves following exposures of D atoms on Ni(110) at 90 K are shown in Fig. 1c. Again, the D_2 TPD curve following a saturation exposure of D_2 gas (from Figure 1a) is shown for comparison as the dashed curve. Like D_2^+ , exposures of D atoms populate the β_2 (350 K) and β_1 (280 K) states. D_2 desorption from the α state, associated with an ordered (1×2) 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) (1×2) phase transition. A comparison of the β_3 and β_2 peak areas following exposures of D atoms and D_2^+ ions shows that D atoms were less efficient at populating the β_3 and β_2 states than D_2^+ . High exposures of D atoms lead to desorption from additional low temperature peaks, labeled as γ_1 (185 K) and γ_2 (195 K), that we attribute to desorption from D bound in subsurface sites. This common origin for γ peaks following exposures of D atoms and D_2^+ ions will be addressed in more detail in Fig. 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 β_1 (280 K) and β_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 β_1 (335 K) and β_2 (370 K) peaks (using the same heating rate in TPD in the two experiments). However, no β_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 α) following 500 eV D_2^+ exposures on Ni(111), which is at a temperature close to our observation of the γ_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 γ_1 (185 K) and γ_2 (210 K) peaks, which are comparable to our γ_1 (185 K) and γ_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 Fig. 1b, except that the γ_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.

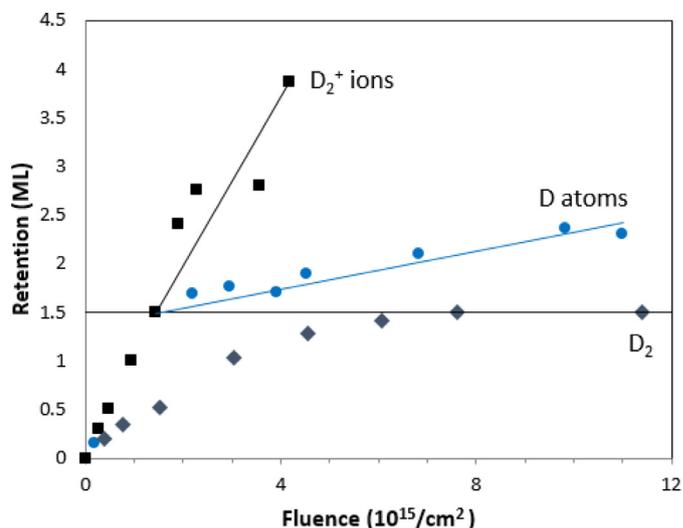


Fig. 2. Uptake curves for D_2 (\blacklozenge), 700 eV D_2^+ ions (\blacksquare), and D atoms (\bullet) on Ni(110) at 90 K. The initial sticking coefficients of D_2 gas and D_2^+ ions were measured to be 0.4 and 1. Setting the initial sticking coefficient of D atoms to be unity up to $\theta_D = 1.5$ ML leads to a sticking coefficient of 0.09 for $\theta_D > 1.5$ ML.

Uptake curves, in which the amount of D (coverage) that is retained by the Ni(110) crystal and that subsequently desorbs as D_2 in TPD for a given fluence (exposure) of D, is shown in Fig. 2 for incident D_2 molecules, 700 eV D_2^+ ions, and D atoms on Ni(110) at 90 K. The initial sticking coefficient of D_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_2^+ 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_2^+ 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.

In the above discussion, we assigned the origin of the γ peaks in D_2 TPD to subsurface D in both Fig. 1b and c, arising from both incident D_2^+ ions and D atoms, even though the D_2 TPD peak temperatures were quite different. Fig. 3 shows that the desorption temperature of the γ_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 Fig. 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.

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.

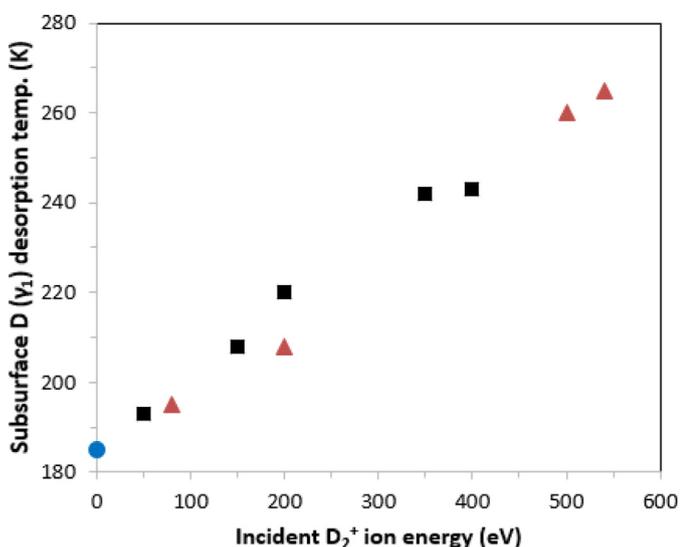


Fig. 3. D₂ desorption temperature in TPD measurements of subsurface deuterium forming the γ₁ feature from exposures to D₂⁺ ions (■) and D atoms (●) on Ni(110) and D₂⁺ ions (▲) on Ni(111) [5,7] for increasing energy of the incident D used to create subsurface D. The γ₁ D₂ desorption temperature remains constant at 265 K for incident energies above 600 eV on both Ni(110) and Ni(111) surfaces.

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 deuterium 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 deuterium atoms and ions. Furthermore, we report that D₂⁺ ions are very efficient at populating a high temperature (435 K) D₂ 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 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. 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.

Acknowledgment

This work was supported by the Air Force Office of Scientific Research through Basic Research Initiative Award no. FA9550-604 14-1-0053.

Supplementary materials

Supplementary material associated with this article can be found, in

the online version, at doi:10.1016/j.susc.2018.04.001.

References

- [1] A.D. Johnson, S.P. Daley, A.L. Utz, S.T. Ceyer, The chemistry of bulk hydrogen: reaction of hydrogen embedded in nickel with adsorbed CH₃, *Science* 257 (1992) 223–225.
- [2] K.L. Haug, T. Bu, M. Gostein, T.R. Trautman, S.T. Ceyer, Catalytic hydrogenation of acetylene on Ni(111) by surface-bound H and bulk H, *J. Phys. Chem. B* 105 (2001) 11480–11492.
- [3] S.P. Daley, A.L. Utz, T.R. Trautman, S.T. Ceyer, Ethylene hydrogenation on Ni(111) by bulk hydrogen, *J. Am. Chem. Soc.* 116 (1994) 6001–6002.
- [4] W. Lin, K. Stocker, G.C. Schatz, Reducing CO₂ to CO and H₂O on Ni(110): the influence of subsurface hydrogen, *J. Phys. Chem. C* 120 (2016) 23061–23068.
- [5] H. Premm, H. Polzl, A. Winkler, Dynamics and kinetics of subsurface absorption and desorption for the system hydrogen (deuterium)–Ni(111), *Surf. Sci. Lett.* 401 (1998) L444–L451.
- [6] S.T. Ceyer, The unique chemistry of hydrogen beneath the surface: catalytic hydrogenation of hydrocarbons, *Acc. Chem. Res.* 34 (2001) 737–744.
- [7] I. Chorkendorff, J.N. Russell Jr., J.T. Yates Jr., Hydrogen implantation in Ni(111)—a study of H₂ desorption dynamics from the bulk, *Surf. Sci.* 182 (1987) 375–389.
- [8] A.D. Johnson, K.J. Maynard, S.P. Daley, Q.Y. Yang, S.T. Ceyer, Hydrogen embedded in Ni: production by incident atomic hydrogen and detection by high-resolution electron energy loss, *Phys. Rev. Lett.* 67 (1991) 927.
- [9] G. Pauer, A. Eichler, M. Sock, M.G. Ramsey, F. Netzer, A. Winkler, Identification of new adsorption sites of H and D on rhodium(100), *J. Chem. Phys.* 119 (2003) 5253.
- [10] D. Kolovos-Vellianitis, J. Kuppers, Kinetics of abstraction of D and O on Cu(110) surfaces by gaseous H atoms, *J. Phys. Chem.* 107 (2003) 2559–2564.
- [11] P. Sandl, U. Bischler, E. Bertel, The interaction of atomic hydrogen with Cu(110), *Surf. Sci.* 291 (1993) 29–38.
- [12] E. Demirci, A. Winkler, Interaction of atomic H and CO with Cu(110) and bimetallic Ni/Cu(110), *Surf. Sci.* 604 (2010) 609–616.
- [13] M.F. Luo, D.A. Maclaren, I.G. Shuttleworth, W. Allison, Preferential sub-surface occupation of atomic hydrogen on Cu(111), *Chem. Phys. Lett.* 381 (2003) 654–659.
- [14] K. Mudiyanse, Y. Yang, F.M. Hoffmann, O.J. Furlong, J. Hrbek, M.G. White, P. Liu, D.J. Stacchiola, Adsorption of hydrogen on the surface and sub-surface of Cu(111), *J. Chem. Phys.* 139 (2013) 044712.
- [15] M.F. Luo, D.A. Maclaren, W. Allison, Migration and abstraction of H-atoms from the Cu(111) surface, *Surf. Sci.* 586 (2005) 109–114.
- [16] D. Kolovos-Vellianitis, J. Kuppers, Abstraction of D on Ag(100) and Ag(111) surfaces by gaseous H atoms: the role of electron–hole excitations in hot atom reactions and the transition to Eley–Rideal kinetics, *Surf. Sci.* 548 (2004) 67–74.
- [17] H. Okuyama, T. Nakagawa, W. Siga, N. Takagi, M. Nishijima, T. Aruga, Absorption of D in the H+D/Pd(100) reaction, *Surf. Sci.* 411 (1998) L849–L854.
- [18] H. Okuyama, T. Nakagawa, W. Siga, N. Takagi, M. Nishijima, T. Aruga, A new reaction channel in H(g)+D(a)/Pd(100): absorption versus abstraction, *Surf. Sci.* 427–428 (1999) 277–281.
- [19] H. Okuyama, T. Nakagawa, W. Siga, N. Takagi, M. Nishijima, T. Aruga, Subsurface hydrogen on Pd(100) induced by gas-phase atomic hydrogen, *J. Phys. Chem. B* 103 (1999) 7876–7881.
- [20] R.J. Behm, K. Christmann, G. Ertl, Adsorption of hydrogen on Pd(100), *Surf. Sci.* 99 (1980) 320–340.
- [21] T.E. Jackman, J. Davies, P.R. Norton, W.N. Unertl, K. Griffiths, Saturation coverage of deuterium on Ni(110), *Surf. Sci.* 141 (1984) L313–L316.
- [22] K. Christmann, F. Chehad, V. Penka, G. Ertl, Surface reconstruction and surface explosion phenomena in the nickel (110)/hydrogen system, *Surf. Sci.* 152–153 (1985) 356–366.
- [23] T.E. Jackman, K. Griffiths, W.N. Unertl, K.H. Davies, D.A. Gurtler, D.A. Harrington, P.R. Norton, Surface phases of Ni(110) induced by adsorption of deuterium, *Surf. Sci.* 179 (1987) 297–321.
- [24] K. Christmann, O. Schober, G. Ertl, M. Neumann, Adsorption of hydrogen on nickel single crystal surfaces, *J. Chem. Phys.* 60 (1974) 4528.
- [25] G. Eilmsteiner, W. Walkner, A. Winkler, Reaction kinetics of atomic hydrogen with deuterium on Ni(110), *Surf. Sci.* 354 (1996) 263–267.
- [26] D.A. Harrington, P.R. Norton, Activated adsorption of deuterium on Ni(110): evidence for a high temperature desorption state, *Surf. Sci.* 195 (1988) L135–L144.
- [27] A.R. Alemozafar, R.J. Madix, CO-induced segregation of hydrogen into the subsurface on Ni(110), *J. Chem. Phys.* 108 (2004) 7247–7252.
- [28] T. Engel, K.-H. Rieder, D.A. King, D.P. Woodruff (Eds.), *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, 4 Elsevier, Amsterdam, 1982, p. 125.
- [29] B. Voigtländer, S. Lehwald, H. Ibach, Hydrogen adsorption and the adsorbate-induced Ni(110) reconstruction—an EELS study, *Surf. Sci.* 208 (1989) 113–135.
- [30] C. Roux, H. Bu, J.W. Rabalais, Structure of the hydrogen-induced Ni(110)-p(1 × 2) H reconstructed surface, *Surf. Sci.* 259 (1991) 253–265.
- [31] H.P. Steinrück, M. Luger, A. Winkler, K.D. Rendulic, Adsorption probabilities of H₂ and D₂ on various flat and stepped nickel surfaces, *Phys. Rev. B* 32 (1985) 5032.