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

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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 adatoms 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 x 1) LEED pattern at a coverage, θH, 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 θH = 1.5 ML, results in a surface reconstruction into a (1 x 2) phase. Heating the (1 x 2) phase above 220 K leads to a streaked (1 x 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 x 2) to the streaked (1 x 2) phase, and β₁ and β₂ states with peaks between 250 and 400 K that are associated with desorption from the (1 x 1) surface and the streaked (1 x 2) phase, respectively [22–24].

Hydrogen uptake past θH = 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 θH = 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...
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 $2 \times 10^{-10}$ 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 15–255 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, ± 0.5° orientation) was cleaned using 1.5 keV Ar$^+$ ions 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$_2$ 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, $\theta$, discussed herein are given in monolayers (ML), where 1.0 ML corresponds to the Ni(110) surface atom density of $1.14 \times 10^{15}$ atoms/cm$^2$. Deuterium coverages, $\theta_D$, 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].

3. Results and discussion

Fig. 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 $\alpha$, $\beta_1$, and $\beta_2$, 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 (1 × 2) “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 Fig. 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 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 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 $\beta_3$ 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 (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 Figure1a) 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. Desorption from the $\alpha$ 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 $\beta_1$ and $\beta_2$ peak areas following exposures of D atoms and D$_2^+$ ions shows that D atoms were less efficient at populating the $\beta_1$ 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 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 $\beta_1$ (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 $\beta_2$ (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 Fig. 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.

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$_2$ 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 is 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 $\gamma$ 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 $\gamma_1$ 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$_2^+$ ions 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.
ions. Furthermore, we report that D2 decreasing energy (up to 600 eV) of the incident deuterium atoms and peaks. The temperature of these peaks increases linearly with incident Ni(110) and D2 remains constant at 265 K for incident energies above 600 eV on both Ni(110) and 90 K by incident D atoms and D2 Subsurface deuterium binding sites on Ni(110) are readily populated at near-surface hydrogen and its reactivity 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.

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Supplementary materials

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