

# The Unique Chemistry of Hydrogen beneath the Surface: Catalytic Hydrogenation of Hydrocarbons

S. T. CEYER

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Received February 27, 2001

## ABSTRACT

Hydrogen atoms emerging from the bulk of Ni metal to the surface are observed to be the reactive species in the hydrogenation of adsorbed methyl radical, ethylene, and acetylene to gas-phase products. Surface-bound H atoms are unreactive. The distinctive chemistry of a bulk H atom arises largely from its significantly higher energy as compared to that of a surface-bound H atom. These results demonstrate that bulk H is not solely a source of surface-bound H in catalytic hydrogenation as proposed 50 years ago, but rather, a reactant with a chemistry of its own.

## Introduction to the Problem of Catalytic Hydrogenation under UHV Conditions

Most of our molecular-level knowledge about chemistry occurring on surfaces derives from experiments that are carried out under ultrahigh-vacuum (UHV) conditions. These conditions are mandated by the need to maintain a well-defined surface as well as by the spectroscopic techniques that are presently available to probe surface reactions at the microscopic scale. They also bring with them the necessity to employ pressures of gaseous reactants that are low, usually less than  $10^{-4}$  Torr. In contrast, practical surface chemistry, such as heterogeneous catalysis, is carried out under conditions where the pressure of the reactants is high, often as high as 100 atm. The problem arises that the surface chemistry observed under a high pressure of gaseous reactants is often different from the surface chemistry observed at low pressure. For example, many surface reactions proceed readily under high-pressure conditions typical of a commercial, heterogeneous catalytic reaction but appear not to proceed under the low-pressure conditions typical of a laboratory experiment, despite favorable thermodynamics. The different chemistry and, in particular, the lack of reactivity at the low pressures<sup>1–3</sup> where UHV surface science techniques are operable is known loosely as the pressure gap.

Recently, considerable progress has been made in uncovering the microscopic processes that give rise to

these differences. For example,  $\text{CH}_4$  dissociatively chemisorbs on Ni(111) under high-pressure conditions but apparently does not in a UHV environment. A barrier to dissociative chemisorption that is surmountable only by the energy of the incident  $\text{CH}_4$  was found to be a reason underlying the apparent lack of reactivity at low  $\text{CH}_4$  pressures.<sup>4–6</sup> Our understanding of this underlying physical principle allowed the high-pressure requirement for  $\text{CH}_4$  dissociation to be bypassed by raising the energy of the incident  $\text{CH}_4$  using molecular beam techniques.<sup>4,5</sup> The ability to effect this dissociation at low pressures in turn enabled UHV techniques such as the vibrational spectroscopy known as high-resolution electron energy loss (HREEL) and beam scattering to be employed to identify the reaction products and the dynamics of  $\text{CH}_4$  dissociation, respectively. It became possible for the first time to determine, by spectroscopic identification of the reaction intermediates,<sup>7</sup> the mechanism of reactions in which  $\text{CH}_4$  is a reactant, such as the synthesis of benzene.<sup>8</sup>

A search for additional plausible explanations for the observed differences between surface chemistry at high and low pressures uncovered a collection of other molecular-level processes, called collision-induced processes. In these processes, a gas-phase molecule collides with an adsorbate. The impact of the collision may cause the adsorbate to dissociate on the surface,<sup>9–11</sup> to desorb molecularly<sup>12–16</sup> or recombinatively from the surface,<sup>17–19</sup> or to absorb beneath the surface.<sup>17,19,20</sup> Such collisions between a gas-phase molecule and an adsorbate-covered catalyst potentially play a significant role in catalytic mechanisms because they are constantly taking place in heterogeneous catalytic environments.

The goal of this discussion is to describe how a microscopic origin for the lack of reactivity of one class of high-pressure catalytic reactions, hydrogenation reactions, has been determined and how knowledge of this origin has been used to effect the reaction under UHV conditions and thereby to determine the reaction mechanism. For example, the hydrogenation of ethylene on a Raney Ni catalyst to form ethane proceeds readily under conditions where the  $\text{H}_2$  pressure is about 1 atm. Because this reaction serves as a prototypical system for industrial hydrogenation,<sup>21</sup> it has been the subject of numerous investigations.<sup>22–28</sup> Perhaps the most influential one is the 1934 study by Horiuti and Polanyi in which a reaction mechanism is proposed.<sup>29</sup> The mechanism depicts the carbon–carbon bond of  $\text{C}_2\text{H}_4$  to be parallel to the surface. Eventually, a coadsorbed H atom migrates up to  $\text{C}_2\text{H}_4$  and reacts, forming a “half-hydrogenated” species which then reacts with a second adsorbed H to form volatile ethane. However, if this simple and attractive mechanism were correct, then it seems reasonable that a coadsorbed layer of  $\text{C}_2\text{H}_4$  and H on Ni(111), formed by exposure to  $10^{-4}$  Torr of  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  in an UHV environment, should result in ethane formation. But, it does not! Although  $\text{C}_2\text{H}_4$  adsorbs with the geometry depicted by the Horiuti–Polanyi mechanism,<sup>30</sup> no ethane is observed.<sup>31–33</sup> In

Sylvia T. Ceyer is the J. C. Sheehan Professor of Chemistry at the Massachusetts Institute of Technology. She received her B.A. *summa cum laude* from Hope College in 1974 and her Ph.D. from the University of California at Berkeley in 1979. She is a physical chemist with research interests in molecule–surface reaction dynamics as related to heterogeneous catalysis, chemical vapor deposition, and plasma etching chemistry.

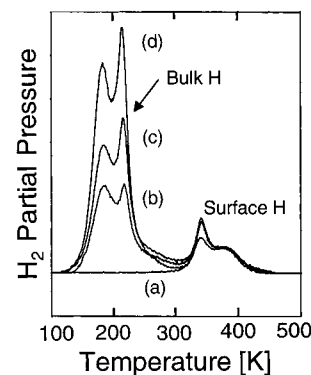
contrast,  $C_2H_4$  hydrogenation readily takes place on Ni(111) at high ethylene– $H_2$  pressures.<sup>34</sup>

Recently, the absence of H absorbed in the bulk of Ni metal after exposure to low-pressure  $H_2$  has been shown to be at least one plausible molecular-level origin for the lack of hydrogenation activity under UHV conditions. This is so because the reactive species in hydrogenating ethylene has been found to be a hydrogen atom emerging from the bulk onto the surface.<sup>31</sup> Hydrogen absorbed in the bulk of Ni catalysts after or during exposure to  $H_2$  at high pressure is plentiful.<sup>35</sup> As long as 45 years ago, positive correlations between the hydrogenation activity of Raney nickel<sup>23,36,37</sup> and Pd catalysts<sup>38</sup> and their hydrogen content were noted, but the exact role of this dissolved hydrogen, here called bulk H, remained unknown.

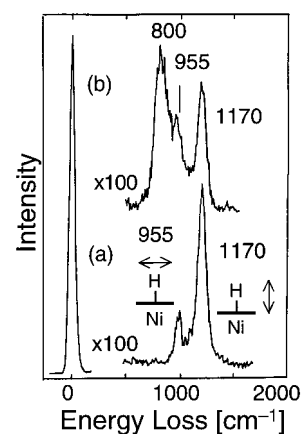
The reason for the dearth of information about these practically important hydrogenation reactions is the inability to carry them out under single-collision conditions, such as afforded by UHV surface science techniques, where microscopic reaction steps are discernible. Specifically, it is the inability to produce bulk H by exposure of most single-crystal transition metals to an ambient gas of  $H_2$  at low pressures that, at the very least, precludes these reactions from being studied. The discussion below describes the physical principle underlying the absence of bulk H and then describes methods that have been discovered to synthesize bulk H under UHV conditions and to detect it spectroscopically. These new capabilities of synthesis and characterization enable the chemistry of bulk H in hydrogenation reactions to be investigated under UHV conditions where the role of bulk H can be unambiguously determined. These investigations have shown that bulk H is not a modifier of the metal electronic structure or solely the supplier of surface-bound H. Rather, bulk H is the reactant in the hydrogenation of the ethylene,<sup>31</sup> acetylene,<sup>39</sup> and methyl radical<sup>18</sup> on Ni(111).

### The Problem of Embedding Hydrogen into Ni under Low-Pressure UHV Conditions

Hydrogen dissolution in a Ni single crystal is apparent from the following study.<sup>40</sup> A small-diameter, thick-walled metal tube whose end is sealed off with a thin disk of Ni with faces of (111) orientation is connected to a source of a high pressure of  $H_2$  ( $> 1$  atm) and is placed in a vacuum chamber. Eventually,  $H_2$  appears in the vacuum chamber. It is obvious that if  $H_2$  was behind the disk at the start of the experiment and in front of the disk at the end, then there must be hydrogen within the Ni disk. But how the hydrogen makes its way into the Ni disk is a very interesting question, because no  $H_2$  is observed to absorb into the Ni bulk if a Ni(111) crystal at 80–300 K is exposed to  $10^{-4}$  Torr of  $H_2$  in a UHV environment. Instead, the  $H_2$  dissociates on the surface until a monolayer (ML) of adsorbed H atoms, here called surface-bound or surface H, is formed, and then the dissociative chemisorption ceases. The Ni crystal does not take up any more hydrogen, and no surface-bound H is observed to dissolve into the bulk. The thermal desorption spectrum of this mono-



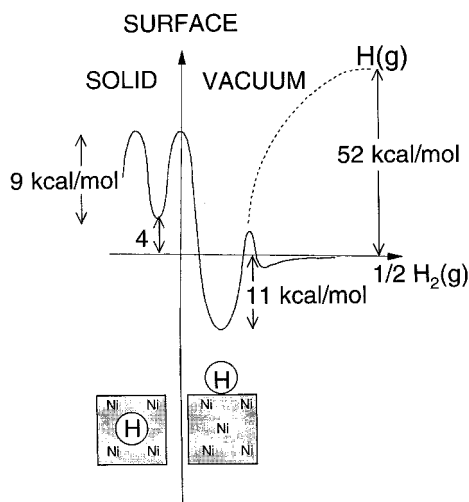
**FIGURE 1.**  $H_2$  partial pressure versus crystal temperature for a heating rate of 2 K/s. (a) Recombination and desorption of 1 ML surface H, formed by exposure to  $H_2$ . (b–d) Recombination and desorption of 1 ML surface H and 1.7, 2.6, and 3.5 ML bulk H, respectively, formed by exposure to gas-phase H atoms.



**FIGURE 2.** (a) Vibrational spectrum of 1 ML surface H. (b) Vibrational spectrum of 1 ML surface H and 1 ML bulk H. Elastic feature at 0  $cm^{-1}$ .

layer, which is the partial pressure at mass 2 as a function of crystal temperature, is shown in Figure 1a. The desorption maxima between 340 and 380 K correspond to the recombination of surface H atoms and their subsequent desorption as  $H_2$ . The vibrational spectrum of this monolayer, as measured by HREELS, is shown in Figure 2a. The features at 1170 and 955  $cm^{-1}$  are the symmetric ( $A_1$ ) and antisymmetric (E) stretch modes of a H atom bound at a 3-fold hollow site. In neither of these spectra is there evidence for bulk H.<sup>41</sup>

The potential energy diagram for the hydrogen–Ni system in Figure 3 provides a plausible explanation for why bulk H is not observed under the low  $H_2$  pressures of a UHV experiment. In order for a gas-phase  $H_2$  molecule incident on a Ni surface to dissociatively absorb, it has to overcome a barrier of 26 kcal/mol. Since the average energy of gas-phase  $H_2$  at 300 K is 40 times lower, it is clear why  $H_2$  dissociative absorption does not occur. However, the occurrence of absorption in the high-pressure permeation experiments<sup>40</sup> seems inconsistent with these energetics! The explanation for this seeming contradiction is that at low pressure, there are too few molecules with energies high enough to overcome the barrier so as to make bulk H observable on a reasonable



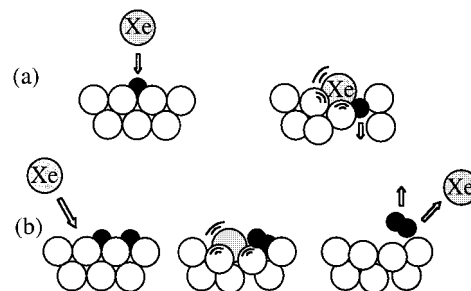
**FIGURE 3.** Potential energy diagram for hydrogen–Ni system. Points to the left of the surface represent a H atom beneath the surface. Points to the right represent a H atom or a  $\text{H}_2$  molecule at or away from the surface.

time scale. At high pressure, the fraction of sufficiently energetic molecules is the same as at low pressure, but because their absolute number is larger, the rate of dissociative absorption increases sufficiently to observe it. Therefore, raising the energy of  $\text{H}_2$  should circumvent the need for high pressures, but because of the technical difficulty of accelerating  $\text{H}_2$ , this route is not chosen here. Instead, two more novel and convenient methods for bulk H synthesis under low-pressure conditions are presented.

### Bulk H Synthesis by Exposure to Gas-Phase H Atoms

Consider a gas-phase H atom incident on the Ni crystal. As can be seen in Figure 3, the initial energy level of a H atom is high above any barrier to absorption, so exposure of a Ni(111) crystal to gas-phase H should result in bulk absorption. Figure 1b–d shows thermal desorption spectra measured after exposure of the crystal held at 130 K to gas-phase H atoms.<sup>41</sup> New desorption features between 185 and 215 K appear.<sup>41,42</sup> Long exposures to atomic H have resulted in the equivalent of over 8 ML of hydrogen desorbing at these low temperatures. This significant increase in hydrogen uptake suggests bulk absorption.

The HREEL spectrum, shown in Figure 2b, also exhibits an additional feature following exposure to atomic H, and it appears at  $800\text{ cm}^{-1}$ .<sup>41</sup> This spectrum is collected from a crystal whose total hydrogen uptake is 2.0 ML, with 1.0 ML of the hydrogen desorbing as the low-temperature feature. The invariance of the surface H vibrational frequencies, which are a sensitive probe of surface coverage, indicate that the surface H remains intact in the presence of the hydrogen that gives rise to the feature at  $800\text{ cm}^{-1}$ . Raising the temperature to 273 K results in the disappearance of the  $800\text{ cm}^{-1}$  feature concurrent with the low-temperature desorption of  $\text{H}_2$ . The resulting HREEL spectrum (not shown) is identical to that of surface H (Figure 2a).



**FIGURE 4.** Schematic of (a) collision-induced absorption and (b) collision-induced recombinative desorption. Open circles are Ni atoms. Black circles are H atoms.

Although not discussed here, measurements of the intensity of the  $800\text{ cm}^{-1}$  mode as a function of the incident electron energy confirm the assignment of this mode to the vibration of hydrogen buried in an octahedral interstitial site beneath the surface.<sup>41</sup> The bulk H does not perturb the two-dimensional unit cell of Ni atoms, nor does it perturb the frequencies of the surface-bound H. The perturbation of the Ni surface electronic structure by bulk H is therefore minimal.<sup>41</sup> These are important pieces of information in understanding the unique chemistry of bulk H.

### Bulk H Synthesis by Collision-Induced Absorption

Now consider a H atom bound at a 3-fold hollow surface site. In order for this H atom to absorb, it has to acquire at least 24 kcal/mol to overcome the endoergicity and the barrier to bulk absorption, as evident from the energy diagram in Figure 3. In principle, this energy could be provided by the impact of energetic inert gas atoms in a process called collision-induced absorption. This new mechanism for absorption is demonstrated as schematically illustrated in Figure 4a.<sup>17</sup> A Xe beam with a kinetic energy above 60 kcal/mol is directed at normal incidence on a hydrogen-covered surface. The resulting HREEL spectrum (not shown) clearly exhibits the loss feature at  $800\text{ cm}^{-1}$  associated with bulk H.

Studies of the dynamics of the collision-induced absorption event reveal that the most effective collisions at producing bulk H are ones in which the Xe atom collides on top of the adsorbed H atom.<sup>17,20</sup> The impact of the collision transfers energy to the surface, which is momentarily distorted so that holes open up, into which the hydrogen can readily diffuse and enter the bulk. Collision-induced absorption is another method to synthesize bulk H in a UHV environment.

### Collision-Induced Recombinative Desorption

In competition with absorption, recombinative desorption occurs, as shown schematically in Figure 4b.<sup>17</sup> The impacts of the inert gas atoms cause the surface H atoms to recombine and desorb as  $\text{H}_2$ , in addition to pounding them into the bulk. The cross section for recombinative desorption is strongly dependent on the incident angle of the inert gas atoms. The cross section is very small at



the normal angle and increases rapidly as the incident angle is increased to  $30^\circ$  away from the normal. The cross section increases because the parallel momentum of the Xe atom increases. At more glancing incidence, the Xe atom moves laterally away from the spot of its initial collision with the surface, thereby clearing a path for the desorbing  $H_2$  and increasing the probability for  $H_2$  to escape into the gas phase.

Therefore, by changing the incident angle, one can choose whether to pound surface H into the bulk or to desorb it as  $H_2$ , because the cross sections for absorption and recombinative desorption have maxima at different incident angles. The discovery of collision-induced recombinative desorption is key to the success of the investigations of bulk H chemistry because it enables the removal of surface H without removing bulk H. Use of the standard method of thermal desorption for removing surface species is not possible because bulk H desorbs at a lower temperature due to its weaker binding to Ni. Collision-induced recombinative desorption is a new tool for the nonthermal removal of chemisorbed species without perturbation of the surface or bulk.

## Ethylene Hydrogenation by Bulk H

With the capabilities to both synthesize and characterize bulk H, it is now possible to explore the chemistry of bulk H with ethylene under UHV conditions.<sup>31</sup> Bulk H is synthesized by exposure to gas-phase H atoms. The surface H that is also produced is removed by collision-induced recombinative desorption which, as discussed above, sweeps the surface clean of hydrogen without perturbing the bulk H. The crystal at 80 K is then exposed to a beam of  $C_2H_4$  to form an adsorbed layer. High-resolution electron energy loss spectroscopy verifies the efficacy of the Xe beam at sweeping the surface clean of H, confirms the presence of both adsorbed  $C_2H_4$  and bulk H, and shows that the C–C bond lies parallel to the surface. The identicalness of this ethylene vibrational spectrum to that of  $C_2H_4$  adsorbed on Ni(111)<sup>30</sup> without bulk H demonstrates that the bulk H does not modify the  $C_2H_4$ –Ni interaction.

With the reactants now synthesized, the crystal is heated at a rate of 2 K/s while a quadrupole mass spectrometer monitors the partial pressures of the desorbing species. These spectra are shown in Figure 5a. The recombination and desorption of hydrogen occurring between 170 and 250 K arises from bulk H, and the remainder arises from surface H. At 180 K, the temperature at which the bulk H emerges onto the surface, ethane is observed to desorb rapidly. The emergence of bulk H onto the surface also causes rapid desorption of  $C_2H_4$ . Up to 65% of the  $C_2H_4$  can be hydrogenated to ethane. No carbon-containing species remain on the surface above 220 K. The bulk H atom appears to be the reactive species for hydrogenation. The unreactivity of surface-bound H for hydrogenation is shown in Figure 5b.<sup>31,43</sup>

In contrast, surface H is very reactive toward exchange with ethylene! The partial pressures of the desorbing

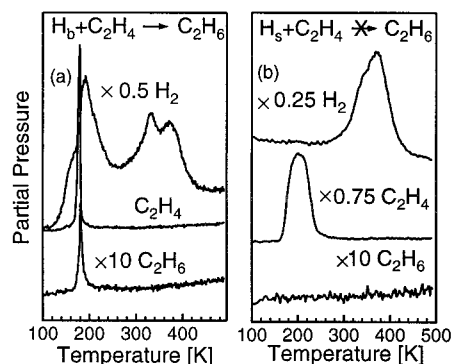


FIGURE 5. (a) Partial pressures versus temperature resulting from reaction of 0.025 ML  $C_2H_4$  adsorbed on Ni(111) with 2 ML bulk H. (b) Reaction of 0.25 ML  $C_2H_4$  and 0.26 ML surface H.

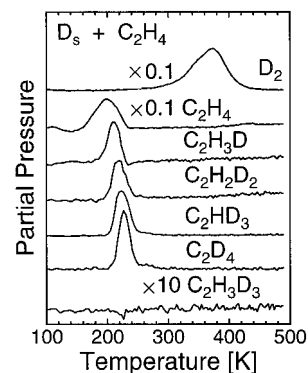


FIGURE 6. Partial pressures resulting from exchange between 0.25 ML  $C_2H_4$  and 0.26 ML surface D.

species from a coadsorbed layer of  $C_2H_4$  and surface D versus crystal temperature are shown in Figure 6. It is clear that all the deuterated ethylenes, from  $C_2H_3D$  to  $C_2D_4$ , are produced by exchange, but no hydrogenation products are formed. The exchange likely occurs in an equilibrium step between the dissociating  $C_2H_4$  molecule and  $C_2H_3$ , because  $C_2H_4$  slowly decomposes to adsorbed  $C_2H_2$  in this temperature range.<sup>32</sup> The observation of exchange is a very important one because it demonstrates that it is not the accessibility of surface H to  $C_2H_4$  that is precluding hydrogenation. Obviously, a surface H (or D) atom is sufficiently mobile to approach  $C_2H_4$  and to interact very strongly with it, even to exchange with it. Rather, the unreactivity of surface H implies that the barrier to hydrogenation via a side-on approach to the lying-down  $C_2H_4$  molecule is just too high for the reaction to be observed under these conditions. In contrast, when the bulk H atom approaches  $C_2H_4$  from underneath, it approaches from the direction in which the rehybridized  $\pi$  orbital is oriented. The barrier to hydrogenation is lower, and the reaction proceeds readily. Indeed, the optimal reaction coordinate for addition of a H atom to gas-phase  $C_2H_4$  is a perpendicular approach to the  $C_2H_4$  plane, in line with the  $\pi$  orbital.<sup>44</sup>

While the barrier to reaction via a side-on approach of a surface H atom is significantly larger than the barrier to reaction from the underside approach of a bulk H, an emerging bulk H atom is also 24 kcal/mol more energetic than a surface H atom, as explained below. Thus, hydro-

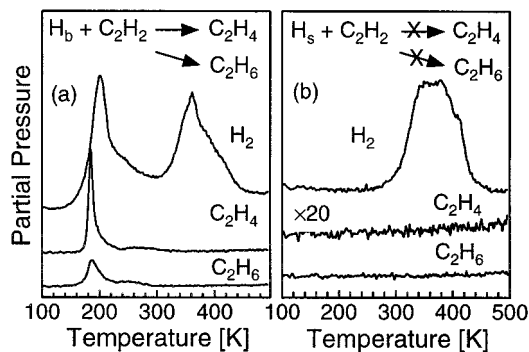


FIGURE 7. (a) Partial pressures versus temperature resulting from reaction of 0.25 ML  $C_2H_2$  with 1.8 ML bulk H. (b) Reaction of 0.13 ML  $C_2H_2$  with 0.7 ML surface H.

generation of  $C_2H_4$  by surface H is stymied not only by a high barrier due to the inaccessibility of the  $\pi$  orbital, but also by the relatively low energy of surface H. The energy difference between a bulk and surface H atom is a critical element in their distinctive reactivities.

### Acetylene Hydrogenation by Surface H and Bulk H

If the direction of approach of a H atom to the  $\pi$  orbitals plays a role in its ability to hydrogenate, then the  $C_2H_2$  molecule provides an interesting test case because it has two mutually perpendicular  $\pi$  orbitals. Like adsorbed ethylene, one of acetylene's rehybridized  $\pi$  orbitals is directed toward the metal and is accessible to a bulk H atom as it approaches from below upon emerging from the bulk. Unlike adsorbed ethylene,  $C_2H_2$  has a second rehybridized  $\pi$  orbital that lies approximately parallel to the surface and is accessible to surface-bound H atoms. Therefore, surface H should be reactive with adsorbed  $C_2H_2$  if the direction of approach of the H atom to the  $\pi$  orbitals of the unsaturated hydrocarbon is a factor in the hydrogenation activity.

Experiments very similar to those on the ethylene system have shown that at temperatures above 260 K, surface H indeed reacts with adsorbed  $C_2H_2$ .<sup>39</sup> In addition, bulk H, as it emerges onto the surface at 180 K, reacts with  $C_2H_2$ .<sup>39</sup> The surprise is that although both kinds of H atoms react, the products are different! Only bulk H hydrogenates  $C_2H_2$  to gas-phase  $C_2H_4$  and  $C_2H_6$ , the products of interest in hydrogenation catalysis.<sup>38</sup> Figure 7 shows the partial pressures of  $C_2H_6$  and  $C_2H_4$  as a function of surface temperature resulting from the reaction of (a) bulk H with  $C_2H_2$  and (b) surface H with  $C_2H_2$ . It is clear that both  $C_2H_4$  and  $C_2H_6$  are formed by the reaction of bulk H with  $C_2H_2$ , whereas no gas-phase products are formed by the reaction of surface H with  $C_2H_2$ . In contrast, surface H reacts with  $C_2H_2$  at 270 K to produce ethynylidyne,  $CCH_3$ , which is an adsorbed species that is known to be a precursor to coke formation. The vibrational spectrum of the species resulting from the reaction of surface H and  $C_2H_2$  is shown in Figure 8.<sup>45</sup>

Why are the product distributions that result from reaction of surface H and bulk H with adsorbed  $C_2H_2$  so

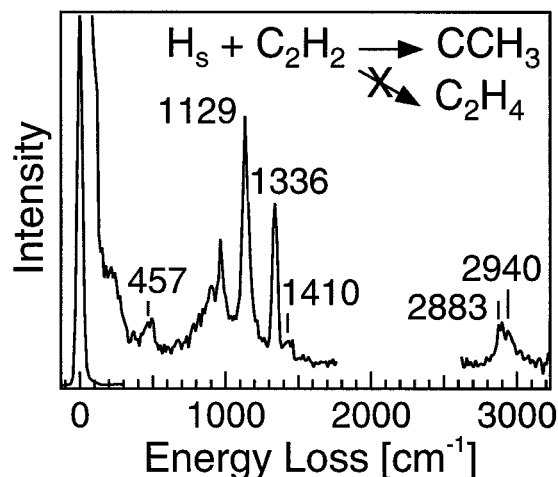


FIGURE 8. Vibrational spectrum predominantly of  $CCH_3$ , formed by reaction of surface H with 0.17 ML  $C_2H_2$  at 270 K. Modes associated with  $CCH_3$  are labeled.

different? The answer lies within the reaction mechanism. The addition of the first H atom from either the bulk or the surface to  $C_2H_2$  results in a vinyl species,  $HCCH_2$ . Although  $HCCH_2$  has not yet been identified spectroscopically in either reaction, it is believed to be the critical intermediate for  $CCH_3$  formation. Its critical role is strongly suggested by the *absence* of  $CCH_3$  production in the reaction of bulk H with  $C_2H_2$ .<sup>31</sup> Because there is no thermodynamically allowed route for  $C_2H_4$  to lose a hydrogen atom during its reaction with bulk H, no  $HCCH_2$  and therefore no  $CCH_3$  can be produced. In contrast, exposure of adsorbed  $C_2H_4$  to gas-phase H atoms readily results in adsorbed  $CCH_3$ ,<sup>45</sup> because the incident H atom abstracts a hydrogen from  $C_2H_4$  to form gas-phase  $H_2$  and adsorbed  $HCCH_2$ , which quickly rearranges to  $CCH_3$ .

Although the precise mechanism for the second step, the conversion of  $HCCH_2$  to  $CCH_3$ , is uncertain, it is clear that a second H atom must add to  $HCCH_2$  to form  $C_2H_4$ . Apparently, the rate of addition of a bulk H atom to  $HCCH_2$  to form gas-phase  $C_2H_4$  competes favorably with conversion of  $HCCH_2$  to  $CCH_3$ , whereas the rate of addition of a surface H atom to  $HCCH_2$  to form gas-phase  $C_2H_4$  is too slow to compete effectively against conversion of  $HCCH_2$  to  $CCH_3$ . The faster rate for addition of bulk H may arise from its higher energy. As shown in Figure 3, when a bulk H emerges onto the surface, it crosses the barrier between the bulk and the surface. At the top of this barrier, a bulk H is 24 kcal/mol more energetic than a surface H. If the emerging bulk H atom encounters an adsorbed  $HCCH_2$ , it can use this 24 kcal/mol of energy to overcome any barrier that may exist to reaction with adsorbed  $HCCH_2$ , and hence add rapidly enough to form ethylene before  $HCCH_2$  rearranges to  $CCH_3$ . In contrast, surface H is not sufficiently energetic to react fast enough with  $HCCH_2$  to form ethylene before  $HCCH_2$  rearranges to  $CCH_3$ .

The distinct product distributions for hydrogenation of  $C_2H_2$  by the two different H atoms emphasize the different energetics of the two H atoms. However, these results are also significant for their demonstration that hydrogenation

of unsaturated hydrocarbons by bulk H is the lower energy pathway. That is, hydrogenation of  $C_2H_2$  by bulk H is complete at 180 K, while the rate of hydrogenation by surface H is just beginning to be measurable at 260 K. Therefore, in high-pressure environments where bulk H is available, the dominant reaction pathway is likely hydrogenation by bulk H over hydrogenation by surface H.

## Relative Energetics of Bulk and Surface H

Certainly, a major key to the unique reactivity of bulk H is its high potential energy relative to that of a surface-bound H. Its high energy is a consequence of both its weaker binding to the bulk Ni atoms and the necessity for the bulk H emerging onto the surface to surmount the barrier at the surface–bulk interface. An emerging bulk H at the top of this barrier is about 24 kcal/mol more energetic than a H atom bound to the surface. This high potential energy of a bulk H can facilitate a reaction that would not otherwise occur for a surface H.

It is important to recognize that the emerging bulk H is transiently energetic. If the emerging bulk H does not encounter an adsorbate, it dissipates its energy to and ultimately equilibrates with the solid and becomes a surface-bound H. Of course, some of the energy of the emerging bulk H may have already dissipated by the time it reacts with the adsorbate. It is also possible, in principle, for there to be some lateral motion of the emerging bulk H atom as it dissipates its energy. It is even possible for the laterally moving bulk H atom to encounter and react with an adsorbate via a side-on approach. For example, a laterally moving bulk H may possibly be reacting with  $C_2H_4$  to form  $C_2H_6$  via a side-on approach, instead of from beneath  $C_2H_4$ , as suggested above. The available experimental data do not eliminate this possibility. What distinguishes this laterally moving bulk H from surface H is its energy. The laterally moving bulk H is still sufficiently energetic to overcome the barrier to its side-on reaction with ethylene, whereas surface H is insufficiently energetic.

The unreactivity of surface H with an adsorbed methyl radical is likely another example of its insufficient energy relative to the barrier to reaction from a side-on approach. No methane is observed as a result of attempts to react a coadsorbed layer of methyl radicals and surface H (or D).<sup>18</sup> In contrast, bulk D (or H) readily reacts with adsorbed methyl radicals to produce methane. Figure 9 shows the partial pressures versus temperature upon reaction of methyl radicals with bulk D. At exactly the temperature at which deuterium moves from the bulk to the surface, 180 K, there is very intense desorption of  $CH_3D$ , the only isotopomer observed.<sup>18</sup> There have been two recent density functional calculations of the energetics of this reaction system.<sup>46,47</sup> Both studies conclude that the reaction is enabled by the high energy of the emerging bulk H atom, although they differ in their conclusions as to the site at which the bulk H emerges.

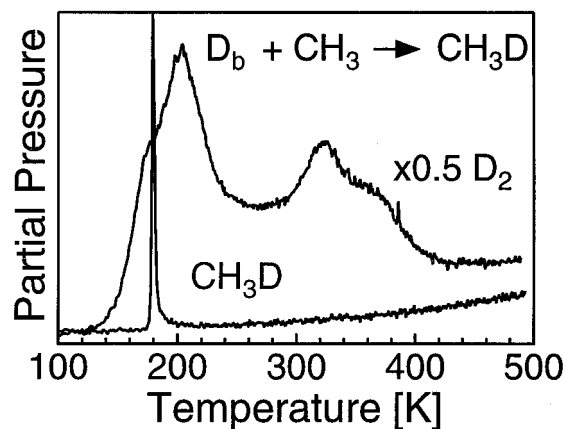


FIGURE 9. Partial pressures versus temperature from reaction of 0.15 ML  $CH_3$  with 2 ML bulk D.

Finally, it is important to note that it is not necessary for the metal to be saturated with hydrogen in order for the energetic hydrogen to be present at the surface. Rather, bulk H just one layer below the surface is sufficient. Therefore, in practical catalytic reactions where bulk H may be a reactant, the equilibrium between gas-phase  $H_2$ , surface H, and bulk H has to be maintained so that there is a constant supply of bulk H just beneath the surface. Such a layer of hydrogen may be associated with a surface reconstruction, as it is in the case of Ni(110) for H coverages between 1 and 1.5 ML.<sup>48</sup> Ethylene is hydrogenated to ethane only by this final half monolayer of hydrogen.<sup>49</sup> Hydrogen with a coverage of less than 1.0 ML is bound to the surface and is observed not to hydrogenate ethylene.<sup>49</sup>

## Evidence from Other Systems for the Unique Chemistry of Bulk Species

Additional evidence has recently accumulated for the importance of bulk H<sup>50</sup> in catalytic hydrogenation reactions. In experiments carried out in Pd membrane reactors, atomic hydrogen can be supplied to the hydrocarbon reactant adsorbed on the Pd membrane either by permeation through the membrane or by exposure to gas-phase  $H_2$ . The hydrogenation activity of pyridine, thiophene,<sup>51</sup> and furan<sup>52</sup> is observed to be higher when hydrogen permeates the membrane. The absence of bulk H in Pd particles<sup>53</sup> severely decreases the activity of CHO production from the reaction of CO and  $H_2$ , and the absence of bulk H in a Pd single crystal affects both the selectivity and activity of the hydrodechlorination of chlorofluorocarbons.<sup>54</sup>

Finally, evidence has been presented for the role of bulk C in hydrocarbon chain growth in the reaction of CO and  $H_2$  over supported and unsupported Ni.<sup>55</sup> Another study of the same reaction argues that the reaction of a bulk C atom with a surface-bound C atom is the critical first step of hydrocarbon chain and carbon nanotube growth.<sup>56</sup> Given that the energy level diagram of the carbon–Ni system is qualitatively similar to that of the hydrogen–Ni system in Figure 3, it is anticipated that bulk C will be shown to exhibit similarly unique chemistry as bulk H.



## Summary

Reactivities of surface-bound H and bulk H have now clearly been distinguished as a result of the capability to synthesize bulk H cleanly in a UHV environment. These results demonstrate that the reactivities of surface-bound and bulk H atoms and their product distributions are distinct. Their distinctiveness arises both from their different directions of approach to the adsorbate and their large difference in potential energy. The fact that an emerging bulk H is a more energetic species than a surface-bound H by 24 kcal/mol makes it likely that reaction channels readily accessible to bulk H will be closed to surface H. The emerging bulk H atom is, in a sense, a unique surface reactant that is present by virtue of the bulk–surface interface. It is an energetic species with a chemistry of its own.

*The U.S. DOE (DE-FG02-89ER14035) supports this work. It was carried out by many talented graduate students and postdoctoral associates whose names appear in the references.*

## References

- Ceyer, S. T.; Beckerle, J.; Lee, M.; Tang, S.; Yang, Q.; Hines, M. Effect of Translational and Vibrational Energy on Adsorption: Dynamics of Molecular and Dissociative Chemisorption. *J. Vac. Sci. Technol.* **1987**, *4*, 501–507.
- Ceyer, S. T. New Mechanisms for Chemistry at Surfaces. *Science* **1990**, *249*, 133–139.
- Ceyer, S. T. Translational and Collision-Induced Activation of CH<sub>4</sub> on Ni(111): Phenomena Connecting Ultra-High-Vacuum Surface Science to High-Pressure Heterogeneous Catalysis. *Langmuir* **1990**, *6*, 82–87.
- Lee, M.; Yang, Q.; Tang, S.; Ceyer, S. T. Activated Dissociative Chemisorption of CH<sub>4</sub> on Ni(111): Observation of a Methyl Radical and Implication for the Pressure Gap in Catalysis. *J. Chem. Phys.* **1986**, *3*, 1693–1694.
- Lee, M.; Yang, Q.; Ceyer, S. T. Dynamics of Activated Dissociative Chemisorption of CH<sub>4</sub> and Implication for the Pressure Gap in Catalysis: Molecular Beam-High-Resolution Electron Energy Loss Study. *J. Chem. Phys.* **1987**, *87*, 2724–2741.
- Beebe, T.; Goodman, D.; Kay, B.; Yates, J. Kinetics of Activated Dissociative Adsorption of Methane on Low Index Planes of Ni. *J. Chem. Phys.* **1987**, *87*, 2305–2315.
- Yang, Q.; Maynard, K.; Johnson, A.; Ceyer, S. T. Structure and Chemistry of CH<sub>3</sub> and CH Radicals Adsorbed on Ni(111). *J. Chem. Phys.* **1995**, *102*, 7734–7749.
- Yang, Q.; Johnson, A.; Maynard, K.; Ceyer, S. T. Synthesis of Benzene from Methane over a Ni(111) Catalyst. *J. Am. Chem. Soc.* **1989**, *111*, 8748–8749.
- Beckerle, J.; Johnson, A.; Yang, Q.; and Ceyer, S. T. Collision Induced Dissociative Chemisorption of CH<sub>4</sub> on Ni(111) by Inert Gas Atoms: Mechanism for Chemistry with a Hammer. *J. Chem. Phys.* **1989**, *91*, 5756–5777.
- Åkerlund, C.; Zoric, I.; Kasemo, B. Collision Induced Desorption and Dissociation of O<sub>2</sub> on Pt(111). *J. Chem. Phys.* **1998**, *109*, 737–745.
- Vattuone, L.; Gambardella, P.; Burghaus, U.; Cemic, F.; Cupolillo, A.; Valbusa, U.; Rocca, M. Collision Induced Desorption and Dissociation of O<sub>2</sub> Chemisorbed on Ag(001). *J. Chem. Phys.* **1998**, *109*, 2490–2502.
- Beckerle, J.; Johnson, A.; Ceyer, S. T. Observation and Mechanism of Collision Induced Desorption: CH<sub>4</sub> on Ni(111). *Phys. Rev. Lett.* **1989**, *62*, 685–688.
- Beckerle, J.; Johnson, A.; Ceyer, S. T. Collision Induced Desorption of Physisorbed CH<sub>4</sub> from Ni(111): Experiments and Simulations. *J. Chem. Phys.* **1990**, *93*, 4047–4065.
- Kulginov, D.; Persson, M.; Rettner, C. T. Dynamics of Collision Induced Desorption: Ar–Xe/Pt(111). *J. Chem. Phys.* **1997**, *106*, 3370–3386.
- Romm, L.; Zeiri, Y.; Asscher, M. Collision Induced Desorption of N<sub>2</sub> from Ru(001). *J. Chem. Phys.* **1998**, *108*, 8605–8614.
- Libuda, J.; Scoles, G. Collision Induced Desorption of Hydrocarbons Physisorbed on Au(111). *J. Chem. Phys.* **2000**, *112*, 1522–1530.
- Maynard, K. J.; Johnson, A. D.; Daley, S. P.; Ceyer, S. T. New Mechanism for Absorption: Collision Induced Absorption. *Faraday Discuss. Chem. Soc.* **1991**, *91*, 437–449.
- Johnson, A.; Daley, S.; Utz, A.; Ceyer, S. T. Chemistry of Bulk Hydrogen: Reaction of Hydrogen Embedded in Nickel with Adsorbed CH<sub>3</sub>. *Science* **1992**, *257*, 223–225.
- Ceyer, S. T. Collision Induced Surface Processes. In *Handbook of Surface Imaging and Visualization*; Hubbard, A., Ed.; CRC Press: Boca Raton, FL, 1995; Chapter 5.
- Kindt, J.; Tully, J. C. Simulations of Collision Induced Absorption of Hydrogen on Ni(111). *J. Chem. Phys.* **1999**, *111*, 11060–11069.
- Satterfield, C. *Heterogeneous Catalysis in Industrial Practice*; McGraw-Hill: New York, 1991; pp 201–205.
- Farkas, A.; Farkas, L.; Rideal, E. Experiments on Heavy Hydrogen IV—Hydrogenation and Exchange Reaction of Ethylene with Heavy Hydrogen. *Proc. R. Soc.* **1934**, *146*, 630–639.
- Kokes, R. J.; Emmett, P. Activity of Raney Nickel as a Function of Hydrogen Content. *J. Am. Chem. Soc.* **1960**, *82*, 4497–4501.
- Dus, R. Reactivity of Ethylene with Selected Forms of Hydrogen Deposit on Evaporated Palladium Films. *Surf. Sci.* **1975**, *50*, 241–252.
- Soga, K.; Imamura, H.; Ikeda, S. Hydrogenation of Ethylene. *J. Catal.* **1979**, *56*, 119–126.
- Fouilloux, P. Nature of Raney Nickel, its Adsorbed Hydrogen and its Catalytic Activity for Hydrogenation Reactions. *Appl. Catal.* **1983**, *8*, 1–42.
- Matsuyama, M.; Ashida, K.; Takayasu, O.; Takeuchi, T. Catalytic Activities of Ni Alloys Expressed by Surface and Bulk Compositions. *J. Catal.* **1986**, *102*, 309–315.
- Molnar, A.; Smith, G. Hydrogen Effects in Organic Hydrogenations. In *Hydrogen Effects in Catalysis*; Paal, Z., Menon, P., Eds.; Dekker: New York, 1988; Chapter 18.
- Horiuti, J.; Polanyi, M. Exchange Reactions of Hydrogen on Metallic Catalysts. *Trans. Faraday Soc.* **1934**, *30*, 1164–1172.
- Hammer, L.; Hertlein, T.; Müller, K. Ordered Phases of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on Ni(111). *Surf. Sci.* **1986**, *178*, 693–703.
- Daley, S.; Utz, A.; Trautman, T.; Ceyer, S. T. Ethylene Hydrogenation on Ni(111) by Bulk Hydrogen. *J. Am. Chem. Soc.* **1994**, *116*, 6001–6002.
- Lehwald, S.; Ibach, H. Decomposition of Hydrocarbons on Flat and Stepped Ni(111). *Surf. Sci.* **1979**, *89*, 425–445.
- Hasse, W.; Günter, H.; Henzler, M. Study of Self-Hydrogenation of Ethene on Clean Ni(111). *Surf. Sci.* **1983**, *126*, 479–486.
- Dalmajmelik, G.; Massardier, J. Catalytic Activity of Single-Crystal Faces: Ethylene and Benzene Hydrogenation on (111), (110) and (100) Faces of Ni. In *Proceedings of the Sixth International Congress on Catalysis*; Bond, G., Wells, P., Tompkins, F., Eds.; Chemical Society: London, 1977; pp 90–100.
- See, for example: *Hydrogen in Metals I and II*; Alefeld, G., Volkl, J., Eds.; Springer-Verlag: Berlin, 1978.
- Smith, H.; Chadwell, A.; Kirslis, S. Role of Hydrogen in Raney Nickel Catalysts. *J. Phys. Chem.* **1955**, *59*, 820–822.
- Kokes, R. J.; Emmett, P. H. Role of Hydrogen in Raney Nickel Catalysts. *J. Am. Chem. Soc.* **1959**, *81*, 5032–5037.
- Palczewska, W. Catalytic Properties of Metal Hydrides. In *Hydrogen Effects in Catalysis*; Paal, Z., Menon, P., Eds.; Dekker: New York, 1988; Chapter 14.
- Haug, K.; Burgi, T.; Trautman, T.; Ceyer, S. T. Distinctive Reactivities of Surface Bound H and Bulk H for the Catalytic Hydrogenation of Acetylene. *J. Am. Chem. Soc.* **1998**, *120*, 8885–8886.
- Comsa, G.; David, R.; Schumacher, B. Angular Dependence of Flux, Mean Energy and Speed Ratio for D<sub>2</sub> Molecules Desorbing from Ni(111). *Surf. Sci.* **1979**, *85*, 45–68.
- Johnson, A.; Maynard, K.; Daley, S.; Yang, Q.; Ceyer, S. T. Hydrogen Embedded in Ni: Production by Incident Atomic Hydrogen and Detection by High-Resolution Electron Energy Loss. *Phys. Rev. Lett.* **1991**, *67*, 927–930.
- Premm, H.; Pölzl, H.; Winkler, A. Dynamics and Kinetics of Subsurface Absorption and Desorption for the System Hydrogen–Ni(111). *Surf. Sci.* **1998**, *401*, L444–L451.
- Son, K.; Mavrikakis, M.; Gland, J. Low-Temperature Hydrogenation of Cyclohexene by Energetic Forms of Hydrogen on Ni(100). *J. Phys. Chem.* **1995**, *99*, 6270–6272.
- Schlegel, H. Ab Initio Molecular Orbital Studies of H + C<sub>2</sub>H<sub>4</sub> and F + C<sub>2</sub>H<sub>4</sub>. *J. Phys. Chem.* **1982**, *86*, 4878–4882.
- Burgi, T.; Trautman, T.; Haug, K.; Utz, A.; Ceyer, S. T. Synthesis and Spectroscopic Identification of Ethylidyne Adsorbed on Ni(111). *J. Phys. Chem.* **1998**, *102*, 4952–4965.
- Michaelides, A.; Hu, P.; Alavi, A. Physical Origin of the High Reactivity of Subsurface Hydrogen in Catalytic Hydrogenation. *J. Chem. Phys.* **1999**, *111*, 1343–1345.

- (47) Ledentu, V.; Dong, W.; Sautet, P. Heterogeneous Catalysis through Subsurface Sites. *J. Am. Chem. Soc.* **2000**, *122*, 1796–1801.
- (48) Christmann, K.; Chehab, F.; Penka, V.; Ertl, G. Surface Reconstruction and Surface Explosion Phenomena in the Ni(110)/Hydrogen System. *Surf. Sci.* **1985**, *152/153*, 356–366.
- (49) Gilnes, A.; Anton, A. Effects of Hydrogen-Induced (1×2) Surface Reconstruction on the Kinetics of Ethylene Hydrogenation on Ni(110). *Surf. Sci.* **1993**, *286*, 122–138.
- (50) Lagos, M.; Ramirez, R. Catalysis and Subsurface Bonding. *Phys. Rev. B* **1988**, *38*, 10042–10043.
- (51) Shirai, M.; Pu, Y.; Arai, M.; Nishiyama, Y. Reactivity of Permeating Hydrogen with Thiophene on a Pd Membrane. *Appl. Surf. Sci.* **1998**, *126*, 99–106.
- (52) Shirai, M.; Arai, M. Hydrogenation of Furan with Hydrogen Atoms Permeating through a Pd Membrane. *Langmuir* **1999**, *15*, 1577–1578.
- (53) Rothaemel, M.; Zanthoff, H.; Baerns, M. Formation of CHO during Interaction of CO and H<sub>2</sub> on Alumina-Supported Pd Catalysts. *Catal. Lett.* **1994**, *28*, 321–328.
- (54) Rupprechter, G.; Somorjai, G. Palladium-Catalyzed Hydrogenation without Hydrogen: Hydrodechlorination of Chlorofluorocarbons with Solid State Hydrogen over Pd(111) and its Implications. *Catal. Lett.* **1997**, *48*, 17–20.
- (55) Barbier, A.; Brum Pereira, E.; Martin, G. A. Role of Bulk H and Bulk C in the Chain Lengthening of Fischer–Tropsch Synthesis over Nickel. *Catal. Lett.* **1997**, *45*, 221–226.
- (56) Nolan, P.; Lynch, D.; Cutler, A. Carbon Deposition and Hydrocarbon Formation on Group VIII Metal Catalysts. *J. Phys. Chem. B* **1998**, *102*, 4165–4175.

AR970030F