HYDROGEN DISSOCIATION ON TRANSITION METAL SURFACES: 
THE EFFECTS OF SURFACE IMPURITIES

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ABSTRACT

The dissociative adsorption of hydrogen on transition metals has been the subject of considerable attention for a number of years by surface scientists. Much of the earlier work concerned the use of techniques such as temperature programmed desorption and work function measurements. These data have been successful in defining the kinetic parameters associated with the adsorption/desorption steps together with information regarding the nature of the metal-hydrogen bond. More recently molecular beam techniques have been employed to examine directly the existence and nature of the H_2 adsorption barrier. This paper will present a limited review of the present understanding of hydrogen dissociation on clean and chemically modified transition metals with emphasis on the authors’ research. In particular, H_2 adsorption on clean tungsten and the influence of electronegative additives (e.g. S, O, C, P, N, Cl) on the chemisorption properties of transition metals, principally nickel, will be discussed. In conclusion, the relevance of these studies to other transition metals will be discussed.

1. Introduction

The relationship between the geometric arrangement of surface atoms and its activity toward making and breaking chemical bonds is a long-standing question. Concepts such as "active centres" [1], "multiplets" [2], or "ensembles" [3-5] have been proposed to characterize the particular configuration of surface atoms required to promote certain chemical transformations. Modern surface science has begun to quantitatively characterize the specific nature of the surface that is prerequisite to its ability to activate chemical bonds. Of particular interest in these studies has been the study of hydrogen dissociation on transition metal surfaces.

Systematic studies can be carried out relating structure to activity by using single crystal surfaces. Although the surfaces of these materials are by no means perfect, their near ideal properties are most attractive for these purposes, particularly when compared to polycrystalline materials which expose different crystal planes and which exhibit a spectrum of structural imperfections. Considerable attention has been given by surface scientists to the question of hydrogen adsorption on transition metals, especially the relationship of the adsorption process to structure as determined from single crystal studies. This paper will review in a restricted manner the status of our understanding regarding hydrogen dissociation, bonding, and desorption from transition metal surfaces, in general, as well as the effect of surface impurities.
2. Energetics of Adsorption

To introduce hydrogen adsorption, it is instructive to briefly discuss [6] the energetics of the dissociation of diatomic hydrogen on a clean surface— as well as associative desorption, which represents the reverse process. Shown in Fig. 1 is a simple one-dimensional potential diagram, proposed by Lennard-Jones [7], which describes the overall energetics. A \( \text{H}_2(\text{D}_2) \) molecule approaching a surface feels a weakly attractive potential. Although a direct determination of the well depth, \( E_1 \), is difficult to obtain, an indirect determination can be made by analyzing molecular beam experiments in which the Debye-Waller factor for the specular beam is measured [6,8,9]. For Pt(111) this kind of analysis for He, \( \text{H}_2 \), and \( \text{D}_2 \) scattering has shown that \( E_1 \) values for \( \text{H}_2 \) and \( \text{D}_2 \) are approximately equal and are, at most, 5 kJ mole\(^{-1} \) [10]. These kinds of measurements give information about the molecular potential at the zero coverage limit.

Figure 1. Potential energy diagram for the interaction of hydrogen with a surface [6].
In the chemisorption process, the $H_2(D_2)$ molecule dissociates and crosses over to the potential curve for chemisorption. This step may be associated with an activation energy $E^*$ as indicated in Fig. 1. The well depth $E_0$ associated with this potential curve can be determined from a variety of experiments [11]. Typical values range from 48 kJ mole$^{-1}$ on Pt(111) [12] to 146 kJ mole$^{-1}$ on W(100) [13]. These values correspond to metal-hydrogen bond energies of 238 and 293 KJ mole$^{-1}$, respectively.

The general accepted picture [14] for dissociative sticking of $H_2$ assumes the antibonding molecular orbital (MO) of a $H_2$ molecule approaching the surface is shifted below the Fermi level ($E_F$). This creates a hole at the adsorbate which is shifted still further down below $E_F$. Tunneling leaves a hole in the solid below $E_F$ which corresponds to an electron-hole excitation of the solid. This effectively transfers the chemisorption energy and enables effective sticking [14,15].

Much of the current understanding of hydrogen on transition metals has developed through the use of thermal programmed desorption (TPD). This technique is one of the oldest and simplest surface techniques, yet extremely powerful in addressing adsorption and desorption phenomena. Thermal programmed desorption [11,16] is conceptually a simple experiment. The surface is dosed to a given coverage with the desired gas, and the temperature of the sample then raised. By following the gas-phase pressure and the substrate temperature as a function of time, one can generate a spectrum of the desorbing gas versus temperature. The work which is to be discussed will be limited primarily to results obtained using this technique. More recently, techniques employing molecular beams and high resolution electron energy loss have made major contributions to our understanding of the interaction of hydrogen with metal surfaces. Because space does not allow, these results will not be addressed in this discussion.

3. **Metal Single Crystal Surfaces**

The literature associated with hydrogen adsorption on transition metal surfaces is extensive thus no attempt will be made here to review this general area. An effort will be made to give the reader a general feel for the experimental approach and the kind of information that is obtainable with the currently available surface techniques. As illustration, two specific transition metals have been targeted for discussion: nickel and tungsten, representative of fcc and bcc metals, respectively. In addition to the topical interest of tungsten to this conference, these metals were chosen because detailed systematic studies addressing structural and impurity effects on $H_2$ chemisorption have been carried out for each.

The variations of the initial adsorption energies of hydrogen on nickel have been studied [17] in great detail and are illustrative of the "structure insensitivity" typically found in hydrogen chemisorption on fcc metals. For the H/Ni system the differences in the activation energies are quite small for different crystal planes. That is, there is little noticeable influence of the surface crystallography on the adsorption/desorption parameters. Recent molecular beam studies
have shown small differences in the measured $E^*$ for H$_2$ dissociation on Ni(110) and N(111). While the barrier to dissociation is negligible for Ni(110), it is 0.1 eV for Ni(111).

For tungsten, the initial heat of adsorption varies between 133 and 167 kJ mole$^{-1}$ [18]. This means that the strength of the metal-hydrogen bond varies between 284 kJ mole$^{-1}$ and 301 kJ mole$^{-1}$, a quite modest change. Despite this apparent modest variation, the chemistry of hydrogen on tungsten shows significant structural complexities. The overall thermal desorption profiles show striking differences as shown in Fig. 2 [19]. Desorption is quite complex with at least 11 peaks from the four planes representing at least 11 desorption processes with activation energies ranging from 58 to 155 kJ mole$^{-1}$. All exchange H$_2$ and D$_2$, and all, with the exception of the B$_1$ peak from W(100), desorb with second-order kinetics. Together these observations indicate that adsorption of hydrogen is dissociative with the adsorbed species being atomic hydrogen. Dissociative adsorption is the general rule for most metals.

![Fig. 2. Hydrogen thermal desorption spectra for saturation coverages on low index planes of W. The dotted curves are the desorption curves calculated on the basis of the activation energies and orders $(x)$ indicated for each peak [19].](image-url)
The origin of the processes leading to the multiple peak structure is not entirely clear from the thermal desorption spectra. One obvious interpretation of the peak multiplicity is the assumption of surface site heterogeneity. Site heterogeneity is interpreted to mean that the hydrogen can be bound differently to different geometrical arrangements of surface metal atoms. For illustration, the unit cells for the four low index planes of tungsten yielding the TPD spectra of Fig. 2 are shown in Fig. 3. On the (100) surface, hydrogen bound to a single metal atom might be quite different from hydrogen bound in the four-fold site. In agreement with this concept is the observation that the most structurally complex surface, W(111), yields the most complex thermal desorption spectrum. A second hypothesis is that multiple peaks in the desorption spectra result from an induced heterogeneity due to lateral interactions between adatoms on adjacent, identical sites. Thermal desorption alone can not distinguish between these two possibilities.

Fig. 3. Unit cells for the four low index planes of W yielding the TPD spectra of Fig. 2. The numerical values are the metal-metal distances for the specific case of tungsten [19].
Work function measurements, which can be related directly to the hydrogen-surface bond, allow us to distinguish between these possibilities. [20]. In the simplest interpretation, the work function is directly proportional to the product of the dipole moment per metal-hydrogen bond and the total number of such bonds. Multiple binding sites will likely have different dipole moments. Thus, sequential filling of these sites should yield breaks in a plot of work function versus hydrogen coverage. In contrast, for induced heterogeneity, where only a single site (and therefore, a single dipole) exists, a smooth variation of the work function with coverage is anticipated. The coverage dependent work function variation corresponding to the spectra in Fig 2, is collected in Fig. 4 [21]. \( W(211) \) and \( W(100) \) are the extreme examples. The smooth change in work function with coverage for \( W(100) \) suggests strongly that no geometrically

![Graph](image)

**Fig. 4** Coverage dependent work function changes obtained using the Kelvin vibrating probe method for the hydrogen adsorption on the four planes in Fig. 3. In coverage dependent TPD as in Fig. 2, the high temperature states fill first. As a result the work function changes with increasing coverage correspond in Fig. 3 to sequential filling of the peaks from high temperature to low temperature, i.e., the work function change at low coverage
corresponds to occupation of only the high temperature state [19].

Distinct sites are sequentially filled. In contrast, a clear break in this kind of plot occurs for W(211) upon completion of one feature (B2) in the thermal desorption spectrum and the onset of the filling of a second feature (B1). Similarly, the multiple breaks in the work function variation for the (111) surface correspond to sequential filling of the multiple thermal desorption peaks. In contrast, a similar plot for the (110) surface exhibits a monotonic change. These results show clearly that smooth surfaces such as W(100) and W(110) exhibit induced heterogeneity while more open surfaces such as W(211) and W(111) show a true site heterogeneity.

In the case of W(211), where the resolution between the TPD peaks is sufficiently large to allow an independent study of each, the existence of multiple sites has been conclusively established. The adsorption kinetics of the two states differ by at least an order of magnitude, and mixed adsorption studies show different behavior between the low and high temperature hydrogen states [22]. Analysis of these data for W(211) lead to the suggestion of a deep trough binding site for the high temperature state of hydrogen. Adsorption into this site is unusual in that it is independent of the amount of hydrogen previously adsorbed. This suggests that initial removal of hydrogen from the gas phase results from impact with the outermost rows followed by a rapid spillover of the hydrogen into the deep trough sites. Ellis and Rye have recently directly confirmed the location of this hydrogen binding site on the W(211) surface by using ion scattering techniques [23]. These techniques exploits the anisotropic nature of the (211) surface. Ion scattering by hydrogen in directions perpendicular to the troughs is strongly inhibited by shielding from the outermost W atoms. In contrast, scattering along directions parallel to the troughs is efficient due to the clear access to the exposed hydrogen.

What is clear from these and other studies is that the size of hydrogen facilitates a probe of the full three-dimensional nature of a surface. The complexity of hydrogen chemistry on W(111), Figs. 2 and 4, is related to the fact that first, second and even third layer W atoms are exposed (see Fig. 3) and accessible to hydrogen. In general, such effects are expected to be more pronounced on the more open bcc metals than for the fcc metals.
5. The Role of Surface Impurities

In defining the role of surface impurities in altering $H_2$ dissociation and adsorption, both structural and electronic effects should be considered. The structural or steric consideration is conceptually simple and depends on the three dimensional nature of a surface for hydrogen adsorption. In addition to the simple site blocking that can always occur through occupation of the site by an adsorbate, one can also have blocking of access to a chemisorption site. For example, the high temperature form of dissociated hydrogen on W(211) is known to occupy a deep trough site, a site which is inaccessible to a larger molecule such as ethylene. Provided that the hydrogen sites are filled first, hydrogen and ethylene can exist independently on this surface. However, if the surface is first covered with ethylene, hydrogen adsorption is precluded despite the fact that free hydrogen sites exist [19].

Structural effects are inherently short range, while electronic effects can exhibit longer range perturbations [25]. Impurities whose electronegativities are greater than those for transition metals generally poison a variety of catalytic reactions [25], particularly those involving $H_2$. Much of this poisoning effect can be attributed to changes in the ability of the poisoned surface to dissociate and adsorb $H_2$.

The effect of preadsorbed electronegative atoms Cl, S, and P on the adsorption-desorption of $H_2$ on Ni(100) has been extensively studied [26,27,28] using TPD, low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). It has been found that the presence of electronegative atoms causes a reduction of the sticking coefficient, the adsorption bond strength and the adsorption capacity of the Ni(100) surface for $H_2$. The poisoning effect becomes more prominent with increasing electronegativity of the preadsorbed atoms [27].

Adsorption of Cl, S and P on nickel causes a reduction in hydrogen adsorption and a shift of the TPD peak maxima to a lower temperature [27]. The effect of preadsorbed Cl, S, and P on the $H_2$ TPD behavior is shown in Fig. 6. The TPD desorption curves represent the total adsorbate desorption for different impurity coverages after an exposure sufficient to saturate the surface. $H_2$ adsorption decreases markedly in the presence of surface impurities. The effects of P, however, are much less pronounced than for Cl or S.

Fig. 7 shows the observed dependence of the total $H_2$ adsorption on impurity coverage. Cl, S, and P cause a reduction of hydrogen adsorption and a shift of the TPD peak maxima to a lower temperature [27]. The extent of this effect increases in the sequence P, S, Cl. As seen in Fig. 4, the reduction of $H_2$ coverage is most apparent for Cl atoms. The similarity in the atomic radii of Cl, S, and P (0.99, 1.04, and 1.10Å, respectively [29], suggests a relationship between electronegativity and the poisoning of chemisorptive properties by these surface impurities.
4. The Role of Steps

From the above discussion it is clear that chemisorption is sensitive to the degree of unsaturation of surface metal atoms. Defects such as steps are another example of such unsaturation, and can be an important parameter in hydrogen chemisorption. For example, the effect of periodic step arrays on the adsorption energy has been studied by Conrad, Ertl, and Latta [24] for a Pd(111) surface. The results are reproduced in Fig. 5. For hydrogen the initial adsorption energy is higher by about 13 kJ mole-1 for the stepped surface and approaches the data for the low index surface with increasing coverage. The authors interpreted these data in terms of a higher binding energy of the H-atoms at the adsorption sites near the steps.

![Graph showing adsorption energy as a function of coverage for H2 on a Pt(111) surface (curve b, open triangles) and on a stepped Pt(111) surface (curve a, dark circles) [24]](image)

Fig. 5. Adsorption energy as a function of coverage for H2 on a Pt(111) surface (curve b, open triangles) and on a stepped Pt(111) surface (curve a, dark circles) [24]
Fig. 6. Effect of varying chlorine, sulfur, and phosphorus precoverage on H₂ thermal desorption from Ni(100). The surface coverage θ refers to the ratio of impurity atoms to surface metal atoms [27].

Fig. 7. Dependence of H₂ adsorption on additive precoverage. Surface coverage (0 or ML) is defined as in Fig. 6 [27].
The relationship between the initial sticking coefficients for \( H_2 \) and the impurity coverage of chlorine, sulfur, and phosphorus is shown in Fig. 8. The general trend is quite similar to that seen for the total hydrogen coverage, that is, the dissociation probabilities vary with the electronegative character of the additive. The most electronegative impurities effect the sticking probabilities most markedly.

![Graph showing variation of initial sticking coefficient of \( H_2 \) as a function of additive precoverage. Dashed line represents the theoretical dependence according to the relationship \( S = S_0 (1 - 40)^2 \) [27].](image)

Fig. 8. Variation of the initial sticking coefficient of \( H_2 \), \( S_0 \), as a function of additive precoverage. Dashed line represents the theoretical dependence according to the relationship \( S = S_0 (1 - 40)^2 \) [27].

Related studies [30] have been carried out in the presence of C and N. These impurities have the same electronegativities as S and Cl, 2.5 and 3.0, respectively. The comparison between the results for C and N and those for S and Cl are entirely consistent with the interpretation that electronegativity effects dominate poisoning of chemisorption by surface impurities with close atomic size, occupying the same adsorption sites. In the case of adsorbed impurities with the same electronegativity but
with different atomic radii (S and C, Cl and N), the effect becomes less pronounced with decreasing atomic radius.

Particularly noteworthy in the above studies is the general observation that those impurities strongly electronegative with respect to nickel, Cl, N, and S, modify the chemisorptive behavior far more strongly than would result from a simple site blocking model. The initial effects of these impurities in Figs. 7 suggest than a single impurity atom successfully poisons as many as ten nickel atoms, a result supporting an interaction that is electronic in nature.

6. Conclusions

It is clear from the above discussion that model studies using metal single crystals and ultrahigh vacuum surface techniques are quite useful in developing an understanding of the fundamental mechanisms by which surface impurities alter the dissociation and bonding of hydrogen to transition metal surfaces. Of particular interest with regards to hydrogen dissociation and chemisorption are the specific bonding site upon which the hydrogen ultimately resides. In the case of tungsten, the multiplicity of these bonding sites, at least for W(211) and W(111), gives rise to multiplicity in the hydrogen desorption spectra as observed by TPD and work function measurements.

The introduction of impurities such as sulfur or chlorine may block sites responsible for H₂ dissociation or bonding of subsequently formed atomic hydrogen. In addition, and this is most certainly the case for chemically modified nickel, a longer range electronic effect can profoundly alter both the efficiency of the surface to dissociate H₂ as well as the capacity of the surface to adsorb hydrogen. This overall electronic effect correlates directly with the electronegativity of the impurity, the most electronegative (i.e. sulfur, chlorine) inhibiting the dissociation and chemisorption most effectively.

These results strongly suggest that low coverages of strongly electronegative impurities on tungsten could significantly alter both the coverage and dissociation probability of H₂. For example, for surface reactions involving WF₆ and H₂, appreciable surface coverages of fluorine are likely present at steady-state conditions. Assuming an analogy exists between impurity effects on nickel and tungsten, then fluorine coverages of a few percent could dramatically alter the kinetics of H₂ dissociation. This attenuation of H₂ dissociation could quite easily lead to this step controlling the overall kinetics of tungsten deposition in WF₆ CVD.

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7. References


