

Catalysis and subsurface bonding

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We analyze the data on hydrogen adsorption and catalyzed water formation on Pt surfaces. Evidence is obtained for the existence of a weakly bound subsurface state of H. A reaction mechanism involving subsurface hydrogen, which can explain the catalytic activity of Pt surfaces in hydrogenation reaction, is put forward.

The catalytic activity of platinum surfaces in hydrogenation reactions makes the H/Pt system especially interesting. Experiments show the existence of two types of hydrogen bonds to Pt surfaces, which at saturation become equally populated. However, whereas one of these types of states (which we will denote as *a* states) is strongly bound and stable at room temperature, the other type (*b* states) is weakly bound and starts desorbing below $T=150$ K.^{1,2} Kasemo *et al.*² show that the weakly bound *b* states, although unstable at $T=273$ K, are partially populated at this temperature when the surface is exposed to an external H_2 pressure p . The total equilibrium coverage $\Theta(p)$ is thus pressure dependent and, on evacuating the chamber, it decreases to half the maximum attainable coverage. The observation of a pressure-dependent population of the *b* states becomes especially interesting after the experiments of Ogle and White,^{3,4} which clearly show a strong dependence of the rates of H_2O formation catalyzed by a Pt(111) surface on the external H_2 pressure. This suggests that the *b* states may have a distinguished role in the catalytic activity of Pt surfaces.

Hydrogen subsurface states have recently been studied in connection with a number of surface problems. They can be understood as a direct consequence of the contribution of the surface modes of vibration^{5,6} or surface relaxation⁷ to the lattice Green function of the host crystal. It has been shown that this contribution notably enhances the self-trapping energy of impurities at the subsurface layer.^{5,6} In this fashion, an *ab initio* method has been developed by which the energy of the subsurface bonded state can be calculated once the elastic properties of the host crystal are given. Recent experiments on H/Pd(110) (Refs. 8 and 9) and H/Nb(111) (Ref. 10) confirm the existence of such states of hydrogen in Pd and Nb and are in excellent quantitative agreement with theory. Very recent evidence has also been provided for the existence of subsurface H in Cu(111).¹¹

In this work we show evidence indicating that (a) the weakly bound *b* states are subsurface states, and (b) that they play the main role in the catalytic activity of Pt in reactions involving hydrogen. The experimental curve $\Theta_b(p)$,² giving the stationary populations of the *b* states,

exhibits a saturation pressure p_1 , for which $\Theta(p_1)=1$, and a kink at this value of p . This qualitative feature, as shown below, allows us to ascribe a subsurface nature to the *b* states.

Calculations for Pt(111) imply that the energy for subsurface hydrogen is close to the binding energy per atom of H_2 molecule.⁵ Consequently, the theory predicts metastable or weakly bound subsurface states of hydrogen in Pt(111). This suggests that the loosely bound *b* states appearing in the experiments are the subsurface states predicted by the theory. We analyze below the adsorption kinetics and show that the only way to fit the available data in H_2 adsorption by Pt(111) is by modeling the *b* states as subsurface states.

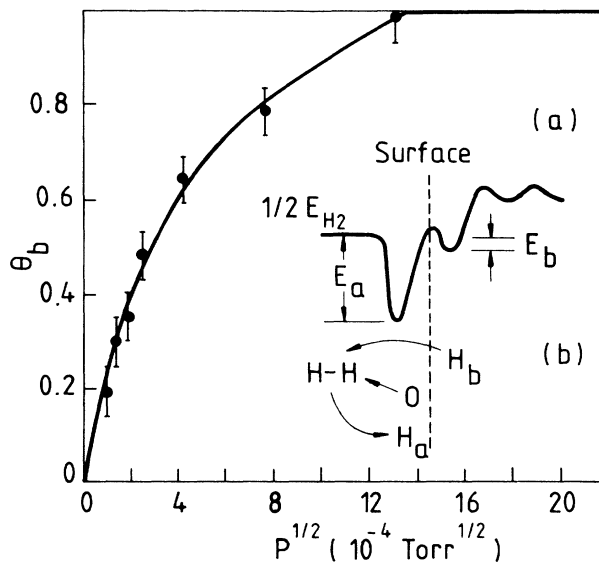


FIG. 1. Final coverage of the *b* state as a function of the hydrogen pressure obtained experimentally (dots), and using the model which assumes the *b* state to be a subsurface state (solid line). Inset (a): energy diagram for a hydrogen atom near the surface of Pt. E_a is the chemisorption energy, E_b is the shallow subsurface bonded energy. Inset (b): schematic mechanism for the catalysis of hydrogen and oxygen to water by Pt surface.

The inset of Fig. 1 shows schematically the energy diagram which follows from interpreting the b states as subsurface states. The kinetic equations governing the hydrogen adsorption are essentially those used in an earlier calculation¹² on the H/Nb system. These calculations were able to explain in a natural way a number of fascinating experiments regarding the absorption kinetics of H in Nb- and Pd-covered Nb systems. The only differences here with Ref. 12 are that the Pt subsurface b states are weakly bound in contrast to the strongly bound Nb subsurface states, there is no bulk absorption, and we incorporate here an additional term which accounts for the H₂ desorption from the metastable b layer. The basic idea is that the H exchange between the H₂ gas and the subsurface b layer needs empty sites in both the chemisorption and the subsurface layers (a and b layers, respectively). The H₂ dissociation is assumed to be of second order for the present calculation. With this assumption, which is not essential for the conclusions of this work, the kinetic equations are

$$\frac{d\Theta_a}{dt} = 2fs_a(1-\Theta_a)^2 + fs_{ab}(1-\Theta_a)^2(1-\Theta_b) - \kappa_{ab}(1-\Theta_b)\Theta_a + \kappa_{ba}(1-\Theta_a)\Theta_b \quad (1)$$

and

$$\frac{d\Theta_b}{dt} = 2fs_b(1-\Theta_a)^2(1-\Theta_b)^2 + fs_{ab}(1-\Theta_a)^2(1-\Theta_b) - \kappa_b(1-\Theta_a)^2\Theta_b^2 + \kappa_{ab}(1-\Theta_b)\Theta_a - \kappa_{ba}(1-\Theta_a)\Theta_b, \quad (2)$$

where Θ_a and Θ_b are the surface and subsurface coverages ($0 \leq \Theta_{a,b} \leq 1$), $f = p / [N_s(2\pi Mk_b T)^{1/2}]$ is the number of H₂ molecules impinging on the surface per unit time and adsorption site, N_s is the number of adsorption sites, M is the mass of the H₂ molecule, and T is the temperature. The coefficients s_a , s_b , and s_{ab} are the probabilities of H₂ dissociation after reaching two empty surface sites (a sites) followed by trapping of the two H atoms in a sites, passage of the two atoms to the b layer, and trapping of one atom in the a layer and the other in the b layer. The coefficients κ_{ab} and κ_{ba} govern the exchange between the two layers and κ_b is the probability of direct desorption from the b layer with formation of H₂.

At equilibrium,

$$\frac{d\Theta}{dt} = \frac{d\Theta_a}{dt} + \frac{d\Theta_b}{dt} = 0. \quad (3)$$

Substituting Eqs. (1) and (2) into Eq. (3) one obtains sim-

ple algebraic equations from the equilibrium coverages $\Theta_a(\infty)$ and $\Theta_b(\infty; p) \equiv \Theta_b(p)$:

$$\Theta_a = 1 \quad (4)$$

and

$$2fs_b + 2fs_b(1-\Theta_b)^2 + 2fs_{ab}(1-\Theta_b) - \kappa_b\Theta_b^2 = 0. \quad (5)$$

Figure 1 shows the experimental data of Ref. 2 for $\Theta_b(p)$ together with an excellent theoretical fit obtained by substituting in Eq. (5) the parameters $s_a = 5.64 \times 10^{-3}$, $s_b = 7.85 \times 10^{-2}$, $s_{ab} = 1.63 \times 10^{-2}$, and $\kappa_b = 5.17 \times 10^{-2} \text{ sec}^{-1}$. These parameters are quite reasonable since the initial sticking coefficient ($s_a + s_b + s_{ab}$) is of the order of 0.1, in good agreement with experimental data^{1,2} at $t \rightarrow 0$ and $s_a < s_b$ as expected in this model. Of particular interest is the saturation pressure $p_1 = 1.85 \times 10^{-6}$ torr beyond which $\Theta(p)$ saturates, which is characteristic of the subsurface nature of the b states. Models assuming the a and b states to be chemisorbed do not produce a reasonable fitting of the data, nor do they imply a saturation pressure.

The existence of weakly bound subsurface H provides an additional mechanism to the well-known ones as a precursor in the catalysis by Pt of H and O to water. In this process a hydrogen molecule gives up one H atom to the chemisorption layer and captures a hydrogen atom from the subsurface layer [see inset (b) of Fig. 1]. The conversion of a b to an a state provides the necessary energy ($E_a - E_b$) to activate another chemisorption species (oxygen in this case) which can react with the unchanged H₂ molecule. This new reaction mechanism [see inset (b)] generates rate curves similar to the ones observed in Fig. 3 of Ref. 1 and gives by far the best energy balance. By simple energetic considerations one expects this mechanism to lower considerably the reaction temperature. This mechanism can be easily extended to more complicated molecules containing hydrogen.

For the kinetic equations for the reaction mechanism it can be easily shown that the rate of H₂O formation starts from zero and has a finite slope at $t = 0$. Therefore, although our proposed mechanism is neither a Langmuir-Hinshelwood nor an Ely-Rideal reaction, the time-dependent reaction rate has the general form of the former type.

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