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Full Length Article

A first-principle study of H adsorption and absorption under the influence of coverage

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ABSTRACT

The investigations of interactions between hydrogen and transition metal surfaces are of vital importance to the comprehension of principals involved in many chemical processes. In this work, the influences of coverage on H adsorption and absorption on and in a series of transition metals have been studied. High enough hydrogen coverage is needed to make H absorption much more feasibly. The pre-adsorbed H adatoms can modify H binding energies as well as H absorption energetics and can be felt very deeply in the 2nd-subsurface. As a result, surface penetration of atomic H and further diffusion into the bulk can be facilitated, and in turn the resurfacing process of absorbed H is blocked.

1. Introduction

In industry, hydrogen can be generated frequently during the production and/or processing of metals [1]. The very simple atomic H can adsorb on metallic surfaces and diffuses between alternative sites [2]. Then two H adatoms on the surface can collide and recombine to form H_2 gas. Alternatively, due to its small size the adsorbed H atom can penetrate into the subsurface and then transit deeper into bulk to form interstitials [3]. The interactions between hydrogen and metals have been investigated extensively through decades, as they are fundamental steps that are of great relevance to a wide variety of chemical processes, including hydrogen embrittlement, hydrogen induced cracking, hydrogen storage, hydrogenation/dehydrogenation reactions, and fuel cell operations [4–11].

Over the past few years, first-principle calculations have been broadly applied to study the behavior of H on/in metals. Ferrin et al. [12], for example, have examined hydrogen adsorption onto the surface and absorption into the subsurface for a number of transition metals. They find that hydrogen adsorption is exothermic with reference to H_2 gas on all metals studied, except for Ag and Au. And the subsurface state is always less stable than the surface state. It is easier for subsurface H to resurface (a process corresponds to H movement from subsurface sites to surface sites) than to diffuse deeper into bulk.

However, work like this has always focused on dilute concentrations of H on/in metals (coverage of 1/4 monolayer (ML) used by Ferrin et al.). Greeley and Mavrikakis [13] using DFT method have found that a very large surface pressure is required to induce the population of subsurface H in Ni(1 1 1). Légaré [14] demonstrate that before the surface is fully covered, no significant repulsion will occur between the H adatoms. Only beyond this coverage of $\theta_H = 1$ ML, population of H in the subsurface can take place, as calculations performed on Pd(1 1 1) [15] show that pre-adsorbed H adatoms can modify the H diffusion energetics at near-surface region and thus block the resurfacing process.

In this work, we have investigated the adsorption and absorption of atomic hydrogen on and into the close-packed fcc(1 1 1) surface of a series of transition metals under different coverages. We show that high H coverage of more than 1 ML is needed to induce H absorption effectively. Large quantities of H covered on the surface can lower the thermodynamic energy differences calculated for H surface penetration as well as for the following diffusion process deep into the 2nd-subsurface. The kinetic activation energy for surface absorption is increased by pre-adsorbed H adatoms, while the relatively larger intrinsic barrier required for the second diffusion step is slightly decreased.

2. Computational methods

All calculations are performed using the BFGSLineSearch optimizer within the Quantum Espresso software package [16], interfaced with the Atomic Simulation Environment (ASE) [17]. Ionic and core interactions are described via relativistic Vanderbilt ultrasoft pseudopotentials [18]. Plane wave basis sets with kinetic energies up to 600 eV are used. The BEEF-vdW [19] exchange correlation functional is selected in

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order to obtain an accurate estimation of adsorption energies [20]. A Fermi-Dirac distribution with a smearing of 0.1 eV is applied. The irreducible Brillouin zone is sampled using a 6 × 4 × 1 Monkhorst-Pack [21] k-points mesh.

Simulations are carried out on close-packed fcc(1 1 1) metal surfaces with optimized lattice constants (see Supporting Information Table S1 for details). The surfaces are modeled by (2 × 3) five-layer periodical slabs, separated by at least 15 Å of vacuum in the direction perpendicular to the metal surface. The two bottom metal layers are fixed, while the top three layers and the H atoms are geometrically relaxed so that the maximum force in any direction on any moveable atom is less than 0.03 eV/Å. Electronic energies are converged to within 0.01 meV. Dipole correction is included in all cases to decouple the electrostatic interaction between periodically repeated slabs. All the calculations involving Ni atoms are spin-polarized.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.06.257.

Zero-point energy (ZPE) corrections are not included in this work. The NEB (nudged elastic band) [22] method is employed to obtain transition state geometries and corresponding barriers for H diffusion. The vibrational frequencies of the transition state help to verify the nature of these transition states given by the NEB method.

In order to investigate the influence of coverage on hydrogen behaviors, we have examined three different surface states. As visualized in Fig. 1(a), θ_H = 1/6 ML means only one H atom adsorbed on the surface fcc site (the most stable adsorption site of the metals studied in this work) in the initial state, which then penetrates into the subsurface, followed by a further diffusion into the 2nd-subsurface. θ_H = 1 ML represents 1 monolayer H atoms occupied on all the fcc sites. Then diffusion occurs to one of these H adatoms, which is highlighted in yellow.

The cyclic voltammetry profiles [23] show that under electro-adsorption conditions, the overpotential deposited H (H_{OPD}) and the underpotential deposited H (H_{UPD}) can coexist on Pt, Pd, Rh and Ir electrodes at potentials below $\overset{\circ}{E}_{HER}$ (the H^+/H_2 reversible potential). The H_{UPD} occupies the threefold hollow site while the H_{OPD} occupies the atop site [24–27], which implies the possibility of more than one monolayer H atoms presented on the surface. Therefore in the third case, besides 1 ML hydrogen atoms taken up all the fcc sites (H_{fcc}), we add one more H adsorbed on the energetically less favorable atop site (H_t) (shown in orange) to make a surface coverage of θ_H = 7/6 ML. (Actually, we have also checked 1 ML fcc-site H plus one H atom adsorbed on the hcp site, while this configuration is quite unstable on most surfaces studied in this work.) It follows that one preadsorbed H_{fcc} (shown in yellow), which is adjacent to the H_t, transits into the subsurface and the weakly bound H_t replaces it at the fcc site simultaneously [23,28].

3. Results and discussions

3.1. Influence on H binding energies

We first investigate the influence of coverage on H binding. The binding energy in each case is defined as the differential binding energy, ΔE_B:

$$\Delta E_B = E(M_{nH+H}) - E(M_{nH}) - 1/2E(H_2) \qquad (1)$$

where $E(M_{nH+H})$ is the total energy for an H atom adsorbed or absorbed on or in the metal surface under surface pre-coverage of n = 0, 5/6 ML and 1 ML, respectively. $E(M_{nH})$ is the energy of the metal surface covered with n ML H adatoms. $E(H_2)$ is the energy of a gas-phase H_2 molecule. A negative value of ΔE_B signifies the adsorption or absorption of hydrogen referenced to gas-phase H_2 is thermodynamically favorable. The results are shown in Figs. 2 and 3.

On surface, the most stable adsorption site is the fcc site for every metals studied in this work. The hcp site is only slightly energetically less stable (a difference of fewer than 0.05 eV) on many of these surfaces. Low coverage H adsorption (θ_H = 1/6 ML) is exothermic with reference to H_2 gas, except for Ag and Cu. Binding on Re is most stable. Results presented here are in good agreement with that shown in previous theoretical studies [29,30] (see Supporting Information Fig. S1).

The sequence of binding stability for surface H adatoms under low coverage is in connection with the very nature of the metallic surface. From the plots of projected density of states (PDOS) on both adsorbed H and surface metal atoms accepting it (see Fig. S2 in the Supporting Information), we can see that the position of the upper *d*-band edge of the noble metals (Ag/Cu) is right below the Fermi Level, leading to

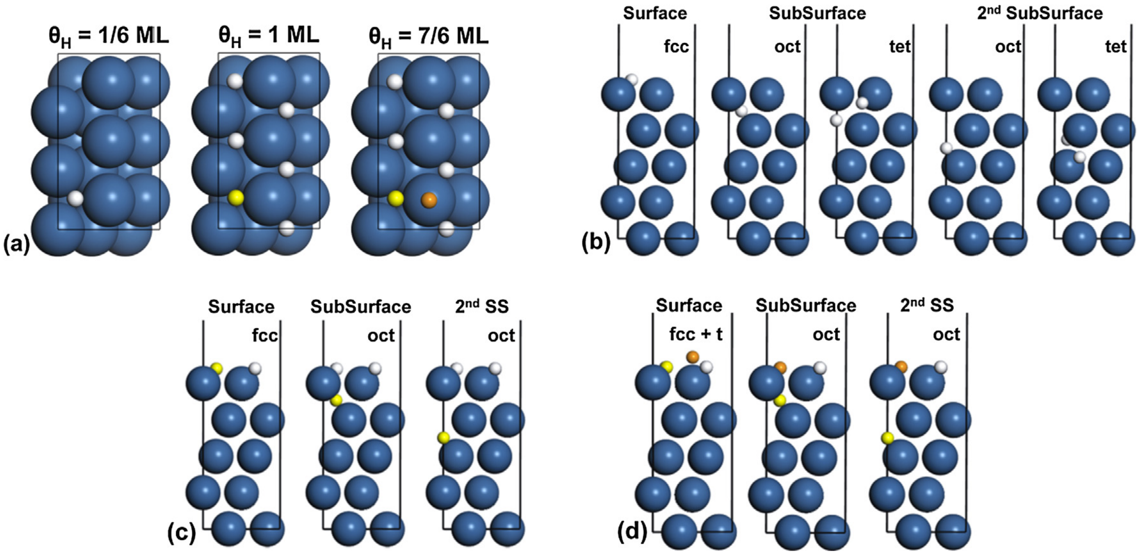

Fig. 1. (a). Initial metal surface state under three different coverages investigated in this work (top view). The unit cell is outlined with a solid line. θ_H = 1/6 ML, only one H atom adsorbs on the surface fcc site. θ_H = 1 ML, 1 monolayer H atoms bound onto all the surface fcc sites. θ_H = 7/6 ML, 1 ML H atoms take up all the surface fcc sites plus one more H adsorbs on the atop site. (b). Configurations for H populated on and in a clean metal surface (side view). The most stable surface adsorption site is the fcc site. Three different probable subsurface (and also 2nd-subsurface) sites have been shown, containing one octahedral (oct) site and two tetrahedral (tet) sites (under-top or under-hcp). (c) and (d) illustrate the pathway for H absorption under total coverage of 1 ML and 7/6 ML (side view), respectively. For simplicity, only the octahedral sites have been shown as representatives. The travelling H atoms are highlighted with colors (yellow and orange) in each case. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)