First-Principles Study of Hydrogen Adsorption on Ru(0001): Possible Occupation of Subsurface Sites

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We have performed an *ab initio* pseudopotential total-energy study of hydrogen adsorption on the Ru(0001) surface. It is found that the surface threefold hollow sites have the lowest energy, as expected for close-packed metal surfaces. However, at higher coverage, the occupation of the subsurface octahedral sites is made possible by the repulsive interaction between nearest-neighbor surface hollow sites. Our results resolve the previous controversy of two hydrogen-binding states observed in the measurements of work-function changes and sticking coefficients.

Ruthenium is a commonly used catalyst in the synthesis of hydrocarbons which involves the catalytic hydrogenation of CO after hydrogen and CO are adsorbed on the metal surface.[1] It is therefore of great interest to study the adsorption of hydrogen on ruthenium in order to obtain detailed information on this catalytic process. There have been considerable experimental efforts[2-10] in studying the adsorption of hydrogen on Ru(0001), which is the close-packed surface of this hcp metal, yet the atomic arrangement and surface stoichiometry have not been fully determined. In this study, we evaluate the total energies of various adsorption sites using *ab initio* pseudopotentials[11] within the local-density-functional approximation[12] and determine possible adsorption sites along with related physical properties.

Some interesting and unusual behavior was found recently[6] in a thorough study of the work-function change ($\Delta\phi$) during adsorption and its correlation with the temperature-programmed desorption spectra. The non-monotonic change of the work function with hydrogen dosage suggests the existence of two different binding *states* with negative (N) and positive (P) outward dipole moments, respectively. These two states are well correlated with the two desorption peaks in the temperature-programmed desorption spectra and exhibit different sticking properties. Initially, adsorption involves mainly the N state which is adsorbed directly with a sticking coefficient proportional to $1 - \theta_N$ (where θ_N is the relative coverage for state N) and is responsible for the initial rise of $\Delta\phi$. With larger H_2 exposures, the adsorption of the P state which has a much smaller sticking coefficient continues and gives rise to a decreasing $\Delta\phi$ which eventually saturates. One way to explain this finding, based on only one adsorption site, is to attribute the apparent two binding states to the lateral interactions between hydrogen atoms.[7] Another possible explanation associates these two binding states with two different adsorption sites, but controversial assignments are found in the literature.[6,7]

The low-energy electron diffraction (LEED) data[4-6] showed a 1×1 pattern at all coverages, which suggests that the ordered phase, if any, is 1×1 and that there is no surface reconstruction. In the measurements by electron energy-loss spectroscopy[2,3] two fundamental frequencies were found for this adsorption system and were assigned respectively to the symmetric (perpendicular to the surface) and asymmetric (parallel to the surface) vibrational frequencies of hydrogen atoms occupying the surface threefold hollow sites. The twofold bridge site will give three nondegenerate vibrational frequencies and is therefore excluded. We considered the surface threefold hollow sites as well as two subsurface sites: the octahedral and tetragonal sites. There are two different hollow sites on the surface: the hcp and the fcc sites. They only differ in the relative positions with respect to metal atoms in the second surface layer. The hcp site is right above the second-layer metal atoms, while the fcc site, in this case, does not have any metal atoms below it. As will be discussed later, we find that the two binding states mentioned above are, in fact, related to two adsorption sites, one being the surface hollow site, the other the subsurface octahedral site.

The ionic pseudopotentials used in the calculation are generated from isolated atoms[11] and are then fitted by Gaussian functions.[13] Localized Gaussian orbitals with three different decays per site are used as the basis for the wave functions. An exchange-correlation functional form suggested by Hedin and Lunqvist[14] is employed in the local-density calculation. The self-consistent procedure is carried out in the momentum space[15] with a supercell consisting of a slab of four ruthenium layers separated by a vacuum region equivalent to the space of five atomic layers. We used the same theoretical methods to study the structural properties of bulk ruthenium[16] as well as the clean Ru(0001) surface[17] and have obtained good agreement with experiment. The surface layer of the clean surface is found to undergo a small contraction,[18] about 2% of the interlayer distance,
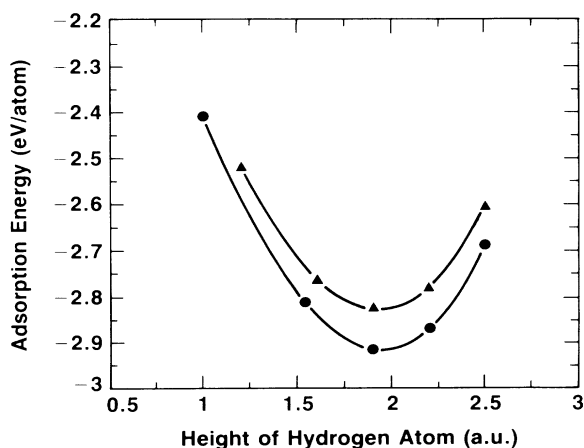
FIG. 1. Adsorption energy of hydrogen at the fcc (circles) and hcp (triangles) threefold hollow sites as a function of height measured from the surface ruthenium layer. The adsorption energy is relative to isolated hydrogen atoms.

with a calculated small relaxation energy of 20 meV.[17] This relaxation of the ruthenium surface layer is neglected since the small relaxation energy is negligible compared with the adsorption energy.

In the calculation, ordered hydrogen atoms are put down on both sides of the slab. The adsorption energy per atom for hydrogen occupying threefold hollow sites, either the hcp or the fcc site, is shown in Fig. 1 as a function of atomic height from the surface ruthenium layer. This energy is obtained by our taking the energy difference between slabs with and without hydrogen and then subtracting the energy of isolated hydrogen atoms. The results for the hcp and fcc sites are similar, with the fcc curve lying about 0.1 eV below the hcp curve. In both cases, the equilibrium position is found to be approximately 1.02 Å, which corresponds to a hydrogen-ruthenium distance of 1.87 Å. This value is 10% longer than the sum of the ruthenium metallic radius and half of the bond length in H_2.

As one pushes the hydrogen atom at the fcc hollow site perpendicularly into the surface, it will reach the subsurface octahedral site. The adsorption energy along this path is plotted in Fig. 2(a), where the octahedral site is indicated by an arrow. It is found that the energy of the octahedral site is higher than that of the surface fcc site by 0.7 eV/atom. Hence subsurface occupation is unlikely under this condition.

In Table I we summarize the adsorption energies and other properties for various adsorption sites with one hydrogen per surface unit cell. These adsorption energies should be compared with the dissociation energy of H_2 which is calculated to be 1.9 eV/atom with the same theoretical methods and same basis orbitals. A hydrogen atom at either the surface hollow site or the subsurface octahedral site has lower energy than in the molecule,
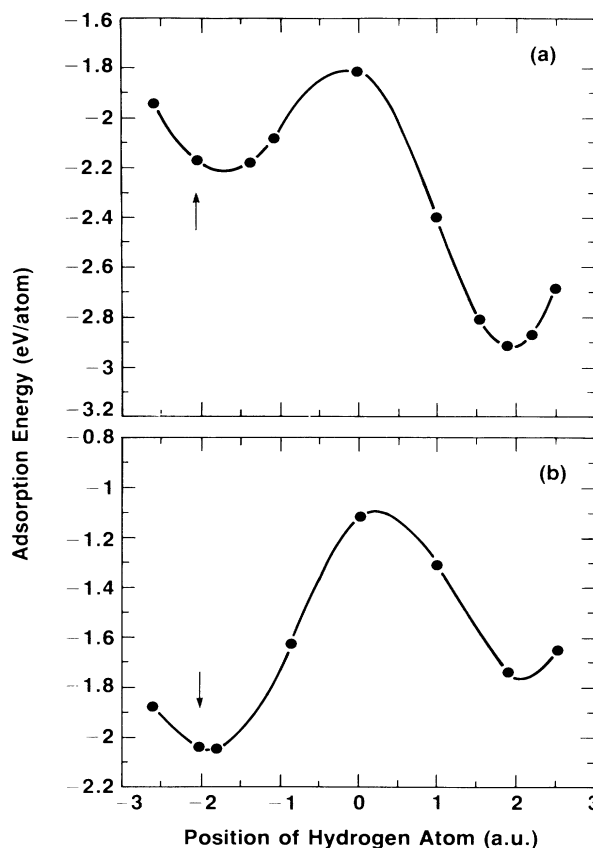

FIG. 2. Adsorption energy of hydrogen on ruthenium as a function of position along the path from the surface fcc hollow site to the subsurface octahedral site (indicated by an arrow) (a) without and (b) with the surface hcp site occupied. The position reference is the surface ruthenuium layer and the adsorption energy is measured from isolated atoms.

while the subsurface tetragonal site has a relatively higher energy. It is most likely that the hydrogen atom will go to the surface hollow site at this coverage since it is both energetically favorable and easily accessible. Note that the calculated work function increases slightly from the clean-surface value for adsorption at either hollow site.

Also listed in Table I are the perpendicular vibrational frequencies deduced from the total-energy curves. The motion of ruthenium atoms has been neglected because of the large mass ratio. No significant difference in the vibrational frequencies is found for the two hollow sites. The calculated equilibrium position and perpendicular vibrational frequency of the fcc site agrees very well with results of a recent linearized augmented plane-wave (LAPW) study.[19]

So far we have considered the occupation of only one of the two hollow sites, but not both. When two hydrogen atoms per surface unit cell are put down on both of the surface hollow sites, it is expected that the repulsive

TABLE I. Calculated equilibrium position h, adsorption energy E_{ad}, work-function change $\Delta\phi$, and perpendicular vibrational frequency $\omega_\perp$ for one hydrogen per surface unit cell on Ru(0001) at various sites. Comparison with other theoretical study and experiment is also made. The experimental frequency listed is the second peak (higher one) in electron energy-loss spectroscopy measurements. The calculated dissociation energy of H_2 is 1.9 eV/atom.

	h (Å)	E_{ad} (eV/atom)	$\Delta\phi$ (eV)	$\omega_\perp$ (meV)
Present study				
fcc	1.03	−2.9	+0.2	140
hcp	1.02	−2.8	+0.2	140
Octahedral	−0.88	−2.2	+0.0	100
Tetragonal	⋯	−1.7	−0.1	⋯
LAPW (fcc)[a]	1.06	−2.4	⋯	140
Experiment	1.10 ± 0.06[b]	−2.90[c] ($\theta \simeq 0$)		141[d]
		−2.65[c] ($\theta \simeq 0.5\theta_{max}$)		138[e]
		−2.51[c] ($\theta \simeq \theta_{max}$)		

[a]Reference 19.   [d]Reference 3.
[b]Reference 5.   [e]Reference 2.
[c]Reference 6.

interaction between them will make this configuration unstable. In fact this is what we find in our calculation. In Fig. 2(b) we show the adsorption energy curve along the same path into the surface as in Fig. 2(a), except that this time there is another hydrogen layer sitting at the surface hcp sites. In this case the subsurface octahedral site is found to have a lower energy than the surface fcc site. The magnitude of the adsorption energy of the octahedral site does not change significantly from Fig. 2(a) to 2(b); it is the rise in energy of the fcc site that is responsible for the change. It should be kept in mind that the energy barrier in Fig. 2 is obtained by moving one layer of atoms simultaneously into the surface and therefore should be treated as an upper limit for the real barrier energy which is coverage dependent. When one single atom instead of a whole layer of atoms goes into the surface, the local ruthenium relaxation may lower the energy barrier considerably.[20]

Shown in Table II are the adsorption properties of some combinations of two hydrogen atoms per surface unit cell. The equilibrium positions are for the hydrogen atoms on the surface and the values are similar to those in Table I. As mentioned above, the adsorption energy refers to the energy of isolated atoms. Within the several cases we studied, the occupation of both the fcc and hcp sites on the surface is relatively unfavorable in energy compared with moving one layer to subsurface sites. Once the octahedral sites are occupied, the energy of hydrogen occupying either fcc or hcp sites on the surface is almost identical in our calculation. It is also interesting to find that the work-function change becomes negative in these cases in contrast to positive changes for

TABLE II. Calculated equilibrium position h, adsorption energy E_{ad}, and work-function change $\Delta\phi$ for two hydrogen atoms per surface unit cell on Ru(0001) at various adsorption sites.

1st/2nd H	h (Å)	E_{ad} (eV/atom) 1st/2nd H	$\Delta\phi$ (eV)
fcc/octahedral	1.02	−2.9/−2.0	−0.2
hcp/octahedral	1.04	−2.8/−2.1	−0.1
fcc/hcp	1.10	−2.9/−1.7	−1.1

the occupation of surface hollow sites alone.

On the basis of the above calculated results, we propose an adsorption sequence for hydrogen on Ru(0001). Initially the hydrogen molecules go to surface threefold hollow sites and dissociate. The calculated difference between the adsorption energy and the molecular dissociation energy is about 1 eV/atom, which is fairly large compared with the experimental migration barrier of 0.25 eV/atom on the surface.[9] Therefore, the hydrogen atoms are expected to be fairly mobile on the surface and they can avoid occupying nearest-neighbor hollow sites if there are empty sites available. At this stage, the work function increases and experiment shows a direct sticking kinetics. When most of the fcc *or* hcp sites are occupied within a certain surface region (but not both) and there are more hydrogen arriving, the additional atoms are likely to go through the fcc hollow sites into the subsurface octahedral sites as shown in Fig. 2(b). Consequently, the work function starts decreasing and a precursor adsorption process is observed. A slight expansion (0.2%) in the distance between the first two ruthenium layers is also found in the LEED data at this stage.[6]

When the temperature is raised and desorption starts, the atoms on the surface are expected to depart first and make some hollow sites available on the surface. Then the energy relation is better described by the curve in Fig. 2(a) than that in Fig. 2(b) and the subsurface hydrogen will come out to occupy surface hollow sites. As a result, the *subsurface sites get evacuated first in desorption.* This is in agreement with the experimental finding that the binding state which gets occupied later in adsorption is depleted first upon desorption.[6]

The experimental work-function changes are of the range of ± 30 meV.[6] In our calculation, the accuracy for work functions is about 0.1 eV and a full coverage is assumed. Therefore, we are not able to make quantitative comparison between the calculated and observed work-function changes, but the sign and the order of magnitude agree.

The occupation of subsurface octahedral sites may have some effect on the vibrational spectra of the system with the surface threefold symmetry preserved. If the subsurface atoms are fixed and we vary the height of the surface atoms occupying the hollow sites, the total-

energy curve gives a perpendicular frequency of 120 meV which is slightly smaller than the result without the subsurface hydrogen (Table I). However, the motions of surface and subsurface hydrogen atoms are expected to be coupled together and the resulting vibrational spectra are presently being investigated.

Recent angle-resolved photoemission study[8,21] found a hydrogen splitoff band below the bulk ruthenium bands as well as some hydrogen-induced extrinsic surface states near $\bar{\Gamma}$ and $\bar{K}$ below room temperature. In our calculation, it is the occupation of threefold hollow sites[21] that accounts for these features in the observed spectra, as found in H/Pd(111).[22] If the subsurface octahedral site is also occupied, an additional splitoff band is found in the calculation with wave functions of predominantly s character centered at the subsurface hydrogen. Therefore, this additional splitoff band has a much smaller photoemission cross section and may be difficult to see experimentally.[23]

In summary, in this total-energy study of hydrogen adsorption, we found that the surface threefold hollow sites have the lowest energy and that the occupation of subsurface octahedral sites is possible when the non-nearest-neighbor hollow sites are all occupied on the surface. This adsorption sequence explains the unusual work-function and sticking-kinetics changes upon adsorption and does not contradict the photoemission and electron energy-loss data. Further experimental and theoretical studies are needed to examine whether this picture holds for hydrogen adsorption on other close-packed transition-metal surfaces.

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