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A. Michaelides, P. Hu, and A. Alavi

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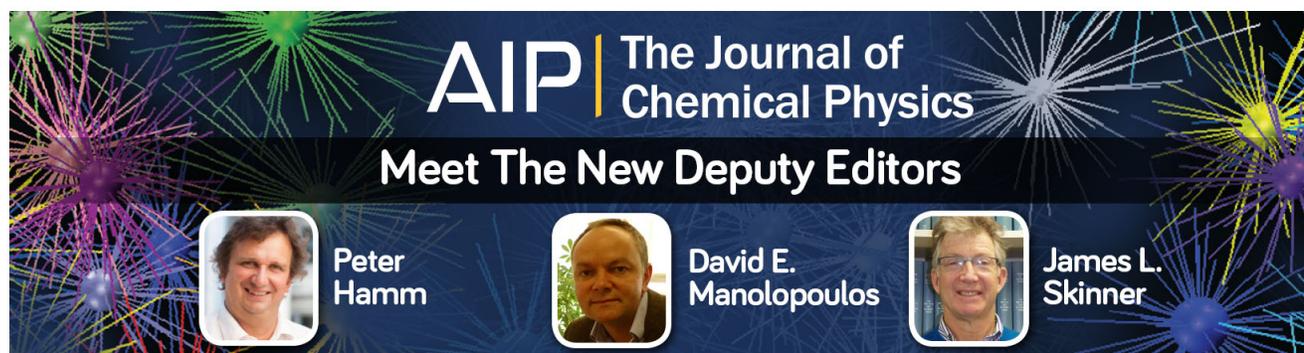
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COMMUNICATIONS

Physical origin of the high reactivity of subsurface hydrogen in catalytic hydrogenationA. Michaelides and P. Hu^{a)}*School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, United Kingdom*

A. Alavi

Atomistic Simulation Group, School of Mathematics and Physics, The Queen's University of Belfast, Belfast BT7 1NN, United Kingdom

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In the catalytic hydrogenation of hydrocarbons, subsurface hydrogen is known experimentally to be much more reactive than surface hydrogen. We use density functional theory to identify low-energy pathways for the hydrogenation of methyl adsorbed on Ni(111) by surface and subsurface hydrogen. The metastability of subsurface hydrogen with respect to chemisorbed hydrogen is mainly responsible for the low activation barrier for subsurface reactions. © 1999 American Institute of Physics. [S0021-9606(99)70528-3]

Hydrogenation is a process of immense scientific and technological importance.¹⁻⁶ In this regard, it has long been speculated that subsurface hydrogen has a reactivity distinct from surface hydrogen.¹ Some years ago, in a series of elegant experiments, Ceyer and co-workers² clearly demonstrated that on Ni(111), subsurface hydrogen could hydrogenate adsorbed methyl to produce methane while surface hydrogen could not. It was suggested that a subsurface hydrogen chemisorbed directly below the methyl group may have a favorable reaction pathway unavailable to surface hydrogen. Since then, it has been found that subsurface hydrogen can hydrogenate other hydrocarbons while surface hydrogen is inactive.³⁻⁵ Theoretical work⁷⁻¹⁰ to date has mainly considered the dissociation of methane on Ni(111), as well as coadsorption of methyl and subsurface hydrogen. But none has addressed the reaction pathways for the recombination reaction involving subsurface hydrogen, and a general explanation as to why subsurface hydrogen is more reactive than surface hydrogen is lacking. In this paper we present the results of a theoretical investigation of this system. We have studied a number of possible reaction pathways and transition states involving both subsurface and surface hydrogens. A rather complex picture emerges. In particular we show that different subsurface hydrogens have very different activation energies to reaction, depending on their initial position relative to the chemisorbed methyl group. By identifying the physical origin of these different activation energies we provide an explanation for the high reactivity of subsurface hydrogen atoms.

We used a finite temperature formulation of DFT,^{11,12} with pseudopotentials and a plane wave basis set. Soft norm-conserving pseudopotentials, generated by a kinetic-energy-filter optimization scheme, were employed and the electronic

orbitals were expanded in a plane wave basis set up to a 550 eV cutoff. Tests for convergence were carried out up to 620 eV. The calculations were done using a Monkhorst-Pack k -point mesh of four points in the surface Brillouin zone, and spot checks for convergence were made using a mesh of nine special k points. Local density approximation (LDA) plus generalized gradient approximation (GGA)^{13,14} calculations were carried out. The procedure we adopted was to perform geometry optimizations using the LDA, and applying the GGA, self-consistently, to the LDA optimized structures to obtain energies. We checked that the properties of the isolated systems were accurately reproduced, including the equilibrium lattice constant of Ni (3.52 Å from LDA, 0.28% error, and 3.55 Å from LSDA 0.68% error), the C-H bond length in both methyl (1.08 Å, 0% error) and methane (1.09, 0% error). The chemisorption energies of methyl on Ni(111) agree well with previous CI calculations^{7,8} (Table I), where direct comparison is available. Our periodic system consisted of four layers of Ni with a $p(2 \times 2)$ unit cell; a monolayer of H placed between the top and second layers, each hydrogen sitting in the octahedral hole below fcc hollow sites of Ni(111); and one methyl group. The bottom two layers of Ni atoms were held in their equilibrium positions, and the remaining atomic coordinates were allowed to relax. The surface magnetism of Ni is strongly reduced by the presence of the monolayer of subsurface H. To verify this, GGS energies were calculated for several LDA optimized structures. The GGS activation energies obtained were similar to the corresponding GGA ones, confirming that the surface magnetism is not important in the presence of subsurface H.

In obtaining reaction pathways for the present system, we first note that there are two possibly distinct types of transition states that can occur. The first involve a *resurfacing barrier*, in which the emerging subsurface H atom is squeezed through a triangle of surface Ni atoms. Such transition states could be located by pushing the emerging H

^{a)}Electronic mail: p.hu@qub.ac.uk

TABLE I. Methyl chemisorption energies (eV) on clean Ni(111), and Ni(111) with a monolayer of subsurface hydrogen.

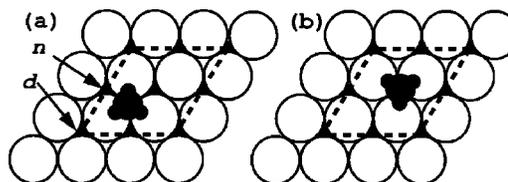
	Clean Ni(111)	Ni(111)+H _B
hcp	1.63 (1.68 ^a)	2.26
fcc	1.65 (1.68 ^a)	2.20 (2.04 ^b)
bridge	1.65 (1.54 ^a)	1.75
top	1.52 (1.47 ^a)	1.97

^aYang and Whitten (Ref. 7).^bYang *et al.* (Ref. 8). Note that in Ref. 8 only a single subsurface H atom, placed in the interstitial directly below the methyl, was considered.

atom through the surface hollow site and allowing for the relaxation of the surface. The second type of transition state is the *recombination* barrier, in which an H atom and methyl come together to react. This TS was located by constraining the C–H distance and minimizing the total energy with respect to all remaining degrees of freedom. In particular, this means that the molecules are free to rotate and translate subject to the above constraint. The transition state (TS) is identical when (i) the forces on the atoms at the TS vanish and (ii) the TS is a maximum along the reaction coordinate but a minimum with respect to all remaining degrees of freedom.

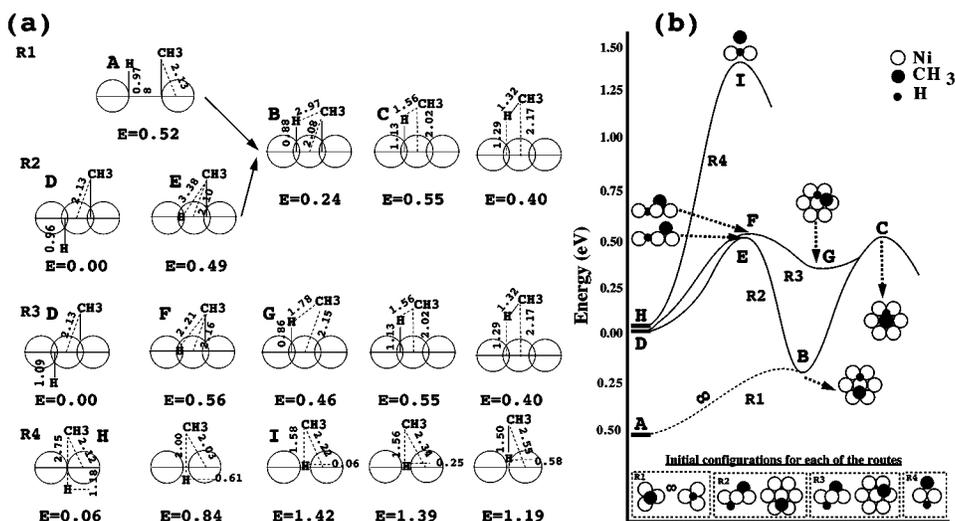
In order to discuss the energetics of the various pathways it is convenient first of all to discuss the chemisorption energies of various stable states with respect to the initial state, consisting of a monolayer of subsurface H and a methyl group on a hcp hollow site. The chemisorption energies of methyl on fcc and hcp hollow sites in the presence of a monolayer of subsurface H (Table I) indicate that, at the present level of calculation, the hcp hollow sites are marginally preferred by 0.06 eV. With the methyl on a hcp hollow, there are two distinct subsurface H atoms that can react with it, labeled *d* and *n* in Fig. 1, respectively.

Several possible reaction pathways have been considered, one involving surface H atoms and three involving subsurface H atoms, all of which react with a chemisorbed methyl. These are schematically shown in Fig. 2. We discuss each in turn. *R1*: This consists of the sequence *B*→*C* (Fig. 2), where H at site *d* reacts with methyl. The initial state (*B*) consists of 0.75 ML subsurface H, a methyl and a surface H, adsorbed at hcp and fcc hollow sites, respectively. This

FIG. 1. Initial $p(2 \times 2)$ geometries for the subsurface reactions. (a) Methyl on hcp hollow; (b) methyl on fcc hollow, over a subsurface H atom. Sites *n* and *d* refer to the neighboring and diametrically opposite sites to the methyl.

choice of initial state is motivated by the desire to have the same number of atoms in the supercell for the surface reaction as the subsurface reactions, enabling a direct comparison between the two. The energy required for step *B*→*C* is 0.79 eV. Taking together the chemisorption energies of the separate hydrogen and separate methyl chemisorbed on Ni with 0.75 ML subsurface H (state A), we find an overall reaction barrier for the process (*A*→*C*) of 1.07 eV. Pertinent points along this reaction pathway are shown in Fig. 2(a) and the energy profile in Fig. 2(b). The structure of the TS, essentially, consists of an activated CH₄ molecule with the C atom on top of a single Ni atom. The pathway for the surface reaction in the absence of any subsurface H has also been calculated.¹⁵ A similar TS to that obtained in the presence of subsurface H was found, with an activation energy of 0.83 eV, in good agreement with the calculations of Yang and Whitten¹⁰ and Kratzer, Hammer, and Norskov,⁹ who found this barrier to be ≈0.85 eV.

R2: In this route the initial state consists of a monolayer of subsurface H with methyl adsorbed at a hcp hollow site. This pathway consists of steps *D*→*E*→*B*→*C*. In the step *D*→*E*→*B*, a subsurface H squeezes through the surface plane of Ni atoms to resurface at site *d*. During this process the Ni surface atoms relax laterally by ~5%. The resurfacing barrier is 0.49 eV. Once the H reaches site *d* the energy drops to 0.24 eV below the initial state. Going from this point to the recombination TS (*B*→*C*) requires 0.79 eV. Some of the geometrical structures calculated along this reaction pathway and the energy profile are also shown in Fig. 2. Significantly, the recombination TS in this route is identical to that of *R1*: i.e., the methyl group moves from the hcp hollow to a top

FIG. 2. Schematic diagrams of some of the points calculated along routes 1–4 (*R1*–*R4*). (a) The circles represent Ni atoms. *R1*–*R3* are viewed along the (112) direction, and the C–Ni distance shown is to the central Ni atom. *R3* is the lowest-energy reaction pathway for the subsurface reaction. All bond distances are in Å. (b) The relative energy profile diagram for the four pathways *R1*–*R4*. The zero of energy is set to the initial energy of the subsurface reaction with the methyl on the hcp hollow site. The labels A–I indicate pertinent points along the reaction pathways.

site. Note that, if instead of the step $B \rightarrow C$ we do $B \rightarrow A$ (i.e., remove the H atom to a hollow site distant from the methyl) the energy drops by 0.28 eV. This shows that in the process $D \rightarrow A$ there is an energy drop of 0.52 eV, and therefore the subsurface H is *metastable* by 0.52 eV with respect to being chemisorbed on the surface at a site distant from the methyl group. Based upon this result we can put the initial state of this route 0.52 eV above the initial state of route 1 (Fig. 2).

R3: The initial state is the same as in *R2*, and the pathway consists of $D \rightarrow F \rightarrow G \rightarrow C$. Here, it is the subsurface hydrogen underneath site n that resurfaces. The barrier for this process ($D \rightarrow F \rightarrow G$) is 0.56 eV. With the H adsorbed at site n the energy of the system is 0.46 eV above the initial. In the process $G \rightarrow C$ the methyl moves to the top site of one of the shared Ni atoms with only a slight displacement of the H, resulting in a recombination TS identical to that in *R2* and *R1*. Going from $G \rightarrow C$ requires only 0.09 eV. We conclude, therefore, that once a H atom is at site n , it requires only 0.09 eV to react. Contrasting this to the pathway involving site d (*R2*) (where 0.78 eV is needed after the H has resurfaced to get to the recombination TS), it is clear that the barrier to reaction is strongly dependent on the site at which H emerges, being low at site n and rather high at site d . In fact, in the pathway involving site n (*R3*), the rate limiting step is the resurfacing barrier (0.56 eV), because the recombination barrier from site n is only 0.09 eV. On the other hand, in the case of site d the recombination barrier (0.79 eV) is higher than the resurfacing barrier (0.49). Overall, therefore, the pathway involving site n will be much favored, and this is the lowest-energy reaction pathway identified. It should be stressed that not every H atom resurfacing at site n will necessarily react. If, for example, such a H atom diffuses away from the methyl group to another site (e.g., site d), the subsequent barrier to reaction will be greatly increased.

R4: The initial state consists of a monolayer of subsurface hydrogen, although this time methyl is adsorbed at a fcc hollow site. As shown in Table I, the energy of this state is 0.06 eV higher than the initial state for *R2* and *R3*. In this route ($H \rightarrow I$), which was originally suggested by Ceyer and co-workers,² the subsurface H attacks the methyl group from directly below. At this TS (I) the H atom is nearly in the plane of the surface Ni atoms (0.08 Å above), and the methyl group is displaced upward by 0.1 Å. The structure of this TS is, therefore, very different from the other recombination TS. Its energy is 1.36 eV higher than the initial state. Therefore, this route is highly unfavorable, even relative to the surface reaction.

It is now evident why subsurface H is more reactive than surface H. Because the transition states accessed by both

surface H and subsurface H are similar, the difference in the activation energies for the reactions must lie in their initial energies. Due to the fact that the subsurface H is metastable with respect to surface H, the initial energy for this reaction is higher and therefore the reaction barrier is lower. Our calculated lowest activation energy (0.56 eV) is in good agreement with an experimentally deduced one (0.52 eV), obtained from the thermal desorption temperature.¹⁶

In conclusion, a complex picture has emerged for this reaction. We have shown that different subsurface H atoms have very different activation energies to reaction, depending on their initial position relative to the methyl group. Certain subsurface hydrogens can react with methyl with a low activation energy because they are metastable with respect to surface hydrogen, by ≈ 0.5 eV. It is essential that they resurface at the correct site, close to the methyl group, otherwise the initial energetic advantage is lost.

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