A systematic DFT study of hydrogen diffusion on transition metal surfaces

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Abstract

Density functional theory calculations of the diffusion of hydrogen atoms on 23 transition metal surfaces in their closed-packed structure have been carried out. The d-metals chosen are all the metals in the 4th, 5th and 6th periods, from Sc to Au, except Mn, Tc, and Hf. Potential energy surfaces of H atom on these metals are constructed and the diffusion barrier from one minima to another is compared with nudged elastic band calculations. Most of the minimum energy paths have a single activation barrier, except on two surfaces where a dip in the bridge position (W and Pt) is observed. Trends in the adsorption and activation energies are observed where the former is explained with the d-band model. All the activation energies for diffusion are relatively low, or from 0.04 eV for Pt to 0.28 eV on Y and Zr. Finally, we estimate the temperature where tunneling effects should start to take place.

Keywords:
Density functional theory calculations
H diffusion
Transition metal surfaces

1. Introduction

Diffusion of hydrogen atoms on metal surfaces is an important process and necessary for many catalytic reactions, such as the (electrochemical) H₂ formation/oxidation [1–9], hydrogenation of nitrogen to form ammonia in the Haber–Bosch process [10,11], or when converting carbon containing species (e.g. CO₂) into useful chemicals (e.g. methanol) [12]. The H diffusion on metal surfaces has been studied extensively, both experimentally [13–17] and theoretically [18–25,16].

Recently, adsorption of hydrogen and its absorption and diffusion into the bulk have been studied systematically on a range of transition metal surfaces with density functional theory (DFT) calculations [26]. In that study, the diffusion into and in the bulk was calculated, whereas in this study, we calculate the diffusion of H on the surfaces. Hence, combining these two studies, one should obtain a comprehensive overview of the energetics and nature of H on and in transition metal surfaces. For the rest of this paper we will only discuss results for H diffusion on transition metal surfaces.

H diffusion on metal surfaces has been a model system for the last few decades where the focus has especially been on studying the quantum nature of the hydrogen nuclei. Since the hydrogen nuclei are light, quantum effects can be observed at elevated temperatures. On the experimental side, the quantum effects of the hydrogen nuclei are observed where the former is explained with the d-band model. All the activation energies for diffusion are relatively low, or from 0.04 eV for Pt to 0.28 eV on Y and Zr. Finally, we estimate the temperature where tunneling effects should start to take place.

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From above it can be seen that H diffusion on metals has been studied extensively. However, since in each case this has only been investigated for one metal at a time, and in total only on a handful of the metals in the periodic table, it is not possible to conclude anything about the trends of H diffusion when the metal substrate is varied. These trends might be e.g. the activation barrier height, the tunneling temperature, or the localization of the hydrogen nuclei.

Recently, correlations in adsorption energy [38] and transition state energy [39] have been invoked. These changes in energetics when moving from one metal to another are all due to the shift of the d-band center of the transition metal, according to the d-band model [40]. Since the initial and final states are different in energy when different species are bound to different metal surfaces, large variations are observed in both the reaction energy and the d-band center when using a metal e.g. far to the left and far to the right of the transition and noble metals. When H is diffusing from one minima to another (e.g. from one FCC hole to another FCC hole), there is, however, no change in the reaction energy when moving from one metal to another, and hence, not much change expected in the activation energy. However, a difference in the detailed morphology of the PES of these metal surfaces can be responsible for both the (de)localization and the tunneling temperature of the hydrogen nuclei.

In this paper, we will present results, all based on the same DFT setup, of H diffusion on 23 metal surfaces in periods 4, 5 and 6 of the periodic table. By this we analyze if there are any systematic trends setup, of H diffusion on 23 metal surfaces in periods 4, 5 and 6 of the periodic table. By this we analyze if there are any systematic trends setup, of H diffusion on 23 metal surfaces in periods 4, 5 and 6 of the periodic table. By this we analyze if there are any systematic trends. We give estimates on the temperature where the H tunneling temperature of the hydrogen nuclei.

The adsorption energy of the hydrogen is calculated with the following equation:

\[ \Delta E = E_{\text{metal}} - E_{\text{H}} - E_{\text{H}^*} / 2 \]

where \( E_{\text{metal}} \) is the energy of the metal without the hydrogen and \( E_{\text{H}^*} \) is the energy of hydrogen in gaseous state.

3. Results

Fig. 2a depicts PES for hydrogen on various metal surfaces relative to \( H_2 \) in gas phase. The bluer the surface is the stronger the hydrogen binds. When taking zero point energy (ZPE) and entropy effects into account, we can calculate the free energy of adsorption. This shifts the adsorption energy of a H atom up by around 0.20–0.25 eV for each metal [45,7]. If the adsorption energy for hydrogen is below

![Fig. 1. a) The crystal structures of HCP(0001) b) FCC(111) c) and BCC(110) metals. The box (solid line) shows the area of the PES shown in Fig. 2, whereas the box (dashed line) shows the area of which the DFT calculations were calculated.](image-url)
−0.2 to −0.25 eV in Fig. 2a, the hydrogen binds to the metal at atmospheric temperature and pressure, but when the adsorption energy is above −0.2 to −0.25 eV the hydrogen adsorption free energy is endothermic. The metals binding H around 0 eV in free energy are good H2 formation catalysts. If the metal binds H too strongly it is difficult to desorb H2 from the surface, and if the metal binds H weakly, it is difficult to get the protons on the surface. In both cases, the catalyst becomes poor H2 evolution catalyst. This leads to the so-called volcano plots for hydrogen evolution [46,7]. From Fig. 2a it can be clearly seen that the Pt-group metals are good H2 evolution catalysts, while the early transition metals bind it too strongly and the noble metals too weakly.

Fig. 2b depicts PES for hydrogen on various metal surfaces scaled from 0 eV for each metal. The bluer the surface is between energy minima (3-fold hollow sites) the lower the energy barriers are and thus the hydrogen travels more easily along the surfaces. For all the metals there is a relatively low barrier to diffuse from one 3-fold hollow site to another through the bridge sites. The on-top sites usually have higher potential energy than the 3-fold hollow sites. This difference is especially great (more than 1 eV) for the first three columns of the periodic table (the Sc, Ti and V columns). For Pt, however, the on-top sites have slightly lower potential energy than the FCC sites, or 0.01 eV. Since the on-top sites have higher ZPE than the 3-fold hollow sites [45], the free energy will become slightly higher for the on-top site and the FCC site becomes the lowest binding site[22,47]. Since the adsorption energy of on-top sites is 0.16 eV lower than the FCC sites on Ir, the small difference in ZPE will not change the adsorption strength, and Ir is the only metal where H prefers the 1-fold on-top site rather than the 3-fold hollow sites.

PES for Pt(111) has been calculated by another research group before and the results compare relatively well [22]. In that study, the PW91 functional was used and the energy of the FCC sites was 0.05 eV lower than the H adsorption energy of the on-top site. Despite this difference, similar anharmonic PES is obtained in both cases.

The activation barrier for H diffusion from an FCC site to an HCP site on Pt(111) is about 0.04 eV with the RPBE functional executed in this study. That is slightly lower than the theoretical values of 0.06 eV [22] and 0.08 eV [16], using the PW91 and the PBE functional, respectively.

When analyzing the PES we noticed that the energy landscape between FCC and HCP holes (hole and hole for BCC metals) is not symmetrical for few metals. Some metals seem to have energy minimum amid the holes, on the bridge sites. We found those unexpected results interesting to look closer into and to understand what caused the difference. We carried out NEB calculations to obtain the minimum energy path (MEP) between the holes. Fig. 3 shows the correspondence between the NEB trajectories and the PES. The energy scales of these PES are not shown, whereas all the PES and NEB profiles for each of the metals are shown in more detail in the Supplementary Information. Most of the metal’s NEB trajectories are similar to the one Cu has, these metals are: Ag, Co, Cr, Fe, Nb, Ni, Pd, Re, Rh, Ru, Sc, Ta, Ti, V, Y and Zr. The other metals, Au, W, Mo, Os, Ir, and Pt have a unique shape of the MEP where Os is categorized with Mo.

Fig. 3 depicts that the trajectories corresponding to the one Cu has, have somewhat symmetrical shape although some have either slightly lower energy in FCC or HCP holes and are thus not fully symmetric.
metals having higher position of the d-states bind H atoms more strongly. The correlation is quite good and as expected from the d-band model the metals). The equation of the line of best fit in Fig. 4 is $y = -0.25x - 0.79$. The correlation is quite good and as expected from the d-band model the metals having higher position of the d-states bind H atoms more strongly.

The values depicted in Fig. 4 for the activation barrier height and the adsorption energy for the FCC holes of the FCC and HCP metals and the holes of the BCC metals are displayed in Table 1. The table also displays the adsorption energy in on-top position and the value of the tunneling temperature which hydrogen atoms are expected to start tunneling through the barrier on each of the metals. The tunneling temperature is calculated with the following equation:

$$T_c = \frac{\hbar}{2\pi k_B} \lambda_1$$

where $\lambda_1$ is the imaginary eigenvalue of the mass-scaled Hessian matrix, which is the mode along the reaction path, $\hbar$ is the reduced Planck’s constant and $k_B$ is the Boltzmann’s constant. The tunneling temperature is between 26 K for Au and 115 K for Ti where no special trend is observed relative to the metal’s position in the d-block.

The inset of Fig. 4 shows the d-band center (in eV) in a periodic table. The d-band center is, however, twenty times greater than the activation energy barriers lie from 0.04 eV for Pt to 0.28 eV for Y and Zr, which means that the diffusion is fast on all the metals. A general trend can be observed, where the barrier height increases when going to the left in the d-block. Since the energy scale of the barrier is quite narrow, we do not make any attempt to correlate that with e.g. the center of the d-band. However, as can be seen from the inset in Fig. 5, the position of the d-band increases in energy when going to the left in the periodic table, same trend as observed for the diffusion barrier height in Fig. 4a. The width of the energy scale of the d-band center is, however, twenty times greater than the activation energy scale of the diffusion barrier, and hence the correlation would be poor. From Fig. 4b we can see the trend for the adsorption energy in FCC holes (hole for BCC metals) for all the metals. Metals tend to have lower adsorption energy (i.e. higher binding energy) as they lie further to the left side in agreement with the d-band model.

Fig. 5 depicts the relationship between the d-band center of the metals and the hydrogen adsorption energy in FCC hole (hole for BCC metals). The equation of the line of best fit is $y = -0.25x - 0.79$. The correlation is quite good and as expected from the d-band model the metals having higher position of the d-states bind H atoms more strongly.

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However, according to Eq. (2) the $T_c$ is directly related to the curvature of the reaction profile at the saddle point or the width of the MEP where narrow paths give higher $T_c$ than if the reaction path is wide. Here we estimate the $T_c = 97$ K for H diffusing on the Ni(111) surface in good agreement with the experimental value of 110 K. It should be noted that this model, Eq. (2), is only an estimate of the tunneling temperature. To validate this further, one would need to perform calculations where the H nuclei is treated quantum mechanically, for instance in an instanton code [28–30]. It is also noted that Eq. (2) and also the instanton theory are only valid for harmonic systems.
However, the NEB profile for Pt and its PES are rather anharmonic and thus it is questionable if such methods would give reliable results.

4. Conclusion

We have calculated the interaction of H adatom with 23 transition metal surfaces in the 4th, 5th, and 6th periods of the periodic table. Adsorption energies at various sites are reported and even the full 2D PESs have been constructed for all the metals. The energy landscape when H is diffusing from one minima to another on the PES is flat (the H diffusion barrier is very low), and the degeneracy of H adsorption sites, is remarkable special. We see some trends for the diffusion activation barriers to get higher when moving to the left in the periodic table. However, since the width of that energy scale is not large (only 0.04–0.28 eV) we do not make any attempt to correlate that with e.g. the d-band center, which has a much larger energy window (−4 to 1 eV). The H adsorption energies do, however, correlate well with the d-band center, as expected. Finally, we estimated the temperature when the H nuclei can be expected to tunnel through the diffusion activation barrier. The temperature is quite low or 26 K (for Au and 115 for Ti). From these estimations we can see that tunneling is of no importance for practical applications, where room temperature or higher temperature is required.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2012.04.028.

References