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Hydrogen diffusion on Fe surface and into subsurface from first principles

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ABSTRACT

The chemisorption of atomic hydrogen on metal surface and into subsurface is of great importance to understand the fundamental diffusion mechanism in heterogenous catalysis and hydrogen-induced embrittlement. Using spin-polarized density functional theory, we show that hydrogen prefers the quasi four-fold hollow site near typical Hollow site on Fe(110) and that four-fold hollow site on Fe(100). A very weak surface reconstruction effect induced by hydrogen coverage is reported. Two three-dimensional (3D) potential energy surfaces (PESs) are constructed for modelling hydrogen diffusion on Fe surface and into subsurface by interpolating *ab initio* energy points (~1200 for each surface). We appraise the accuracy of PES and plot some contours of potential energies at different adsorption heights including the important subsurface regions. Furthermore, possible minimum energy pathways for hydrogen diffusion on Fe surface and into subsurface are searched out based on these 3D PESs using a mesh method. These pathways are in good agreement with those obtained from the nudged elastic band method. Some trapping regions into subsurface for hydrogen chemisorption are shown and the diffusion coefficient is estimated by classical transition state theory.

1. Introduction

Hydrogen chemisorption on iron (Fe) is of particular significance and practical interest, not only as a reactant in Fe-catalyzed Fischer-Tropsch synthesis [1], but also as a common impurity to cause fracture in steel [2]. The fundamental understanding of hydrogen diffusion on Fe surface and into subsurface can provide great motivations on exploring catalytic properties and tuning material properties. In recent years, hydrogen adsorption on common low-index Fe surfaces and some simple grain boundaries (GBs) have been extensively investigated from experimental [3–7] and theoretical methods [8–17]. With low energy electron diffraction (LEED) measurements [3–7], experiments at much low surface temperatures (eg., from 35 K to 140 K) have mainly confirmed some important thermodynamics information about hydrogen adsorption: the adsorption site, the binding energy, the weak surface reconstruction and so on.

Because of its low solubility and high mobility, the effective diffusion paths and diffusion coefficients are difficult to directly measure due to the technical limitations in spatial and time resolution of experimental measurements. Consequently, the adsorption and diffusion properties of hydrogen on iron surface and into subsurface remain open and largely encourage to model it using the fast development of theoretical approximations. Some earlier theoretical works about hydrogen adsorption on iron surfaces [8–12] have the excellent agreement with the experimental results by using density functional theory from first principles [11–13]. Fe(110) and Fe(100) surfaces are two stable low-index surfaces of iron with low surface energy. Jiang et al. [11,12] first performed a spin-polarized density functional theory study of hydrogen adsorption and diffusion energetics on Fe(110) and Fe(100) surfaces. They confirmed the experimental findings and predicted some possible penetration pathways for hydrogen into these two surfaces as well as into bulk Fe. These pathways were searched out using the climbing image nudged elastic band (CI-NEB) [18–20]. At the atomic level, it is very expensive but important to elucidate hydrogen diffusion pathways on Fe surface particularly into the subsurface region using *ab initio* methods [21]. However, such expensive computational cost of *ab initio* approaches usually make them prohibitive if computational models become larger. An alternative approach is attempting to construct a full-dimensional potential energy surface (PES) for modelling the interaction potential energy between the reactant and surface [22–28].

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Recently, some theoretical groups have used the corrugation reducing procedure (CRP) approach to develop some simple cheap PESs for H/Pd(111) [22,29], N/Fe(110) [30] and N/W(110) [31]. They gave some in-depth investigations on the single atom interacting on metal surfaces and explained some important surface catalytic reactions such as the Eley-Rideal mechanism [32].

In this work, we have revisited hydrogen diffusion on Fe(110) and into subsurface as well as Fe(100) by constructing two three-dimensional (3D) PESs using a spline interpolation method. A clear picture of possible diffusion pathways for hydrogen on Fe surface and into subsurface is given in detail. Significantly, some interesting results about hydrogen diffusion into the subsurface region are shown such as some stable trapping sites for hydrogen chemisorption. The article is organized as follows. In Section 2 the brief description of density functional theory used in this work is introduced, in Section 3 we demonstrate some results about the hydrogen adsorption on Fe(110) and Fe(100) surfaces as the increasing in the hydrogen coverage. The accuracy of PES and possible diffusion pathways are then addressed. Furthermore, we compare the diffusion pathways obtained from PES and NEB methods, and roughly estimate the diffusion coefficients using classical transition state theory. Discussions and conclusions are given in Section 4.

2. Computational method

For the interaction of a single atom on a metal surface and into subsurface, all *ab initio* total energy calculations were carried out based on density functional theory (DFT) within the framework of VASP (Vienna *ab initio* simulation packages) code [33,34] which uses a plane wave basis set for the electronic orbitals. The electronic exchange and correlation was described within the generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) functional [35]. The interaction of the valence electrons with the ionic cores was treated within the projector augmented-wave (PAW) method [36]. A supercell of a rigid Fe surface was modeled by a five-layer slab and a (2×2) unit cell with a vacuum space between consecutive slabs corresponding to about six metal atomic layers. A Monkhorst-Pack grid [37] of $5 \times 5 \times 1$**k**-points was used. The cut-off energy was employed as 450 eV. An electronic smearing was introduced within the Methfessel-Paxton scheme [38] with $N = 1$ and $\sigma = 0.1$ eV. Spin-polarized effect was taken into account due to ferromagnetism. The reference potential energy ($E_{DFT} = 0.0$ eV) refers to the configuration of one hydrogen atom placing at 6.0 Å above the equilibrium rigid Fe surface, unless otherwise specified. The current set up is very reasonable for needing plenty of *ab initio* DFT energy points for constructing a multi-dimensional PES [28].

To search out possible minimum energy pathways of hydrogen diffusion on Fe surface and into subsurface, we adopt a mesh method to split the PES into a lot of grids and obtain the minimum potential energy in each dimension. We then perform some NEB calculations to search out the minimum energy pathways by interpolating eight images for hydrogen diffusion from Fe surface into subsurface. In addition, in order to find out the transition state of hydrogen diffusion on iron surface, we divide the DFT optimization into two steps: in the first step, after the normal reaction pathway optimization, the structure of that image with the highest potential energy along minimum energy pathway was used as an input structure for more precise determination of the transition state by minimizing all the residual forces until to the convergence criterion of 0.01 eV/Å within a quasi-Newton method; in the second step, the saddle point will be identified as the required transition states through the frequency analysis (*i.e.* saddle point should be characterized by only one negative eigenvalue of the Hessian matrix). For the zero-point energy (ZPE) correction, this work only considers the frequency of hydrogen on the adsorption site and keeps its environment unrelaxed. The ZPE is obtained by summing up the zero-point vibrational frequency of hydrogen, *i.e.*, $\mathrm{ZPE} = 0.5\Sigma h\nu_i$, where ν_i is a real vibrational frequency.

3. Results and discussions

3.1. Adsorption of hydrogen atoms on Fe(110) and Fe(100) surfaces

To investigate hydrogen adsorption on Fe surface, two important single crystal surfaces, Fe(110) and Fe(100) surfaces, are focused here. By means of DFT calculations, we present some theoretical results about geometries of hydrogen adsorption on Fe(110) and Fe(100) surfaces with the increasing in the hydrogen coverage (*i.e.*, θ_H) in Table 1. The average adsorption energy of hydrogen is defined as

$$E_b = (E_{H_n/\mathrm{Fe}} - E'_{H_n/\mathrm{Fe}})/n, \tag{1}$$

where $E_{H_n/\mathrm{Fe}}$ is the total energy of hydrogen adsorption on Fe surface, $E'_{H_n/\mathrm{Fe}}$ is the total energy of hydrogen placing at a height of 6.0 Å above Fe surface, n is the number of hydrogen atoms. First of all, we investigated the single hydrogen adsorption on a rigid clean surface, *i.e.*, at a hydrogen coverage θ_H of 0.25 monolayer (ML). From DFT calculations, we obtained the corresponding adsorption energies and geometries. As shown in Fig. 1, on Fe(110) and Fe(100) surfaces, there are three typical high symmetry adsorption sites, *i.e.*, Top site, Brg site and Hollow site. In principle, the higher the coordination number of a site has, the more stable it is. We obtained the hydrogen adsorption energy of −2.880 eV on the four-fold Hollow site (0.25(I) in Table 1) of Fe(110) and −2.645 eV on Fe(100), respectively. The height of the adsorbed hydrogen atom above Fe(110) surface is about 0.971 Å and that above Fe(100) surface is much smaller with about 0.393 Å. However, on Fe(110) surface, the lowest adsorption energy site is not exact Hollow site but near this Hollow site. It is the quasi four-fold adsorption site (0.25(II) in Table 1) that has been confirmed by the previous theoretical work [11,12] and LEED experiments [3–7]. Our DFT results show that the lowest adsorption energy for hydrogen on Fe(110) surface is −2.937 eV, very close to the previous theoretical value [39]. It is near that Hollow site with the distance of 0.475 Å. It is the Site 9 that is shown in Fig. 1 (c). The heights of hydrogen on these two adsorption sites are very similar. In order to verify this result, we optimized the hydrogen adsorption configuration on the Site 9 of Fe(110) and calculated the vibrational frequency of hydrogen as well as that on the Hollow site. From DFT calculations, the adsorption hydrogen on Hollow site has the vibrational frequencies of 1148 cm^{-1}, 1052 cm^{-1} and an imaginary frequency of 549 cm^{-1}. However, on the most stablest quasi-four fold site, three real vibrational frequencies of hydrogen are 1046 cm^{-1}, 824 cm^{-1} and 504 cm^{-1}. It is clear to see the Hollow site is a saddle point for hydrogen adsorption on Fe(110) surface. The diffusion barrier between the quasi-four fold site and the Hollow site is only 36 meV (57 meV) with (without) the zero point vibrational energy correction. It is easy to overcome for hydrogen diffusion at a room temperature. Our calculated vibrational frequencies of hydrogen are in good agreement with the prior experiments. One experiment performed by Baro et al. [5] showed that a symmetric stretching vibration of hydrogen on Fe(110) surface at 300 K is 1060 cm^{-1} and an asymmetric stretching vibration is 880 cm^{-1}. In addition, on Fe(100) surface, the Hollow site is the exact most stablest adsorption site. Three real vibrational frequencies of hydrogen are respectively 1143 cm^{-1}, 357 cm^{-1} and 341 cm^{-1}. Hydrogen atom is strongly trapped on the four-fold Hollow site.

When the hydrogen coverage θ_H is increased to 0.5 ML, it is found that the average adsorption energy per hydrogen slightly decreases due to the weak attractive interaction between hydrogen atoms. On