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Unconventional behavior of gas molecules on Fe (1 1 1)

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ABSTRACT

The main contents of atmosphere are studied concerning their adsorption behavior on (1 1 1) surface of γ-Fe and carbon doped γ-Fe. Fe (1 1 1) is found to be highly reactive to all the considered gases except helium. Van der Waals (vdW) interactions, which were usually neglected previously, are found to play a crucial role in the gas adsorption behavior. The carbon impurity significantly affects the chemical bonding between these molecules and Fe (1 1 1) but has a negligible effect on the vdW contribution. These findings offer important clues for tuning the reactivity of Fe (1 1 1).

1. Introduction

Iron is the most important and the most widely used metal as a structural material [1–4]. At room temperature, iron's stable phase is the body centered α-Fe, which constitutes most part of iron in use [5–7]. α-Fe has been extensively studied both experimentally and theoretically, with vast understanding accumulated that has profoundly promoted practices of mechanical processing, anti-corrosion, etc [8–11]. However, the high temperature phase of iron, the face centered γ-Fe (also known as austenite) has been seldom studied, which actually plays an increasingly important role as the non-structural material in catalysis field [12–15]. Traditionally, the use of γ-Fe is limited only in reactions that happen at very high temperature, e.g., ammonia synthesis reaction. However, researchers have now successfully prepared γ-Fe film on Cu and Rh substrates at room temperature by ultrafast thermal deposition, further extending the application of γ-Fe into the field of low-temperature catalysis [16–20]. Egawa et al. studied the co-adsorption and reaction of CO and NO on γ-Fe film in the temperature window from 200 K to 1100 K, and discussed its potential for being integrated into the tail gas treating unit (TGTU) [20]. They observed high density of states located just below the Fermi level of γ-Fe, which underlies the strong combination of γ-Fe with CO and NO, and the high chemical reactivity and catalytic efficiency of γ-Fe.

However, the high chemical reactivity of γ-Fe causes the problem of preservation, or anti-corrosion in atmosphere. Bernasek studied the reaction pathway of CO and H_2O on iron surface, indicating a complex reaction mechanism that depends on adsorption sites, co-adsorbed species, and site-conversion processes [21]. Considering the constitutions of atmosphere, the corrosion mechanism of γ-Fe would probably be even more complex with a series of synergetic reactions involving different gas species such as O_2, H_2O and CO_2. As the initial step of corrosion, the adsorption behavior of gas often determines whether the corrosion would happen and the specific pathway of corrosion [22]. It is therefore of great necessity to study the adsorption behavior of atmospheric gas on Fe (1 1 1) before learning the corrosion behavior of γ-Fe. However, such studies are scarce and scattering.

Another issue of anti-corrosion that we are concerned about is the protected object itself. In fact, what people use in reality is not pure iron, but iron containing different elements, known as steel. The most common impurity is carbon atom, with the concentration up to 2.11% wt in austenite at high temperature. What's more, the carbon impurity tends to segregate at the surface area, further complicating the anti-corrosion study of iron [23]. Thus, the study of gas adsorption on carbon doped γ-Fe is in particular necessity [24,25].

In this paper, we studied the adsorption of O_2, H_2O, CO_2, H_2, O_2, N_2, CO and He on (1 1 1) surface of γ-Fe and carbon doped γ-Fe, using density functional theory (DFT) augmented with van der Waals (vdW) TSsurf (Tkatchenko-Scheffler surface) method [26]. Our results demonstrated that Fe (1 1 1) is highly active to gas molecules even the ones with full shell electronic structures such as CO_2 and N_2. We also found that both the vdW interactions and the carbon impurity are critical for the adsorption of the considered gases. These results provide important clues and insights for further anti-corrosion study and practice of γ-Fe.

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2. Computational method and model

All first principle calculations are performed with the spin unrestricted, Perdew-Burke-Ernzerhof (PBE) functional [27], implemented in the CASTEP code [28]. We build the 4 × 4 × 1 supercell with 5 atom layers to represent γ-Fe (1 1 1) substrate. To determine the appropriate substrate thickness, we tested the adsorption energy of CO_2 on a serials of models with 4, 5 and 6 atom layers, and find that 5 is adequate for obtaining converged results. Among the 5 layers, the top 3 layers are allowed to relax, and the bottom 2 layers are fixed. The vacuum thickness is set to be 20 Å to reduce the spurious interaction between periodic images. To simulate the influence of carbon impurity, we used two models, namely, substrate A and substrate B. For substrate A, it contains only Fe atoms. For substrate B, it contains a carbon impurity atom except Fe atoms to model the conditions closer to the realistic condition than the substrate A. The integration in reciprocal space is performed on 2 × 2 × 1 Monkhorst-Pack k point meshes; the cutoff energy of plane wave basis set is 450 eV; the energy convergence criteria of optimization is 5×10^{-6} eV/atom, and the force convergence criteria of optimization is 0.01 eV/Å. We use the TSsurf method to take into account of the vdW interactions. It is a screened vdW method that includes the many-body collective response of the substrate electrons and goes beyond the pair-wise approximations [26].

We define the adsorption energy of adsorbates to be:

$$E_{ad} = E_{tot}(sub + mol^{*}) - E_{tot}(sub) - E_{tot}(mol^{iso})$$

where $E_{tot}(sub + mol^{*})$ is the total energy of adsorbed system, $E_{tot}(sub)$ is the total energy of substrate A/B with the clean surface, and $E_{tot}(mol^{iso})$ is the total energy of an isolated molecule. E_{ad} can be divided into two parts, E_{chem} and E_{vdW}.

$$E_{ad} = E_{chem} + E_{vdW}$$

E_{chem} results from the superposition of electron cloud, and it is equal to the PBE value numerically. E_{vdW} results from van der Waals contribution.

3. Results and discussion

3.1. The structure of substrates

Fig. 1(a) and (b) show the most stable structures of γ-Fe (1 1 1) and γ-Fe (1 1 1) with carbon impurity. We decide to use one C atom out of 80 Fe atoms (0.267%wt) to simulate the influence of C impurity on the substrate, as the austenite Fe based alloy at room temperature generally contains 0.02–1.0%wt carbon impurity [15]. The binding energy of the impurity carbon atom is −0.58 eV (taking the graphite as reference), which demonstrates the stability of the alloy. In addition, we also build another two impurity contained models with carbon concentration equals to 0.533% wt and 0.171% wt to detect the influence of carbon concentration on Fe substrate. It turns out that a little variation of the extremely low carbon concentration does not cause dramatic change of the chemical activity of Fe based alloy in the test of gas adsorption (details in Fig. S1 of supporting information). Therefore, the model with one C atom out of 80 Fe atoms can be a typical representative for studying the adsorption performance. Notably, we considered different adsorption/interstitial sites for the carbon atom in substrate B. We found that the carbon atom prefers the octahedral interstitial site in the subsurface after relaxation, with energy of over 0.28 eV lower than the surface adsorption sites, and the energy barrier from surface site to subsurface site is as high as 1.01 eV (Fig. S2 of supporting information). This is different from the results on bcc iron where surface adsorption site is more preferred [23], but close to those on other fcc metals like Cu, Pd, and Ni [29]. For an isolated gas molecule, there are 4 different adsorption sites on substrate A, denoted as T (top site), B (bridge site), F (fcc hollow) and H (hcp hollow). The adsorption sites of substrate B is more complex because of the existence of carbon impurity atom, for each adsorption site T, B, F and H, there can be nearest/s nearest/third nearest adsorption site to carbon atom.

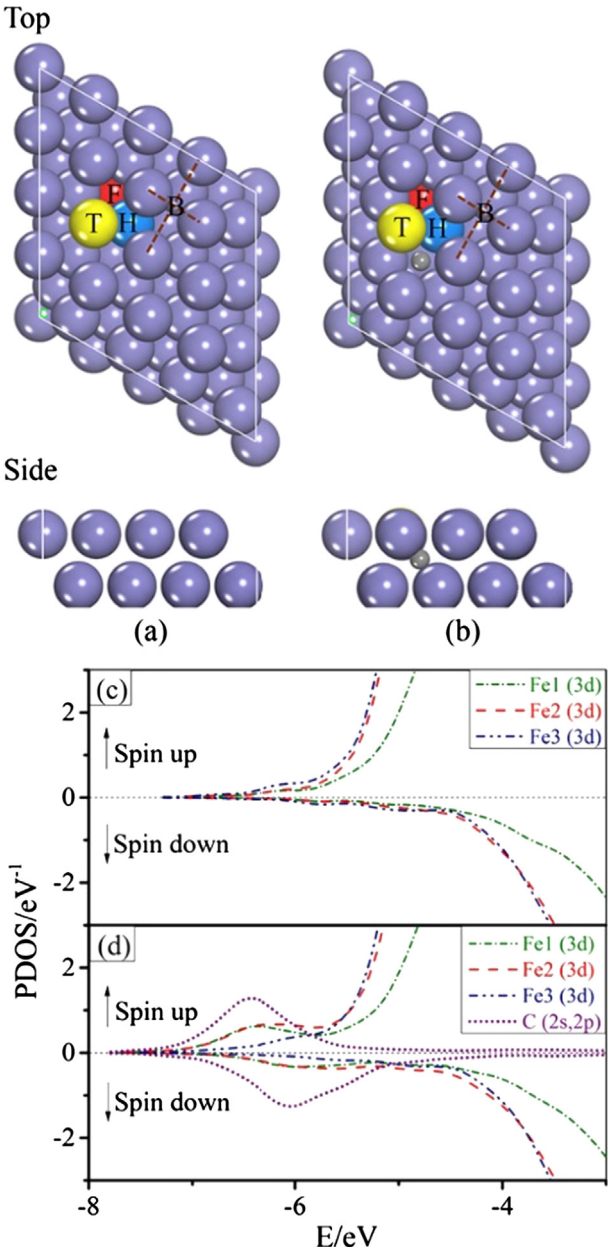

Fig. 1. Schematic top and side views of (a) substrate A and (b) substrate B. The four adsorption sites are T, F, H, B. PDOS of (c) substrate A and (d) substrate B. Fe1 (3d), Fe2 (3d) and Fe3 (3d) represent the d band of top layer, sub-layer and third layer, respectively. The Fermi level is at the 0 eV, however, not shown in the figure because of magnification.

To reveal the influence of carbon impurity on the electronic structure of γ-Fe (1 1 1), we calculated the PDOS of substrate A and substrate B and show them in Fig. 1(c) and (d), respectively. The PDOS of the top three iron layers are displayed separately. In both substrates, the d band level of the top layer is slightly higher than that of the other two layers. The difference between the two substrates is caused by the carbon impurity, which introduces extra carbon energy levels into the substrate B. The carbon orbital has an evident coupling with the d band of the first iron layer and a slight coupling with the d band of the second iron layer, whereas the third and deeper iron layers are barely affected by the carbon interstitial.