

N. NUNOMURA<sup>\*,‡</sup>, S. SUNADA<sup>\*</sup>

## DENSITY FUNCTIONAL THEORY STUDY OF THE INTERACTION OF HYDROXYL GROUPS WITH IRON SURFACE

### BADANIE WZAJEMNEGO ODDZIAŁYWANIA GRUP HYDROKSYLOWYCH NA POWIERZCHNI ŻELAZA ZA POMOCĄ TEORII FUNKCJONAŁU GĘSTOŚCI

The electronic interaction of hydroxyl groups with Fe(100) surface is modelled using a density functional theory (DFT) approach. The adsorption energies and structures of possible adsorption sites are calculated. According to our calculations of the adsorption energies, the interaction between oxygen atom of OH species and surface iron atom is shown to be strong. It is likely to be due to the interaction of the lone-pair electrons of oxygen and the 3d orbital electrons of iron atom. At low coverage (0.25ML), the most favorable adsorption sites are found to be two-fold bridge sites, and the orientation of the O-H bond is tilted to the surface normal. Further, the adsorption energy is found to be decreasing with the increasing OH group coverage.

**Keywords:** density functional theory, hydroxyl groups, iron surface, adsorption energy

Wzajemne oddziaływanie elektronowe grup hydroksylowych na powierzchni Fe(100) modelowano stosując metodę teorii funkcyjonału gęstości (ang. density functional theory; DFT). Dokonano obliczeń energii adsorpcji oraz struktury potencjalnych centrów adsorpcji. Na podstawie otrzymanych wyników stwierdzono, że pomiędzy atomem tlenu grupy OH, a powierzchnią atomu żelaza występuje silne oddziaływanie. Jest to prawdopodobnie spowodowane oddziaływaniem wolnej pary elektronowej tlenu z elektronami atomu żelaza na orbitalach 3d. Przy niskim poziomie pokrycia (0,25 ML), najbardziej uprzywilejowane centra aktywne stanowią podwójne pozycje mostkowe, a orientacja wiązania O-H jest prostopadła do powierzchni. Ponadto energia adsorpcji zmniejsza się wraz ze wzrostem ilości grup OH na powierzchni.

## 1. Introduction

Comprehension of the interaction between water molecules and the metal surface is an important issue from the viewpoint of electrochemistry, corrosion and catalytic science. Iron is a common and useful element, and its characteristics have been studied by many researchers, such as magnetic property, surface oxidation [1] and model catalyst [2]. For theoretical study, Eder *et al.* [3] presented first-principles analysis of initial stages of iron-oxidation caused by water on iron surfaces. In their results, it was shown that water molecule dissociates spontaneously into hydrogen atoms and hydroxyl groups at low coverages. Experimentally, Hung *et al.* [4] studied the adsorption and decomposition of water on the Fe(100) surface using low-energy electron diffraction (LEED), temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). They reported that the dissociation of water is complete at 250 K, forming an ordered  $p(1\times 2)$ -OH overlayer with O-H bond tilted from the surface normal. However, the iron corrosion mechanism has not been completely understood from an atomic scale. Participation of oxygen and water molecules is imperative for

corrosion process. In a previous study [5], we discussed the adsorption of water molecules with pre-covered oxygen atom on the iron surface. We found that repulsive interactions give rise to a reduction in the adsorption energy of water molecules with increasing oxygen coverage. Moreover, the hydroxylation process on the Fe(100) surface was clarified by our molecular dynamics simulations.

In the present study, after the dissociation of water, we focus on the interaction of OH groups with the Fe surface using density functional theory (DFT) calculations.

## 2. Computational methods

We performed DFT calculations within the generalized gradient approximation (GGA) of the PBE [6] form for electron exchange and correlation, using Spanish Initiative for Electronic Simulation of Thousands of Atoms (SIESTA) [7]. SIESTA is a DFT code for large systems based on atomic orbital basis set. The effects of core electrons and nuclei were described using pseudopotentials of the Troullier-Martins type [8]. The energy cutoff for the grid computation of numeri-

<sup>\*</sup> INFORMATION TECHNOLOGY CENTER, UNIVERSITY OF TOYAMA, 3190 GOFUKU, TOYAMA, JAPAN

<sup>\*</sup> GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR RESEARCH, UNIVERSITY OF TOYAMA, 3190 GOFUKU, TOYAMA, JAPAN

<sup>‡</sup> Corresponding author: nori2@itc.u-toyama.ac.jp

cal integrals was set to 350 Ry. Double-zeta with polarization functions (DZP) basis set was used as electronic wave functions. The localization radii of the basis function were determined from an energy shift of 100 meV. We used a Monkhorst-Pack [9]  $7 \times 7 \times 1$  mesh with Fermi-Dirac smearing occupations (smearing temperature of 300 K) to sample the Brillouin zone. The clean Fe(100) surface was modeled in a  $[2 \times 2]$  supercell geometry, employing an asymmetric slab consisting of eleven Fe layers. For the lattice parameter we used the calculated equilibrium value of  $a = 2.882 \text{ \AA}$  for bulk bcc Fe. A vacuum region of  $20 \text{ \AA}$  ensures the decoupling of consecutive slabs. Hydroxyl molecules were adsorbed on one side of the slab. Dipole corrections along the perpendicular axis of the slab have been applied to remove dipole effects due to non-symmetry of the slab. During structure optimizations all atoms were allowed to relax until the forces on unconstrained atoms converged to less than  $0.01 \text{ eV/\AA}$ .

### 3. Results and discussion

The adsorption energy ( $E_{ads}$ ) per OH group was calculated as

$$E_{ads} = \{E(\text{OH/slab}) - [N \cdot E_{slab} + E(\text{OH})]\} / N, \quad (1)$$

where  $E(\text{OH/slab})$  is the total energy of the OH group covered surface,  $E_{slab}$  is the energy of the clean Fe surface,  $E(\text{OH})$  is the energy of an OH group and  $N$  is the number of OH in the simulation cell.

The different adsorption sites examined for OH group adsorption on the Fe(100) surface are shown in Figure 1. Coverages of 0.25, 0.5 and 1ML using  $[2 \times 2]$  supercell were studied.

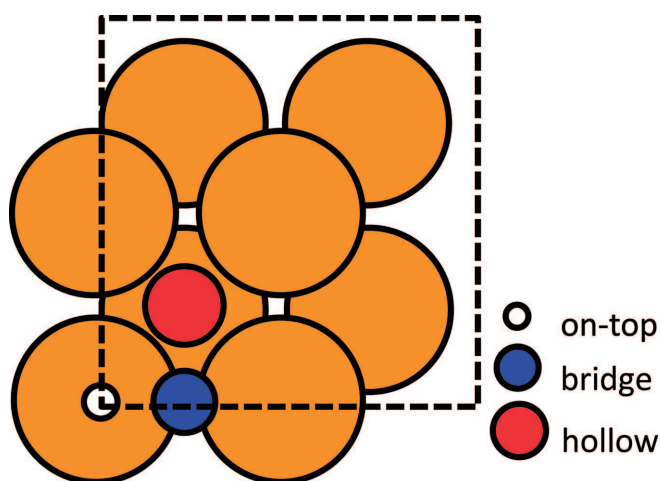


Fig. 1. Top view of adsorption sites of OH groups on the  $[2 \times 2]$  supercell Fe(100) surface. The large orange circles indicate iron atoms. The white, blue and red circles show the on-top, two-fold bridge and four-fold hollow sites, respectively

Calculated adsorption energies and geometries for the different adsorption sites as a function of coverage are listed in Table 1.

For low coverage (0.25ML), the most stable adsorption sites are found to be two-fold bridges, and at full coverage (1ML) the most stable sites are fourfold hollows. In all the

adsorption sites, the adsorption energy of OH is larger than the results of hydrogen and oxygen atom adsorption [3]. As we can see, the adsorption energy  $E_{ads}$  decreases as OH coverage increases. This can be interpreted as existence of a repulsive effective interaction between OH groups. We found that Fe-O bond lengths are reduced with increasing coverage and O-H bond lengths are not dependent on the coverage. The most stable geometric structure at 0.25ML coverage is shown in Figure 2.

TABLE 1

Adsorption energies ( $E_{ads}$ ) for the Fe(100) surface adsorption sites as a function of OH coverage. The normal distance  $Z_O$  of oxygen atom to the averaged Fe surface and O-H bond-length  $d(\text{O-H})$  are additionally shown

Coverage		on-top	bridge	hollow
0.25ML	$E_{ads}(\text{eV})$	-4.32	-4.71	-4.48
	$Z_O(\text{\AA})$	1.96	1.59	1.32
	$d(\text{O-H})(\text{\AA})$	0.97	0.97	0.98
0.5ML	$E_{ads}(\text{eV})$	-4.16	-4.47	-4.44
	$Z_O(\text{\AA})$	1.84	1.42	1.29
	$d(\text{O-H})(\text{\AA})$	0.97	0.97	0.98
1ML	$E_{ads}(\text{eV})$	-3.40	-4.07	-4.11
	$Z_O(\text{\AA})$	1.77	1.36	1.02
	$d(\text{O-H})(\text{\AA})$	0.96	0.97	0.98

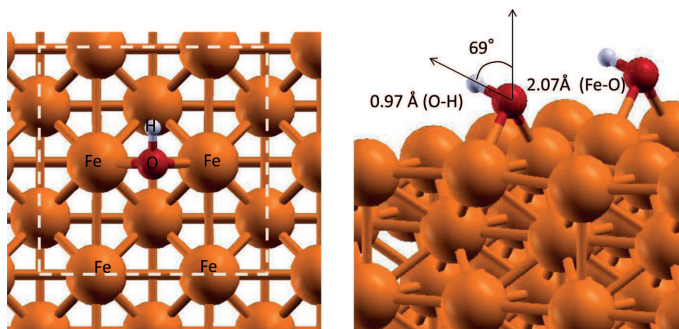


Fig. 2. Top view and side view of the most stable structure at 0.25ML coverage. The large spheres represent the iron atoms, while oxygen atoms and hydrogen atoms are depicted by middle red spheres and small white spheres

The oxygen atom of OH group is bonded to iron atoms on the surface, and the bond angle of OH is tilted 69 degree to the surface normal direction. The most stable configuration turns out to be similar to the one reported by Eder *et al.* [3]. The obtained absorption structures of OH groups are also in agreement with experimental results [4].

In order to investigate electron accumulation and depletion between OH groups and the surface Fe atoms, we have analyzed the electron density difference ( $\Delta\rho$ ) on the surface using the formula

$$\Delta\rho = \rho(\text{OH/slab}) - \rho(\text{OH}) - \rho(\text{slab}), \quad (2)$$

where  $\rho(\text{OH/slab})$ ,  $\rho(\text{OH})$  and  $\rho(\text{slab})$  are the electron densities of the total system, the isolated OH molecule, and the isolated clean Fe(100) slab. Figure 3 illustrates the result of the induced

electron density difference by OH adsorption. This figure was produced using VESTA package [10].

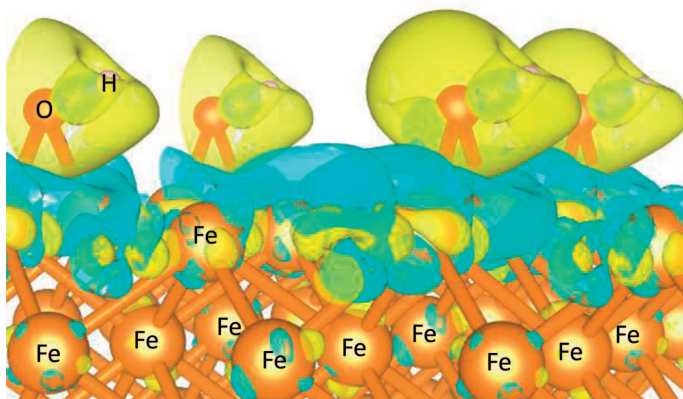


Fig. 3. Isosurface variations in the adsorption-induced electron density change are shown with an isosurface level of  $\pm 0.0028a_0^{-3}$  ( $a_0$ : Bohr radius). A light blue (yellow) indicates negative (positive) value. Regions of electron accumulation (depletion) have positive (negative) values

For iron atom, the topmost layer mainly is contributed. The results shown in Figure 3 indicate that the electron transfer occurs from hydrogen and surface iron atoms to oxygen atom. As we can see, not only the first surface layer but also the second layer is concerned in electron charge transfer. The depletion in the electron density of hydrogen atoms would be affected the bonding of O-H.

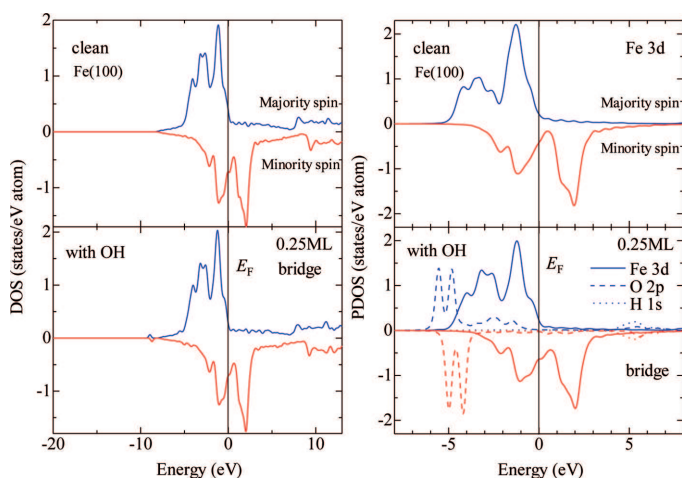


Fig. 4. Total density of states (DOS) and partial density of states (PDOS) for clean and OH adsorbed Fe(100) surface. The energy zero has been set to the Fermi energy ( $E_F$ )

Figure 4 shows total density of states (DOS) and partial density of states (PDOS) of the clean and OH group adsorbed Fe(100) surface obtained from spin-polarized calculations. Although the DOS is almost changeless, the difference of both for PDOS is distinct. The PDOS analysis suggests that the driving forces for the adsorption are the formation of Fe-O coordination bonds with Fe(3d)-O(2p) hybridization.

#### 4. Conclusions

We have addressed the geometric and electronic structures of the adsorption of hydroxyl group on the Fe(100) surface by first-principles calculations based on DFT. In conclusion, our calculations show that the adsorption structure of OH group on the Fe surface is most stable in the bridge sites at low coverage, and the orientation of the O-H bond is tilted to the surface normal. Furthermore, we found that the adsorption energy is reduced with increasing OH coverage. From the results of electron density difference, it turned out that electron transfer happens from a surface atom and hydrogen to an oxygen atom. The electronic structure analysis indicated that the change around the Fermi energy is due to strong binding of hybridization between Fe 3d and O 2p orbitals.

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