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Controlled FCC/on-top binding of H/Pt(111) using surface stress

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ABSTRACT

The preferred binding site of H/Pt(111) has been shown to be change from the on-top to FCC as the Pt(111) surface goes approximately from a state of compressive to tensile strain. A chemical analysis of the system has shown that for both FCC and on-top bound cases the H s—Pt s and H s—Pt d interactions have a similar importance in determining the preferred binding position. It has been seen that FCC-bound H forms a distinct state below the Pt d-band, whereas the on-top bound H does not.

1. Introduction

The controllability of surface reactions is an important research field, particularly in the design of efficient and durable oxygen reduction reaction (ORR) catalysts. Seminal contributions by Stamenkovic et al. who investigated the reactivity of $Pt_3Ni(111)$ [1] and Pt_3M (M = Ni, Co, Fe, Ti, V) [2] have demonstrated the considerable effectiveness of Pt-based materials [3] as ORR catalysts, and have secured their importance within the broader field of nano-catalysis [4].

The nanoparticles used in this field are often metallic alloys which commonly demonstrate segregation [5] where the surface composition of the nanoparticle is different from its bulk. Cases often arise when the surface is no longer an alloy but a pure metal. Segregation effects have been seen specifically on Pt_3Ni samples [6] but also have been seen on a range of other Pt-alloys [7] including Pt_xNi_{1-x} [8], Pt-Ti [9], Sn-Pt [10], Fe-Pt [11], and Pt_3Co [12].

The properties of a purely metallic overlayer formed on an alloy sample can display significantly different properties to those of the parent metal. A well-documented example of this is a shifting of the d-band centre [13]. Changes in the position of d-band can accompany changes in the surface stress – see, for example, Shiihara and Kohyama [14] – which arise because of the lattice mismatch between the purely metallic overlayer and the alloy bulk. However, a delicate balance exists between the degree of lattice mismatch and the structural, electronic and catalytic behaviour of the surface. Recent work [15] has demonstrated that the compressive strain that permeates through pure Pt shells formed on Pt-Ni nanoclusters is negligible when the pure Pt shell is greater than 4 atomic layers. The models are complex, and are divided into compressive/tensile strain effects, which are due to the pressure changes within the crystal, and ligand effects, which are due to hybridisation of orbitals between atoms of different species. A clear understanding of ligand effects does not exist partly because of difficulties experimentally separating the two classes of effects [16] and partly because of the relative complexity of the ligand effects compared to the straightforward shifting of the d-band centre [17]. Further ligand effects arise when an adsorption event occurs and bonding occurs between the adsorbate and the substrate. Early studies [18] of H/Fe(110) have shown that Fe-H bonding involves mainly the Fe 4s and H 1s orbitals, with the surface d-states only playing a minor role.

The current work seeks to investigate the effect of strain and adsorbate substrate ligand effects. It will preclude ligand effects that act between metal atoms in the surface and selvedge regions and those in lower layers. The work is organised in the following way: initially, an overview of the computational details is given. Then, the results are reported and discussed in two sections: the first focussing on the surface binding energies and structures, and the second focussing on the work function of, and bonding at the surface. The current work finally then presents its conclusions.

2. Theory

The density functional theory (DFT) simulations presented in this work were performed using the plane-wave Quantum Espresso package [19]. The electron exchange-correlation was described using the generalised gradient approximation (GGA). Brillouin zone

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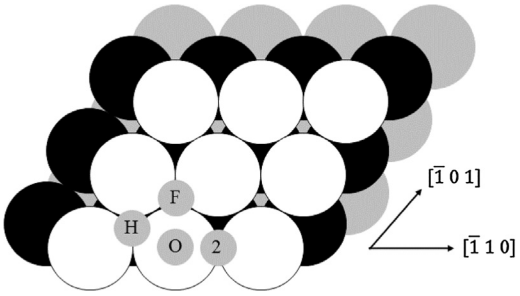

Fig. 1. Structural diagram of the H/Pt(111) adsorption system. The large white, black and grey circles denote Pt atoms in the surface and subsurface layers, respectively, and the small grey circles denote H atoms. The labels 'H', 'F', 'O' and '2' denote binding in the HCP, FCC, on-top and two-fold bridge sites, respectively.

integration was performed on a $(6 \times 6 \times 1)$ grid using a first-order Methfessel-Paxton [20] smearing of 0.02 Ry. The kinetic energy cut-offs for wave-functions and for charge density and potential were set to 75 Ry and 300 Ry, respectively. Using norm-conserving PBE pseudopotentials [21] the equilibrium bulk lattice constant of Pt was determined to be $L_0 = 3.980$ Å. This compares with the experimental value of the lattice constant of 3.92 Å. A preliminary set of spin-polarised simulations were performed and no evidence of magnetisation was found. Consequently all the results contained in this work are from non-spin-polarised calculations.

The surface was modelled using slabs containing 7 layers of Pt atoms with H atoms bound in equivalent positions on either side of the slab. Fig. 1 shows the binding positions of the H atoms within the unit cell. Subsequent slabs were separated by a vacuum whose width was approximately 10 lattice constants. A (3×3) surface supercell was used and each of these supercells contained only a single H atom. This low surface hydrogen coverage (1/9 ML) was used to reduce the effect of lateral interactions. During relaxation, only the central layer of Pt atoms was restrained; all Pt atoms in the 3 layers either side of the central layer of atoms were unrestrained.

The H binding energy was defined as

$$E = \frac{1}{2}\left(E_{H/Pt} - E_{Pt} - 2E_H\right) \tag{1}$$

$E_{H/Pt}$ is the total energy of the (3×3)-H/Pt(111) slab, E_{Pt} is the total energy of a clean, fully relaxed (3×3)-Pt(111) slab and E_H is the total energy of an isolated H atom. The factors of 2 and 1/2 account for the binding of H atoms on either side of the slab.

Changes in the crystal pressure were simulated by expanding and contracting the lattice the lattice constant L used in each DFT simulation. L was calculated using Eq. (2):

$$L = (1 + \sigma)L_0 \tag{2}$$

σ is the lattice distortion and $\sigma \in [-0.05, 0.05]$. The range of σ was defined by considering Vegard's law [22] which relates the lattice constant of an alloy to the stoichiometric average of the lattice constants of its components. For Pt_3Ni the lattice constant predicted by Vegard is 3.814 Å based on experimental lattice constants of 3.912 Å and 3.52 Å for Pt and Ni, respectively. The lattice distortion range used in the current simulations will therefore firmly capture the range relevant to Pt_3Ni as well as leaving the study accessible to the analysis of other surface segregated alloys, or of strained parent metal surfaces.

The zero-point energies (ZPE's) were calculated using phonons calculated using the small displacement method [23]. Quantum Espresso, using the same parameters outlined at the beginning of this section, was used to provide the total energies required for this calculation. Convergence was achieved when a $3 \times 3 \times 1$ supercell was used together with a Brillouin zone sampling of $16 \times 16 \times 16$. ZPE integration was performed across all phonon modes. The zero-point energy difference between systems containing H bound in either the FCC or the on-top positions was defined by

$$\Delta_{ZPE} = \frac{1}{2}\left(E_{ZPE,\,FCC} - E_{ZPE,\,on\text{-}top}\right) \tag{3}$$

$E_{ZPE,\,FCC}$ and $E_{ZPE,\,on\text{-}top}$ are the zero point energies of hydrogenated seven Pt layer (3×3)-H/Pt(111) slabs with H atoms bound in either the FCC or the on-top positions on either side of the slab, respectively. The factor of 1/2 in Eq. (3) accounts for the binding of H atoms on either side of the slab and consequently Δ_{ZPE} is the difference in zero-point energy per H atom.

The work function φ was calculated for both hydrogenated and clean Pt slabs using [24]

$$\varphi = V(\infty) - E_F \tag{4}$$

$V(\infty)$ is the potential at a height of approximately five lattice constants above the surface Pt layer and E_F is the Fermi energy. $\varphi_{H/Pt}$ and φ_{Pt} are defined as the work function of the hydrogenated and clean Pt slabs, respectively. The bond order was calculated by evaluating the integral of the crystal orbital overlap population (COOP) curve up to the Fermi energy [25].

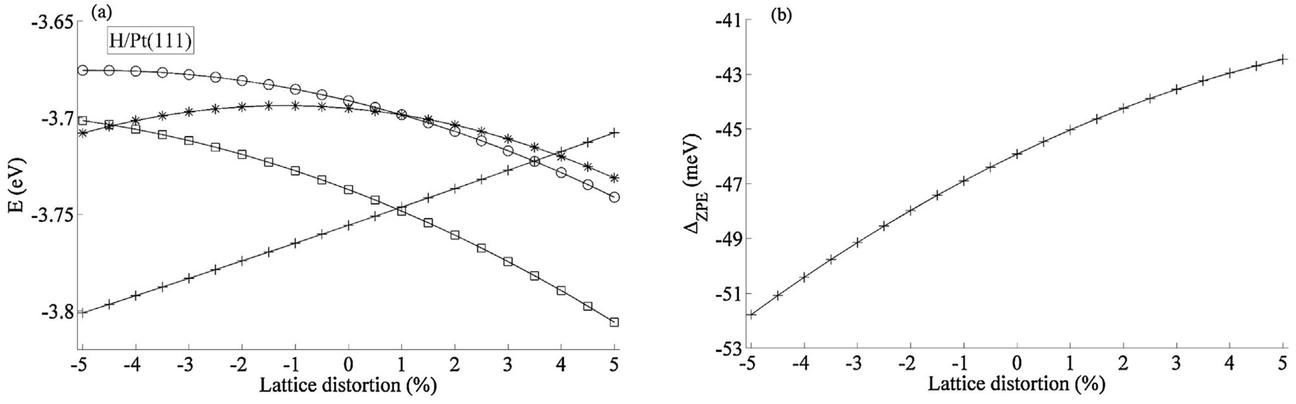

Fig. 2. (a) H binding energy E for the (3×3)-H/Pt(111) system as a function of change in the surface lattice parameter (lattice distortion). H binding in the FCC/HCP/2-fold bridge/on-top binding sites are denoted by squares, circles, asterisks and '+' signs, respectively. (b) Difference in the zero point energy (ZPE) Δ_{ZPE} between unit cells of (3×3)-H/Pt(111) containing H atoms bound in either the FCC or the on-top site. In both (a) and (b) the solid connecting lines are intended as a guide for the eye.