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Strain engineering of H/transition metal systems

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ABSTRACT

The effects of both compressive and tensile surface strain on the hydrogenated low-index faces of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt and Au has been investigated using density functional theory (DFT). Changes in the preferred H binding site have been observed on the Pd, Ir and Pt surfaces when the surface lattice constant is strained by up to 2%, and on Fe, Rh, Ag and Os surfaces for larger strains of up to 5%. A complete discussion of the variance of the hydrogen binding energy, charge, density of states and local geometry with strain is presented. The exchange-correlation, electrostatic and kinetic contributions to the binding energy are delineated and their respective contributions are discussed. The mechanism which determines the preferred binding site for each system under strain is shown to be complex.

1. Introduction

The controllability of surface reactions has been a goal for surface science since its inception. The topic has developed significantly in the recent years as strain engineering has started to demonstrate some elements of the required controllability in an effective way [1–3].

One of the earlier studies of the effects of strain looked at oxygen adsorption on Ru(0001) [4] and showed that oxygen adsorbs preferentially in the on-top position in regions of tensile strain and generated the surface strain by forming sub-surface cavities using sputter-anneal cycles. Ar^+ ion sputtering has been used more recently [5] to distribute stress across Au(100) surfaces and an increase in chemical reactivity was seen at the defected, or locally stressed, sites. Strain has also been seen across the surfaces of metallic nanoparticles – for example, Pd@Pt [6], Pt [7] and Au [8,9] – and both oxide nanoparticles and thin-films [10,11].

Comparative studies have addressed the behaviour of surface energies when the underlying bulk atoms are in a non-equilibrium, or stressed state. This behaviour can be induced by growing thick metallic layers on top of a support layer with a different lattice constant using, for example, repeated atomic layer deposition cycles [12], or by mechanically applying surface-parallel strain to the system [13]. This technology is established in the semiconductor and metal-oxide-semiconductor field [14] but is less well understood for purely metallic surfaces. Recent studies [15] have shown that the application of bulk strain is effective in controlling the binding site preference of H across catalytically active metallic surfaces and similar studies have shown H-binding site shifts in the bulk [16]. The binding energy of hydrogen to TiO2 [17] has recently shown to be sensitive to the strain state of the surface.

The behaviour of surface energy when the bulk atoms are stressed is therefore not directly predicable, and also of considerable importance when looking towards the applications of surface technology. The interest of the current work is to look at the behaviour of hydrogen on strained transition metal surfaces. Hydrogen is a key component in numerous industrial processes as well as remaining at the forefront of proposed energy storage technologies [18]. Applications of hydrogen technology have commonly used nanoparticles as intermediates and the characteristics of these nanoparticles, including shape, size and composition, will affect their performance [19–22]. Controlling these characteristics will consequently alter the way that the nanoparticle will interact with the gaseous medium. Methods of affecting control are necessarily indirect and effected in part by changes to the way that the nanoparticles are grown. Global restructuring phenomena are becoming identified with recent studies [23] classifying a group of binary alloy materials as stable towards strain.

The current work will approach the effect of strain on surface reaction from a fundamental point view. The existing literature of fundamental hydrogen adsorption on unstrained systems is extensive – a recent review [24] contained 443 references. However, the current work will explore hydrogen adsorption on strained substrates by computationally deforming a sequence of low index transition metal surfaces and scrutinise the interactions of these surfaces with hydrogen. The remainder of this work is divided into three main sections: the computational details are outlined in Section 2; Section 3 will discuss the hydrogen binding energy E and its exchange-correlation part E_{XC}, structural investigations, and studies of the surface bonding and the work function change that accompany hydrogenation. The key findings of the work will then be elucidated in Section 4.

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2. Computational details

The plane-wave density functional theory (DFT) simulations presented in this work were performed using the Quantum Espresso package [25]. Brillouin zone sampling was performed on a (6×6×1) grid using a first-order Methfessel-Paxton smearing of 0.02 Ry [26]. The Fe, Co and Ni simulations for spin-polarised whereas all other simulations were not as Fe, Co and Ni are the only magnetic substrates considered in the current work. Norm-conserving pseudopotentials were used for the Cu, Ru, Rh, Pd, Os, Ir or Pt simulations [27] and ultrasoft pseudopotentials were used for the Fe, Co, Ni, Ag and Au simulations [27,28]. Recent studies [29] have shown that these pseudopotentials give extremely high precision equilibrium (zero-strain) lattice constants for each of the elements considered in the current work, with variations between the computational and experimental values of the lattice parameter of < 0.10 Å for all systems. A wave-function kinetic energy cut-off of 50–100 Ry was used for all simulations and a charge density/potential kinetic energy cut-off of 4× that amount was used for the simulations that used norm-conserving pseudopotentials, and 12× that amount for the simulations that used ultra-soft pseudopotentials. The GGA approximation was used exclusively throughout this work.

Fig. 1 shows the surface structures investigated in the current work. For a sequence of FCC systems – Ni, Cu, Rh, Pd, Ag, Ir, Pt and Au – the hydrogenated hexagonal (111) and square (100) surfaces were simulated, as well as the hydrogenated hexagonal HCP Co(0001), Ru(0001) and Os(0001), and the BCC Fe(100) surfaces. All investigations were performed using (2×2) surface unit cells and 7 layer slabs, separated by a vacuum of approximately 12 atomic layer spacings. The amount of lattice strain σ was defined as

$$\frac{L}{L_0} = 1 + \frac{\sigma}{100} \tag{1}$$

L and L_0 are the strained and un-strained lattice constants, respectively. Throughout the current work, strain σ was numerically treated as a percentage and $\sigma \in [-5\%, \ldots, +5\%]$. During relaxation only the central layer of metal atoms were constrained. The remaining atoms were allowed to relax freely. Because of the small unit cell size the possibility of in-plane reconstructions was not investigated; however, significant reconstruction effects were not anticipated. This is because within the group of metals investigated, few would be expected to reconstruct under the range of strains used. The notable exception to this is Au though that only undergoes reconstruction for large surface unit cells.

The hydrogen binding energy was defined as

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

$E_{H/metal}$ is the total energy of the (2×2) hydrogenated transition metal slab, E_{metal} is the total energy of a clean, fully relaxed (2×2) transition metal 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. E_H was determined to be −0.92 Ry and was obtained by placing a single H atom in a 10 Å×10 Å×10 Å cubic unit cell and performing a single self-consistent field calculation.

The total energy $E_{KS}[n]$ of a system described by Kohn-Sham density functional theory can be written

$$E_{KS}[n] = T_S[n] + \int n(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{XC}[n] \tag{3}$$

$T_S[n]$ is the kinetic energy of the system, $v_{ext}(\vec{r})$ is the external potential and $n(\vec{r})$ is the electron density. To elucidate the importance of the terms on the right hand side of Eq. (3) the hydrogen binding energy Eq. (2) can be re-written to only consider the exchange-correlation components

$$E_{XC} = \frac{1}{2}(E_{H/metal,XC} - E_{metal,XC} - 2E_{H,XC}) \tag{4}$$

E_{XC}, $E_{H/metal,XC}$, $E_{metal,XC}$ and $E_{H,XC}$ are the exchange-correlation components of E, $E_{H/metal}$, E_{metal} and E_H, respectively. Quantitatively, the relative importance of the exchange-correlation energy $E_{XC}[n]$ can be evaluated using by comparing its contribution to the binding energy against the kinetic $T_S[n]$ and electrostatic contributions. The electrostatic contributions are the external and Coulomb contributions, which are the single and double integrals on the right hand side of Eq. (3), respectively. The average fractional kinetic and electrostatic component of the binding energy is given by

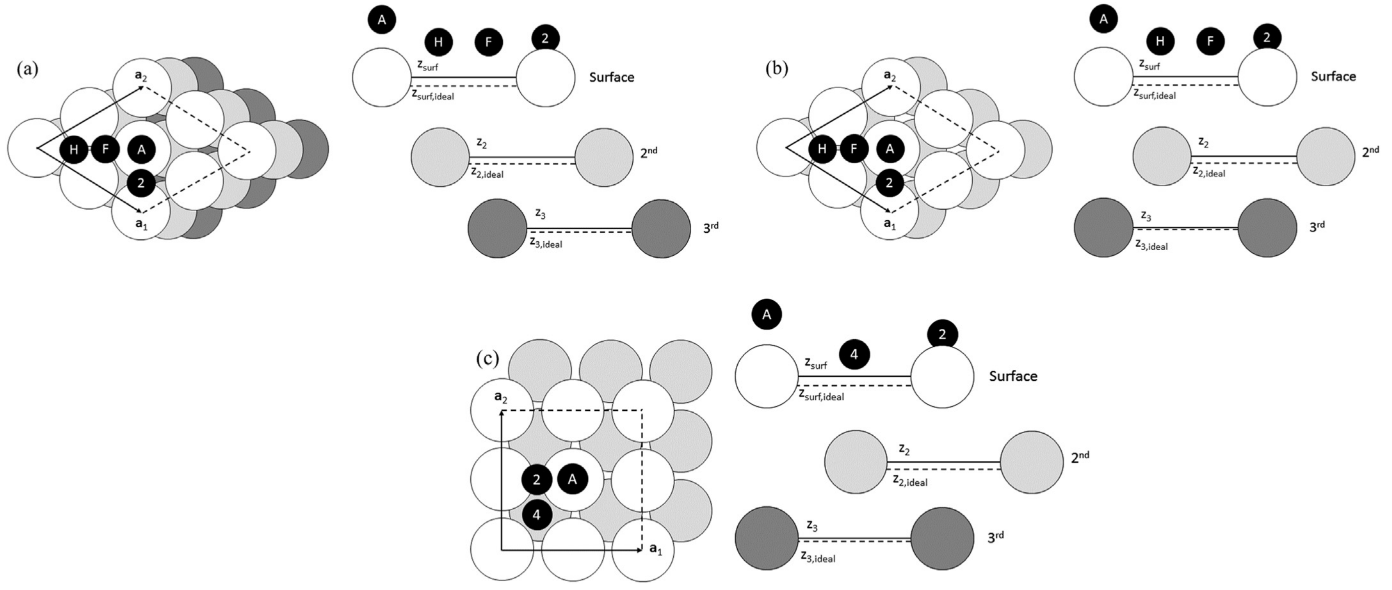

Fig. 1. Structures of the (a) FCC (111), (b) HCP (0001), and the (c) FCC (100) and BCC (100) (2×2)-H/transition metal systems investigated in this work. The surface, second and third layer transition metal atoms are shown by white, light grey and dark grey circles, respectively. The black circles represent H atoms whose labels denote binding in the 'H' HCP, 'F' FCC, 'A' atop, and '2' 2-fold bridge sites for structures (a-b), and the '2' 2-fold bridge, '4' 4-fold hollow and 'A' atop sites for structure (c). z_{surf} and $z_{surf,ideal}$ are the actual and ideal bulk terminated surface layer heights, respectively, and similar notation is used for the height of the atoms in the second and third layers.