Bond length effects during the dissociation of O₂ on Ni(111)

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Abstract

The interaction between O₂ and Ni(111) has been investigated using spin-polarised density functional theory. A series of low activation energy ($E_A = 103$ to 315 meV) reaction pathways corresponding to precursor and non-precursor mediated adsorption have been identified. It has been seen that a predominantly pathway-independent correlation exists between O-Ni bond order and the O₂ bond length. This correlation demonstrates that the O-O interaction predominantly determines the bonding of this system.

Keywords

Oxidation; Nickel; Ni(111); Oxygen; Nudged Elastic Band; NEB; Surface dissociation

Introduction

Surface oxidation is an almost ubiquitous challenge because of the very large number of applied topics within this field – for example, in controllable growth on the Pt-group metals [1] and catalysis [2] - as well as the vigorous and very much ongoing studies of the mechanisms that control these processes. A central theme in these studies has been the early suggestion [3] that adsorbate-substrate interactions are inadequate to explain the observed growth of oxygen structures on Pt. Interactions were inferred to exist between the chemisorbed oxygen and non-dissociated O₂ resulting in local O₂ dissociation channels. More recent studies of the O₂/Pt(111) system [4] have shown explicitly that the adsorption energy is controlled by O-O interactions. Similar lateral effects have been demonstrated on the (100) surface of Pt, Pd, Rh, Ni and Ir [5]. The origins of these interactions vary between systems with studies on Al(111) [6] highlighting the importance of charge transfer whereas contemporary studies on Ni(111) [7] have indicated that the initial oxygen spin state affects the initial oxygen sticking coefficient.

Indeed, the adsorption of oxygen on Ni surfaces, and specifically Ni(111), has attracted a sustained interest. Adsorption of O₂ on Ni(111) has been seen to be independent of the rotational state of the O₂ molecule [8]. However, range of adsorption channels have been observed experimentally dependent on translational O₂ energy [9] and which switched between island growth and Langmuir kinetics. These observations complemented earlier studies which discussed the possibility of a precursor state [10] as a mechanism for regions where $\partial S/\partial E_{Trans} < 0$, i.e. the sticking coefficient of the O₂ molecules decrease as incident translational energy of the molecules increases.

The current work will address these issues by evaluating a series of energetically similar adsorption channels across the surface and then further the study by elucidating the significant features of each adsorption process. The study is divided into 4 sections: after a description of the computational methods an investigation of the interactions between molecular O₂ and Ni is presented. Using benchmarks from this study an effective range of possible reaction channels are then investigated in studies of dissociative adsorption together with an analysis of the mechanisms of dissociation for each case. The highlights of this work are then reviewed and concluded.

Computational Details

The calculations in this work were performed using the Quantum Espresso DFT code [11]. Norm-conserving pseudopotentials [12] generated according to the method of Troullier-Martins [13] and with the PBE exchange-correlation functional [14] were used for both Ni

and the O. The kinetic energy cut-offs for wave-functions and for charge density and potential were set to 75 Ry and 300 Ry, respectively. Brillouin zone integration was performed on a (6×6×1) grid using a first-order Methfessel-Paxton [15] smearing of $\sigma = 0.02$ Ry. The equilibrium bulk lattice constant of Ni was determined to be 3.553 Å which compares to the experimental value of 3.52 Å. The nudged elastic band (NEB) studies were performed with 7 images per reaction pathway and the climbing image scheme was invoked after initial NEB simulations established an approximate path.

The Ni surface was modelled using (3×3) surface unit cells and either 3 or 4 layer slabs separated by a 10 layer spacing vacuum. The large vacuum region was necessary to ensure that the initial and early stage images during the NEB studies were not affected by subsequent slabs. Preliminary studies of atomic oxygen adsorption showed that the lowest energy binding position for low coverages ($\theta=1/9$ ML) of oxygen to be the 3-fold hollow, with a slight preference for the fcc site in agreement with recent studies [16]. During these simulations the outermost two Ni layers were relaxed. Consequently the final images of all the NEB pathways involved oxygen atoms bound in 3-fold positions. The final O-Ni distances were 1.835-1.91 Å for higher oxygen coverages (two oxygen atoms/unit cell, $\theta=2/9$ ML). The variance in this result was due to the relative locations of the two oxygen atoms, which are shown as the final dissociated O atoms in fig. 3. A combination of non-spin polarised and collinear LSDA simulations were performed in order to ease the computational burden, particularly during the NEB studies. A low mixing parameter $\beta = 0.02$ was used during the spin-polarised studies following recent studies of Pd [17] to ensure that the system did not artificially lock-up in an incorrect magnetic state.

Bond orders were calculated by integrating the overlap population as a function of energy. In order to clearly extract the impact on bond order of the lower energy oxygen p states the limits of the bond order integral were altered. For the F_{HS} reaction path the limits were either $E-E_F = [-30, -3.25]$ eV (BO_{partial}) or $E-E_F = [-30, 0]$ eV (BO_{full}). It is for this reason that a vertical dotted line is shown at $E-E_F = -3.25$ eV in fig. 5. The same limits for BO_{full} were used for all other reaction paths but the upper limit for BO_{partial} was varied slightly between reaction paths to compensate for variations in the work function of the final surface.

The magnetisation μ was calculated using the formula

$$\mu = \int_{-\infty}^{E_F} [n_+(E) - n_-(E)] dE \quad (1)$$

where $n_+(E)$ and $n_-(E)$ were the energy-resolved oxygen p and Ni d states in the spin up and down orientations, respectively. The total magnetization μ_T was evaluated over all states. In the current work, the total magnetization μ_T was calculated over the all atoms per 3×3 slab

including both the surface and the bulk Ni atoms whereas the magnetization μ was only evaluated for the oxygen atoms and the Ni atoms in the surface layer.

Results and Discussion

I. Molecular O₂-Ni Interactions

Fig. 1 shows the high-symmetry orientations used to investigate the non-dissociative interaction between molecular O₂ and Ni(111). Preliminary studies showed that the equilibrium bond length of gas phase O₂ was 1.215 Å, which compares to the experimental value of 1.21 Å. In order to determine the interaction between non-dissociated O₂ and Ni(111) a series of simulations were performed where the O-O bond length was fixed at this equilibrium length and the height of the O₂ molecule above the Ni(111) surface was varied.

The resulting potential energy curves are shown in fig. 2. Within the resolution of the figure the potential energy curves above either of the 3-fold sites (fcc and hcp) were seen to overlay and consequently only single curves for each of these sites are included. Additionally little dependence was seen on the rotation of the O₂ molecule particularly for the curves which do not contain an attractive component. This agrees with experimental reports [8] which indicated that the rotational state of O₂ has no effect during its dissociation on Ni(111).

It can be clearly seen in fig. 2 that molecular adsorption can occur in more than one way. The O₂ molecule can become trapped in physisorbed state: this is the case for the 3F_{||} and 2S curves where a potential well of depth 16 and 22 meV, respectively, exists. The remaining curves show no evidence for this type of well. This is consistent with recent experimental reports [9] which indicated that the mechanism of O₂ dissociation is strongly dependant on the incident energy of the O₂ molecule. Low incident energies (< 2.3 eV) are seen to result in islanding whereas higher incident energies adsorption produces direct adsorption. The change in reaction mechanism could now be interpreted in terms adsorption along different reaction channels, as fig. 2 suggests two potential mechanisms for O₂ dissociation dependant on the orientation of the incident molecule.

II. Dissociative O₂→2O Adsorption Channels

To investigate the mechanisms of O₂ dissociation a series of climbing-image nudged elastic band (CI-NEB) simulations were performed. In these simulations initial O₂ images were set with the O-O axis either parallel or perpendicular to the Ni(111) surface. The investigated group of surface parallel images are summarised in fig. 3. An additional simulation was performed with the O-O axis oriented along the short 2-fold bridge direction as opposed to orientation along the long 2-fold bridge direction (2L-F/H) shown in fig. 3. However, the reaction channel contained a barrier of 0.6 eV and was consequently precluded from further analysis. Surface perpendicular images were also investigated above each of the high-

symmetry Ni(111) adsorption sites; however, barriers in excess of 0.6 eV occupied each of these reaction channels and consequently they too were subsequently precluded.

The heights of the initial images were determined using the potential energy curves in fig. 2. For reactions involving 2-fold (2L-F/H) and 3-fold symmetry (F_{HS} and F_{LS}) the height of the initial O_2 image above the Ni(111) surface was 2.24 Å and 1.73 Å, respectively. These heights were selected to coincide with the potential energy minima shown in fig. 2. For all other reaction channels the initial O_2 images were set at 3 Å above the Ni(111) surface.

Fig. 4 shows the resulting reaction pathways. The energetic parameters for these pathways are summarised in table 1 and show that particularly low energy paths exist along the F_{HS} and O-F/H pathways. This latter pathway is similar to those on Pt(111) [18] which observed that pathways starting from a top site have the smallest activation energy E_A . However, comparison of the lowest energy routes with the precursor state of the molecule has shown that no clear correlation exists between E_A and the presence of an attractive well in the molecular energy curves shown in fig. 2. This is very much consistent with the experimental observation that more than one adsorption channel is accessible.

Further insight into the adsorption process is obtained by considering the density of states of the oxygen atoms and of the surface Ni atoms that are closest to the oxygen atoms during the NEB simulations. These curves are shown in fig. 5 for the O-F/H channel. It can be seen that the significant interaction develops between the Ni d and the O p states as the reaction progresses. The importance of the Ni d-O p interaction is in agreement with other studies of O/Ni interfaces [19]. In the initial state, fig. 5 (a), a group of oxygen p states lie below the Ni 3d band at energies of -6 to -9 eV. These are accompanied by higher energy p states which lie within the Ni 3d band, either below or above the Fermi energy. At the transition state, fig. 5 (b), the low energy O p states have increased in energy and now overlap with the Ni d states. By comparison with the O p states in the final state, fig. 5 (c), the hybridisation of these O p states with the Ni d states is incomplete during the transition compared to the hybridisation at the final state.

This observation can be accurately shown by evaluating the O/Ni bond order. This is shown in fig. 6. Two formulations of the bond order are presented in order to separate the contribution from the low lying O p states which are in the region -6 to -9 eV in the initial state, and the higher energy O p states. For this reason the partial bond order BO_{partial} was evaluated by only integrating to $E - E_F = -3.25$ eV whereas the full bond order BO_{full} was evaluated by integrating up to the Fermi level.

A strong correlation between O/Ni bond order and the O_2 bond length can be seen in fig. 6. Significantly, this correlation is extremely similar for each considered reaction paths. This is evidenced by the fact that the bond order curves for different reaction paths overlap very

closely. The most significant variance in these curves is due to the high energy spin up O p state which causes the very large differences between figs. 6 (a) and (c). The correlation effect is still very much visible in these curves but has changed form. The correlation effect is also seen to undergo a transition as the O₂ bond lengths approach approximately 2Å.

This transition is also seen in the magnetisation μ of the O₂ molecule and of all the surface Ni atoms and is shown in fig. 7. In comparison to the bond order calculations, the magnetisation μ was evaluated for all the surface Ni atoms as the clean surface of Ni is ferromagnetic. The trend in magnetisation shown in fig. 7 is not the same as the trends in total magnetisation μ_T presented in table 1 where μ_T is seen to decrease through the sequence initial state→transition state→final state. This is because μ_T contains d components due to the bulk Ni atoms, and components due to the remaining angular momentum states. These states are not included in an analysis of the bonding where the key interactions are between the Ni d and O p states [19]. An O s moment exists at approximately $E-E_F = -20$ eV which is significantly below the energy required for a covalent interaction between itself and the O p/Ni d states and, as such, is precluded. However, the contribution of this moment, and others, explains the differences between the μ_T presented in table 1 and the magnetisations μ presented in fig. 7.

The transition of these effects as the O₂ bond lengths approach 2Å is compared with the transition state bond lengths of 1.280 – 1.816 Å presented in table 1. The sizable difference between these two length scales can be discussed in two ways. The p and d states considered in this study are directional so perfect equivalence between the bond orders presented in fig. 6 for different reaction paths can only be achieved if the systems are equivalent sterically. The second view is that the bond orders are in fact non-equivalent but that the component that contributes to the transition state is minor and bound by the simulation error of fig. 6. The current work, however, does not attempt to further analyse the nature of the O/Ni bond. The reason for this is because studies of the bonding in the known O/Ni(111) are of current research interest [16]. To extend this base to an in-depth analysis of a series of reaction pathways will be necessarily verbose and potentially inaccurate because of the currently known issues surrounding high precision simulation of O/Ni systems. However the existing observations have shown exceptionally clearly that the O₂ bond length is key explaining O₂ dissociation on Ni(111). It potentially suggests that vibrational activation of the incident O₂ molecule may effectively control the O/Ni reaction. This complements current attempts at reaction control using spin polarisation [7] and earlier studies which used rotational excitation [8].

Conclusions

In the current work the interaction between O₂ and Ni(111) has been investigated in both the physisorption and chemisorption regimes. A pair of high-symmetry precursor states have been identified with the O₂ molecule oriented parallel to the surface above either the 3-fold or the short 2-fold bridge sites. Using the length scales determined in the physisorption study the climbing image nudged elastic band method has been used to identify possible reaction channels between the O₂ and Ni(111). Low activation energy reaction channels have been seen to exist above both 3-fold and on-top position with $E_A = 209\text{-}251$ and 103 meV, respectively.

A strong correlation has however been identified between the O-Ni bonding and the O₂ bond length for reaction channels starting above each of the 3-fold, 2-fold and on-top positions. A definite transition in the nature of the O-O interaction is seen as the O-O bond length exceeds 2 Å and this is accompanied by a transition in the magnetic state of the surface Ni atoms. The consequences of this transition have been discussed.

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Fig. 1. Molecular O_2 -Ni(111) systems. The large clear (black) circles denote Ni atoms in the surface (second) layer. The grey circles denote oxygen arranged such that the molecular axis is either parallel to the surface ($\text{O}_{\parallel}$, 2S, 2L and $3\text{F}_{\parallel}$) or perpendicular (2, 3F, 3H and O).

Fig. 2. Potential energy curves for the non-dissociated O_2 -Ni(111) system. The black (grey) curves correspond to O_2 oriented parallel (perpendicular) to the Ni(111) surface. Using the notation defined in fig. 1, the surface parallel curves correspond to O_2 in the $O_{||}$ (black ‘o’ circles), 2S (black long dashes), 2L (black ‘+’ addition signs) and $3F_{||}$ (black solid line) configurations; the surface perpendicular curves correspond to O_2 in the 2 (grey solid line), 3F and 3H (grey long dashes) and O (grey dots). d_{O_2-Ni} is the surface-perpendicular distance between the outermost layer of Ni(111) and the centre of mass of the O_2 molecule.

Fig. 3. Surface parallel-oriented O_2 -Ni(111) reaction channels. The grey dumb-bells are the initial unreacted O_2 molecules and the grey circles with a black outline are the final dissociated O atoms. The large clear (black) circles denote Ni atoms in the surface (second) layer. Four reaction channels are presented: high (F_{HS}) and low (F_{LS}) symmetry reaction across the fcc 3-fold site, and reactions across the on-top (O-F/H) and long 2-fold (2L-F/H) sites.

Fig. 4. Reaction paths for surface parallel-oriented O_2 -Ni(111). Using the notation defined in fig. 3, the high-symmetry F_{HS} (black solid line) and low-symmetry F_{LS} (black dotted line) 3-fold and the long 2-fold (2L-F/H) (black long dashes) and on-top (O-F/H) (grey solid line) pathways are presented. The illustrations in this figure show the relative positions of the oxygen and nickel atoms (clear and grey circles, respectively). Reaction coordinates of zero and one correspond to un-dissociated gas phase molecular oxygen and adsorbed oxygen, respectively.

Fig. 5. Spin-polarised projected density of states for the oxygen p states (solid) and the nearest neighbour surface Ni d states (dotted) in the (a) initial, (b) transition and (c) final states of the O-F/H reaction channel. The projections are the sum of the p states over both oxygen atoms and of the d states of Ni atoms that lie closest to either of the oxygen atoms during the reaction, respectively. The vertical dashed line is included to clearly define partial bond order ($\text{BO}_{\text{partial}}$). Curves (a-c) of this figure are offset vertically for clarity.

Fig. 6. (a,b) Partial (BO_{partial}) and (c,d) full (BO_{full}) spin polarised bond orders between the O p and Ni d states as a function of O_2 bond length. In (a) and (c) ((b) and (d)) the oxygen p states are spin up (down). The following notation is used for each reaction channel: F_{HS} (circles), F_{LS} (diamonds), 2L-F/H (squares) and O-F/H (+).

(a)

(b)

(c)

(d)

Fig. 7. Magnetisation of the (a) O_2 molecule and (b) the surface Ni layer as a function of O_2 bond length. The following notation is used for each reaction channel: F_{HS} (circles), F_{LS} (diamonds), 2L-F/H (squares) and O-F/H (+).

(a)

(b)

Table 1. Summary of the energetic, structural and magnetic transition state properties. Gas phase O₂ bond length was 1.21 Å. E_A is the activation energy for dissociation along a particular reaction path and μ_T is the total magnetisation per (3×3) unit cell.

		Reaction path			
		F _{HS}	F _{LS}	2L-F/H	O-F/H
E _A (meV)		209	251	315	103
μ _T (μ _B / unit cell)	Initial	-25.41	-23.47	-23.23	-22.98
	Transition	-25.76	-25.69	-25.65	-23.45
	Final	-26.58	-26.58	-25.73	-26.34
O ₂ bond length at transition state (Å)		1.816	1.559	1.589	1.280