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Charge transfer and adhesion in Rh/MgO(001)

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Abstract. *Ab initio* density functional calculations are reported for Rh adlayers on MgO(001) at coverages of 1, 1/2 and 1/8 monolayers. It is shown that charge is transferred from oxide surface to the Rh adatoms. The transfer ranges from 0.06 *e* to 0.27 *e*, depending upon adsorption site and coverage. In comparison, transfers of 0.08 *e* from adatom to surface and 0.32 *e* surface to adatom are found for monolayer coverages of Mg and O, respectively. With the Rh adatoms, significant charge polarization of both Rh and the surface are also seen, but it is never-the-less found that the adhesion energy is linearly related to the charge transfer, with the most stable adsorption site at any particular coverage being the one at which the charge transfer is a maximum.

1. Introduction

There is a great deal of interest in the deposition of transition metal adatoms and adlayers on both metal and metal oxide substrates. One particularly interesting system is Rh deposited on MgO, which is of practical interest in catalysis [1-3], for example. We have recently presented a series of studies of Rh/MgO(001) [4-6] using *ab initio* Density Functional Theory (DFT). We have studied three different adsorption sites, (above surface O, above surface Mg and above the Mg-O-Mg-O square hollow), at three different coverages (1, 1/2 and 1/8 monolayers (ML)). See figure 1 for geometries. We have calculated relaxed structures and the Rh/MgO adhesion energy,

$$E_{adh} = - E^{T}(\mathrm{Rh/MgO}) + \left[E^{T}(\text{clean MgO slab}) + E^{T}(\text{Free Rh layer})\right] \qquad (1)$$

where E^T is a total energy of the supercell. We have shown that the O site is the most stable, at all coverages, followed by the hollow and then the Mg site and we have shown that all cases are magnetic except for 1 ML at the O site. We have studied the evolution of the magnetic moment as a function of the Rh ⇔ MgO surface distance and its relationship to the adhesion, showing that the magnetism of Rh/MgO and the adhesion behaviour are not directly linked. Understanding what *does* affect the adhesion remains very important, however, so in this paper we report the charge transfer between Rh and MgO upon adhesion and relate it to the calculated adhesion energies. In section 2 we outline our method, giving results and discussion in section 3. In section 4 we conclude.

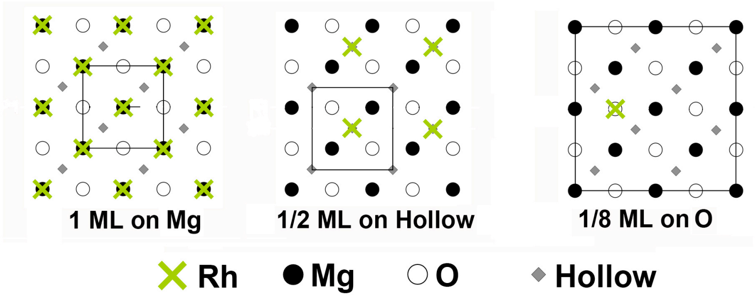


Figure 1. MgO(001) surface, showing the three Rh adsorbtion sites: Mg, Hollow and O sites, at examples of the three coverages used: 1 ML, 1/2 ML and 1/8 ML. The square indicates the surface (x,y) supercells used.

2. Method

We use spin polarized plane wave *ab initio* DFT, with the VASP code [7,8]. Core electrons are treated using the PAW method [9,10] and exchange and correlation using the PW91 form [11] of the Generalized Gradient Approximation (GGA). The plane wave cut-off was set at 500 eV and structures were relaxed until forces were below 0.01 eV/Å. For the 1 and 1/2 ML coverages, we use a 1×1 crystallographic unit cell in the x and y directions, with 8 MgO layers along z. For the lowest coverage (1/8 ML) a 2×2 supercell with 4 MgO layers was used (see figure 1) following checks with 8 layers. In both cases the vacuum gap was set at 15 Å. The unit cell dimensions were kept fixed at the optimized bulk lattice parameter of 4.25 Å. Brillouin zone integrations were done using a 6×6×1 Monkhorst-Pack grid [12] with a Gaussian smearing factor of $\sigma = 0.1$ eV. We have previously showed [5] that these models and parameters lead to total energy errors of up to ~0.1 eV but to errors in total energy differences (such as E_{adh}) of below 0~.01 eV. The charge transfers reported here are "Bader" charges, derived using the "Atoms in Molecules" theory of R Bader [13].

Table 1 Charge transfers from the MgO surface to the Rh adatom.

	O site	Mg site	Hollow site
1 ML	0.19	0.09	0.10
1/2 ML	0.19	0.06	0.17
1/8 ML	0.27	-[a]	-[a]

[a] charge transfers not evaluated for 1/8 ML at Mg and hollow sites.

3. Results

Our calculated Bader charge differences for Rh are shown in table 1. (Details and charge differences for the other ions in the system will be reported elsewhere [6].) We find that there is always charge transfer to the Rh adlayer from the MgO surface. At the most stable site (the O site) the transfer for 1 ML coverage is 0.19 e, rising to 0.27 e at 1/8 ML coverage. That this transfer is *from* the surface *to* the Rh is rather striking, as Rh thus becomes slightly *anionic*. For comparison, if we replace the Rh with a 1 ML adlayer of Mg atoms above the O site (with full relaxation) then we find a charge transfer of 0.08 e from the Mg adatom to the surface. On the other hand, an O adatom receives 0.32 e from the surface, (again, for 1 ML at the O site with full relaxation,) which is of the same sign and order of magnitude as the transfer to the Rh adatoms.

In figure 2 we plot the adhesion energy (E_{adh}) against the charge transfer. It turns out to be linear. It is therefore tempting to conclude that a large proportion of the interaction energy is closely connected to the charge transfer itself, with other sources of interaction contributing only to a smaller extent. Indeed, the energy axis intersect is *negative*, suggesting that the contributions to E_{adh} which are *not* linear in the charge transfer are actually repulsive. It certainly appears from this correlation that there can be no adhesion if there is less than ~0.07 *e* charge transfer.

However, showing linearity is not the same as showing cause; it may simply be that both E_{adh} and the charge transfer are linear in something else which is more fundamental. For example, figure 3 shows a charge density difference (Δρ) map (taken from [4-5]), which shows that considerable charge polarization and reorganization occurs in addition to the transfer itself. This must also contribute significantly to E_{adh}. Indeed, charge transfer is likely to lead to charge polarization and vice versa, and it is hard to differentiate between the two. On the other hand, it *is* true to say that if just the charge transfer is measured, then figure 2 allows us to make a direct estimation of E_{adh}. From figure 2 one can also say that the most stable site for a particular coverage is that site at which the charge transfer is a maximum.

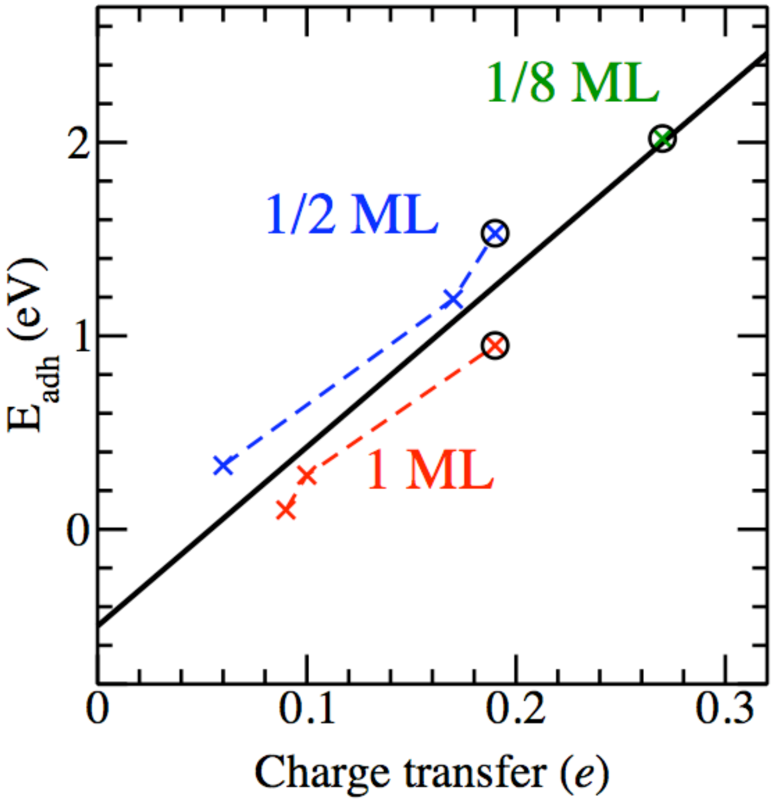


Figure 2. Adhesion energy, E_{adh}, as a function of electron transfer from the MgO surface to the Rh adatom. Circled data points are for the O site. The solid line is a linear fit to the calculated points. The E_{adh} values are taken from [4, 6].

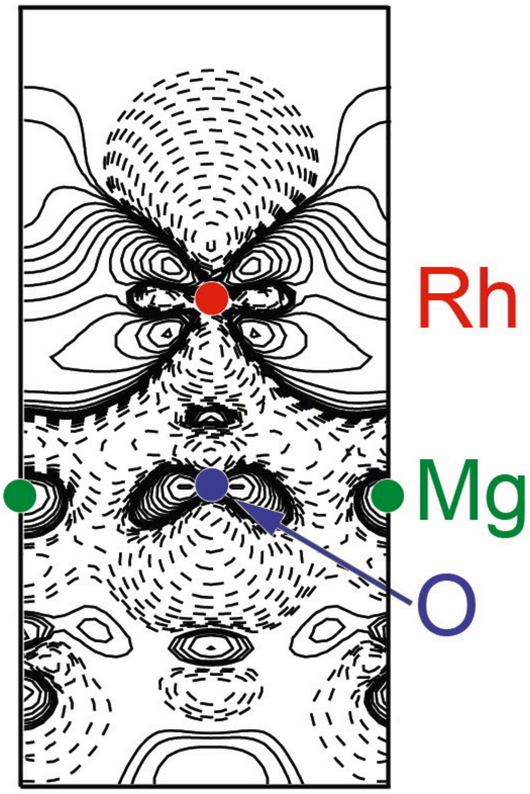
4. Conclusions

We have shown that when Rh adheres to the surface of MgO(001), charge is always transferred to the Rh from the oxide surface, and that this charge transfer is linearly related to the adhesion energy E_{adh}. The amounts of charge actually transferred are fairly small (always below 0.3 *e*) so we certainly cannot talk of ionic bonding of the Rh atom to the surface. Likewise, the Δρ map in figure 3 (and others in [4-5]) indicate that charge is depleted between Rh and the surface, rather than being built up, suggesting that there is no significant covalent contribution to the bonding either. Rh adhesion on MgO(001) is therefore not via the formation of either ionic or covalent bonds. Instead, it seems to be due to a mixture of charge transfer and polarization effects, and possibly other contributions such as correlation effects. However, it does appear that the main contributions to the adhesion are linear in the charge transfer itself.

Figure 3. The charge density difference

$$\Delta\rho = \rho(\mathrm{Rh/MgO}) - \rho(\mathrm{Free\ Rh\ layer}) - \rho(\mathrm{clean\ MgO\ slab})$$

where ρ is the calculated charge density. Shown for 1 ML Rh at the O site on MgO(001). Taken from [5].



References

[1] Wang H Y, Ruckenstein E 1999 *J. Catal.* **186** 181.
[2] Baerns M, Buyevskaya O V, Mleczko L, Wolf D 1997 *Stud. Surf. Sci. Catal.* **107** 421
[3] Solymosi F, Cserenyi J, Ovari L 1997 *J. Catal.* **171** 476
[4] Nokbin S, Limtrakul J, Hermansson 2004 *Surf. Sci.* **566-568** 977
[5] Castleton C W M, Nokbin S, Hermansson K 2007 *Surf. Sci.* **601** 1218
[6] Nokbin S, Castleton C W M, Limtrakul J, Hermansson *In preparation.*
[7] Kresse G, Hafner J 1993 *Phys. Rev. B* **47** 558.
[8] Kresse G, Furthmueller J 1996 *Phys. Rev. B* **54** 11169.
[9] Blöchl P E 1994 *Phys. Rev. B* **50** 17953.
[10] Kresse G, Joubert D 1999 *Phys. Rev. B* **59** 1758.
[11] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J, Fiolhais C 1992 *Phys. Rev. B* **46** 6671.
[12] Monkhorst H J, Pack J D 1976 *Phys. Rev. B* **13** 5188
[13] Bader R F W *Atoms in Molecules: A Quantum Theory* 1990 (New York: Oxford University Press).