Lowering Effective Coordination Promotes Adsorption of NO on Rh(100) and Rh/MgO(100) Surfaces

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We have studied the adsorption of NO, and the coadsorption of N and O, on four physical and hypothetical systems: unstrained and strained Rh(100) surfaces and monolayers of Rh atoms on strained and unstrained MgO(100) surfaces. We find that as we go from Rh(100) to Rh/MgO(100), via the other two hypothetical systems, the effective coordination progressively decreases, the d-band narrows and its center shifts closer to the Fermi level, and the strength of adsorption and co-adsorption increases. Both strain and the presence of the oxide substrate contribute significantly to this. However, charge-transfer is found to play a negligible role, due to a cancelling out between donation and back-donation processes. Our results suggest that lowering effective coordination of Rh catalysts by strain, roughening or the use of inert substrates might improve reaction rates for the reduction of NO to N₂.

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I. INTRODUCTION

Though catalysts are crucial to the operation of many industrial and commercial processes, our understanding of the factors that make a good catalyst is still incomplete. Both the electronic and geometric structures of the catalyst are known to be important, and in recent years, it has become evident that coordination number can have a large effect on catalytic activity. The general understanding is that lower coordination leads to higher activity, though there are exceptions.

Industrial catalysts usually consist of small particles supported on a substrate. The presence of the substrate introduces additional factors, such as charge transfer between the catalyst and the support, a change in the local environment of catalyst atoms, and geometrical strain imposed by the presence of the substrate.

In this paper, we have studied some of these issues by performing calculations to study the adsorption of NO, as well as the co-adsorption of N and O, on a variety of realistic and hypothetical Rh(100) surfaces. These configurations constitute the initial and final states in the dissociation of NO, which is a crucial step in the reduction of nitrogen monoxide to nitrogen, for example in three-way catalysts in automobiles. Rh is perhaps the best catalyst for this process, but it is also by far the most expensive precious metal. It is therefore desirable to gain a better understanding of what makes a good catalyst, so as to guide one in developing new catalysts that use less or no Rh.

Towards this end, and in an attempt to gauge the contributions made by the chemical nature of the substrate, as well as strain, we have studied adsorption and co-adsorption on four kinds of (100) surfaces: (i) the surface of an unstrained Rh crystal; (ii) the surface of a Rh crystal that has been stretched (expanded) so as to be commensurate with an MgO(100) surface; (iii) a monolayer of Rh on MgO(100), with both the Rh and the substrate’s in-plane spacing fixed to be that of Rh(100); and (iv) a monolayer of Rh on MgO(100), with all in-plane spacings fixed to be that of MgO(100). Note that straining systems (i) and (iii) leads to systems (ii) and (iv) respectively, while changing the substrate from Rh to MgO converts systems (i) and (ii) to systems (iii) and (iv) respectively. Qualitatively, it seems apparent that as one proceeds from system (i) to system (iv), the surface Rh atoms become progressively less coordinated; this idea is put on a quantitative footing further below.

Another factor – magnetism – seems likely to play a role in these systems. Bulk Rh is “almost” ferromagnetic. There has been a long-running controversy over whether or not the Rh(100) surface is magnetic. However it seems clear that Rh monolayers and clusters are magnetic. This raises the question of what possible role magnetism may play in the operation of Rh catalysts; this issue is also dealt with in this paper.

Though the adsorption of NO on Rh(100) has been studied by previous authors, we are not aware of any systematic programme of calculations that is similar in spirit to ours.

II. METHOD

Our calculations have been performed using ab initio density functional theory, using the PWscf package of the Quantum-ESPRESSO distribution. The spin-polarized version of the Kohn-Sham equations were solved using ultrasoft pseudopotentials and a plane-wave basis with a cut-off of 30 Ry. Exchange and correlation effects were treated using the Generalized Gradient Approximation (GGA) in the form suggested by Perdew, Burke and Ernzerhof. In order to improve convergence, a Methfessel-Paxton smearing with a width of 0.03 Ry was used.

Most results for the Rh(100) and Rh/MgO(100) slabs
FIG. 1: Schematic diagrams showing the geometries considered for adsorption studies. The grey, white and black circles represent Rh, O and N atoms respectively. The NO occupies different sites, and is oriented differently, in the six cases depicted here. (a), (b) and (c) show top views of configurations where the NO sits horizontally on the Rh substrate, while (d), (e) and (f) show top views of configurations where the NO sits vertically on the substrate; in these, the N atoms are not visible, as they sit directly below the O atoms. The picture (g) shows a side view of configuration (e).

were obtained by using a \((1 \times 1)\) asymmetric supercell containing four Rh layers, of which the outermost two (towards the adsorbate) were allowed to relax, while the inner two were kept fixed at the appropriate bulk separation. However, some tests were also performed with symmetric slabs containing eight layers of Rh atoms. Brillouin zone integrations for such \((1 \times 1)\) surface cells were carried out using a \((12 \times 12 \times 1)\) Monkhorst-Pack mesh.

The adsorption and co-adsorption studies were carried out using slabs with larger unit cells, viz., \((2 \times 2)\) and \((2 \times 3)\), together with corresponding k-point meshes \([6 \times 6 \times 1]\) and \([6 \times 4 \times 1]\) respectively. For systems (i) and (ii), we found that a slab containing four Rh layers was sufficient to give well-converged adsorption energies; however, for one particular adsorption geometry, we found it necessary to use a slab with five Rh layers. All the results presented below for adsorption and co-adsorption on systems (iii) and (iv) were obtained using a slab containing one layer of Rh atoms over four MgO layers.

In adsorption studies, six different geometries were considered; these are shown in Fig. 1, while Fig. 2 shows the three different geometries for the co-adsorption studies. These two figures show (schematically) the geometry prior to relaxation; after relaxation (in the absence of symmetry constraints) the geometries remained roughly similar, though bond lengths changed.

As we will show in the next section, in cases (ii), (iii) and (iv), the Rh(100) surface was found to be magnetic. In such cases, one needs to worry about the possibility that the bottom surface acquires a magnetic moment and is thus no longer representative of a bulk-like layer. To mitigate this, in these cases we deposited a layer of H atoms on the bottom surface, which has the effect of quenching magnetization on that surface.

We obtained a value of 3.85 Å for the lattice constant of bulk Rh, which is in excellent agreement with the experimental value of 3.80 Å and previous theoretical values of 3.87 Å. Our value implies that the distance between nearest-neighbor (NN) Rh-Rh distance within the monolayer would be increased to 3.00 Å, which corresponds to a strain of 9.9%.

For MgO, we obtained a lattice constant of 4.25 Å, which is identical to the value obtained in previous calculations and in good agreement with the experimental value of 4.21 Å. Note that this would imply that if a Rh monolayer were to be deposited commensurately with an MgO(100) substrate, the NN Rh-Rh distance within the monolayer would be increased to 3.00 Å, which corresponds to a strain of 9.9%.

For NO in the gas phase, we obtained a binding energy of 7.13 eV, and an N-O bond length of 1.17 Å. For comparison, the experimental values are 6.5 eV and 1.15 Å respectively.

In all these cases, it can be seen that our results are in good agreement with both experiments and previous calculations, lending support to the validity of our approach.

III. RESULTS

A. Preliminary Tests: bulk Rh, bulk MgO and gas-phase NO

We obtained a value of 3.85 Å for the lattice constant of bulk Rh, which is in excellent agreement with the experimental value of 3.80 Å and previous theoretical values of 3.87 Å. Our value implies that the distance between nearest-neighbor (NN) Rh atoms on the (100) surface is 2.73 Å, while the interlayer distance between bulk-like layers in a Rh(100) slab is 1.93 Å.

For MgO, we obtained a lattice constant of 4.25 Å, which is identical to the value obtained in previous calculations and in good agreement with the experimental value of 4.21 Å. Note that this would imply that if a Rh monolayer were to be deposited commensurately with an MgO(100) substrate, the NN Rh-Rh distance within the monolayer would be increased to 3.00 Å, which corresponds to a strain of 9.9%.

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In all these cases, it can be seen that our results are in good agreement with both experiments and previous calculations, lending support to the validity of our approach.

B. Case (i) - Unstrained Rh(100) surface

For the surface energy of the clean and unstrained Rh(100) surface [case (i)], we obtain a value of 1.12 eV per surface atom, which agrees exactly with the value obtained in a previous calculation and is also in reasonably good agreement with the experimental value of 1.27 eV per surface atom. We find that the first in-
terlayer spacing \(d_{12}\) is contracted by 3.5% with respect to the bulk interlayer spacing of 1.93 Å; this is similar to the contraction of 4.0% found in an earlier study\(^{19}\), but more than the contraction of 1.4% ± 1.4% reported experimentally.\(^{22}\) We find that the next two interlayer spacings, \(d_{23}\), and \(d_{34}\), are both expanded by 0.77%; the next interlayer spacing \(d_{45}\) is very close to the bulk interlayer spacing. We find that the surface is not ferromagnetic, which is in agreement with several previous studies,\(^{6,7}\) though it disagrees with some reports in the literature.\(^{23}\)

Following previous authors,\(^{24}\) we define an effective coordination number for the surface as:

\[
n_c = \sum_j \rho_{Rh}^at(R_{ij})/\rho_{Rh}^at(R_{bulk})
\]

where, \(\rho_{Rh}^at(R)\) is the atomic charge density of an isolated Rh atom as a function of \(R\), the distance from the nucleus, and the sum is taken over all the nearest neighbor atoms \(j\) around a surface Rh atom \(i\). \(R_{ij}\) is the distance between atoms \(i\) and \(j\), and \(R_{bulk}\) is the NN distance for bulk Rh. For case (i), we find \(n_c = 8.49\). This is slightly increased with respect to the nominal surface coordination (the number of nearest neighbor atoms for a surface atom) of 8, due primarily to the contraction of \(d_{12}\) relative to the bulk interlayer spacing.

We define the adsorption energy as \(E_{ads} = E_{NO-Rh(100)} - E_{Rh(100)} - E_{gas}^{NO}\), where \(E\) is the value obtained from \textit{ab initio} calculations for the total energy of the corresponding configuration. In agreement with previous results,\(^{2,19}\) we find that the most favorable adsorption geometry on an unstrained Rh(100) slab is the “vertical bridge” (VB) \([\text{corresponding to Figs. 1(c) and (g); the adsorption geometry is also shown in Fig. 3a}]). With a \((2 \times 2)\) unit cell \(\text{(i.e., a coverage of 1/4 ML)}\), we obtain \(E_{ads} = -2.59\) eV in this geometry; and the N-O bond length is increased slightly from the gas-phase value of 1.17 Å to 1.20 Å. The most next favorable adsorption geometry is the “horizontal hollow” (HH) \([\text{see Fig. 1(a)}]\) with \(E_{ads} = -2.47\) eV, and an N-O bond length of 1.31 Å in the latter geometry. The details of the adsorption geometries for both VB and HH are given in Table 1. All these values are in excellent agreement with a previous study.\(^{19}\)

We have also investigated the geometry and energetics of the co-adsorption of N and O on this surface. We find that both N and O prefer to occupy four-fold hollow sites, as has also been reported in a previous paper.\(^{25}\) In Table 1, we show how the co-adsorption energy, defined as \(E_{coads} = E_{N+O-Rh(100)} - E_{Rh(100)} - E_{gas}^{NO}\), varies with adsorbate coverage and adsorption geometry. We find that the N and O atoms prefer to occupy next-nearest-neighbor hollow sites over nearest-neighbor hollow sites. Also, the magnitude of \(E_{coads}\) increases as the coverage is decreased. These observations suggest that there is a repulsive interaction between the N and O atoms after dissociation of NO. We note that in a previous study,\(^{12}\) a coadsorption energy of -3.50 eV was obtained at a coverage of 1/16 ML, which is in keeping with our conclusions here.

C. Case (ii) - Stretched Rh(100) surface

When an in-plane expansion of 9.9% is imposed on a \((1 \times 1)\) Rh(100) slab, we find that the bulk interlayer spacing \(\approx d_{12}\) is reduced by 11.3% with respect to the unstrained case and becomes equal to 1.71 Å. Upon allowing all interlayer distances to relax in an eight-layer slab, the first three interlayer spacings \(d_{12}, d_{23}\), and \(d_{34}\) are reduced to 1.59, 1.76 and 1.73 Å respectively. These are contracted significantly, with respect to the bulk interlayer distance in unstrained Rh(100), by 17.3, 8.9 and 10.5 % respectively. The net effect of having longer intralayer distances but shorter interlayer distances at the surface is that now the effective coordination \(n_c = 6.65\), i.e., as a result of stretching, the effective coordination has decreased on going from case (i) to case (ii).

In Fig. 4, we show the layer-resolved magnetization per atom of a symmetric \((1 \times 1)\) stretched eight-layer slab \((\text{stars})\). Interestingly, the stretched Rh(100) surface is now magnetic with surface magnetization of 1.0 \(\mu_B\)/atom. In order to reduce computational load, it is a common practice to consider asymmetric slabs where some of the bottom layers are fixed at their bulk positions. The circles in Fig. 4 show the magnetization per atom in a \((1 \times 1)\) four-layer slab with the bottom two layers fixed at 1.71 Å interlayer spacing and the top two
TABLE I: The Rh-Rh bond length \(d_{Rh-Rh}\), the Rh-N bond length \(d_{Rh-N}\), the Rh-O bond length \(d_{Rh-O}\) and the N-O bond length \(d_{N-O}\) of NO on different adsorption sites for the four cases. The number given below each case denotes the Rh-Rh in plane distance for the clean surfaces. \(Rh_N\) and \(Rh_O\) indicate the distances between two Rh atoms bonded to N and O atoms respectively. All distances are given in Å.

| System | Site and geometry | \(d_{Rh-Rh}\) (Å) | \(d_{Rh-N}\) (Å) | \(d_{Rh-O}\) (Å) | \(d_{N-O}\) (Å) |
|--------|------------------|------------------|------------------|------------------|------------------|
| case (i) | VB | 2.74 | 1.96 | - | 1.20 |
| (2.73) | HH | 2.75 (\(Rh_N\)) | 1.98 | 2.21 | 1.31 |
| case (ii) | VB | 2.70 | 1.96 | - | 1.20 |
| (3.00) | HH | 3.13 (\(Rh_N\)) | 1.98 | 2.22 | 1.32 |
| case (iii) | VB | 2.75 | 1.93 | - | 1.20 |
| (2.73) | HH | 2.70 (\(Rh_N\)) | 1.95 | 2.15 | 1.33 |
| case (iv) | VB | 2.56 | 1.94 | - | 1.21 |
| (3.00) | HH | 2.66 (\(Rh_N\)) | 1.95 | 2.18 | 1.34 |
|       |       | 2.59 (\(Rh_O\)) |          |          |          |

TABLE II: Dependence of coadsorption energy \(E_{coads}\) on coverage and adsorption geometry. The first row corresponds to a coadsorption of N and O in a 2×2 unit cell in next-nearest-neighbor hollow sites, while the second and third rows (a) correspond to results for the geometries depicted in Figs. 2(a) and (b) respectively. Here, \(C = \) coverage of N = coverage of O.

| Coverage | \(E_{coads}\) (eV) | \(r_{N-Rh}\) (Å) | \(r_{O-Rh}\) (Å) |
|----------|------------------|------------------|------------------|
| 1/4 ML   | -3.20            | 2.03             | 2.14             |
| 1/6 ML (a) | -3.10          | 1.99, 2.10      | 2.04, 2.35       |
| 1/6 ML (b) | -3.34          | 2.03, 2.04      | 2.14, 2.17       |

Adsorbing H on the bottom surface also turns out to be crucial in correctly predicting the stable adsorption geometry for NO. In the absence of H, it is found that the VB and HH configurations are degenerate, with both having an adsorption energy \(E_{ads} = -2.83 \text{ eV}\); however, when H is adsorbed on the bottom surface, the VB (with \(E_{ads} = -2.86 \text{ eV}\)) is found to be clearly favored over the HH (with \(E_{ads} = -2.71 \text{ eV}\)); for the reasons stated above, we believe that the set of numbers obtained with H atoms on the bottom surface is more to be trusted. This stable adsorption geometry is depicted in Fig. 8(b).

In order to gauge the effects of magnetization on adsorption energies, we also performed non-spin-polarized (NSP) calculations. We found that the magnitude of \(E_{ads}\) increases in the absence of magnetization; however, the difference between the VB and HH geometries is maintained: with NSP calculations, the former gives \(E_{ads} = -2.96 \text{ eV}\), while the latter gives \(E_{ads} = -2.82 \text{ eV}\).

We found that NO adsorption leads to a significant distortion in the position of Rh atoms (see Table I). When NO is adsorbed in the VB configuration, the Rh-Rh distance for the two Rh atoms bonded to N is reduced significantly, from 3.00 Å to 2.70 Å. However, for the HH configuration, the distances between the two Rh atoms bound to N and O increase to 3.13 and 3.21 Å respectively. The internal bond length in NO is increased in all cases; to 1.20 Å for the VB and to 1.32 Å for the HH configuration. Note that this also suggests that it might be easier to break the N-O bond in the HH configuration.

Next, we co-adsorb N and O on this surface. The coadsorption geometries considered by us are shown in Fig. 2. When we start from a configuration where N and O are at NN hollow sites (see Fig. 2(a)), the O atom moves away from N, and sits at the bridge site which is equidistant.
from the N atom and its image. This configuration represents the most favorable co-adsorption geometry, with $E_{\text{coads}} = -3.47$ eV. The second most favourable configuration is one where both N and O sit at NNN hollow sites (Fig. 2(b)): here $E_{\text{coads}} = -3.33$ eV. Unlike in case (i), the stretched Rh(100) surface also has a local minimum when both the atoms sit at bridge sites (see Fig. 2(c)). This is the configuration that the system assumes just after the dissociation of NO, and corresponds to $E_{\text{ads}} = -3.24$ eV. As in case (i), the magnitude of $E_{\text{ads}}$ is increased by $\sim 0.3$ eV in the first two adsorption geometries upon performing an NSP calculation; however, in the third case, $E_{\text{ads}}$ is essentially unchanged. It is also worth noting that changes in interatomic distances are slight when comparing spin-polarized (SP) and NSP calculations.

D. Case (iii) - Monolayer of Rh on MgO(100), at Rh(100) lattice constant

The third case we consider is again an artificial one. We consider first an MgO(100) substrate that has been strained (compressed) in-plane, so that it has the same in-plane lattice constant as in case (i). As a result of this in-plane compression, we find that the first two interlayer spacings are both increased by 8.15% relative to the interlayer spacing in unstrained MgO. There is also a noticeable rumpling of Mg-O layers near the surface. We define the rumpling as $\Delta z = (z_O - z_Mg)/d_0$, where $z_O$ and $z_Mg$ are the z-coordinates (normal to the surface plane) of O and Mg respectively, and $d_0$ is the bulk interlayer spacing. Then, the outermost MgO layer has $\Delta z = 2.0\%$, while the second MgO layer has $\Delta z = -0.1\%$. Note that the rumpling is opposite in the two outermost layers: in the topmost layer, oxygen atoms are displaced further away from the substrate than Mg atoms, whereas for the second layer, the reverse is true.

When a monolayer of Rh is deposited pseudomorphically on this compressed MgO substrate, it binds with a binding energy $E_{\text{bin}}$ of -3.59 eV per Rh atom. Here, the binding energy has been defined by $E_{\text{bin}} = E_{\text{Rh:MgO}} - E_{\text{MgO}} - E_{\text{Rh}}$, where $E_{\text{Rh:MgO}}$ is the total energy of the Rh/MgO slab, $E_{\text{MgO}}$ is the energy of the MgO slab alone, and $E_{\text{Rh}}$ is the energy of an isolated Rh atom in the gas phase. The Rh atoms sit atop the oxygen atoms of the outermost MgO layer, with a Rh-O separation of 2.22 Å. The deposition of the monolayer changes both the rumpling and the relaxation of the outermost MgO layers. The first two layers now display a rumpling of -4.2 % and 0.7% respectively; note that the deposition of Rh has actually reversed the direction of rumpling. There is also a change in interlayer spacings, with the distance between the two outermost MgO layers now expanded by 9.55% relative to the interlayer distance in unstrained MgO, while the expansion of the next interlayer spacing is now reduced slightly, from the value of 8.15% (in the absence of the Rh adlayer) to 8.05%. The Rh monolayer in this case is found to be magnetic, with a magnetic moment of 1.5 $\mu_B$/atom.

In principle, placing metal atoms on an oxide substrate can lead to charge transfer. In Fig. 4(a), we have plotted the redistribution of charge upon placing a layer of Rh atoms on an MgO substrate. In this figure, red and dark blue regions represent areas where the charge has increased and decreased respectively. It is interesting to note that one observes both red and dark blue lobes on both the Rh layer and the topmost Mg-O layer; this is because of the simultaneous presence of donation and back-donation between the adsorbate (Rh) and the substrate (MgO), as is well-known for such systems. Interestingly, these two processes essentially cancel out for this system, the net charge transfer, as calculated by Lowdin population analysis, is only 0.015 electrons per Rh atom between the Rh overlayer and the MgO substrate.

The effective coordination $n_e$ is now lowered to 5.51. Note that $n_e$ is lower for both cases (ii) and (iii) relative to
to case (i); however, the lowering in case (iii) (which is due to the replacement of the Rh substrate by an MgO support), is more significant than in case (ii) (where it is due to stretching the system to the lattice constant of MgO). Similarly, the magnetic moment is larger in case (iii) than in case (ii).

Upon adsorbing NO on this compressed Rh/MgO(100) system, we find that the most favorable adsorption geometry is the HH [depicted in Fig. 3(c)], with $E_{ads} = -3.38$ eV, which is larger in magnitude than the adsorption energy of -3.17 eV for the VB configuration. Note that this is in contrast to the most favored adsorption geometry for both cases (i) and (ii); it is now favorable for both N and O to bind to Rh atoms.

For the VB case, the distance between the two Rh atoms bound to the N (Rh$_N$) increases slightly from 2.73 Å to 2.75 Å. On the contrary, for the HH geometry, the distance between the same pair of Rh atoms decreases to 2.70 Å, while that between the Rh atoms attached to the O atom (Rh$_O$) increases to 2.95 Å; this is because, as a result of strong binding between NO and the Rh atoms, the Rh$_N$ pair is pulled out of the surface.

Moreover, upon adsorbing NO, the magnetization of the Rh atoms is quenched. For the HH NO adsorption geometry, this reduction is as follows: for the two Rh atoms to which N is attached, the reduction is by 74%, for the two Rh atoms to which O is attached, it is by 45%, and for the two Rh atoms which are furthest from NO, the reduction is only by 9%.

Once again, we find significantly enhanced binding upon performing an NSP calculation, with $E_{ads} = -4.07$ eV and -3.82 eV for the HH and VB geometries respectively.

The co-adsorption energies are -4.64 -3.32 eV when the N and O atoms are in the NN hollow (Fig. 2(a)) and bridge (Fig. 2(c)) sites respectively.

E. Case (iv) - Monolayer of Rh on MgO(100), at MgO lattice constant

Upon putting a pseudomorphic layer of Rh atoms on an unstrained MgO(100) substrate, we find that Rh atoms again preferentially occupy the sites atop O atoms. The binding energy for this configuration, defined as in case (iii), is found to be $E_{bin} = -3.27$ eV per Rh atom; this is somewhat less in magnitude than the value of -3.99 eV obtained in a previous study. The Rh-O distance is found to be 2.25 Å, which is larger than the value of 2.10 Å reported earlier. Both the Mg and O atoms in the topmost layer move outwards, away from the substrate, so that the mean interlayer distance between the top two MgO layers is increased by 0.73% relative to the bulk interlayer spacing. However, there is a considerable rumpling (Mg atoms are higher up on the surface than oxygen atoms), with $\Delta z = -4.0\%$, of the topmost MgO layer; this is in good agreement with one earlier reported value of -4.3% but somewhat less than the value of -6.1% obtained in another study. The rumpling is reduced to +1.0% in the MgO layer below this one. Note that for both layers the rumpling is reversed with respect to that observed for a bare MgO(100) surface.

For a Rh atom in case (iv), we obtain $n_e = 3.59$. Note that this is significantly lowered with respect to the value of 8.49 obtained in case (i), due to a combination of two factors: the replacement of substrate Rh atoms by Mg and O atoms, and the stretching to the MgO lattice constant.

Once again, we find that the surface Rh atoms are magnetic, with a moment of 1.5 $\mu_B$/atom.

In Fig. 3(b), we present a plot of charge transfer for the Rh/MgO system. From this figure, it is evident that, as in case (iii), there is both donation and back-donation between the overlayer Rh atoms and the O atoms in the MgO substrate. Once again, these two processes effectively cancel out, and there is a net charge transfer of only 0.018 electron per Rh atom from the oxygen to the Rh atom.

Next, we study the adsorption of NO on this Rh/MgO(100) system. As in case (iii) above, we find that it is now most favorable for the NO atom to lie horizontally on the surface: $E_{ads} = -4.08$ eV and -3.87 eV for the HH and VB geometries respectively. In Fig. 3(d) we have depicted the lowest-energy adsorption geometry, corresponding to the HH configuration.

With the adsorption of NO on 1 ML of Rh on MgO, the Rh atoms to which the NO is attached come closer together for both the HH and VB geometries (see Table 1). We speculate that this may be because Rh-Rh bonds are under considerable tensile stress when deposited pseudomorphically on MgO; the adsorption of NO breaks the symmetry and allows the Rh atoms bonded to NO to come closer together.

As in case (iii), upon adsorbing NO, the magnetization of the Rh atoms is quenched. Out of the six Rh atoms present in the unit cell, the spin polarization of each of the two Rh atoms to which N is attached is negligible, while those to which O is attached is reduced by about 81% and the spin polarization of the two Rh atoms which are furthest from NO is reduced by about 28%. Similar effects have also been observed previously, by us for NO adsorbed on small Rh clusters and by Hass et al. in their studies of NO adsorption on a hypothetical monolayer of Rh atoms. Apart from the fact that the latter group of authors worked with a monolayer of Rh (i.e., there was no substrate), there are other differences between our calculations and theirs: they did the calculations for NO adsorbing in the VB geometry alone, fixed the Rh-Rh distance at the value for bulk Rh, and did not relax the coordinates of NO. While they found that the magnetic moments on all the atoms of the monolayer are negligible, we find that the magnetism of those Rh atoms which are attached to the NO molecule is very strongly suppressed, while in the other Rh atoms there is a slight reduction.

As in the previous cases, the magnitude of $E_{ads}$ in-
increases upon performing an NSP calculation; one obtains values of -4.38 and -3.93 eV for the HH and VB configurations respectively.

Upon co-adsorbing NO on this Rh/MgO slab, we find that it is preferable for both the N and O to be at NN hollow sites rather than at NN bridge sites; the former leads to a co-adsorption energy of -4.74 eV, while the latter leads to a co-adsorption energy of -4.10 eV.

### IV. DISCUSSION OF TRENDS

We have seen that as we go from case (i) to case (iv), the effective coordination $n_e$ decreases progressively and significantly. This decrease in effective coordination is accompanied by (and, in our interpretation, causes) a significant increase in the strength of adsorption of NO and co-adsorption of N and O. Our main results are encapsulated in Fig. 6. In the panel on the left-hand-side, we have presented our results for the adsorption energy of NO on these systems. The open circles represent results for the vertical bridge geometry, and the filled circles those for the horizontal hollow geometry. The following features are evident from this graph: (a) for a given geometry, the magnitude of $E_{ads}$ increases monotonically as $n_e$ is decreased; (b) the slope of this graph is larger for the HH than for the VB; this can be rationalized as being due to the fact that for the HH, both the N and O are bonded to Rh atoms, whereas for the VB, only N is bonded to Rh atoms; (c) as a consequence of this the HH geometry becomes more favorable at lower $n_e$; (d) the slope of the lines connecting cases (i) and (ii) is less than that connecting (ii), (iii) and (iv). This last observation can be attributed to the fact that in case (i) the substrate is non-magnetic, whereas in case (ii) it is magnetic. In the absence of magnetism, adsorption is stronger, and the points corresponding to cases (ii), (iii) and (iv) would be shifted downwards, and one would have obtained a roughly straight line connecting the points from the four cases considered by us; since these three points have, however, been shifted upwards by the presence of magnetism, the slope connecting (i) and (ii) is reduced. The main conclusion from this graph is that the adsorption energy scales more-or-less linearly with effective coordination; we note further that the Rh(111) surface has a larger $n_e$ (9.15) and weaker $E_{ads}$ (-2.18 eV) than all four cases considered by us.

Similar conclusions about co-adsorption can be drawn from the right-hand-side panel, where the co-adsorption energy is found to vary monotonically with $n_e$. The variation is less linear for this case, presumably because of changes in co-adsorption geometry.

The adsorption energy decreases as we go from (i) to (iv) due to two reasons: (a) the strength of adsorption increases as the coordination is decreased, and (b) the horizontal hollow geometry, which leads to stronger binding to the substrate and a weaker and longer NO bond, becomes more favored at low effective coordination. However, these effects would have been even more marked if the substrate were to remain non-magnetic: in every case, we have seen that NSP calculations (where magnetism is suppressed) point to stronger adsorption than SP calculations.

For the VB geometry, the N-O bond length is found to be $\sim 1.2$ Å, whereas for the HH geometry, the bond length is increased to $\sim 1.3$ Å, suggesting that it should be easier to break the N-O bond in the latter case.

Our results show that strain and the presence of the oxide substrate contribute to the increased strength of adsorption primarily through their effect on $n_e$, and that both effects contribute to roughly the same extent. In the case of the magnesia substrate considered by us, charge transfer plays a negligible role, since the donation and back-donation mechanisms essentially cancel out. This may not be true for more active oxide substrates, such as titania and ceria.

It seems intuitively obvious that when Rh atoms have a lower effective coordination, they will bind adsorbates more strongly, thus making it easier to break bonds within the adsorbate. An alternative and equivalent way of looking at this effect is to consider the effect of lower coordination on the density of states. In Fig. 7 we show how the spin-polarized $d$-band density of states of the surface Rh atoms changes as we go from case (i) to case (iv) – it can be seen that the lowering of $n_e$ results in a progressive narrowing of the $d$-band. The $d$-bandwidth and position of the $d$-band center have been shown to be a good predictor of catalytic activity.

In Fig. 8(a) we show how the position of the $d$-band center shifts with effective coordination. We see that as we go from case (i) to case (iv), the reduction in $n_e$ is accompanied by an approximately linearly proportional shift in the $d$-band center, bringing it closer to the Fermi
FIG. 7: (Color online) Rh d-band projected density of states (DOS) for the four cases. Positive and negative values denote the DOS for spin-up and spin-down electrons respectively.

level. In Fig. 8(b) we show that the adsorption energy varies in a monotonic (and approximately linear) way with the d-band center.

V. SUMMARY AND CONCLUSIONS

We have studied the adsorption of NO and the co-adsorption of N and O on strained and unstrained Rh surfaces with and without the presence of an MgO substrate. Both strain and placing a monolayer of Rh atoms on the oxide substrate lead to a significant lowering in the effective coordination of surface Rh atoms; doing both [i.e., placing a monolayer of Rh atoms pseudomorphically on an MgO(100) substrate] leads to the largest decrease in effective coordination $n_e$. Further, both strain and the presence of the substrate (either separately or together) have the effect of making the surface Rh atoms magnetic. Every decrease in $n_e$ is accompanied by (and, presumably, causes) a decrease in the d-bandwidth of Rh atoms, a shift of the d-band center towards the Fermi level, and a strengthening of the adsorption of NO and the co-adsorption of N and O.

We note that the effective coordination $n_e$ is a quantity that can be very simply computed, especially if the structure is known – it is not even necessary to perform an ab initio density functional theory calculation in order to compute it. Therefore it can serve as a simple guide or rule-of-thumb in order to design systems where the strength of adsorption or co-adsorption takes on a desired value.

Thus, lowering the effective coordination seems to be a good strategy to increase the strength of adsorption and co-adsorption, and thus, conceivably, lower the barrier to dissociation of the NO bond. One can think of several ways of reducing effective coordination: e.g., by using rough surfaces, by placing Rh atoms on an inert oxide substrate, and by using Rh nanocatalysts where the Rh particles are sufficiently small so as to be significantly under-coordinated. However, most of these strategies to reduce $n_e$ also favor magnetism, which competes with bonding. This suggests that an optimal value of $n_e$ should be aimed for, where the coordination is low enough so as to favor a significant strengthening of Rh-NO bonds and weakening of the N-O bond, yet the adverse effects of magnetism are not too evident.

We are in the process of computing dissociation barriers, in order to verify our expectation that lowering effective coordination will also weaken the N-O bond and thus catalyze the reduction of NO to $N_2$.

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