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Oxygen chemisorption on metal surfaces using the cluster model: Basis set effects

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Summary. Previous calculations on Ni_5O have indicated large effects on the oxygen binding energy from *d* orbital relaxation. In these calculations the basis set was quite restricted, in particular the metal *d* orbitals were described by a single contracted basis function. In the present study the effect on the oxygen and the cluster binding energies of increasing the nickel basis set has been investigated. When the *d* basis is changed from totally contracted to triply split the cluster binding energy increases by 9 kcal/mol, or 1.8 kcal/mol per nickel atom, and the oxygen chemisorption energy increases by 3 kcal/mol to 45 kcal/mol. A completely contracted description of the *d* orbitals is thus adequate for metal clusters. This result also supports the notion that the *d* orbitals are not important for the covalency of the surface-oxygen bond.

Key words: Oxygen chemisorption – Metal surfaces – Cluster model

1. Introduction

In theoretical studies of chemisorption and surface reaction phenomena it is common to use cluster models, i.e. clusters of suitably arranged atoms, to simulate a metal surface [1–11]. The convergence of certain surface properties with the size of the cluster thus becomes a central issue. Previous studies of cluster convergency have shown that a number of chemisorption properties can be calculated with a high degree of accuracy using clusters with less than 50 metal centers [12]. However, simplifications always become necessary if the cluster is larger than 5–10 metal atoms. The effective core potential (ECP) method, where the metal atoms are effectively described as one-electron systems, has proven to be both efficient and accurate for Cu and Ni surfaces [5–11].

In our opinion two criteria are essential for a cluster model based on a simplified treatment of the metal atoms. The basic equations used in the model should be the same as those used in standard *ab initio* calculations (SCF, MCSCF, CI), and the model should yield results in good agreement with all-electron calculations on relevant systems. The first criterion, which in general is fulfilled by the ECP approaches, is important if a surface reaction is to be understood in terms of generally accepted quantities such as covalency, ionicity, overlap, Pauli repulsion etc. Simplified cluster models, based on e.g. one-electron ECP's, should in fact be regarded as approximations to all-electron calculations, rather than models of the surface per se. At least initially, it is more important for model calculations to agree with all-electron results than with experiment, and comparisons with good-quality all-electron results for small clusters is thus of utmost importance for the development of cluster models.

One early finding from all-electron calculations on small metal clusters was that chemisorption properties could be very dependent on the description of the *d* orbitals in the cluster [6]. The difference in the oxygen chemisorption energy between calculations where all the *d* orbitals were kept frozen in their atomic shape and where they were fully relaxed was 16 kcal/mol for Cu_5O [8] and 44 kcal/mol for Ni_5O [6]. In spite of the large *d*-orbital relaxation effects, only minor covalency effects involving the *d* orbitals could be found in the cluster-adsorbate bond. However, the metal basis sets used in these studies were rather restricted, in particular a single zeta (totally contracted) description of the metal *d* orbitals was employed. The basis set used was of the Tatewaki–Huzinaga type [13] with a totally contracted five component *d* function optimized on the $^3D(d^9s^1)$ state of the Ni atom. Since the all-electron calculations are of fundamental importance for the cluster model it is essential that they are of a high quality, and in view of the importance of the *d* orbitals the small basis set used may be inadequate. In order to elucidate the role of the *d* orbitals in the substrate-oxygen bond for oxygen chemisorbed on a transition metal surface we decided to carry out large basis set calculations on the Ni_5 and the Ni_5O systems.

2. Computational details

The calculations presented in this work were all carried out at the SCF level of approximation (CI effects at the all-electron level have been investigated in a separate study for Cu_5O [14]).

Oxygen chemisorbs at the fourfold hollow position on the Ni(100) surface [15]. The smallest unit appropriate for modelling the fourfold hollow position on Ni(100) consists of four Ni atoms in a square arrangement and one Ni atom below the center of the square. The chemisorption process is modelled by placing an oxygen atom at various heights above the center of the square. While the full point group symmetry of this system is C_{4v}, the present calculations were for technical reasons carried out in the C_{2v} subgroup, and symmetry was not retained for degenerate states of E symmetry. However, the energy differences between symmetry restricted and symmetry unrestricted calculations are minor, as verified for e.g. Pt_5O [16]. The symmetry labels of orbitals and states in the following refer to the C_{4v} point group.

The electron configuration of Ni_5O is most easily discussed if the valence and the *d* electron configurations are considered separately. The valence electron configuration of the ground state of Ni_5 and Ni_5O at the SCF level have previously been found to be $^4A_2; (1a_1)^2(2a_1)^1(1e)^2$ and $^2E; (1a_1)^2(2a_1)^2(3a_1)^2(1e)^4(2e)^1$ respectively [6]. In the ground state of the cluster the open *d*-type orbitals on the four surface Ni atoms have been found to be of a_1, e and b_2 symmetry, and on the Ni atom below the square of a_1 symmetry (i.e. of $2z^2 - x^2 - y^2$ type) [21]. If the *d* electrons are high-spin coupled, which is a natural choice since nickel is ferromagnetic, the full symmetry of the system becomes $^9B_2$ for the bare cluster and ^7E for Ni_5O.

Our previous all-electron calculations on the Ni_5O system [6] were carried out using a modified version of the MIDI-3 basis set suggested by Tatewaki and Huzinaga [13]. The modified basis set is of single zeta quality in the core region, and has a totally contracted 3*d* orbital. For the 3*d* orbital one diffuse *d* function was added and the contraction coefficients were determined in a calculation on the [^{3}D; d^4s^1] state of the Ni atom. To this basis set two diffuse *p* functions were added. In order to minimize possible basis set superposition errors, which may become serious in connection with non-energy optimized basis sets [20], the calculations were carried out keeping the 1*s*-3*p* atomic orbitals in the nickel atoms frozen in their atomic shapes. In [6] we used a *d*-shell occupation with a singly occupied d_{xy} orbital (of b_2 symmetry) on the nickel atom below the surface square. In the present study calculations have been carried out both for this ground state and for a state where the *d*-hole on the bottom Ni was placed in the d_{xy} orbital (i.e. in the b_2 symmetry orbital).

The basis set used for nickel was the 13*s*, 7*p*, 5*d* basis set suggested by Hyla-Kryspin et al. [17], augmented by two diffuse *p* functions with exponents 0.112 and 0.031 and one diffuse *d* function with exponent 0.16. This basis set was contracted to 5*s*, 3*p*, 3*d* or 5*s*, 3*p*, 1*d* using the general contraction scheme suggested by Rafenetti et al. [18]. For oxygen Dunning's 9*s*, 5*p* atomic basis set [19], augmented by one diffuse *p* function with exponent 0.057669 and one polarizing *d* function with exponent 1.0 was used. This basis set was contracted to 3*s*, 4*p*, 1*d* using a general contraction scheme.

3. Results and discussion

The bonds between the cluster and the adsorbate are, as discussed in [6–7], best characterized as covalent although polarized toward the adsorbate. The oxygen charge is about −1 but the oxygen atom does not have any radical character in the bound state. The ground state of Ni_5O has one singly occupied orbital of e symmetry, but this orbital is localized on the cluster.

The present results and the results obtained previously with the smaller Tatewaki–Huzinaga basis set are shown in Table 1. The sensitivity to the choice of the electron configuration of the *d* shells appears to be quite small. The energy

Table 1. Chemisorption energies and equilibrium distances

Basis set[a]	*d*-hole[b]	*d*-basis	r_e (a.u.)	B_e Ni_5O (kcal/mol)	B_e Ni_5 (kcal/mol)	ω_e cm^{-1}
T–H	*xy*	single Z	1.92	41.6	17.8	381
H–K	*xy*	single Z	(1.9)[c]	41.7	28.2	—
H–K	x^2-y^2	single Z	1.89	42.5	29.8	367
H–K	x^2-y^2	triple Z	1.94	45.3	38.8	382

[a] T–H and H–K refer to the basis sets of Tatewaki and Huzinaga [13] and of Hyla-Kryspin et al. [17]. See also text

[b] The *d*-hole of the bottom Ni atom

[c] Not geometry optimized

difference between the ground state and the state with an open d orbital of b_2 symmetry on the bottom Ni atom was very small: only about 1 kcal/mol for both the cluster and the oxygen binding energies.

The results appear to be fairly sensitive both to the size of the contracted and the primitive basis for the binding energy of the pure Ni_5 cluster. The cluster binding energy obtained with the basis set of Tatewaki and Huzinaga was 17.8 kcal/mol, while the cluster binding energy from the present study, for the same electron configuration (with an open d_{xy} orbital on the bottom Ni) using a fully contracted d function based on the larger primitive basis, is 28.2 kcal/mol. The ground state electron configuration (i.e. with an open $d_{x^2-y^2}$ orbital on the bottom Ni) yields a slightly higher cluster binding energy, 29.1 kcal/mol. It should be kept in mind that the size of the contracted basis sets are the same in these two calculations. The difference in cluster binding energy (obtained with a fully contracted d orbital) may at first seem large. However, one difference between the previous and the present calculations is that in the former case the $1s$-$3p$ orbitals were kept frozen whereas they were allowed to relax in this work. The present calculations, in contrast to the earlier ones, thus include polarization of the core orbitals and also possible basis set superposition errors involving the core orbitals. Such effects, which can be expected to be of the order of a few kcal/mol/atom, are additive with the number of atoms in the cluster. A calculation on the Ni_5 cluster using the Tatewaki–Huzinaga basis set but with a completely relaxed core yielded an energy lowering of 15 kcal/mol, or 3 kcal/mol/atom, in reasonable agreement with the 2 kcal/mol/atom binding energy increase in going from the Tatewaki–Huzinaga basis with a frozen core to the fully contracted basis set of Hyla–Kryspin et al. When the d basis set is triply split the cluster binding energy increases by another 9 kcal/mol to 38.8 kcal/mol. This energy lowering is most likely due to polarization of the $3d$ shells in the cluster.

The oxygen chemisorption energy is much less affected than the binding energy by the changes in the basis sets. The effect of changing the primitive basis set but keeping the d orbital fully contracted is negligible (0.1 kcal/mol). The effect on the oxygen chemisorption energy of splitting the d shell is surprisingly small, 3 kcal/mol, and the effect on the equilibrium substrate-adsorbate distance is quite modest (a bond distance increase from 1.89 to 1.93 a.u.). The potential surface is very flat around the equilibrium position (the vibrational frequency is 382 cm^{-1} in our best calculation), which makes the difference in equilibrium geometry essentially insignificant. The small effects induced by the larger flexibility of the d shells is also reflected by the calculated vibrational frequency which changes from 367 cm^{-1} to 382 cm^{-1} when the d basis is increased.

Possible basis set superposition errors in the calculated chemisorption energy were investigated by the counter-poise method for the totally contracted d orbital case. A calculation on the pure cluster, carried out with an oxygen basis set at 1.9 a.u. above the surface, yielded a decrease of the total energy by 1.2 kcal/mol. This superposition error is not of any consequence for the chemisorption energies but may explain the slight lengthening of the oxygen to surface distance obtained when the d shell was split.

In the simplified ECP-based cluster models it is implicitly assumed that the d electrons do not contribute to the covalency in the cluster-adsorbate bond. This has indeed been shown to be the case of Cu_5O, where a CSOV analysis [22] yielded a d contribution to the covalency of at most 2–4 kcal/mol [23]. A corresponding analysis is more difficult to carry out for the Ni_5O system because of the open shell d orbitals. However, if the d orbitals were important for the covalent part of the oxygen-cluster bond, larger effects resulting from a splitting of the *d* shell would have been expected. It is not reasonable to believe that a fully contracted *d* shell, taken from an atomic calculation, would be adequate to describe the radial polarization of the *d* orbital which would most likely occur if *d* covalency were important. The present results thus support the notion that *d* covalency is not important in the bonding between a nickel surface and an oxygen atom.

The question of the *d* orbital contribution to the covalency in the cluster-adsorbate bond is very important for cluster modelling. At a first sight it may appear that a prerequisite for our cluster model is that the *d* orbitals are inert during the chemisorption process. Clearly the *d* orbitals are not inert in the case of oxygen chemisorption on a nickel surface, since the chemisorption energy increases by some 40 kcal/mol when the *d* orbitals are relaxed [6]. However, if the *d* relaxation effect is cluster-specific, i.e. not directly involving the adsorbate, it can always be modelled by some cluster-specific operator. Since the *d* orbital relaxation does not involve important charge transfer or covalency effects it must be interpreted as a polarization of the *d* orbitals, presumably resulting from Pauli repulsion (i.e. the orthogonality constraint) between the *d* orbitals and the adsorbate. A polarization of the *d* orbitals in the cluster is a property of the cluster itself, and hence it should be possible to model this effect by some operator which does not depend explicitly on the adsorbate. In [6] we have suggested a modification of the ECP operators which has been successfully applied for a number of adsorbates on Cu and Ni. If 3*d* covalency effects prove to be important for some adsorbates, a less general ECP, which describes the interaction with the specific adsorbate, can always be used, although the generalizability of the results in this case will of course be more limited. This may be the case for multiply bound adsorbates such as N or C. However, it may also be difficult to apply the simple cluster model using only one-electron ECP's for these adsorbates for another reason. Both C and N adsorb very close to the surface, which in fact becomes structurally reorganized, and an all-electron description of the nearest neighbours may be necessary also at the hollow sites for these adsorbates.

4. Conclusions

The results of this investigation suggest that an adequate description at the SCF level of chemisorption on nickel and copper surfaces can be obtained with fully contracted metal *d* orbitals. The binding in the cluster proper is somewhat more sensitive to a reasonable flexibility of the metal *d* orbitals. Going from a totally contracted to a triply split *d* function induced an increase in the binding energy of 9 kcal/mol. Taken per atom, this binding energy increase is still small, 1.8 kcal/mol. The good performance of the totally contracted *d* basis set, in spite of the large relaxation energies encountered upon relaxing the *d* orbitals, indicate that the relaxation of the *d* orbitals involves *s*-*d* type mixing rather than radial relaxation. The small effect on the oxygen binding energy from splitting the *d* shell is consistent with reasonably small covalent contributions from the *d* orbitals in the cluster-oxygen bond.

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