

Effect of the Madelung potential in the structure and bonding of metal–oxide systems: Cu on MgO(100)

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Abstract

In this paper we use different cluster models to study the chemistry of the metal–oxide interface. These models permit us to show that the main differences between the CuMgO and CuOMg molecules and the Cu/MgO(100) system arise from the Madelung potential. A quantitative description requires to explicitly consider the extended nature of the ions surrounding the active site although for different physical reasons. For Mg sites the inclusion of O^{2-} nearest neighbors permits an adequate representation of the frontier orbitals while for O^{2-} sites explicit consideration of nearest Mg^{2+} cations avoids artificial charge density polarization produced by the point charges simulating the Madelung field. The present study shows that the Cu/MgO(100) interaction is weak, of intermolecular or Van der Waals origin. This implies a Volmer–Weber model for the growth of Cu on MgO(100).

Keywords: Copper; Magnesium oxide; Madelung potential

1. Introduction

Supported metals are of great interest in heterogeneous catalysis but also in other technological fields like microelectronics. In the past, it was argued that supported metals should be employed in heterogeneous catalysis because its use enabled to reduce the amount of the often very expensive catalytic material. However, this is not the only reason since it is nowadays well known that it is possible to change the activity and selectivity of a catalytic metal by changing the nature of the support [1]. Supports are usually ionic materials and more generally metal

oxides. Interactions between metals and metal oxides have been divided into three types depending on their strength. Metal–support interactions are believed to be originated by purely electronic effects, the strong interaction appearing when the oxide can be reduced and the weak one when non-reducible oxides are involved [2]. A huge amount of experimental data is demanding theoretical studies that may help to validate current interpretations [3,4]. In spite of this fact, the theoretical framework in which it would be possible to handle with these highly complex systems is only slightly emerging.

The simplest way to describe ionic solids is by representing each ion as a point charge, the resulting model being merely a distribution of point charges. This oversimplified description

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takes into account the most important contribution to the bonding in ionic solids which is the Madelung potential. Of course, the ionic model neglects direct or covalent chemical bond and finite ion size effects. However, various detailed quantum chemical studies of simple oxides such as MgO to BaO or Al_2O_3 show that effects neglected in the ionic model contribute to the total energy by only a small amount [5–8]. Therefore, one should expect that the Madelung potential will also make a large contribution to the metal–oxide interaction. In a previous work, we have studied the interaction of atomic Cu with the MgO and CaO diatomic molecules [9]. In each case, we found two stable species which correspond to the Cu–MO and Cu–OM ($\text{M} = \text{Mg}, \text{Ca}$) orientations, respectively. For both orientations, a strong interaction was found although the chemistry was very different in the M- and O-bonded complexes. These molecular systems are not directly related to the metal–oxide interaction but, as shown later, will be very useful to understand it. This is because, as stated above, the largest contribution to bonding in bulk MgO is precisely the Madelung potential and, from the point of view of theory, it is quite simple to just add this term to the Cu–MgO and Cu–OMg molecular complexes to obtain a first model of the metal–oxide interface. Other effects, such as the finite ion size, can be added by replacing some of the point charges used to represent the Madelung potential by extended ions.

Although experimental studies suggest that the interaction is more likely to occur at the defective sites [10] we will be only concerned with the perfect MgO(100). This is to compare with previous theoretical studies modeling which lead to rather different conclusions. Thus, UHF calculations by Bacalis and Kunz [11] predicted a weak interaction between Cu and the surface with a shallow minimum approximately 8 bohr above the surface and 0.04 eV deep. On the other hand, Li et al. [12] used the local density approximation, LDA, method and concluded that the interaction was very strong, 1.4 eV, for the

dissociation energy, and Cu much closer to the surface (3.70 bohr). Finally, Pacchioni and Rösch [13] used gradient corrected LDA techniques, or DFT-GC, to study Cu and Ni on MgO(100) and found that Cu chemisorption energy on both cation and anion sites was small but noticeable, of ≈ 0.3 eV; also, they found quite short equilibrium distances, 4.89 and 4.04 bohr, respectively. We should stress the fact that, in spite of methodological differences, models employed in Refs. [11–13] are not comparable and more information is needed not only to obtain reliable values for the geometrical and energetic aspects of the interaction but also in the mechanisms governing the formation of the metal surface bond which in the view of these widely spread results is far from being understood.

In this work, we will use different cluster models to represent the interaction of atomic Cu with the MgO(100) surface. In particular, we will investigate which are the similarities and differences in the chemistry of the Cu–MgO and Cu–OMg molecules and on that of the metal–oxide interface. We will be specially concerned with the role of the Madelung field and show that it is largely responsible for the differences between both systems.

2. Cluster models for the Cu/MgO(100) system

In order to understand the modifications induced by the ionic support we have made use of two different models. In the first model, we try to explore the electrostatic effects due to the Madelung potential. In order to compare the Cu–MgO(100) system with the triatomic molecules Cu–O–Mg and Cu–Mg–O studied previously [9], we start with a model of MgO(100) which contains just two atoms, Mg (or O) in the first layer and O (or Mg) in the second layer, but surrounded by an array of point charges representing the electrostatic or Madelung potential. A similar model was used

recently to study the chemical bond of bulk alkaline–earth oxides and using the dipole moment curves as measure of ionicity [14]. This model has the beauty of being extremely simple and stoichiometric; however, notice that the present model is for the (100) surface and not for the bulk as in Ref. [14]. The total model for MgO(100) includes 676 lattice points distributed as $13 \times 13 \times 4$. Among these lattice points there are two atoms and 674 point charges. In order to further understand the effect of the Madelung potential we will use two different values of the Madelung potential. This is achieved by simply using different values for the point charges. Two extreme cases are considered; in the first one, hereafter referred to as Model-1, we use ± 2.0 values and thus represent a fully ionic material while in the second case, and in spite of the large body of evidence showing the large ionic character of MgO (see for instance Refs. [5–8,10], and references therein), we use ± 1.0 which represents a lower ionicity, this will be referred to as Model-2. Finally, in Model-3 we include the finite size of the ions in the first layer by explicitly considering the first four nearest neighbors in the first layer thus leading to $[\text{MgO}_5]^{8-}$ and $[\text{OMg}_5]^{8+}$ clusters (see Fig. 1). The total net charge of these $[\text{MgO}_5]^{8-}$ and $[\text{OMg}_5]^{8+}$ clusters includ-

ing the array of point charges is, evidently, zero and the superindex serves just to indicate that the number of electrons included is that corresponding to a fully ionic model although the cluster wave functions are flexible enough to distribute the electronic charge between centers if this effect lowers the total energy. Therefore, Model-3 does also include possible, very small, covalent effects. In all cases, the Mg–O distance, for both cluster atoms and ions represented by point charges, was fixed at the bulk experimental value and no relaxation nor reconstruction was considered.

For each one of the models above described we have obtained the potential energy curve for the interaction of atomic Cu above either the Mg or O site of the MgO(100) surface cluster model. The study of the potential energy curve and of the nature of the interaction will provide new and useful information about the metal–oxide interface.

3. Computational approach

The electronic structure of the different models described in the previous section as representative of the Cu/MgO(100) interface has been studied by means of *ab initio* quantum

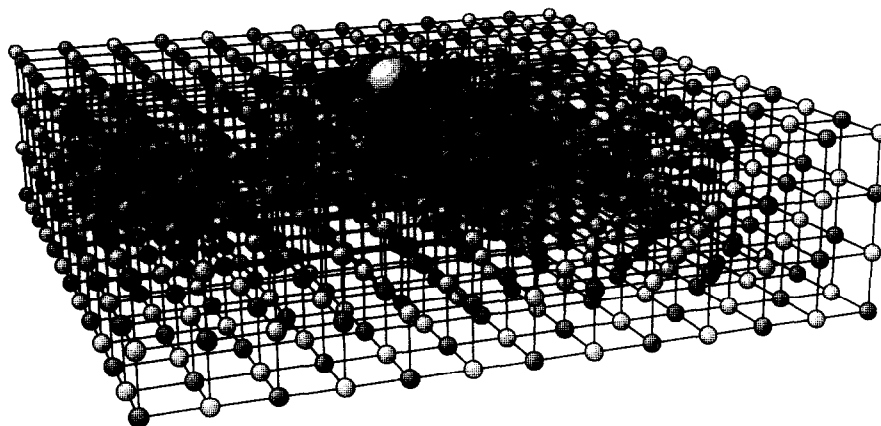


Fig. 1. Schematic representation of the cluster model of the MgO surface. This corresponds to Model-3(O) thus including $[\text{OMg}_5]$ and the array of 670 point charges. Pictures for Model-1(O) or Model-2(O) will be identical but substituting the four edge first layer atoms by point charges. Clusters representing the cation centered Model- $n(\text{Mg})$ situations are almost identical to this one with exception of the ion size.

chemical methods. All electron Hartree–Fock self consistent field wave functions, in the restricted open shell, ROHF, formalism, have always been considered. The one electron basis functions or molecular orbitals, MO's, have been expressed in a rather large basis set of contracted Gaussian type orbitals, CGTO's. The basis sets used in the present work are the same previously used to describe the Cu–MgO, Cu–OMg, Cu–CaO and Cu–OCa molecular complexes [9]. For Cu we used a 8s, 6p, 4d contraction of the 14s, 11p, 6d primitive set of Wachters [15] modified by Bagus et al. [16] by adding two CGTO's to represent the Cu 4p atomic character and a diffuse d as recommended by Hay [17]; the final basis is indicated as [8s, 6p, 4d/14s, 11p, 6d]. For O we use a [9s, 5p/4s, 3p] previously used by Broughton and Bagus [18] in their study of core-level shifts in bulk MgO and more recently used by Bagus et al. to describe excited states [19] and excitons also in MgO [20]. Finally, for Mg and Ca we used, respectively, the [13s, 8p/6s, 3p] and [15s, 10p, 1d/7s, 5p, 1d] sets with exponents and coefficients taken by Pacchioni et al. [21].

Using the atomic basis sets above described, ROHF calculations were performed to search stable structures on the potential energy surface. In all models it was assumed that Cu interacts directly above either cation or anion sites. Given the linear geometry of the isolated molecular complexes, this is a reasonable assumption. Therefore, the only geometrical parameters to be determined are the perpendicular distance to the surface and the vibrational frequency for the frustrated translation which indeed is obtained assuming infinite mass for the substrate. Dynamical correlation effects on the calculated energies have been explicitly accounted for by using simple second order perturbation theory in the framework of the Moller–Plesset partition of the electronic Hamiltonian. However, we must remark that here the ROHF wavefunction is taken as the zeroth-order; we will refer to this approach as ROHF-MP2. The adequacy of the ROHF wave function to represent the electronic

structure of these systems, at least as a zeroth-order wave function, can be investigated by looking at the first-order contribution of the single and diexcited determinants; except for the gas-phase diatomic MgO, which needs a multi-reference description [9], there are no excitations contributing to the first-order wave function by more than 0.5%. Consequently, the ROHF-MP2 has been used in all correlated calculations.

Once the equilibrium geometries were determined, the chemical bond determining the stable structures of the Cu–MgO unit in different surroundings was studied by means of a series of methods of theoretical analysis. This includes the constrained space orbital variation [22–24], CSOV and the corresponding orbital transformation (Ref. [25]; see applications in Refs. [26,27]). ROHF calculations were carried out using HONDO8.5 package [28] whereas ROHF-MP2 calculations were carried out using the HONDO-CIPSI chain of programs [29].

4. Results and discussion

For the atop interaction of Cu on a MgO(100) perfect surface it is logical to consider both the cationic and anionic sites. These will be referred to as Model-*n*(Mg) for Cu interacting directly above a cationic site of Model-1, Model-2 or Model-3; similarly Model-*n*(O) will denote interaction directly above a cationic site on a given model. For each model, the optimum Cu–surface distance, vibrational frequency for the motion of Cu perpendicular to the surface and the interaction energy is given in Table 1. In all cases, the MgO distance for the surface models has been fixed at the bulk value. The distance between Cu and either Mg or O is always larger than that corresponding to the isolated triatomic molecule, and the interaction energy is always much smaller than that for the molecular complexes. Very approximately, the interaction of Cu above MgO(100) is of 0.2–0.4 eV only, to be compared to 1.2 or 2.3 eV for

Table 1

Calculated equilibrium distance, r_e , interaction energy, D_e , and vibrational frequency, ω_e , for Cu on MgO(100) as represented by Model- n (Mg) and Model- n (O) cluster models ($n = 1-3$). For a description of the different models see Section 2

Model	Method of calculation	r_e (Bohr)	D_e (eV)	ω_e (cm^{-1})
Model-1(Mg)	ROHF	—	—	—
	ROHF-MP2	6.90	0.03	20.1
Model-2(Mg)	ROHF	6.01	0.17	186.6
	ROHF-MP2	5.70	0.20	53.2
Model-3(Mg)	ROHF	6.18	0.09	264.8
	ROHF-MP2	5.24	0.35	72.0
Model-1(O)	ROHF	4.29	0.28	217.6
	ROHF-MP2	3.79	0.59	130.8
Model-2(O)	ROHF	3.87	0.89	171.0
	ROHF-MP2	3.64	1.19	184.3
Model-3(O)	ROHF	4.67	0.09	363.0
	ROHF-MP2	4.01	0.40	120.4

CuMgO and CuOMg molecules, respectively. At the ROHF level, the interaction through Mg is repulsive for Model-1 although a shallow minimum appears for both Model-2 and Model-3. However, at the correlated ROHF-MP2 level the three models lead to attractive curves with equilibrium distances smaller than the ROHF ones although, again, the interactions energies are small. The interaction through O is attractive for the three models for both ROHF and ROHF-MP2 levels of computation.

The fact that the behavior is roughly similar for the three different models and for the interaction through either Mg or O indicates that the Madelung potential is responsible for the large difference, qualitative and quantitative, with respect to the molecular complexes. We must recall that while Cu-OMg can be viewed as a largely ionic bond the Cu-MgO was better described as a covalent interaction [9]. However, mainly as a result of the Madelung potential, the three models lead to very weak interactions. Now, let us consider this Madelung potential effect in more detail. We first notice that for Model- n (Mg), changes from Model-1 to Model-2 or Model-3 are similar. However, Model-2 and Model-3 are very different; Model-2 includes only 25% of the Madelung potential corresponding to a fully ionic system whereas

Model-3 includes 100% of this Madelung potential, as Model-1, but it contains also the finite size of the anions surrounding the central Mg cation. It is well established that MgO may be adequately described as a fully ionic system [5–8]. Therefore data calculated from Model-2 have to be taken with caution and the useful information is that a very large reduction, by 75%, of the Madelung potential does only slightly affect the quantitative, ROHF-MP2, description of the interaction above a Mg site. Clearly, differences between Model-1 and Model-3 alert us on the danger of using models which are too simple. The formation of the bond in the triatomic molecule Cu-Mg-O arises from the interaction between the 4s electron belonging to the Cu and the MgO highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO [9]. In Model-1, and also in Model-2, the LUMO can only be the Mg 3s orbital. However, in bulk MgO the conduction band orbitals, here represented by the LUMO, are extended in space and have no resemblance to a purely atomic 3s Mg orbital [19,20]. This extended character of the MgO conduction band orbitals begins to develop in Model-3 simply because the O^{2-} anions are big enough so that there is no physically space left for a 3s like orbital.

Now, let us briefly discuss the Model- n (O) cases. Here, reduction of the Madelung potential by about 75% does only produce modest changes in the Cu-O distance but largely increases the interaction energy (Table 1). It is worth to point out that the smallest Cu-O distance and largest interaction energy appears precisely for Model-2. Again, this is a result of a too simplified representation of MgO. In fact, the lack of surface Mg^{2+} nearest neighbor for the O^{2-} surface anion permit the O^{2-} electronic density to artificially polarize towards the point charges representing these cations. This charge density polarization reduces the Pauli repulsion and results in a too short equilibrium distance and a too large interaction energy.

Before ending this discussion, it is worth to

briefly comment the basis set superposition error, BSSE, effects on the calculated energies. While the overall picture is not changed after correcting the D_e values by the well known counterpoise method, consideration of BSSE leads to even smaller values. This is in agreement with the description of the interaction as a weak one. For both Model-3(Mg) and Model-3(O) the ROHF D_e values are similar and small and almost vanish after taking BSSE into account. At the ROHF-MP2 the situation is similar though a net bond exists after taking BSSE into account; the uncorrected D_e values are 0.35 and 0.40 eV, respectively; the BSSE corrected values are 0.10 and 0.21 eV. The fact that almost no binding appears at the ROHF level and the modest values obtained after including electronic correlation effects suggest that the Cu/MgO(100) interaction is, in fact, best described as weak and originated by electrostatic (charge-induced dipole, etc.) mechanisms. This interpretation is supported by the rather large calculated equilibrium distances and by the vibrational frequencies which are drastically changed from ROHF to ROHF-MP2, a clear indication that bonding is dominated by correlation effects and, hence, of Van der Waals like character. This is in agreement with the recent DFT results of Pacchioni and Rösch [13].

Further arguments for a weak, Van der Waals like, interaction are provided by the corresponding orbitals and CSOV analyses. The corresponding orbital analysis show that there is no orbital mixing, the orbitals of the supersystem, Cu and Model- n , are basically the superposition of those of the two subsystems, the only orbital which appears to be slightly different is the Cu 4s and this is a result of the polarization induced by the substrate. This is supported by the CSOV analysis which, without entering into fine details, shows that, in all cases, the only noticeable contributions are Cu polarization, ≈ 0.06 to 0.18 eV for Model-3(Mg) and Model-3(O), and that charge donation from Cu to Model-3, ≈ 0.08 to 0.06. Similar values are found for the donation from Model-3 to Cu but this is mainly

originated by BSSE because of the limitations of the basis sets used to describe the O^{2-} anions.

5. Conclusions

In this paper we have used different cluster models to study the chemistry of the metal–oxide interface. From the discussion in the previous section, it is clear that the main differences between the CuMgO and CuOMg molecular complexes and the models for Cu on MgO(100) cationic or anionic sites arises from the Madelung potential. This can be deduced even using models as simple as Model-1. However, a quantitative description requires also to explicitly consider the extended nature of the ions surrounding the active site although for different physical reasons. For Mg sites the inclusion of O^{2-} nearest neighbors permits an adequate representation of the frontier orbitals while for O^{2-} sites explicit consideration of nearest Mg^{2+} cations avoids artificial charge density polarization produced by the point charges simulating the Madelung field. We must notice that sometimes an artificial large reduction on the Madelung potential leads to results which compare fairly well with those of the extended model, cases represented by Model- n (Mg), while in some other occasions large discrepancies do appear (see results for Model- n (O)). Therefore, one must be aware of fortuitous coincidences. In some cases, artificially reduced potentials have been used to obtain values for observable quantities that compare better with experimental results. The present analysis shows the danger of using this kind of approach.

In summary, present calculations for Cu on MgO(100) models show that the interaction of intermolecular or Van der Waals origin is weak and that bonding differences between this metal–oxide interface and the isolated CuMgO and CuOMg molecules arises mainly from the Madelung potential although nearest neighbor

ions have to be explicitly considered to avoid misinterpretations. We would like to end this paper by noting that our conclusions are in agreement with those reached by Pacchioni and Rösch [13] on their DFTCG study on the Cu/MgO(100) interface but also with a very recent study of the interaction of Cu, Ag and Au on NaCl(100) [30]. All these studies suggest a weak interaction between the metal and the support. Contrarily to the strong metal–metal bonding, this weak metal–support interaction is of electrostatic and dispersive origin and points out that, for these systems, the growth of the metal will be better described through the Volmer–Weber model [31].

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