Ab Initio Cluster Model Calculations on the Chemisorption of CO_2 and SO_2 Probe Molecules on MgO and CaO (100) Surfaces. A Theoretical Measure of Oxide Basicity

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Abstract: A comparative study of the basic character and of the chemical reactivity of the oxide site of the MgO and CaO (100) surfaces has been performed on the basis of *ab initio* cluster model calculations. Two molecules, CO_2 and SO_2, have been chosen as probes of the basic character of the O^{2-} surface site. The latter was modeled by a OM_5 cluster, with M = Mg or Ca, embedded in the proper Madelung field. We found that CO_2 and SO_2 exhibit completely different reactivities with the two surfaces. On MgO, the two probe molecules form a weakly bound surface complex, while on CaO, we observe the formation of strongly bound sulfite and carbonate species. The reason for the different reactivities has been analyzed in detail. A decomposition of the interaction energy into electrostatic, polarization, and charge transfer contributions shows that CaO is a better base than MgO. This is also the reason why CO_2 and SO_2 are more strongly bound on the heavier oxide. The ultimate reason for the different surface reactivities of MgO and CaO, however, is not of chemical nature and can be simply explained in terms of electrostatic stabilization of the surface anion. The O^{2-} ion at the surface is stabilized by the Madelung potential of the ionic crystal. This is smaller in CaO than in MgO, thus leading to a higher basicity and reactivity of CaO. In this respect, a regular surface site of CaO behaves similarly to a low-coordinated defect site of MgO. We also show that there is a direct relationship between the lattice constant of the ionic crystal and the surface basicity. This may be relevant in the context of the acid-base properties of strained oxide thin films grown on metal substrates.

1. Introduction

The acidic or basic nature of a metal oxide largely determines its catalytic activity toward an adsorbed species.[1] The characterization of the acidic-basic properties of a metal oxide surface is therefore of considerable practical importance. The basic strength of a solid surface is usually defined as the ability of the surface to convert an adsorbed electrically neutral acid, from a solution or from the gas phase, to its conjugate base.[1] In other words, the basicity of an oxide is defined as the ability of the surface to donate electronic charge to the adsorbed molecule. One widely used method to determine the basicity of an oxide consists in the titration of the surface with benzoic acid in the presence of an indicator.[1] In principle, the method is very similar when the titrating "acid" is not in solution but is a gas-phase molecule like carbon dioxide, nitric oxide, or phenol.[1] For instance, the amount of CO_2 irreversively adsorbed on the surface of a thermally pretreated and dehydroxylated CaO surface provides a measure of the density of basic sites, considered to be O^{2-} sites, on the surface.[2,3]

In a series of seminal papers,[4] Tanabe and co-workers have studied the basic properties of alkaline-earth-metal oxides. Studying reactions like the conversion of benzaldehyde into benzyl benzoate over MgO, CaO, SrO, and BaO surfaces, they found a very good correlation between catalytic activity and surface basicity. In particular, it was shown that the order of base strength is MgO < CaO < SrO < BaO.[4]

A more physical measure of surface basicity is given by X-ray photoelectron spectroscopy, XPS.[5-7] The O 1s binding energy, BE, is used to measure the charge density around the anion. In particular, if the O 1s BE is low, typically <530 eV, it is assumed[8] that the compound is largely ionic and that the charge of the oxide anion is close to −2; this leads to a large intraatomic screening and to a shift of the core level BE to smaller values. This is the case for instance of BaO (528.5 eV).[8] Oxides where the O 1s BE is >530 eV, e.g., SiO_2 (532 eV) or Al_2O_3 (531.5 eV), are assumed[8] to be more covalent and the corresponding oxide anions on the surface less basic. However, measures of surface basicity based on XPS measurements are not free from ambiguities. We have recently shown[9] that one important contribution to the O 1s core level BE in dominantly ionic oxides is the Madelung potential and that the observed shift in the O 1s BE as one goes from MgO (530.9 eV) to BaO (528.5 eV) is largely due to the change in the Madelung potential and not to the different ionic degrees.[9]

An important aspect of the basicity of an oxide is also connected to the nature and the density of the surface defects. It is well known that surface defects, like less-coordinated steps, corners, or even vacancies, are the sites where most of the chemistry takes place.[10,11] These sites can exhibit an acidic-basic behavior

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substantially different from that of the regular surface sites.[10] Therefore, it becomes important to establish some general rules to rationalize and predict the acidic–basic character of various surface sites as well as of different oxides.

In this paper we report the results of *ab initio* cluster model calculations on the reaction of two "probe" molecules like CO_2 and SO_2 with the fully dehydroxylated (100) surfaces of MgO and CaO. In particular, we focus our attention on the five-coordinated oxygen sites, O_{5c}^{2-}, of the ideal, unreconstructed surface of the two alkaline-earth-metal oxides. The aim of the paper is twofold. First, we want to compare the different reactivities of CO_2 and SO_2 with the MgO and CaO solid surfaces. This is an important class of reactions considering that, for instance, the industrial abatement of SO_2 from coal combustion emissions is based on this process. Second, we want to compare the different reactivities of the two surfaces. This second point is relevant in order to formulate a general, simple explanation for the different acid–base behavior of the two surfaces. We will show that the ultimate reason for the different basicities and reactivities of MgO and CaO is not of chemical nature, but can rather be explained by simple electrostatic arguments.

The paper has been organized as follows. In section 2 we describe the details of the computations and the basic features of a procedure adopted to decompose the interaction energy and to identifiy the relative importance of different bonding mechanisms in the two oxides. In sections 3.1 and 3.2 we discuss the chemisorption of SO_2 and CO_2, respectively, at the O^{2-} surface sites of MgO and CaO. In section 3.3 we analyze the reasons for the different behavior of CaO compared to MgO. Some general conclusions on the basicity of ionic solids are drawn in the last section.

2. Computational Details

To study the adsorption of CO_2 and SO_2 at the (100) surfaces of MgO and CaO, we have used two cluster models,[12] $[OMg_5]^{8+}$ and $[OCa_5]^{8+}$, where a surface O^{2-} ion is surrounded by its five nearest-neighbor M^{2+} cations. The total charge of the cluster reflects the largely ionic nature of the oxide, formed by M^{2+} and O^{2-} ions. The cluster is then "embedded" in a 13 × 13 × 4 array of point charges, PC = ±2, placed at the lattice positions. This array of PC's is large enough to ensure that the Madelung potential in the chemisorption region is reproduced with reasonable accuracy.[13,14] The entire system, cluster + PC's, is neutral. In doing this, we have assumed perfect ionicity for the MgO and CaO crystals. *Ab initio* Hartree–Fock and configuration interaction calculations for cluster models[15] and periodic systems[16] support this view. PC arrays may give artificial dipolar fields outside the surface. It is therefore important to check the validity of the model against periodic calculations, larger clusters, or other embedding methods. Detailed comparisons on the adsorption on MgO_5 + PC models of a surface cation have shown virtually no difference with respect to larger clusters or periodic slab calculations.[17] This makes us confident that the conclusions of the present study are not dependent on the choice of the models used. Furthermore, similar cluster models have been successfully used for the study of the adsorption of CO,[13] CO_2,[18] and SO_2[19] on the regular surface sites of the MgO (100) surface.

We have determined all electron Hartree–Fock, self-consistent field, SCF, wave functions for the free clusters and for the clusters with an adsorbed molecule, namely, $[OM_5]^{8+}/CO_2$ and $[OM_5]^{8+}/SO_2$, with M = Mg or Ca. The following Gaussian type basis sets were used to construct the molecular orbitals: Mg^{2+} [13s8p/6s3p],[14] Ca^{2+} [11s7p/7s4p],[20] O^{2-} [11s7p1d/5s3p1d],[14,19] C [9s5p1d/4s3p1d],[21] S [13s9p1d/6s4p1d],[20] O (of CO_2 and SO_2) [9s5p1d/4s3p1d].[21] Thus, different basis sets were used for the O atoms of the adsorbed molecules and of the surface oxide anion to account for the different spatical extents of the electronic charge in the two cases. Previous studies[18,19] have shown that these basis sets are flexible enough to avoid the occurrence of large basis set superposition errors, BSSE.[22] The BSSE for these systems is typically on the order of 0.10–0.15 eV.[18,19] Since we are interested in semiquantitative comparisons of different systems more than in the accurate determination of the adsorption energies, we have not introduced BSSE corrections in this work.

Table 1. Geometries and Dissociation Energies, D_e, of CO_2 and SO_2 on OMg_5 and OCa_5 Cluster Models of MgO and CaO (100) Surfaces (See Also Figures 1 and 3)[a]

		z-($MO–XO_2$) (Å)	r-(X–O) (Å)	α-(OXO) (deg)	γ-(O–XOO) (deg)	D_e (eV)
SO_2	SCF		1.409	119		
	MP2		1.475	119		
	exptl		1.431	119		
OMg_5/SO_2 surface	SCF	1.905[b]	1.436	115	101	0.21
	MP2	1.905[b]	1.480	116	103	–0.04
	SCF[c]	2.387	1.418	117	92	0.33
OMg_4/SO_2[d] step	SCF[c]	1.684	1.466	118	96	1.80
OCa_5/SO_2 surface	SCF	1.905[b]	1.441	114	109	1.23
	MP2	1.905[b]	1.484	115	112	1.02
	SCF[c]	1.800	1.447	115	110	1.30
CO_2	SCF		1.141	180		
	MP2		1.201	180		
	exptl		1.162	180		
OMg_5/CO_2 surface	SCF	1.376[b]	1.218	135		–0.77
	MP2	1.376[b]	1.255	134		–0.87
	SCF[c]	1.525	1.202	140		–0.62
OMg_4/CO_2[e] step	SCF[c]	1.398	1.224	134		1.60
OCa_5/CO_2 surface	SCF	1.376[b]	1.226	131		1.00
	MP2	1.376[b]	1.262	130		0.88
	SCF[c]	1.412	1.222	132		1.02
OMg_5(exp)/CO_2[f] surface	SCF	1.376[b]	1.225	135		0.48
	SCF[c]	1.397	1.224	136		0.49

[a] Results are given also for a model of MgO with an expanded lattice, OMg_5(exp). [b] Distance nonoptimized. [c] Full geometry optimization. [d] From ref 18. [e] From ref 19. [f] The MgO substrate ions and PC's are placed at the CaO lattice positions; see text.

The optimal geometry of the adsorbed molecule has been determined for each case by performing a full geometry optimization by means of analytical gradient techniques; the atoms of the substrate cluster have been fixed at their lattice positions. Surface relaxation effects have not been considered here since it has been shown previously[14b,18] that they do not affect to a significant extent the chemisorption properties. Sections of the potential energy surface, PES, have been generated by fixing the distance of the C or of the S atom of CO_2 and SO_2, respectively, from the surface and by varying the other geometrical parameters of the adsorbed molecule.

The importance of correlation effects on both the adsorption energies and geometries has been evaluated by performing second-order perturbation theory (MP2) calculations. For closed shell systems this is known to be a reasonable approach. Unfortunately, MP2 analytical gradients were not available, and a partial optimization has been performed pointwise by separately optimizing distances, bond angles, and dihedral angles, in this order. We found that the MP2 distances are considerably longer than the SCF ones, Table 1, while the changes in the bond angles are much less pronounced. The computed dissociation energies, D_e, are not too different in SCF and MP2, indicating that correlation effects do not change the picture of the bonding obtained within the one-electron approximation.

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This conclusion allows us to obtain a deeper insight into the nature of the bonding through the analysis of uncorrelated, SCF wave functions. We have performed a decomposition of the interaction energy, E_{int}, and of the dipole moment, μ, in order to establish the relative importance of the MO (M = Mg, Ca)/XO_2 (X = C, S) charge transfer mechanisms, and hence of the basicity of the MgO and CaO surfaces. This has been done according to the constrained space orbital variation, CSOV.[23-25] Denoting the two interacting fragments, i.e., the OM_5 cluster and the XO_2 adsorbate as A and B with SCF wave functions $\Psi_A{}^0$ and $\Psi_B{}^0$, respectively, the CSOV analysis starts with the zero-order wave function $\Psi_{AB}{}^0 = A_{AB}\Psi_A{}^0\Psi_B{}^0$, i.e., an antisymmetrized product of the fragments' occupied molecular orbitals. This step is often denoted as frozen orbital, and the corresponding energy is defined as $E_{int}(FO) = E_A{}^0 + E_B{}^0 - E_{AB}{}^0(FO)$. Here a positive value of E_{int} indicates the formation of a stable bond. The term frozen orbital indicates that no relaxation of the charge densities of the two fragments is allowed at this step. Thus, E_{int}(FO) accounts for the electrostatic and Pauli repulsion energies between the two frozen fragments placed near equilibrium distance.

In the following steps the wave function $\Psi_{AB}{}^0$ is relaxed by successively allowing the mixing of the occupied, Occ, and virtual, Virt, orbital spaces, such as $Occ_A/Virt_A$ or $Occ_B/Virt_B$. This accounts for the polarization of one fragment, due to the variation of the occupied MOs in its own space. The mixings $Occ_A/Virt_B$ and $Occ_B/Virt_A$, on the other hand, measure the extent of charge transfer from A to B and *vice versa*. The sum of ΔE_{int} for each mechanism should be as close as possible to the final, unconstrained, full SCF E_{int} value. When the sum of the various ΔE_{int} values is substantially different from the full SCF E_{int}, the individual mechanisms are strongly coupled and a different definition of variational spaces, or another cycle of variations, is required.[25] Further, the order of the constrained variations is not unique, and changes in the ΔE_{int} values may occur depending on the fragment which has been varied first. To account for this uncertainity, we have performed the CSOV in two different ways, varying the fragment A first followed by the fragment B, and *vice versa*. Here we report only one order of variations since the conclusions are the same when a reverse order is used.

The calculations were performed on IBM/RISC 6000 workstations with the HONDO8 program package[26] for the geometry optimization and the MP2 calculations and with the PSHONDO program package[27] for the CSOV analysis.

3. Results and Discussion

3.1. SO_2 Chemisorption. SO_2 is a bidentate molecule, with a permanent dipole moment, which can interact in several different ways with the surface of an ionic crystal like MgO or CaO. A detailed account of the bonding modes of SO_2 with the regular and defective, basic and acidic, sites of MgO has been reported elsewhere.[19] Here we consider only the case of adsorption at the $O_{5c}{}^{2-}$ sites and we compare MgO with CaO. This will provide a first basis for the discrimination of the different reactivities of the two surfaces.

The optimal geometrical parameters and the dissociation energies, D_e, computed at the SCF and MP2 levels are given in Table 1. The SO_2 molecule is adsorbed on both MgO and CaO with the S atom almost perpendicular to the O^{2-} anion and the two O atoms pointing toward the nearest surface cations, Figure 1. In this conformation the SO_2 molecule is almost parallel to the surface plane. The interaction, however, is quite different in MgO and CaO. On CaO SO_2 forms a stable surface sulfite with a D_e of more than 1 eV; on MgO it is only weakly bound, by 0.33 eV, Table 1. This latter value is further reduced to 0.20 eV if one takes into account the BSSE.[19] The MP2 D_e values for CaO/SO_2 and MgO/SO_2 are about 0.3 eV smaller than the SCF ones.

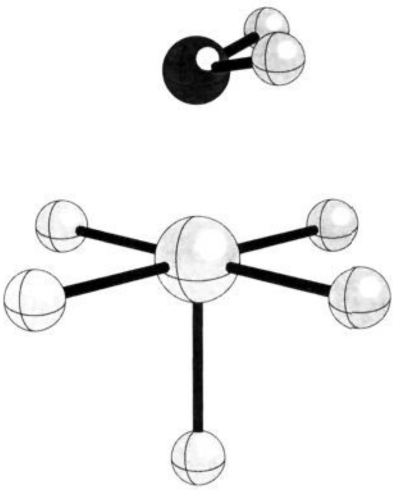

Figure 1. $[OM_5]^{8+}/SO_2$ cluster model (M = Mg or Ca) of the interaction of SO_2 with a five-coordinated $O_{5c}{}^{2-}$ site of MgO and CaO surfaces. The cluster is embedded in a large array of point charges (not shown) to reproduce the Madelung potential at the adsorption region.

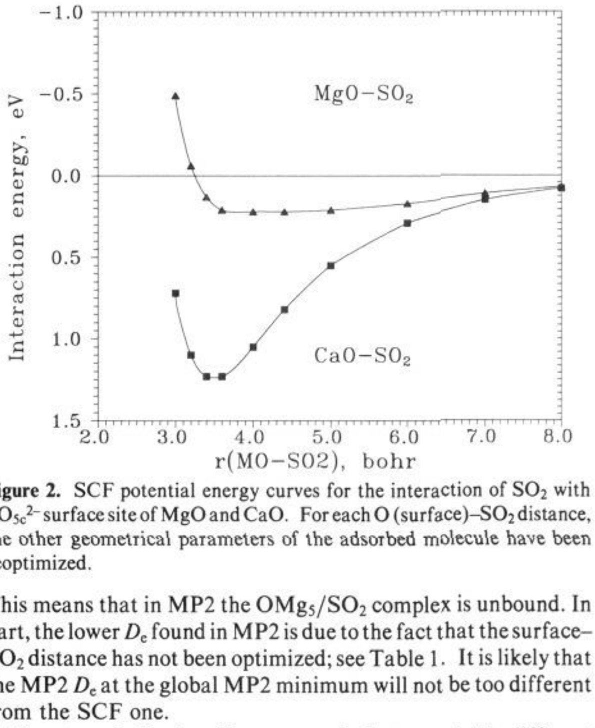

Figure 2. SCF potential energy curves for the interaction of SO_2 with a $O_{5c}{}^{2-}$ surface site of MgO and CaO. For each O (surface)–SO_2 distance, the other geometrical parameters of the adsorbed molecule have been reoptimized.

This means that in MP2 the OMg_5/SO_2 complex is unbound. In part, the lower D_e found in MP2 is due to the fact that the surface–SO_2 distance has not been optimized; see Table 1. It is likely that the MP2 D_e at the global MP2 minimum will not be too different from the SCF one.

Thus, two similar bonding geometries but completely different stabilities are found for SO_2 adsorbed on MgO and CaO. In both cases the molecule is slightly perturbed by the interaction with the substrate, as shown by the moderate elongation of the S–O bonds compared to free SO_2. In MgO, however, the system can be described as a weak complex, while in CaO a strong chemisorption bond is formed.

The different characters of the interaction can be further shown by a section of the PES obtained by computing the interaction energy at several fixed surface–SO_2 distances; for each distance the other geometrical parameters have been reoptimized. The potential energy curve for MgO/SO_2 is very flat, see Figure 2, suggesting a largely electrostatic interaction at long distances. The structure represented in Figure 1, however, is not a global minimum for SO_2 on MgO. In fact, an isolated SO_2 molecule prefers to bind at the MgO (100) surface with the two oxygen atoms bridging two adjacent Mg^{2+} acid sites.[19] In this conformation, the SO_2 is electrostatically bound to the surface by about 1/2 eV.[19] This means that on the regular, nondefective MgO

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Table 2. CSOV Analysis for SO_2 Adsorbed on OMg_5 and OCa_5 Cluster Models[a]

	OMg_5/SO_2		OCa_5/SO_2	
step	$E_{int}/\Delta E_{int}$	$\Delta\mu$[b]	$E_{int}/\Delta E_{int}$	$\Delta\mu$[b]
(1) frozen orbital	−4.02/−		−4.04/−	
(2) MO substrate polarization	−3.12/+0.90	−0.24	−3.19/+0.85	−0.21
(3) MO → SO_2 charge transfer	−1.09/+2.03	−1.00	−0.35/+2.84	−1.28
(4) SO_2 polarization	−0.22/+0.87	+0.05	+0.80/+1.15	+0.01
(5) SO_2 → MO charge transfer	+0.04/+0.26	+0.02	+0.99/+0.19	+0.01
(6) full SCF	+0.22/+0.18	−0.37	+1.18/+0.19	−0.38
ΔE(SO_2 activated − SO_2 free)	0.12		0.09	

[a] The analysis is performed for a geometry close to the minimum. [b] Only the z component of the dipole moment is reported. The x component is always smaller than $|0.2|$ au.

surface SO_2 is more strongly bound to the surface cations than to the oxide anions or, in other words, that the basicity of the O^{2-} ions is too low to form a stable surface sulfite. On the other hand, the chemistry of the MgO surface sites is completely different from that of the low-coordinated step sites where the interaction with SO_2 leads to the formation of a stable surface sulfite.[19]

This is an important observation because the surface O_{5c}^{2-} sites of CaO behave as the step O_{4c}^{2-} sites of MgO. In fact, SO_2 forms a stable surface sulfite, with a desorption energy of about 1.3 eV, on a surface O_{5c}^{2-} site of CaO. At large distances the interaction is electrostatic, but as the SO_2 molecule approaches the CaO surface a strong dative bond is formed, as it will be shown below.

The reason for the different reactivities of MgO and CaO can be better understood by decomposing E_{int} and the dipole moment μ according to the CSOV procedure described in section 2. The CSOV analysis has been performed for a geometry close to equilibrium. The SO_2 unit has been computed with the geometry of the adsorbed state. This geometry is slightly distorted compared to the free gas-phase molecule, Table 1, and the corresponding energy is about 0.1 eV higher than for the optimal gas-phase structure; see Table 2.

The first step of the CSOV, the frozen orbital (FO) step, is the sum of two terms: (a) the electrostatic attraction between the nonuniform electric field at the surface and the SO_2 charge distribution and (b) the Pauli repulsion due to the nonbonding overlap of the occupied orbitals. E_{int} at the FO step is repulsive, by about 4 eV, for both MgO/SO_2 and CaO/SO_2, Table 2, indicating that for this geometry the Pauli repulsion dominates over the electrostatic attraction. Next we have considered the substrate polarization, CSOV step 2, which is similar, about 0.9 eV, for the two clusters OMg_5 and OCa_5. This polarization reflects the change in the shape of the surface O^{2-} ion to reduce the initial FO repulsion. The following step, step 3, is the most important one for the purpose of this analysis. In fact, it measures the extent of the charge transfer from the oxide to adsorbed SO_2. The contribution of this mechanism to E_{int}, ΔE_{int}, is 2 eV in MgO and 2.8 eV in CaO. Thus, a larger charge transfer is found in CaO. This is further shown by the change in the vertical component of the dipole moment, $\Delta\mu_z$. The SO_2 molecule being oriented along the z axis, a negative $\Delta\mu_z$ indicates flow of charge from the substrate to the adsorbate. In both cases, $\Delta\mu_z$ is large, −1 au for MgO and −1.3 au for CaO, but consistently with the ΔE_{int} value, we found that CaO is a better "base" than MgO.

In the remaining steps 4 and 5 the polarization of the SO_2 molecule and the charge transfer from SO_2 to the substrate are measured. These contributions are similar in MgO and CaO. The SO_2 polarization gives a stabilization which is comparable to that of the OM_5 polarization, about 1 eV. Much smaller is the contribution of the charge transfer from SO_2 to the cluster. It is woth noting that since O^{2-} has its valence completely filled, the energy gain due to the $SO_2 \rightarrow OM_5$ charge transfer, about 0.2 eV, is, in large part, the result of the BSSE and does not reflect a real donation of charge from the molecule to the surface.

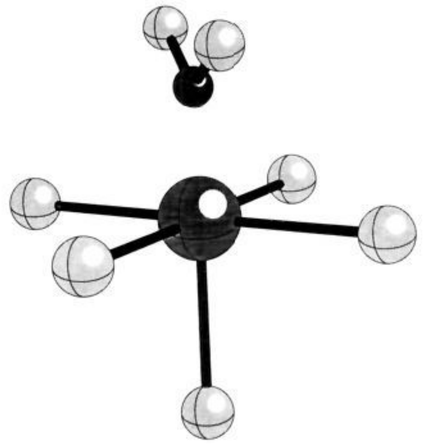

Figure 3. $[OM_5]^{8+}/CO_2$ cluster model (M = Mg or Ca) of the interaction of CO_2 with a five-coordinated O_{5c}^{2-} site of MgO and CaO surfaces. The cluster is embedded in a large array of point charges (not shown) to reproduce the Madelung potential at the adsorption region.

The total interaction energy obtained by summing up all the individual contributions described above is reasonably close to the E_{int} value obtained with no constraints at the full SCF step, Table 2. This is a sign that the decomposition is reliable since the individual bonding mechanisms are not strongly coupled to each other. At the geometry where the CSOV was performed, the full SCF E_{int} value is 0.22 eV for MgO and 1.18 eV for CaO. The difference in adsorption energies for the two surfaces, about 1 eV, comes almost entirely from the charge donation step. Thus, the CSOV provides a clear cut analysis of the origin of the different reactivities of MgO and CaO toward SO_2.

3.2. CO_2 Chemisorption. At a O_{5c}^{2-} site of MgO, CO_2 forms a surface complex where the O–C–O unit is considerably distorted from the gas-phase linear structure; in particular, the C–O distance is stretched by 0.06 Å and the O–C–O angle is reduced to 130°, see Figure 3 and Table 1. This surface complex, however, is unstable toward dissociation into OMg_5 and free CO_2: it corresponds to a local minimum on the PES.[18] The minimum is separated by a small barrier from the limit of dissociation into OMg_5 and CO_2; see Figure 4. This barrier is not an artifact of the one-electron approximation. In fact, MP2 calculations do also show the barrier. Previous studies have shown that the reactivity is totally different when one considers the low-coordinated step sites of MgO where the interaction with CO_2 leads to the direct formation of a stable surface carbonate with no barrier.[18]

The reaction of CO_2 with the O_{5c}^{2-} site of CaO has been considered for comparison. As already observed for SO_2 adsorption, we found a dramatic difference in the reactivity of CaO compared to MgO. In fact, on CaO CO_2 adsorbs strongly with a D_e of 1 eV (0.9 eV in MP2); see Table 1 and Figure 4. The geometrical parameters of the adsorbed CO_2, however, are not too different from those of the corresponding MgO/CO_2 surface complex, despite the completely different stabilities of the two species (the surface carbonate is unstable by 0.6 eV in MgO and is stable by 1 eV in CaO, Table 1). It is also very interesting to note that the shapes of the potential energy curves for the two oxides, Figure 4, are qualitatively similar, with a barrier which separates the minimum near the surface from the dissociation limit.

The origin of this double minimum in the curve becomes clear when, for each CaO–CO_2 distance z, one decomposes the interaction energy, $E_{int}(z)$, into the sum of two contributions.

Table 3. Optimal Geometrical Parameters for the Interaction of CO_2 with a Surface O_{5c}^{2-} Ion of MgO ($[OMg_5]^{8+}$) and CaO ($[OCa_5]^{8+}$) for Some Selected O(surface) – CO_2 Distances[a]

	OMg_5[b]		OCa_5		OMg_5(exp)[a]	
$r(O{-}CO_2)$ (Å)	r(CO) (Å)	α(OCO) (deg)	r(CO) (Å)	α(OCO) (deg)	r(CO) (Å)	α(OCO) (deg)
1.270	1.229	131	1.238	128	1.238	132
1.482	1.206	138	1.215	134	1.213	138
1.693	1.185	146	1.195	142	1.191	145
1.905	1.166	155	1.176	150	1.170	154
2.117	1.153	163	1.160	158	1.155	162
2.328			1.150	166	1.148	169
2.646	1.143	176	1.144	173	1.143	175
3.704	1.141	180	1.142	179	1.142	180

[a] Results are given also for a model of MgO with an expanded lattice, $[OMg_5(exp)]^{8+}$ (see text). [b] From ref 18.

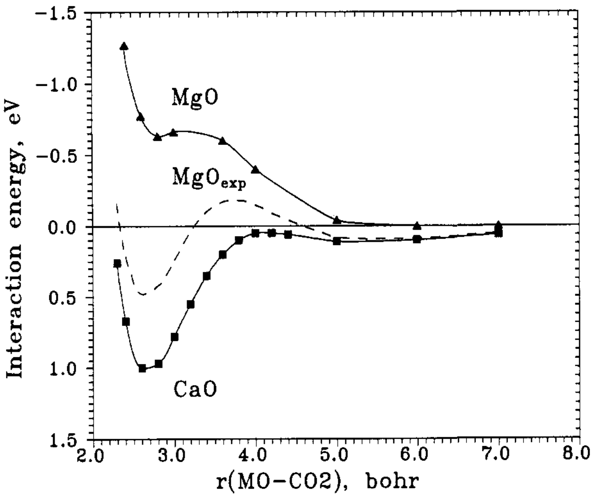

Figure 4. SCF potential energy curves for the interaction of CO_2 with a O_{5c}^{2-} surface site of MgO and CaO. For each O(surface)–SO_2 distance, the other geometrical parameters of the adsorbed molecule have been reoptimized. The dotted curve represents the interaction of the CO_2 molecule with an expanded MgO substrate cluster, in which the lattice constant was set equal to that of the CaO bulk crystal.

The first term is the energy necessary to "activate" the free CO_2 molecule, $E_{act}(z)$. This has been determined by computing the energy of a free CO_2 molecule with the same geometry which CO_2 assumes when it is adsorbed on the cluster for that particular distance z. The second term is the binding energy, $E_{bin}(z)$, between this "activated" CO_2 molecule and the surface. Thus,

$$E_{int}(z) = E_{act}(z) + E_{bin}(z)$$

Clearly the first term is purely repulsive, while the second term is attractive, at least when the surface–CO_2 distance is not too short. At very short distances in fact also the interaction between the "promoted" molecule and the surface is dominated by the Pauli repulsion. The three curves $E_{int}(z)$, $E_{act}(z)$, and $E_{bin}(z)$ are shown in Figure 5. The cost to bend and stretch the CO_2 molecule as in the surface CaO/CO_2 complex for $z \simeq z_e$ is about 3 eV. The energy gain for the interaction of this activated CO_2 molecule with the cluster is about 4 eV, and the total result is a net bonding of about 1 eV, Figure 5. In MgO the cost to bend and elongate the CO_2 molecule is very similar; the fact that the surface complex is unbound means that the interaction with the substrate is much weaker, as will be shown below.

Also the origin of the small barrier becomes clear from the analysis of the curves of Figure 5. At a surface–CO_2 distance of about 4 bohr, where the small barrier is found, the CO_2 molecule begins to bend significantly (the O–C–O angle becomes $\simeq 160°$ and smaller, Table 3). This bending has a high energetic cost, and the slope of the $E_{act}(z)$ curve has a sudden change, Figure 5. The cost for the bending is only partially recovered by the interaction with the substrate because the $E_{bin}(z)$ curve shows a smoother behavior in this region. The result is the appearance of a barrier around this particular surface–CO_2 distance.

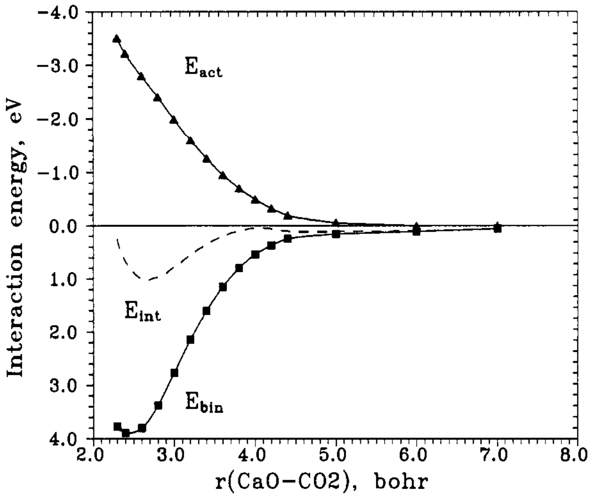

Figure 5. Decomposition of the SCF $[OCa_5]^{8+}/CO_2$ interaction energy curve, $E_{int}(z)$ (dotted line), into the sum of the energy required to activate the CO_2 molecule, $E_{act}(z)$, and the binding energy between the activated CO_2 molecule and the surface, $E_{bin}(z)$.

Table 4. CSOV Analysis for CO_2 Adsorbed on OMg_5 and OCa_5 Cluster Models[a]

	OMg_5/CO_2		OCa_5/CO_2	
step	$E_{int}/\Delta E_{int}$	$\Delta\mu$	$E_{int}/\Delta E_{int}$	$\Delta\mu$
(1) frozen orbital	-8.65/–		-7.75/–	
(2) MO substrate polarization	-6.25/+2.40	-0.52	-5.69/+2.06	-0.42
(3) MO → CO_2 charge transfer	-0.90/+5.35	-1.02	+0.95/+6.64	-1.28
(4) CO_2 polarization	+0.98/+1.88	-0.04	+3.23/+2.28	-0.13
(5) CO_2 → MO charge transfer	+1.30/+0.32	+0.07	+3.46/+0.23	+0.04
(6) full SCF	+1.59/+0.29	-0.30	+3.79/+0.33	-0.33
ΔE(CO_2 activated – CO_2 free)	2.35		2.77	

[a] The analysis is performed for a geometry close to the minimum.

The interaction of CO_2 with the MgO and CaO surfaces shows the same behavior described in the previous section for SO_2: while the O_{5c}^{2-} site of MgO is rather unreactive, strong chemisorbed sulfites and carbonates form at the corresponding site of CaO. Also in this case we can analyze the interaction by means of the CSOV analysis; see Table 4. At the FO step, the energy is repulsive by about 8 eV in both MgO and CaO. This strong repulsion is due to the fact that we used as starting points the cluster and the activated CO_2 molecule computed at the same geometry of the local minimum near the surface, Table 1. This promoted molecule has an energy which is 2.35 (MgO) and 2.77 (CaO) eV higher than free CO_2, Table 4. At the FO step the interaction between this deformed CO_2 molecule and the substrate cluster is highly repulsive. To reduce the initial repulsion, the O^{2-} on the surface polarizes, a mechanism which stabilizes the system by about 2 eV. The polarizations are not very different

Table 5. Madelung Potential at Various Sites of MgO and CaO Surfaces

		Madelung potential, eV	
site	Madelung constant[a]	MgO (r = 2.106 Å)	CaO (r = 2.399 Å)
O_{6c}^{2-} bulk	1.747	23.89	20.97
O_{5c}^{2-} surface	1.681	22.98	20.18
O_{4c}^{2-} step	1.591	21.76	19.10
O_{3c}^{2-} corner	1.344	18.38	16.13

[a] From ref 29.

in MgO and CaO, and are about twice as large as for SO_2, Table 2, because of the much larger initial repulsion in the CO_2 case. A very large stabilization occurs at the CSOV step 3 where charge transfer from the oxide to CO_2 is allowed. This step leads to an energy gain of 5.35 eV in MgO and 6.64 eV in CaO. Also the $\Delta\mu$ value is about 25% more negative in CaO than in MgO; see Table 4. Hence, the same picture emerges from the CSOV analysis of the OM_5/CO_2 and OM_5/SO_2 interactions: CaO is a better donor than MgO. More precisely, it is possible to estimate that CaO has a basic character which is about 25–30% larger than that of MgO.

The polarization of CO_2, the fourth step of the CSOV, contributes about 2 eV to the overall stabilization, and no other important bonding mechanism are found; see Table 4. The final, full SCF value for the interaction between the activated CO_2 molecule and the unreconstructed substrate cluster is 1.59 eV in MgO and 3.79 eV in CaO. In order to compute the D_e with respect to the free, unperturbed fragments, one must substract from this value the energetic cost to "promote" the CO_2 molecule, 2.35 eV in MgO and 2.77 eV in CaO. The result is a OMg_5/CO_2 surface complex which is unbound by about 0.8 eV and a OCa_5/CO_2 surface carbonate which is bound by about 1 eV. Once more, the CSOV shows that the different stabilities between the two chemisorbed species are, to a large extent, due to the different efficiencies of the charge donation mechanism in MgO and CaO.

3.3. Reasons for the Different Reactivities of MgO and CaO Surfaces. The previous discussion has shown unambiguously that the O_{5c}^{2-} sites of the MgO and CaO (100) surfaces exhibit very different chemical reactivities toward the adsorption of CO_2 and SO_2. Since the O^{2-} ion has been treated exactly in the same way in the two models, its different chemical behaviors must reflect a dramatic change in the influence of the surroundings when one goes from MgO to CaO. Both MgO and CaO bulk crystals, but also the corresponding (100) surfaces, are usually regarded as highly ionic, with a nominal charge of the ions not too different from ±2. Theoretical calculations performed at various levels of sophistication are consistent with the view of almost perfect, and not very different, ionicities of the two oxides.[15,16] The small deviations from ideal ionicity, in any case, are not large enough to justify the completely different chemical reactivities found in this study. Thus, the reason for this trend cannot be of chemical nature and must be looked for in the different electrostatic potentials at the two surfaces.

The bulk Mg–O distance is 2.106 Å, and the Madelung potential at the MgO surface is 22.9 eV, Table 5. The CaO lattice constant, 2.399 Å, is ≃ 14% longer, and the Madelung potential at a surface site decreases to 20.2 eV.[28,29] The O^{2-} ion is not stable in the gas phase and exists only in ionic crystals by the effect of the Madelung potential. Thus, a smaller value of the Madelung potential implies that the oxide anion is less stable on the CaO than on the MgO surface. The first consequence is that the electron cloud of the O_{5c}^{2-} anion in CaO is more spatially diffuse and can overlap more efficiently with the accepting orbitals of the incoming molecule, Table 6. In other words, the electrostatic potential felt by an adsorbed molecule is considerably more negative on a O_{5c}^{2-} site of CaO than on the same site of MgO; see Table 6. It is worth noting, however, that the value of the electrostatic potential is quite dependent on the cluster model used.[30]

Table 6. Electrostatic Potential, EP (eV), and Charge Density, CD (au), at Various Heights from the Surface Oxide Anion in OMg_5, OMg_5(exp), and OCa_5 Cluster Models of the Respective (100) Surfaces

	OMg_5		OMg_5(exp)		OCa_5	
z (Å)	EP	CD	EP	CD	EP	CD
2.0	−3.28	0.0398	−3.60	0.0382	−5.09	0.0417
2.5	−2.98	0.0142	−3.27	0.0134	−4.50	0.0157
3.0	−2.13	0.0054	−2.36	0.0052	−3.34	0.0064
3.5	−1.40	0.0021	−1.57	0.0020	−2.34	0.0027
4.0	−0.90	0.0008	−1.00	0.0008	−1.61	0.0011
5.0	−0.40	0.0001	−0.39	0.0001	−0.77	0.0002
7.5	−0.14	0	−0.06	0	−0.22	0
10.0	−0.12	0	−0.06	0	−0.14	0
100.0	−0.03	0	−0.03	0	−0.03	0

Another sign of the different basic properties of a surface O_{5c}^{2-} ion in MgO or CaO is the energy of the donor orbital, the cluster highest occupied molecular orbital, HOMO. This orbital, largely an O $2p_z$ orbital slightly mixed in with the 2s one, has the proper symmetry to interact with the acceptor orbitals of CO_2 and SO_2, and the bonding with these molecules can be simply viewed as a HOMO–LUMO interaction.[18,19] The HOMO lies at −11.0 eV in MgO and at −8.5 eV in CaO. The difference, 2.5 eV, is about the difference in the Madelung potential between the two surfaces, Table 5. Thus, charge can be donated to an adsorbed molecule at a lower energy cost in CaO than in MgO. This is exactly what has been found with the CSOV decomposition of the interaction energy between CO_2 and SO_2 and the two surfaces.

It is worth noting that the Madelung potential at a O_{5c}^{2-} site of the CaO (100) surface is intermediate between that of a step and of a corner site of MgO;[28,29] see Table 5. On this basis, the chemical reactivity of a regular surface site of CaO is expected to be closer to that of a defect, low-coordinated site than to that of the corresponding surface site of MgO. Indeed, the reactivity of the CO_2 and SO_2 molecules with these sites fully supports this view.[18,19]

The origin of the higher basicity and chemical reactivity of CaO is therefore of electrostatic and not of chemical nature. Given the very high ionicity of MgO and CaO in the last analysis, this is due to the different cation–anion distances in the two oxides or to the average coordination if different sites on the same surface are considered. To further check this conclusion, we have performed a computational experiment where the CO_2 molecule interacts with a "modified" MgO substrate. This is represented by a $[OMg_5]^{8+}$ cluster where all the distances, of both ions and PC's, are expanded to the CaO lattice separation. In this way we obtain a hybrid system where the Madelung potential created by the PC's is that of CaO, but the central O^{2-} ion is surrounded by Mg^{2+} neighbors placed at the CaO lattice positions. We call this new cluster $[OMg_5(exp)]^{8+}$ to indicate that an expanded lattice was used. We have computed a section of the PES in the same way as for CO_2 on MgO and CaO; see Figure 4. The new curve lies in between those of OMg_5/CO_2 and OCa_5/CO_2. On this expanded MgO substrate the CO_2 molecule is bound to the surface by about 0.5 eV; this adsorption minimum is separated from the dissociation limit by a small barrier as already found in MgO and CaO, Figure 4. The reactivity of the $[OMg_5(exp)]^{8+}$ cluster is thus intermediate between that of the two oxides because the position of the donor orbital and the electrostatic potential are intermediate between the two limit situations; see Table 6. This provides strong, compelling evidence of the importance of the Madelung potential for the basicity of the surface.

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The fact that the reactivity of the OMg_5(exp) cluster is not the same as that of the OCa_5 one, despite the fact that the ions and the PC's are in the same positions, suggests that another important factor which determines the chemical behavior of the oxide anion is the compression of the ions or, in other words, the proper representation of the Pauli repulsion at the adsorption site. The Mg^{2+} ions are considerably smaller than the Ca^{2+} ones. Thus, by replacing Ca^{2+} with Mg^{2+}, the repulsion with the oxide anion is strongly reduced. The O^{2-} ion polarizes toward the Mg^{2+} neighbors so that the charge density outside the surface, along the *z* direction, decreases; see Table 6. Consequently, the reactivity toward an adsorbed species is reduced with respect to the model of the real CaO surface.

4. Conclusions

We have presented the results of *ab initio* cluster model calculations on the interaction of SO_2 and CO_2 with the oxide anion sites of the regular, dehydroxylated, (100) surfaces of MgO and CaO. The five-coordinated $O_{5c}{}^{2-}$ sites of MgO and CaO exhibit very different chemical reactivities. In particular, the $O_{5c}{}^{2-}$ site of MgO shows a very low tendency to donate charge to an adsorbed CO_2 or SO_2 probe molecule and thus to act as a base. The interaction is weak and does not imply the formation of a stable chemisorbed species. The reactivity of the same site of the CaO surface is totally different and is reminiscent of that of the low-coordinated defect sites of MgO.[18] The $O_{5c}{}^{2-}$ site of CaO reacts with both SO_2 and CO_2 to form sulfite and carbonate species, respectively. These surface complexes are strongly bound to the surface, and the bond can be viewed as a HOMO–LUMO interaction where electronic charge flows from the substrate orbitals to the empty orbitals of the adsorbate. The analysis of the bonding mechanisms shows unambiguously that a different charge donation occurs at the two surfaces: the donor ability, or basicity, of CaO is found to be about 25% larger than that of MgO.

The reason for these different basicities and reactivities is not of chemical nature but can rather be ascribed to the different electrostatic (Madelung) potentials at the two surfaces. The $O_{5c}{}^{2-}$ ion is less stable on the CaO than on the MgO surface because in the former case the cation–anion distances are larger and the Madelung potential is smaller. This results in a more diffuse charge distribution around the oxygen and in a lower cost for the charge transfer from the donor orbital of the surface anion.

Since the Madelung potential further decreases in SrO and BaO surfaces, it is possible to predict an increasing basicity along the series MgO < CaO < SrO < BaO. This is also the trend experimentally observed by Tanabe and Fukuda studying the catalytic activity of these oxides.[4] The novel aspect of the present work is that this trend can be easily predicted and explained by simple electrostatic arguments, with no need to make use of ambiguous explanations like the partial charge on the oxygen atom, a quantity very difficult to determine both theoretically and experimentally.[15] The extent and even the trend in charge separation of alkaline-earth-metal oxides is a controversial subject. Recent theoretical studies indicate a very small but increasing covalency as one goes from MgO to BaO.[15] This would correspond to a higher charge density around the oxygen atom in MgO than in BaO, in contrast to the experimental basicity trend. On the other hand, the calculations[15] show that the deviations from the ideal ionicity are small, less than 10%, so that several electronic properties can be simply explained in terms of electrostatic models.[9,31] In other words, the electrostatic contributions are much more important than the chemical ones in determining the chemistry of these ionic surfaces.

Another important value of the present model is that it can be easily applied to other oxide sites of an ionic surface like kinks, steps, edges, corners, etc. by simply evaluating the Madelung potential of each site. To a first approximation, it is possible to infer that to a lower value of the Madelung potential corresponds a higher basicity of the surface site.

Finally, we have shown that an expansion of the MgO lattice, and hence a decrease of the Madelung potential, leads to an enhanced basicity and reactivity of the surface O^{2-} site. This may be an important observation in the context of the pseudomorphic growth of oxide thin films on metal surfaces. The deposition of oxide thin films on substrates with slightly larger lattice constants may result in a stretched oxide layer with an acid–base character different from that of a crystallographic face of the bulk crystal.

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