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Periodic DFT study of acidic trace atmospheric gas molecule adsorption on Ca and Fe doped MgO (001) surface basic sites

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Abstract

The electronic properties of undoped and Ca or Fe doped MgO (001) surfaces, as well as their propensity towards atmospheric acidic gas (CO₂, SO₂ and NO₂) uptake was investigated with an emphasis on gas adsorption on the basic MgO oxygen surface sites, O^{surf}, using periodic Density Functional Theory (DFT) calculations. Adsorption energy calculations show that MgO doping will provide stronger interactions of the adsorbate with the O^{surf} sites than the undoped MgO for a given adsorbate molecule. Charge transfer from the iron atom in Fe doped MgO (001) to NO₂ was shown to increase the binding interaction between adsorbate by an order of magnitude, when compared to that of undoped and Ca doped MgO (001) surfaces. Secondary binding interactions of adsorbate oxygen atoms were observed with surface magnesium sites at distances close to those of the Mg–O bond within the crystal. These interactions may serve as a preliminary step for adsorption and facilitate further adsorbate transformations into other binding configurations. Impacts on global atmospheric chemistry are discussed as these adsorption phenomena can affect atmospheric gas budgets via altered partitioning and retention on mineral aerosol surfaces.

Introduction

MgO is an important compound in the environment and is found in the form of mineral periclase with measured concentrations in the continental crust of ~3.7%.¹ MgO is also a typical atmospheric mineral dust aerosol component.² Mineral aerosol is produced over deserts by natural processes³ and, once airborne, can be transported over long distances.⁴ In addition, mineral dust can originate from anthropogenic sources with small ambient particulate matter levels higher in large city environments.⁵ As natural minerals are rarely pure in the environment, naturally-occurring MgO can have varying concentrations of other elements substituted into its crystalline lattice with Ca and Fe reported as main dopants with concentrations of Fe as high as 5–10 wt%.^{6,7} Currently, the reactivity of doped mineral dust and their components, such as Ca and Fe doped MgO, towards atmospheric gas surface uptake is not well understood.

It is well known that mineral aerosol particles will act as reactive sinks for trace atmospheric gases via heterogeneous uptake. Thus, surface reactions on mineral dust particles can affect atmospheric chemistry and gas phase budgets via reactions on aerosol particles.⁸ Additionally, alterations to mineral dust surface composition upon gas/surface uptake can change the reactive nature and the radiative impacts of the aerosol particles on climate.⁹ Furthermore, uptake of trace atmospheric acidic gases, such as CO₂, SO₂ and NO₂, on basic

mineral surface sites can reduce the acidity of rain as well as direct climate effects due to removal of important greenhouse gases from the atmosphere, of which CO₂ is the most significant greenhouse gas¹⁰ and is considered in the current study.

Adsorption of CO₂, SO₂ and NO₂ on mineral dust components has been thoroughly investigated using laboratory^{11,12} and theoretical methods^{13,14} or combination thereof. Additionally, adsorption properties and speciation of CO₂,^{15–20} SO₂^{15,18,19,21–23} and NO₂^{19,24,25} on undoped MgO has been investigated extensively both experimentally and theoretically, providing a foundation for further investigations on more complex and environmentally relevant, doped MgO systems. Fundamentally, MgO surfaces possess both acidic and basic surface sites. Acidic gas adsorption on MgO, however, will predominantly be determined by the interaction of the acidic adsorbate atoms with basic MgO (001) surface sites.²⁶ Due to the purely ionic Mg-O bond character, electron rich surface oxygen sites, O^{surf}, will act as strong bases by donating electrons to the adsorbing molecule, whereas electron deficient magnesium sites, Mg^{surf}, will act as weak electron acceptors.²⁷ Hence, to a first approximation, O^{surf} can be considered as the most important reactive site of the MgO surface responsible for the binding of acidic atmospheric gases via electron pair donation. Other factors that can affect MgO surface acidity/basicity are adsorbed hydroxyl groups resulting from water dissociation at the surface.^{28,29} These surface hydroxyls are amphoteric in nature. For example, surface hydroxyls will act as electron donors via nucleophilic attack on an acidic CO₂ molecule. Furthermore, surface hydroxyl sites, depending on their location on steps, corners and kinks, will have different coordination numbers, thermal stabilities and, consequentially, reactivities.³⁰ Collectively, acidic gas adsorption on natural MgO containing surfaces will be complex due to the variety of reactive surface sites available on the MgO surface, the degree and nature of hydroxylation, the presence of natural dopants and the coordination number of surface sites. Thus, systematic computational studies are necessary for elucidating the various mechanisms of surface adsorption.

In this work we focus on the effects of doping the MgO surface using common naturally-occurring dopants, such as Ca and Fe, on the propensity of the MgO surface to reactive uptake of three of the most common acidic gases found in the atmosphere, including CO₂, SO₂ and NO₂. It has already been shown that dopants change MgO surface properties.³¹ A typical example was reported by Orlando *et al.*³² where Li doping of MgO resulted in the formation of a very reactive O[−] species in the surface layer that exhibited a relatively small energy barrier (18 kcal/mol) for methane deprotonation. This type of enhanced reactivity due to doping within the mineral surface layer is expected to occur in natural environments where MgO is present as an atmospheric aerosol component. The resulting doped MgO surfaces can affect adsorption properties of acidic gases, such as CO₂, SO₂ and NO₂, thus altering their removal rate from the atmosphere. With this in mind, we performed periodic density functional theory (DFT) calculations to elucidate initial adsorption mechanisms of acidic gases on Ca and Fe doped MgO surfaces.

Theoretical methods

The periodic *ab initio* solid state program suite CRYSTAL'09 was used in all calculations.^{33,34} This program uses functions localized at atoms as the basis for expansion of the crystalline orbitals via linear combination of atomic orbitals (LCAO). Basis sets used for Mg and O are based on previous work³⁵ with an additional d-exponent of 0.5 added to O, whereas those for Ca, Fe, C, S and N were obtained from the University of Torino CRYSTAL basis set library³⁶ (accessed Fall 2011). Namely, Ca (86-511d21G),³⁷ Fe (86-411d41G),³⁸ C (6-31d1G),³⁹ S (86-311d1G),⁴⁰ and N (6-31d1G)³⁹ all electron basis sets were used.

Spin unrestricted Hartree-Fock formalism and hybrid UB3LYP^{41,42} Hamiltonian was used in all calculations. B3LYP functional has been shown to reproduce well MgO properties, including bandgap and vibrational frequencies.⁴³ The DFT exchange–correlation contribution is evaluated by numerical integration over the unit cell volume. Radial and angular points of the grid were generated through Gauss–Legendre radial quadrature and Lebedev two-dimensional angular point distributions with a pruned grid of 75 radial and 974 angular points. The level of accuracy in evaluating the Coulomb and Hartree–Fock exchange series was controlled by five parameters,³³ and values of 7, 7, 7, 7, 14 were used. The reciprocal space integration was performed by sampling the Brillouin zone with the 6×6×1 Pack–Monkhorst net.⁴⁴ The Fermi energy (E_F) was defined as the top of the valence band, while the bandgap was defined as the difference between the bottom of the conduction band and the top of the valence band. In all figures, E_F was aligned with zero x-axis value.

By far the most stable MgO surface plane is (001) with 1.16 J/m² and the closest higher index plane higher in surface energy by 0.15 J/m².⁴⁵ As such, the MgO (001) surface was modeled as an infinite slab with periodicity in two dimensions as a reactive acidic gas adsorption surface. The initial structure was built using experimental crystallographic MgO (periclase) data with a 4.21 Å cell parameter and a 2.11 Å Mg–O bond length.⁴⁶ A supercell was constructed with dimensions of 8.93×8.93 Å having 9 Mg–O units in every layer and was propagated parallel to the (001) plane. Dopant position was selected in the second, subsurface layer, similar to Li doped MgO model used earlier.³² More importantly, doped MgO modeled here and present as atmospheric aerosol component originates from the Earth's crust under high temperature-low oxygen pressure conditions. Under these conditions, intrinsic (self-diffusion)⁴⁷ or extrinsic (counterdiffusion)⁴⁸ diffusion mechanisms, facilitated by the structural oxygen defects, proceed with the resulting dopant penetration depth in the order of microns⁴⁷. Any long range interactions between the dopant atom and the adsorbing molecule will vanish quickly with dopant localization depth while dopant atom in the surface layer will have almost the same properties towards adsorbing molecule as its pure oxide. Thus of interest in this work was dopant-surface oxygen-adsorbate interaction which would possess properties different from that of bulk MgO or dopant oxide. Structure optimizations were performed using analytical energy gradients with respect to atomic coordinates within a quasi-Newton scheme combined with the Broyden–Fletcher–Goldfarb–Shanno scheme for Hessian updating.^{49–52} Convergence was checked on both gradient components and nuclear displacements and was signaled when RMS gradient was 0.0003 Hartree/Bohr and RMS displacement was 0.0012 Bohr. Symmetry, where available, was fully exploited in all calculations.

The adsorption energies of the adsorbed molecules on undoped and Ca or Fe doped MgO (001) surfaces were calculated as the energy difference between the total energies of the MgO (001) surface with molecule adsorbed and those of the molecule in gas geometry and unreconstructed MgO (001) surface themselves, such that, $E_{\text{adsorption}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{molecule}}$. Adsorption energies were basis set superposition error (BSSE)⁵³ corrected by removing nuclear charge and the shell electron charges of the selected atoms but leaving the basis set at the atomic position.

Results and Discussion

Structural and electronic properties of undoped and Ca or Fe doped MgO (001) surfaces

Atomic position optimization was performed using a 5 layer MgO supercell propagated parallel to (001) plane. Figure 1 shows the representative computed structure with the view oriented perpendicular to the surface. A box outlines the region of interest where Mg substitution with Ca and Fe and gas adsorption was modeled. As a result of the optimization, O^{surf} atoms underwent almost negligible outward relaxation of 0.01 Å, whereas Mg^{surf}

atoms relaxed inwards by 0.05 Å with an Mg-O bond length of 2.06 Å (Figure 1b). The Mg-O bond length between the 2nd and 3rd layers remained 2.11 Å, whereas the O-Mg bond length was slightly shorter at 2.10 Å. The total surface relaxation energy during the atomic position optimization per 90 atom supercell was -18.01 kcal/mol. Lateral Mg-O bond lengths, e.g. those parallel to (001) plane, remained essentially unchanged, close to 2.11 Å. From this perspective, bulk-to-surface relaxation did not perturb the symmetry of the MgO₆¹⁰⁻ coordination unit with the Mg atom situated in the 2nd layer maintaining an octahedral environment. The calculated total Mulliken charges were 9.89, 9.92, 10.10 and 10.09 e⁻ for O^{surf}, O^{bulk}, Mg^{surf} and Mg^{bulk}, respectively, which can be used for comparison with gas adsorbed structures. The total Mg-O bond population overlap between the atoms in the 1st layer, as well as those in the 1st and 2nd layers was 0.01 e⁻ indicating ionic bonding.

Substitution of the 2nd layer Mg atom with Ca (Figure 1c) resulted in the elongation of all metal-oxygen bonds in the vicinity of the Ca atom. Equatorial Ca-O bonds increased from 2.11 Å in MgO to 2.21 Å in the Ca doped MgO. Even further distortion was observed in the axial directions with the Ca-O bond length between 1st and 2nd layer of 2.28 Å and that between 2nd and 3rd layers of 2.24 Å. Although these Ca-O bond lengths are much shorter than those in CaO (lime) at 2.41 Å,⁵⁴ they introduce partial stress into the doped MgO structure. This can be attributed to the different ionic radii of Mg²⁺ and Ca²⁺ atoms (86 and 114 pm, respectively).⁵⁵ The Ca atom, while doped in MgO, can be considered to have a distorted octahedral coordination with axial Ca-O at equivalent bond lengths. More importantly, upon doping the MgO surface with Ca, the O^{surf} site coordinated to the Ca atom (O5 in Figure 1c), changes its electronic properties to accommodate the longer Ca-O bond and relaxes outwards. The calculated total Mulliken charge was 9.82 e⁻, lower than that of other oxygen atoms in the 1st layer (9.89 e⁻) and the undoped MgO. Finally, the O^{surf} atom (O5 in Figure 1) coordinated to Ca has larger displacement, ~0.16 Å higher in the z-axis, above the other (001) surface oxygen atoms in the MgO (001) surface relative to the undoped MgO. These results collectively indicate that the reduced electron charge and the “enhanced” sterics will make the O^{surf} atom react differently with respect to gaseous uptake relative to the O^{surf} atom in the undoped MgO surface.

Upon substitution of an Mg for Fe in the 2nd layer and optimization of atomic positions, the octahedral coordination around the dopant atom was altered. The axial Fe-O bond lengths changed very little from 2.11 Å in the undoped MgO to 2.11 and 2.12 Å with respect to O^{surf} and O^{bulk} in the Fe doped MgO. However, equatorial bonds elongated to 2.15 Å. The total Mulliken charge on Fe1 atom was 24.22 e⁻ effectively showing a Fe²⁺ electron configuration. The O5 atom was situated slightly higher than the rest of O^{surf} atoms by 0.04 Å relative to the undoped MgO surface. Due to the effective Fe²⁺ configuration, the Fe1 atom had 3.74 unpaired electrons with the partial electron spin donated to the surrounding oxygen atoms of ~0.04 e⁻.

Total, difference with respect to the superposition of ionic densities, and spin electron charge density maps were plotted (Figure 2) to better understand the observed unpaired electron localization in the Fe doped MgO. Unpaired electrons in Fe doped MgO were mostly localized on Fe1 atoms with some density donated to the octahedrally coordinated oxygen atoms. Importantly, the O^{surf} atoms in the Fe doped MgO surface possess some spin density, thus potentially making it available to an adsorbing molecule. Difference maps with respect to the superposition of ionic densities (Figure 2, right) show the basicity of the O^{surf} atoms with an increased electron density extending into the surface due to the absence of counterbalancing attraction by the Mg atom, absent above O^{surf}. Additional electron polarization between Ca, Fe and equatorial oxygen atoms can be observed with a very distinct change in the region between O^{surf} and Fe atoms. The latter shows that substitutional doping in the 2nd layer can profoundly affect electronic properties of the O^{surf}.

Further electronic structure information can be obtained from the density of state (DOS) plots shown in Figure 3. The UB3LYP calculated bandgap for MgO in this work was 10.3 V, larger than the experimentally-determined value of 7.81.⁵⁶ This overestimation is due to the incomplete Gaussian basis set used in this work to avoid linear dependencies. Nevertheless, the hybrid functional describes bandgap related properties much better than Hartree-Fock or pure functionals alone and qualitative description is provided here.⁵⁷ The MgO valence band is primarily comprised from O2p and the conduction band is due to the mixing of empty Mg and O states. With Ca atom doping, a very small change is introduced into the valence band composition and the conduction band is primarily the combination of Ca4s and Ca3d states. It is worth noting that the bottom of the conduction band is now a sharp band from the Ca atom. Thus, the nature of charge acceptance from the adsorbing gas molecule would change.

A more complicated electronic structure emerges from Fe doping of the MgO (001) surface as inferred from the atomic DOS plot shown in Figure 3c. The nature of the valence band is altered due to the defect states in the bandgap localized on Fe and neighboring O atoms. Band energy at the Fermi level for Fe doped MgO is due to the mixing of O and Fe states with several empty bands situated 4–6 eV above it. Contributions to Fe DOS from 3d-orbitals are shown in Figure 3d with Mulliken AO populations tabulated in Table 1. It can be seen that the state at the Fermi level is due to the beta spin x^2-y^2 Fe 3d-orbitals. These orbitals point towards the nearest oxygen neighbors thus maximizing electron-nuclei attraction. Thus the Fermi level is due to the electrons in the axial Fe-O bonds. From Table 1 it can also be seen that the x^2-y^2 subshell is doubly populated. While Mg atom is octahedrally coordinated in bulk undoped MgO, presence of the surface causes symmetry to be decreased and thus the $t_{2g}-e_g$ degeneracy is broken. It can be seen from earlier discussion and Figure 1d, the Fe coordination symmetry is now reduced to C_{4v} , in agreement with equal 2.15 Å equatorial bond lengths. In that case, Fe 3d xy , yz and xz (t_{2g}) orbitals split in energy with xz and yz still remaining degenerate as can be seen in Figure 3d.

Adsorption of CO₂, SO₂ and NO₂ on undoped and Ca and Fe doped MgO (001) surfaces

CO₂ adsorbed on undoped and Ca or Fe doped MgO (001) surfaces are shown in Figure 4 and the corresponding bond lengths, total Mulliken population, bond overlap population and the charge and spin density parameters are tabulated and reported in Table 2. Only a representative section of the slab pertaining to the adsorbed molecule is shown for clarity. From Figure 4, we find that CO₂ adsorbs via electron donation from the surface basic site, O^{surf}, to form an adsorbed monodentate-like carbonate structure. This adsorption mechanism involves electron density donation to the CO₂ $2\pi_u$ orbital with its components $6a_1$ molecular orbital (out of plane bending) becoming lower and energy.⁵⁸ The geometry of the adsorbed monodentate-like is similar in all three cases with a C1-O5 bond length of 1.44, 1.42 and 1.43 Å for undoped, Ca and Fe doped MgO, respectively. The electron density donation from the O5 atom to C1 in Figure 4 can be also seen in Table 2, where the total Mulliken population on the O5 atom is $\sim 9.34 e^-$. This value is much lower relative to the case with no adsorbed CO₂ ($\sim 9.86 e^-$). Hence, $\sim 0.5 e^-$ is being donated to the adsorbing CO₂ molecule to form a bond. This electron donation has a profound effect on the local coordination of the O5 atom. In nearly all three adsorbed CO₂ cases, the Mg-O5 bond lengths increase from 0.10 to 0.15 Å due to the decrease in charge difference between the atoms involved in the Mg-O5 bond. Population overlap of Mg-O5 is zero still showing purely ionic bonding character. In general, C1s total Mulliken population remains almost the same ($\sim 5.20 e^-$) in CO₂ adsorbed on undoped and Ca or Fe doped MgO (001) surfaces. For the Fe doped MgO, the total Mulliken population on Fe ($24.21 e^-$) and the number of unpaired electrons ($3.73 e^-$) remain approximately the same relative to the surface without adsorbed CO₂. The elongation of Fe1-O5 bond from 2.11 to 2.28 Å upon CO₂ adsorption, as well as change of

two equatorial bond lengths from 2.15 to 2.08 Å is an evidence of Jahn-Teller distortion and the profound effect of the adsorbing molecule on the local structure, as well as the electronic properties of the Fe doped MgO. Here x^2-y^2 Fe 3d-orbital becomes only half-occupied with the other electron now shared between xz and yz .

Adsorption energies of adsorbed CO₂ were calculated to evaluate doping effects on the adsorption strength between the MgO surface slab and the CO₂ molecule. Results are reported for CO₂, SO₂ and NO₂ adsorption in Table 3, including results for individual total energies of the surface models with adsorbates. It can be seen that the BSSE corrected adsorption energy, $E_{\text{adsorption}}$, for CO₂ decreases by 5.81 and 3.25 kcal/mol from undoped to Ca and Fe doped MgO with -8.77, -14.58 and -12.02 kcal/mol, respectively, hence showing a lower calculated adsorption energy (stronger adsorption) of CO₂ on Ca and Fe doped MgO than in undoped case. As an internal test, $E_{\text{adsorption}}$ was also calculated using larger basis sets on all atoms, including two additional d-exponents on Mg, and the calculated $E_{\text{adsorption}}$ was found to increase in magnitude by ~4 kcal/mol (weaker interaction) but the difference of ~5 kcal/mol between CO₂ adsorbed on MgO and that of Ca doped MgO was still maintained. Recent reported calculated adsorption energies of CO₂ on MgO (001) terrace ranged from 3.1 kcal/mol using cluster type¹⁷ to -3 kcal/mol using GGA plane wave with PW91 functional,⁵⁹ showing a weak attractive or repulsive coordination due to the lower basicity of highly coordinated terrace site⁶⁰ and in agreement with values reported in early work.¹⁸ Thus, the CO₂ binding interaction with the basic O^{surf} sites in Ca and Fe doped MgO is enhanced relative to the undoped MgO surface. However, the total energy change in the CO₂ configuration upon adsorption is small (~0.6 kcal) in all three cases, as well as the difference in C1-O5 bond length (~1.43 Å) between the three models. This result rules out the possibility that the stronger interaction energy between adsorbed CO₂ and the undoped, Ca and Fe doped MgO (001) surface is due to adsorbate rearrangement itself. Accordingly, the next probable largest contributor to the adsorption energy could be the rearrangement of the surface slab, particularly in the proximity of the O5 atom. However, this is not the case since the total energy difference between the optimized MgO (001) supercells (shown in Figure 1) and those optimized with CO₂ adsorbed (but adsorbate removed in single point calculations) was found to be very close at -25.08, -23.29 and -25.82 kcal/mol for undoped, Ca and Fe doped MgO (001) supercells, respectively, e.g. the difference was much smaller than that between the calculated adsorption energies.

The last probable contributor to the increase in interaction energy could be due to polarization effects upon doping. To assess this effect, we plotted the total electron density maps and those computed as a difference between the MgO (001) surface with CO₂ adsorbed and their respective components, adsorbed CO₂ and MgO (001) in the same atomic coordinates. These maps are shown in Figure 5, left and right, respectively. The total energy maps show adsorbed CO₂ forming a carbonate ion, CO₃²⁻, on the surface. Additionally, a small electron density overlap between CO₂ oxygen atoms and Mg^{surf} can be seen which could further stabilize the adsorbed molecule. Indeed, O-Mg^{surf} bond lengths of 2.16 to 2.20 Å can be observed as a secondary interaction between CO₂ and the MgO (001) surface in Figure 4. This effectively shows polydentate bridging binding configuration, similar to previously reported of CO₂ in various organometallic compounds.⁶¹ Most interestingly, the electron density difference maps (Figure 5, right) show clear polarization of the electrons towards the adsorbing CO₂ molecule, with negative density (less electrons) situated below the O5 atom in the undoped MgO (001) surface. In Ca and Fe doped electron density difference maps, there is additional polarization between the dopant atom and O5, also including axial oxygen atoms surrounding the dopant atom. We believe that this additional electron polarization is responsible for the ~ 5 kcal/mol increase in the CO₂ interaction energy with the Ca and Fe doped MgO (001) relative to the undoped MgO case.

Figure 6 shows the optimized structures of adsorbed SO₂ on undoped and Ca or Fe doped MgO (001) surfaces. The corresponding bond lengths and the charge and spin density parameters are reported in Table 2. SO₂ adsorption on MgO basic sites proceeds via O^{surf} (O5) electron density donation to the S1 atom, thus forming an adsorbed sulfite species. This is in agreement with previous experimental data⁶² and confirmed by the total Mulliken population analysis reported in Table 2 where it can be seen that O5 possesses ~9.30 e⁻ in all three cases. This result is very similar to that of CO₂ adsorption. Bond lengths in the adsorbed SO₂ molecule are 1.56 Å while those of the O5-S1 bond are ~1.84 Å. Thus, in contrast to CO₂ adsorption, adsorbed SO₂ does not form a planar complex perpendicular to the MgO surface making the molecular geometry of the adsorbed SO₂ trigonal pyramidal. Calculated adsorption energy for SO₂ on O^{surf} atoms was -17.06, -24.60 and -19.91 kcal for undoped, Ca and Fe doped Mg (001) (Table 3, E_{adsorption} column). In addition, a secondary interaction between Mg3-O6 and Mg4-O7 could be inferred from the short ~2.09 Å bond length between these atoms. This bond length is within the order of Mg-O bond in the crystal (2.11 Å), thus drawing some electron density towards O6 and O7 atoms and weakening O5-Mg3 and O5-Mg4 bonds, increasing their lengths to 2.38 Å. As shown in Table 3, the calculated adsorption energy was larger for Ca and Fe doped MgO relative to undoped MgO, similar in the energy ordering to the case of CO₂ adsorption. These values are consistent with the literature reported of -16.8 kcal/mol¹⁹ indicating SO₂ adsorption stronger than that of CO₂ primarily due to the longer S-O bonds in SO₂ and resulting secondary acid-base interaction with surface Mg atoms.⁵⁹

NO₂ coordinated to undoped, Ca and Fe doped MgO (001) surfaces was modeled and the resulting structures are shown in Figure 7. The corresponding bond lengths and charge and spin density parameters are reported in Table 2. NO₂ adsorption on MgO (001) O^{surf} sites should yield surface nitrate species. This interaction was reported to have a low adsorption energy of -10.2 kcal/mol and a large surface-adsorbate separation of 2.62 Å using PW91 functional.²⁴ Our calculated value of -0.19 kcal/mol reported in Table 3 shows no interaction between the NO₂ molecule and the surface, consistent with the rich NO₂ coordination chemistry reported earlier.⁵⁹ The magnitude of this interaction can be described as physisorption, well in agreement with experimental observations where adsorbed NO₂ was only transformed into nitrate at elevated temperatures.⁶³ This is also substantiated by the total Mulliken population analysis reported in Table 2 where NO₂ adsorbed on the undoped and Ca doped MgO surfaces result in a smaller electron density transferred from O5 to the NO₂ molecule relative to the case in which CO₂ and SO₂ are the adsorbates. Secondary interactions of O6 and O7 atoms with the surface Mg3 and Mg4 were observed with the bond length of 2.38 Å in all cases and adsorption energy of -2.67 kcal/mol in Ca doped MgO. The adsorption energy determined for NO₂ on the Ca doped MgO surface is higher by ~2.5 kcal/mol than for NO₂ adsorbed on the undoped MgO surface.

NO₂ adsorption on the Fe doped MgO (001) surface was found to be dramatically different from adsorption on the undoped and Ca doped MgO (001) surfaces. The adsorption interaction for NO₂ on the Fe doped MgO surface was also very different from interactions theoretically observed for CO₂ and SO₂ on the same surface. As shown in Figure 7, upon NO₂ adsorption on Fe doped MgO, a strong inward relaxation of the O5 atom was observed with the Fe1-O5 bond length at 1.89 Å. This bond length is much smaller than in the case without the NO₂ molecule interacting with the surface (2.18 Å). All equatorial Fe-O bonds also became shorter and very similar in length (2.07 to 2.10 Å). The total Mulliken charge of the O5 atom became 9.70 e⁻ upon accounting for NO₂/surface interactions. This value is larger than that for CO₂ and SO₂ adsorption on the same surface and much closer to that of the Fe doped MgO (001) surface (9.86 e⁻) with no molecules adsorbed. This result possibly indicates that electron density is not transferred from the O5 to N1 to facilitate a bonding interaction or that the O5 acted as an electron density transfer atom from Fe1 to N1. The

most prominent change happens to the Fe1 atom and manifests itself as the increase in total spin from $3.72 e^-$ to $4.29 e^-$ and the total Mulliken population decreasing from $24.21 e^-$ to $23.77 e^-$ (Table 2). This, concurrently with the increase in total Mulliken charge on the N1 atom from $6.54 e^-$ to $6.85 e^-$, shows charge redistribution (transfer) from the Fe1 atom located in the 2nd layer of the Fe doped MgO (001) surface to the NO₂ molecule. There is no spin density left on the N1 atom with the total Mulliken population ($6.85 e^-$) closer to that of a neutral nitrogen atom ($7 e^-$). Furthermore, the total number of electrons on the NO₂ molecule is $23.99 e^-$ whereas for NO₂ adsorbed on the undoped MgO (001) surface there is a total of $23.35 e^-$ localized on NO₂. This effectively shows that NO₂ has obtained some electron density from Fe1, thus effectively becoming NO₂⁻, as confirmed by no unpaired electrons on N1. Most importantly, charge transfer results in an increased adsorption energy of -37.64 kcal/mol in Fe doped MgO (001) when compared to -2.67 kcal/mol in Ca doped MgO (001). It cannot be excluded that, in the NO₂ adsorption case (especially Fe doped MgO (001)) due to the inherently weak adsorbate-surface interactions, there are other adsorbate configurations with respect to the O5 atom that might be located during optimization, depending on the initial geometry guess. One other NO₂ optimization on Fe doped MgO (001) resulted in an Mg-O coordinated structure that was 11.58 kcal/mol lower in energy (more stable) than the bonded N1-O5. This result is not surprising as Mg-O bonds are stronger than those of N-O. All reported structures, however, resulted in the absence of unpaired electron density on N1 and $\sim 4.26 e^-$ localized on Fe1, thus showing electron transfer from the NO₂ molecule to the surface regardless of the adsorbate configuration. Collectively, our results show a profound effect on both electronic and structural properties of MgO (001) surface during NO₂ adsorption on O^{surf} sites.

Conclusions and Atmospheric Implications

The structural and electronic properties of undoped, Ca and Fe doped MgO (001) surfaces, and the differences in their propensity towards the acidic atmospheric gas (CO₂, SO₂ and NO₂) adsorption were investigated with emphasis on gas adsorption on basic oxygen surface sites. Monodentate-like coordination was observed for all adsorbates with SO₂ and NO₂ exhibiting secondary interactions with surface Mg atoms. Thus, it can be inferred that trace atmospheric gas adsorption onto O^{surf} basic sites is a preliminary step for further adsorbate transformation, such as more stable Mg-O bond formation. Importantly, adsorption energy calculations showed that MgO doping will provide stronger interactions between the adsorbate and the surface than in the undoped MgO case for a given adsorbate molecule. Since mineral dust in the environment is rarely pure and will have structural defects and impurities, this can affect trace atmospheric gas partitioning rates and stability and implies potentially enhanced uptake relative to previous laboratory studies on pure minerals as model mineral aerosol components. Additionally, our results show that charge transfer from the iron atom in the Fe doped MgO (001) surface to NO₂ results in the formation of adsorbed NO₂⁻ and an increase the binding attraction between adsorbate and the surface by an order of magnitude relative to the undoped and Ca doped MgO (001) surface. This result suggests that the nature of NO₂ adsorption on MgO surfaces can be significantly altered depending on the identity of the dopant atom. In this case, adsorption changes from physisorption to chemisorption via charge transfer, contrary to the currently accepted weak NO₂ adsorption on dust surfaces. This is in agreement with previous XAFS data where Fe mixing into MgO was found to alter the nature of CCl₄, atmospheric pollutant molecule, adsorption.⁶⁴ Thus, our results indicate that trace metal doping in atmospheric mineral aerosol as it occurs naturally in the environment needs to be accounted for in laboratory and theoretical studies as well as global atmospheric chemistry models in order to better understand the heterogeneous chemistry of naturally-occurring mineral dust aerosol.

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Figure 1.

(a) A 5 layer 2×2 supercell (side view) of MgO (001) and the UB3LYP optimized geometries for (b) undoped and (c) Ca or (d) Fe doped MgO (001) surfaces. Only relevant atoms are shown.

Figure 2.

Total difference (spin) (left) and atomic difference (right) electron charge density maps of the MgO (001) supercell, and the Ca and Fe doped MgO (001) supercells. The spin density map for Fe doped MgO is shown in purple and superimposed on top of the black total density maps. In the total charge density maps, the maximum, minimum and increment between the two contour lines are 0.1, -0.1 and 0.01 electrons/bohr³, respectively. In the charge density difference maps, the maximum, minimum and increment between the two contour lines are 0.015 , -0.015 and 0.001 electrons/bohr³, respectively. Continuous, dashed and dot-dashed lines correspond to positive, negative and zero values of the plotted function, respectively.

Figure 3. Total and atomic density of state (DOS) plots for the (a) undoped and (b) Ca or (c) Fe doped MgO (001) surfaces. (d) shows the Fe doped MgO (001) d-orbital DOS plot. The Fermi level (top of the valence band) was set to zero.

Figure 4. The UB3LYP optimized geometries of CO₂ adsorbed on (a) undoped and (b) Ca or (c) Fe doped MgO (001) surfaces. Only relevant atoms are shown.

Figure 5.

Electron charge density total (left) and difference (right) plots of CO_2 adsorbed on undoped and Ca or Fe doped MgO (001) surfaces. Difference represents $(\text{surface} + \text{CO}_2) - \text{surface} - \text{CO}_2$. In the charge density difference maps, the maximum, minimum and increment between the two contour lines are 0.015, -0.015 and 0.001 electrons/bohr³, respectively. Continuous, dashed and dot-dashed lines correspond to positive, negative and zero values of the plotted function, respectively.

Figure 6.
The UB3LYP optimized geometries of SO_2 adsorbed on (a) undoped and (b) Ca or (c) Fe doped MgO (001) surfaces. Only relevant atoms are shown.

Figure 7. The UB3LYP optimized geometries of NO_2 adsorbed on (a) undoped and (b) Ca or (c) Fe doped MgO (001) surfaces. Only relevant atoms are shown.

Table 1

UB3LYP calculated frontier d-orbital populations of the Fe doped MgO (001) supercell.

d AOs	$2z^2-x^2-y^2$	xz	yz	x^2-y^2	xy
Spin					
$\alpha+\beta$	1.10	1.02	1.02	1.97	1.06
$\alpha-\beta$	0.88	0.96	0.96	0.01	0.91

UB3LYP calculated bond length, charge and spin parameters of undoped and Ca or Fe doped MgO (001) supercell with CO₂, SO₂ and NO₂ adsorbed.

Table 2

Property and selected atom		Doping atom and adsorbed molecule											
		Mg			Ca			Fe					
		CO ₂	SO ₂	NO ₂	CO ₂	SO ₂	NO ₂	CO ₂	SO ₂	NO ₂	CO ₂	SO ₂	NO ₂
Total Mulliken population, e ⁻	O5	9.34	9.33	9.64	9.31	9.27	9.54	9.35	9.34	9.70			
	O6, O7	8.72	8.73	8.40	8.74	8.73	8.42	8.73	8.73	8.57			
	Me (Mg5, Ca1, Fe1)	10.09	10.09	10.09	18.34	18.35	18.35	24.21	24.21	23.77			
	Cl (S1, N1)	5.21	15.24	6.55	5.18	15.23	6.54	5.21	15.25	6.85			
Total spin, e ⁻	O5	-	-	0.22	-	-	0.26	-	-	0.20			
	Fe1	-	-	-	-	-	-	3.73	3.72	4.29			
	N1	-	-	0.36	-	-	0.35	-	-	0.00			
Bond length, Å	O6(O7)-C1 (S1, N1)	1.25	1.56	1.23	1.26	1.56	1.23	1.26	1.56	1.27			
	O5-C1 (S1, N1)	1.44	1.84	2.27	1.42	1.82	2.19	1.43	1.85	2.37			

Table 3

UB3LYP calculated BSSE corrected adsorption energies of CO₂, SO₂ and NO₂ adsorbed on the undoped and Ca or Fe doped MgO (001) supercell.

Complex	E _{total} , Hartree	E _{surface} , Hartree	E _{gas molecule} , Hartree	E _{adsorption} , ^a kcal/mol
MgO+CO ₂	-12582.592242	-12394.034149	-188.515754	-8.77
Ca doped MgO+CO ₂	-13060.026511			-14.58
Fe doped MgO+CO ₂	-13646.061689			-12.02
MgO+SO ₂	-12942.579660	-12871.460652	-548.481330	-17.06
Ca doped MgO+SO ₂	-13420.017490			-24.60
Fe doped MgO+SO ₂	-14006.050253			-19.91
MgO+NO ₂	-12599.055672	-13457.499119	-205.003539	-0.19
Ca doped MgO+NO ₂	-13076.486423			-2.67
Fe doped MgO+NO ₂	-13662.604020			-37.64

^aBSSE corrected values.