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Electronic properties and reactivity of simulated Fe³⁺ and Cr³⁺ substituted α -Al₂O₃ (0001) surface

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Abstract

Metal oxide based minerals naturally contain transition metal impurities isomorphically substituted into the structure that can alter the structural and electronic properties as well as the reactivity of these metal oxides. Natural α -Al₂O₃ (corundum) can contain up to 9.17% (w/w) Fe₂O₃ and 1.81% (w/w) of Cr₂O₃. Here we report on changes in the structural and electronic properties of undoped and doped α -Al₂O₃ (0001) surfaces using periodic density functional theory (DFT) methods with spin unrestricted B3LYP functional and a local atomic basis set. Both structural and electronic properties are altered upon doping. Implications for doping effects on photochemical processes are discussed.

As metal oxides are major components of the environment, including atmospheric mineral aerosol, DFT was also used to study the effect of transition metal impurities on gas/surface interactions of a model acidic atmospheric gas molecule, carbon monoxide (CO). The theoretical results indicated that the presence of Fe³⁺ and Cr³⁺ impurities substituted on the outer layer of natural corundum surfaces reduces the propensity toward CO adsorption relative to the undoped surface. However, CO-surface interactions resemble that of bulk α -Al₂O₃ when the impurity is substituted below the first surface layer. The presence and location of the mineral dopant was found to significantly alter the structural and electronic properties and gas/surface interactions studied here.

Introduction

Undoped corundum (α -Al₂O₃), characterized as perfectly colorless and transparent, is rarely found in nature. Transition metal ions, such as Cr³⁺, Fe³⁺, Fe²⁺ and Ti⁴⁺, are often substituted into the corundum crystal structure which can alter the physical, chemical, electronic, and optical properties of the material.¹ Additionally, synthetic doping of corundum can lead to customization of materials used in the semiconductor, optics, and ceramic industry.^{2–4} Of particular interest are doping with transition metals such as Cr³⁺ and Fe³⁺ as they are isovalent with Al³⁺ and form oxides (hematite, α -Fe₂O₃, and eskolaite, α -Cr₂O₃) that are isostructural with α -Al₂O₃.

In the atmospheric environment, alumina is the most abundant component of mineral dust aerosol⁵ and is also emitted into the atmosphere from rocket plumes.⁶ Mineral dust aerosols provide abundant reactive atmospheric surfaces that can serve as sinks or reaction centers

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Supporting Information. Supporting Information contains tables S1 and S2 with slab convergence parameters and d-orbitals populations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

for heterogeneous chemistry, particularly for trace acidic gases. Alumina particles as models for atmospheric aerosols have been shown to adsorb and reactively transform CO,⁷ CO₂,^{8–10} SO₂,^{11,12} and NO₂^{13–19} with and without presence of other atmospherically relevant gases (see Usher et al.²⁰ for a comprehensive review). Acid anhydrides, such as carbon monoxide (CO) or nitrogen dioxide (NO₂), are particularly interesting due to their abundance as trace reactive gases in the atmosphere. Carbon monoxide, CO, is an important atmospheric gas that originates from both natural and anthropogenic sources, most prominently from fossil fuel burning and vehicle exhaust. Additionally, as CO is a product of fuel combustion, mixing of CO with alumina surfaces are known to occur in rocket plumes.⁶ CO has also been used to probe acidity and basicity of various surfaces, such as zeolite and metal oxide surfaces.^{21–24} Ballinger and Yates²⁵ showed that Lewis acid sites formed by dehydroxylation of Al₂O₃ upon adsorption of CO on Al³⁺ sites occurs by CO 5σ orbital (primarily associated with the carbon atom) electron donation into an acceptor orbital on Al³⁺. Thus, it can be proposed that trace atmospheric gas adsorption can alter the structure and properties of alumina surfaces in the atmosphere.

Computational and experimental methods have been used to study the structure, relaxation and electronic properties of the undoped (0001), low index, α-Al₂O₃.^{26–38} Fewer studies have explored atomic, molecular adhesion and adsorption on the same surfaces^{39–53} with particular interest in H₂O adsorption,^{27,47,52,54,55} while doping effects were primary of interest of the bulk material due to the changes in the bandgap related properties.^{56,57} or dehydroxylation effects.⁵⁸ However there is still a need for computational and experimental studies of other gaseous molecules on undoped and doped model corundum surfaces as partition interactions commonly occur in the environment.

Transition metal doping affects corundum color via metal induced electronic transitions, suggesting modification of the electronic structure. Particle catalyzed oxidation of atmospheric pollutants has been proposed previously to compete with homogeneous gas-phase reactions with or without ionizing atmospheric radiation present.⁵⁹ It can be envisioned that, depending on the transition metal localization (surface vs bulk), adsorptive and reactive properties of corundum towards trace atmospheric gases can also be affected. In this work, we have used solid state density functional methods to model undoped and Cr³⁺ and Fe³⁺ doped corundum (0001) surfaces. Electronic properties of the modeled surfaces were determined and their effects of CO adsorption, as well as the changes of structural and electronic properties with the adsorbed gas were observed and discussed.

Theoretical methods

Periodic *ab initio* solid state program suite CRYSTAL'09 was used in all calculations.^{60,61} CRYSTAL'09 uses localized functions of atoms as the basis for expansion of the crystalline orbitals by linear combinations of atomic orbitals (LCAO). All-electron Gaussian type basis sets were used. Basis sets have been obtained from the University of Torino CRYSTAL basis set library⁶² (accessed Spring 2011). Specifically, the 85-11d1G basis set was used for Al,⁶³ 86-411d41G for Fe,⁶⁴ 86-411d41G for Cr⁶⁵ and 6-31d1G for O and C⁶⁶. Basis sets for Fe and Cr were used in structural calculations of α-Fe₂O₃ and α-Cr₂O₃,^{64,65} hence optimized for corundum structural calculations. The hybrid B3LYP^{67,68} Hamiltonian was used in all calculations. The DFT exchange–correlation contribution was 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,⁶⁰ 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.⁶⁹

Structural optimizations were performed using analytical energy gradients with respect to atomic coordinates and unit-cell parameters,^{70–72} within a quasi-Newton scheme combined with the Broyden–Fletcher–Goldfarb–Shanno scheme for Hessian updating.^{73–76} Convergence was checked on both gradient components and nuclear displacements and was signaled when the RMS gradient was 0.0003 Hartree/Bohr and RMS displacement was 0.0012 Bohr. Both cell parameters and atomic positions were optimized in bulk structure optimization which was then used to construct supercells propagated parallel to (0001) surface. Symmetry was fully exploited in all calculations. All calculations were performed using spin unrestricted formalism (UB3LYP notation further in text). By definition, the Fermi level was set as the top of the valence band.

Surface slabs of 6, 12, 18, 24 and 30 layers were created to check structural and electronic property convergence with the surface slab thickness (*vide infra*). Surface slabs were terminated with a distorted-tetrahedron coordinated Al atom with 3 O atoms and an unsaturated bond vacancy. For doping and adsorption calculations, bulk-optimized α -Al₂O₃ cell parameters were taken and 2×2 supercells were created of 18 layer thickness. Optimization of supercells was performed in fixed cell parameters, only atomic positions were allowed to relax. All structures and electron densities were visualized using the J-ICE program.²¹

Results and Discussion

Undoped α -Al₂O₃ (0001) surface

The undoped α -Al₂O₃ (0001) surface was constructed from a fully optimized bulk Al₂O₃ crystal. Experimental⁷⁷ and UB3LYP optimized bulk α -Al₂O₃ cell parameters are shown in Table 1. It can be seen that UB3LYP optimized crystalline cell parameters reproduce experimental parameters quite accurately with a relative error of 0.8% and 0.6% for *a* and *c*, respectively. To obtain computational artifact free data, structural and electronic parameters, such as Al–O bonds lengths, atomic charges and bandgap values were converged with the thickness of the slabs ranging from 6 to 30 layers (Table S1, Supporting Information) and an 18 layer surface slab was further considered in all further computations. Al–O bond lengths and bandgap values were particularly sensitive to the thickness of the slab. While it has been shown that modeling ionic crystal structures require very few layers to obtain a reliable description of surface properties,³⁸ the electronic properties, which are of particular interest in this work, converged in an 18 layer surface slab resulting in a band gap of 8.31 eV. Early theoretical and experimental work that focused on aluminum oxide electronic properties reported bandgap values ranging between 5 to 9.9 eV (see Evarestov et al.⁵⁸ and references therein) and are in very good agreement with another experimentally reported value of 8.8 eV⁷⁸ thus showing high accuracy of the selected UB3LYP functional and atomic basis sets of α -Al₂O₃ electronic properties.

With an appropriate thickness of 18 layers of α -Al₂O₃ (0001) surface slab established, a 2×2 supercell, made by multiplying lattice vectors by an integer of 2, was constructed. Supercells are used to model defects in crystalline materials; the supercell used here contained a total of 120 atoms, including 48 Al and 72 O atoms. The dimensions of the primitive cell were 9.596 Å × 9.596 Å with an angle of 120° and volume of 79.74 Å³. Supercell had 2-D periodicity. To avoid the uncertainty arising from an insufficient supercell size, where dopant atoms or defects in neighboring supercells start interacting,⁷⁹ dopant atoms were separated between 2×2 supercells by 9.60 Å. A similar distance was found to be adequate for metal dopant electronic structure modeling in an aluminophosphate framework material.⁸⁰

Figure 1a and 1b represent top and side views, respectively, of the α -Al₂O₃ (0001) 18 layer 2×2 supercell structure. During optimization, outer layer Al atoms strongly relaxed inward

by 0.74 Å to compensate for the absence of an octahedral bonding configuration. Almost exactly the same value (0.72 Å) of the outer Al atom relaxation in α -Al₂O₃ (0001) was shown very recently by Kurita et al.³⁷ using a combination of GGA and ionic pseudopotentials. The next layer of Al atoms relaxed by 0.04 Å showing that structural properties of the bulk are readily achieved. Figure 1c shows the total and atom density of states (DOS) calculated from the optimized α -Al₂O₃ (0001) 18 layer 2×2 supercell. The results confirm the insulating nature of corundum. Valence orbitals are largely comprised of oxygen contributions with a small mixing of Al valence orbital character, situated at approximately -2 eV. The conduction bands have predominantly Al 3s character, approximately 8 eV above the E_F, with an O 2p contribution situated approximately 11 eV above E_F. Similarly, Evarestov et al.⁵⁸ summarized Al₂O₃ band structure with upper valence bands being due to O 2p orbitals and the bottom of conduction band predominantly due to Al 3s orbitals. Notably, this magnitude of the bandgap is too large for solar radiation to overcome and no charge transfer can be achieved when α -Al₂O₃ (0001) surfaces are present in the environment. Figure 1d shows the 2D total electron density map of the four layer Al-Al-Al-Al column of the optimized α -Al₂O₃ (0001). Our results indicate partial Al-O electron overlap. It can also be seen that greater overlap of the electron densities is present between the first layer Al-O atoms, than those in the 2nd and 3rd layer. Overlap population analysis showed a 0.35 e⁻ overlap for Al-O in the first layer and 0.21 e⁻ overlap for latter, shorter Al-O bond lengths due to the surface reconstruction being responsible for greater degree of covalency between surface Al-O bonds.

Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001) surfaces

Compiled¹ experimental data on dopant composition and concentrations in natural mineral corundum are shown in Table 2. The most common impurity elements in naturally-occurring corundum, modeled in this work as α -Al₂O₃ (0001) dopants, are Fe³⁺ with concentrations of up to 9.17% Fe₂O₃ w/w followed by Cr³⁺, up to 1.81% Cr₂O₃ w/w, with Si, Ti and Ca occurring at somewhat lower concentrations. The propensity of α -Al₂O₃ doping towards Fe³⁺ and Cr³⁺ can be related to the isostructural character of these metal oxides. Crystal ionic radii of Al³⁺, Fe³⁺ and Cr³⁺ are 0.675, 0.69 and 0.755 Å,⁸¹ respectively, thus resulting in similarly sized corresponding metal oxide unit cells (4.7602, 5.038 and 4.9307 Å, respectively)^{77,82,83} which is favorable for isomorphic substitutions. In α -Al₂O₃ (0001) surface termination, there is one vacancy for every two atoms of aluminum. To investigate structural and electronic changes with dopant depth from the surface, one aluminum atom was substituted with an Fe³⁺ or Cr³⁺, as shown in Figure 2. The dopant atom was substituted at depths of one, two, and three layers. The Al in the 1st layer was a distorted tetrahedron coordinated outer Al atom and exhibited the most structural relaxation upon optimization. The 2nd and 3rd layers were considered to occur at the two Al atoms directly underneath the surface Al, perpendicular to the surface. The distances between the 1st and 2nd, and the 2nd and 3rd layer Al atoms after 18 layer (0001) surface slab optimization were 3.15 and 2.67 Å, respectively. Prior to optimization, they were 3.84 and 2.68 Å, respectively. Properties of outer surface Al³⁺ and the substituted Fe³⁺, Cr³⁺ atoms in the first layer can thus be compared to the lower layers to probe effects of impurity depth on structural and electronic properties as well as gas/surface interactions. All three layers are shown in Figure 2 with the blue atom labeled as a dopant. Structural and electronic parameters of optimized Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001) 18 layer 2×2 supercells with different dopant depth locations are tabulated in Table 3. It can be seen that total atomic charges of Fe³⁺ and Cr³⁺ are ~24 and 22 e⁻, respectively, with total charge density decreasing by ~0.2 e⁻ upon penetration beyond the first layer. This result coincides with the total density increase of the surrounding dopant oxygen atoms and a slight increase in the unpaired electron density on Fe³⁺ but not on Cr³⁺, as it can be seen from Table 3. Finally, while in the reconstructed surface Me-O

bonds are relatively short at ~ 1.8 Å, they elongate by ~ 0.2 Å with the dopant atom situated in deeper layers.

Electronic properties of the doped surfaces were further investigated to infer any changes in the bandgap upon doping. Figure 3 shows the total and atom DOS computed for Fe^{3+} and Cr^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001) 18 layer 2×2 supercells. Also shown are the corresponding plots of charge density contributions from each band superimposed on the structure. It can be seen that several new bands appear in the bandgap with the substitutional doping. First, a new occupied band appeared at the Fermi level due to the mixing of iron (chromium) and oxygen valence orbitals. Second, two new bands appear at ~ 4 and 6 eV above E_F in the Fe atom DOS due to the empty beta spin Fe 3d (Cr 3d) orbitals. The nature of the E_F is also altered, but differently for Fe^{3+} and Cr^{3+} . For Fe^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001), most of the charge density at the E_F is localized at the dopant nearest neighbor oxygen atoms with very little charge density on the dopant atom itself. For Cr^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001), occupied bands at E_F are heavily localized on the dopant atom. All of the states in the bandgap are due to the empty metal 3d orbitals.

An important observation can be made when comparing DOS plots for the selected dopant between the three layers. Fe 3d beta spin energies do not change with iron atom being substituted into the deeper layers of the surface, whereas Cr 3d alpha band at 4 eV above E_F shifts to higher energy by ~ 2 eV when going from the 1st layer substituted into the 2nd and 3rd layer substituted structures. Additionally, two bands in beta spin appear to split upon Cr substitution from the 1st to the 2nd layer. These results show that the electronic properties of Fe^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001) are not sensitive to the location of the dopant atom, whereas the Cr^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001) electronic properties become dependent on the dopant depth. Normally, corundum type compounds, such as $\alpha\text{-Al}_2\text{O}_3$, have octahedral coordination of metal ions in the bulk,⁸⁴ due to the slightly distorted surrounding oxygen atoms octahedra.⁸⁵ Fe^{3+} has a $3d^5$ electron configuration and there is no crystal field splitting energy (CFSE) difference between octahedral and tetrahedral coordination, whereas Cr^{3+} has a $3d^3$ electron configuration with CFSE favoring octahedral coordination. Thus, the splitting of the band located at 6 eV (Figure 3d–f) upon substitution beyond the 1st layer is a result of the CFSE effect on Cr dopant atom. UB3LYP computed d orbital populations are shown in Table S2 Supporting Information for total and spin difference. It can be seen that there is very little change in atomic orbital populations in Fe^{3+} dopant case with x^2-y^2 alpha spin becoming slightly depopulated and xy beta spin becoming slightly more populated. There is, however, much greater change in the Cr^{3+} dopant case where xz, yz orbitals gets slightly depopulated and with x^2-y^2 and xy becoming more populated, in accordance with the change in the DOS features (Figure 3).

Figure 4 shows the 2D total and spin density maps for the Fe^{3+} and Cr^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001) 18 layer 2×2 supercells. It can be seen that there is significant spin density transferred to the surrounding O atoms in the Fe DOS, especially when the Fe atom is located in the 1st layer (Figure 4a). This result is consistent with the data reported in Table 3 and can be attributed to the lack of octahedral coordination which leads to higher spin densities being transferred to neighboring O atoms. Additionally, spin density around the Fe atoms is quite symmetrical. Less spin density is transferred to neighboring O atoms upon Cr doping. The asymmetric nature of the spin density on the Cr atoms is due to the different d subshells contributing unpaired electrons.

To take a closer look into the dopant atom frontier d-orbital distribution contributions from each 3d subshell are shown in Figure 5 as the atomic population DOS. Small contributions to DOS just below the Fermi level upon Fe doping are due to xz, yz, x^2-y^2 and xy orbitals. Alpha spin $2z^2-x^2-y^2$ is fully populated and located in the -2 to -4 eV region, whereas its

beta spin has a sharp unpopulated contribution to the DOS at ~ 4 eV above E_F , overlapping with majority component xz and yz. The x^2-y^2 and xy unpopulated band is located ~ 5.5 eV above E_F . In the 1st layer, the Cr doped structure frontier d-orbital contribution is different from those of the Fe doped α -Al₂O₃ (0001) with an occupied defect band just below the Fermi level split into two (Figure 5a and c, respectively). $2z^2-x^2-y^2$ is a majority contributor to the first part of the split band and the remaining four 3d subshells contributing to the higher energy part of the split band. A new empty band at ~ 4.5 eV alpha spin is due to all four d-orbital contributions: xz, yz, x^2-y^2 and xy. Additionally, all unoccupied beta spin Cr d-orbitals have very similar energies, ~ 6 eV. These split into two bands with the majority $2z^2-x^2-y^2$ component becoming of lower energy upon octahedral configuration with Cr atom located in 2nd and 3rd layers. This phenomenon is not apparent for Fe doped α -Al₂O₃ (0001) where no band shifting appears upon substitution below the first surface layer. However, there is a difference in relative contributions to the bands: the $2z^2-x^2-y^2$ component becomes a major contributor to ~ 4 eV above E_F band when going from Fe 1st layer to 2nd layer doping. Additionally, yz and xz increase in energy, therefore becoming a major contributor to the ~ 5.5 eV above E_F beta component. So while the relative band positions remained the same for Fe³⁺ doped α -Al₂O₃ (0001) between 1st and 2nd layer, their composition became more even, which is consistent with going from the asymmetric tetrahedra (1st layer) to the more symmetrical octahedral (2nd layer) metal atom coordination.

Importantly, the presence of the new band at the Fermi level shows a change in the nature of the highest occupied valence orbitals switching from bulk O 2p to largely having a localized Fe 3d character. Furthermore, empty states in the bandgap can act as electron acceptors via photon absorption followed by electron excitation since the bandgap effectively decreases to ~ 4 eV, yet still higher than the visible part of the solar spectrum.

CO adsorption on undoped and Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001) surface

Figure 6 shows the total and atomic DOS of Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001) 18 layer 2 $\times$ 2 supercells with CO molecules adsorbed to the surface. The results show two new bands in the bandgap (observed in all spin configurations) in addition to the bands from the dopant atoms. The new bands represent contributions from the adsorbed CO molecule, some of which mix with the dopant atom unoccupied bands upon first layer doping (Figure 6a and d). This mixing is somewhat more pronounced for Fe³⁺ doping than for Cr³⁺ doping. Additionally, there is no band splitting at the E_F in Cr³⁺ doped 1st layer. Importantly, CO empty bands, especially upon doping the 1st layer, are now low enough in energy (~ 3.5 eV with respect to the Fermi level) to accept any photoexcited electrons from the highest valence orbitals in the presence of solar light. The nature of the charge transfer would be different in both Fe³⁺ and Cr³⁺ cases, since O 2p orbitals are major contributors to the highest valence orbitals in Fe³⁺ doped α -Al₂O₃ (0001) whereas Cr3d orbitals are major contributors in the Cr³⁺ doped α -Al₂O₃ (0001).

Electronic structure is essentially not affected for CO adsorbed on Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001), consistent with the weak nature of the adsorption. There is a change, however, in Me-C bond length where CO is coordinated to Fe³⁺ and Cr³⁺ dopant atoms (1st layer) and Al³⁺ atoms (with dopant atoms in 2nd and 3rd layers). It is most pronounced in Cr³⁺ case with Me-C bond length decreasing from 2.50 to 2.18 Å. C-O bond length remained 1.13 Å showing little charge donation from surface metal atom to the CO molecule.

Figure 7 shows the 2D electron density difference maps for Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001) 18 layer 2 $\times$ 2 supercells with CO adsorbed. Difference here represents (surface+CO)-surface-CO. It can be seen that there is a clear electron polarization in all cases upon CO

adsorption from carbon towards surface atoms on which adsorption is occurring. There is a clear difference in electron density polarization when CO is adsorbed on the first layer dopant atoms. Much less electron density is displaced across the molecule from CO oxygen atom towards Cr-C bond, than there is in Fe-C case, suggesting weaker interactions between CO and the surface doped α -Al₂O₃ (0001). Finally, surface oxygen atoms coordinated to the dopant metal have very little polarization upon CO adsorption whereas greater polarization occurs with dopants in the 2nd and 3rd layer.

BSSE corrected binding energies were estimated for CO adsorbed to undoped and doped α -Al₂O₃ (0001) are tabulated in Table 4. Here binding energy was calculated as a difference between the optimized slab and CO complex and the sum of slab and CO (in adsorbed geometry) energies. This is warranted by the rigidity of the adsorbing CO. Consistent with results shown in Figure 6, the calculated binding energies are lower when the dopant is substituted into the first layer. Estimated binding energies were -10.78 and -3.33 kcal/mol for 1st layer doped Fe³⁺ and Cr³⁺, respectively, with the binding energy almost equal to that of the undoped cluster at -12.97 kcal/mol with dopants deeper within the surface. This result suggests that doped α -Al₂O₃, such as those found in nature, has a lower affinity for acidic gases relative to pure α -Al₂O₃. Thus, implications arise when using pure α -Al₂O₃ for experimental measurements of gas/surface interactions representing natural α -Al₂O₃ surfaces.

Very recently, Blomqvist et al.⁸⁶ used generalized gradient approximation (GGA) in combination with plane wave basis set to study CO and transition metal (Ag and Pd) ad-atom co-adsorption on the α -Al₂O₃ (0001) surface. The estimated binding energy of CO was -11.53 kcal/mol (independently of the surface site) in good agreement with the value of -12.97 kcal/mol determined in this work. Adsorption of the 1st layer Fe³⁺ and Cr³⁺ dopants can be generalized and compared with that on pure α -Fe₂O₃ (0001) and α -Cr₂O₃ (0001). The carbon bonded configuration was found to be stable only on α -Fe₂O₃ (0001) via GGA +U and plane wave calculations with -12.29 kcal/mol.⁸⁷ Concurrently, CO adsorption on α -Cr₂O₃ (0001) was calculated to result in -3.11 kcal/mol binding energy,⁸⁸ also in agreement with data reported in this work. Collectively, this shows that 1st layer Fe³⁺ and Cr³⁺ dopants will exhibit adsorptive properties similar to those of bulk α -Fe₂O₃ and α -Cr₂O₃ while quickly reverting to the adsorptive properties of α -Al₂O₃ with deeper layer doping. In this regard, $E_{\text{surface relative}}$ energies shown in Table 4 are of particular interest as they show that the Fe³⁺ dopant will energetically prefer the 1st layer by 6.05 and 3.75 kcal/mol with respect to 2nd and 3rd layers, respectively. However, Cr³⁺ will be in the most energetically stable configuration in 2nd and 3rd layers, in agreement with the CFSE governed 3d level splitting discussed earlier and illustrated in Figure 3. Exactly the same order is obtained, albeit at slightly different values, when doped surfaces are optimized without the CO adsorbed. This has large implications when considering gaseous acidic molecule adsorption on α -Al₂O₃ (0001) surfaces doped with Fe³⁺ and Cr³⁺. Effectively, our data shows that the Cr³⁺ dopant will be situated within deeper layers of the surface without directly affecting gas adsorption, whereas the Fe³⁺ dopant will prefer the top layer and result in weaker adsorption of CO.

Conclusions

In this work, α -Al₂O₃ (0001) surface doping with Fe³⁺ and Cr³⁺ has been shown to alter its structural, electronic and reactive properties. While there was only slight Me-O bond length change in the local coordination of the dopant atom from that of undoped, electronic structure was profoundly altered. E_F changed its nature from the bulk O2p to that of predominantly dopant localized with several new bands in the bandgap due to the empty d-states from the dopant atoms.

Location of the dopant with respect to the surface had a significant effect on the electronic structure of the Cr^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001), while very little effect on the electronic structure of the Fe^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001) was observed. When adsorbed CO molecule was modeled, its calculated binding energy changed with the dopant and its localization depth. In both cases, weaker adsorption energy was calculated for 1st layer dopant coordinated CO molecules than that of the undoped surface. It can be proposed that natural Fe^{3+} and Cr^{3+} dopant rich $\alpha\text{-Al}_2\text{O}_3$ (0001) surfaces will bind CO weaker than pure $\alpha\text{-Al}_2\text{O}_3$ (0001) surfaces, thus decreasing its retention time and partition from the atmosphere. Importantly, when Fe^{3+} was present in the 1st layer with CO molecule adsorbed, the effective bandgap value decreased to 3.4 eV (365 nm), right at the edge of the incident solar spectrum. This result in turn shows that Fe^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001) might be involved in photochemical charge transfer to CO thus completely changing the nature and the extent of adsorption. Finally, while the models used in this work have been shown to represent the ideal $\alpha\text{-Al}_2\text{O}_3$ (0001) surface well, under atmospheric conditions these surfaces will have molecularly adsorbed, as well as dissociated H_2O which will interact with CO and affect its adsorption. Theoretical work to understand the electronic structure and adsorption towards atmospheric gases of hydroxylated $\alpha\text{-Al}_2\text{O}_3$ (0001) surfaces are underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Unoptimized α - Al_2O_3 (corundum) 18 layer (0001) 120 atom supercell structure from the (a) top and (b) side views. Also shown are the (c) total and atom density of states (DOS) and (d) total electron density map plots. Grey – Al and red – O atoms.

Figure 2. Pictorial representation of α - Al_2O_3 (0001) surface supercell fragment with Fe^{3+} and Cr^{3+} doped in (a, d) 1st, (b, e) 2nd and (c, f) 3rd layers, respectively, with dopant metal ion position shown. Grey – Al, red – O and blue Fe(Cr) atoms. Only a representative portion of the supercell is shown.

Figure 3.

Atom and total density of states (DOS) plots of α - Al_2O_3 (0001) surface supercell doped with Fe^{3+} and Cr^{3+} doped in (a, d) 1st, (b, e) 2nd and (c, f) 3rd layers, respectively. Fermi level was offset to zero. 3D charge density maps of bands of interest obtained from the energy range projected density matrix are also shown.

Figure 4.

Total and spin electron density plots of α - Al_2O_3 (0001) surface slabs doped with Fe^{3+} and Cr^{3+} doped in (a, d) 1st, (b, e) 2nd and (c, f) 3rd layers, respectively. Spin density maps are shown in purple and superimposed on top of black total density maps. Continuous, dashed and dot-dashed lines correspond to positive, negative and zero values of the plotted function.

Figure 5. Dopant atom frontier d-orbital density of states (DOS) plots of α - Al_2O_3 (0001) surface supercell doped with Fe^{3+} and Cr^{3+} in the (a, c) 1st and (b, d) 2nd layers, respectively. The Fermi level was offset to zero.

Figure 6.

Atom and total density of states (DOS) plots of α - Al_2O_3 (0001) surface supercell doped with Fe^{3+} and Cr^{3+} in the (a, d) 1st, (b, e) 2nd and (c, f) 3rd layers, respectively, with CO molecules adsorbed. The Fermi level was offset to zero. 3D charge density maps of bands of interest obtained from the energy range projected density matrix are also shown.

Figure 7.

Charge density difference plots of the α - Al_2O_3 (0001) surface supercell doped with Fe^{3+} (left) and Cr^{3+} (right) in the (a, d) 1st, (b, e) 2nd and (c, f) 3rd layers, respectively, with CO molecules adsorbed. Continuous, dashed and dot-dashed lines correspond to positive, negative and zero values of the plotted function. The maximum, minimum and increment between the two contour lines are 0.015, -0.015 and 0.001 electrons/bohr³, respectively. Topmost three atoms are shown in red for clarity.

Table 1Structural data of UB3LYP optimized bulk α -Al₂O₃

Cell parameter ^a	Experimental ^b	Calculated	Relative error, %
a, Å	4.7602	4.7979	0.8
c, Å	12.9933	13.0665	0.6

^aSpace group R-3c^bExperimental parameters taken from Lewis et al.⁷⁷

Table 2Common elements present in natural corundum (α -Al₂O₃)^a

Compound (element)	Concentration, weight %
Fe ₂ O ₃ (Fe ³⁺)	0.00–9.17
Cr ₂ O ₃ (Cr ³⁺)	0.00–1.81
SiO ₂ (Si ⁴⁺)	0.20–0.94
TiO ₂ (Ti ⁴⁺)	0.00–0.37
CaO (Ca ²⁺)	0.00–0.34

^a Only impurities above 0.1 weight % are shown. Adopted from Deer et al.¹ and references therein

Table 3
Structural parameters of UB3LYP calculated Fe^{3+} and Cr^{3+} doped $\alpha\text{-Al}_2\text{O}_3$ (0001)

	1 st layer		2 nd layer		3 rd layer	
	Fe^{3+}	Cr^{3+}	Fe^{3+}	Cr^{3+}	Fe^{3+}	Cr^{3+}
Atomic charges, e^-	Me	22.13	23.79	22.04	23.78	22.03
	O	-	9.52	9.47	9.48	9.42
		9.41	9.48	9.42	9.47	9.42
Unpaired electrons, e^-	Me	2.93	4.28	2.94	4.28	2.94
	O	-	0.13	0.01	0.13	0.01
		0.27	0.02	0.08	0.08	0.00
Me-O bond length, Å		-	1.94	1.96	1.92	1.95
		1.79	2.06	2.00	2.11	2.02

Table 4

UB3LYP calculated BSSE corrected binding energies of CO adsorbed on undoped and Fe³⁺ and Cr³⁺ doped α -Al₂O₃ (0001)

Complex	E _{total} , Hartree	E _{surface} , Hartree (E _{surface} relative, kcal/mol) ^a	E _{adsorbate} , Hartree	E _{binding} , kcal/mol
1 st layer Fe ³⁺ doped Al ₂ O ₃ +CO	-18195.861871	-18082.564562 (0.00; 0.00)	-113.280136	-10.78
2 nd layer Fe ³⁺ doped Al ₂ O ₃ +CO	-18195.847060	-18082.544699(6.02; 7.50)	-113.280628	-13.64
3 rd layer Fe ³⁺ doped Al ₂ O ₃ +CO	-18195.849090	-18082.547794(3.75; 5.42)	-113.280679	-12.94
1 st layer Cr ³⁺ doped Al ₂ O ₃ +CO	-17976.664340	-17863.379357(13.26; 10.41)	-113.279670	-3.33
2 nd layer Cr ³⁺ doped Al ₂ O ₃ +CO	-17976.690122	-17863.388869(0.00; 0.00)	-113.280677	-12.91
3 rd layer Cr ³⁺ doped Al ₂ O ₃ +CO	-17976.689886	-17863.388301(0.36; 0.36)	-113.280670	-13.12
Al ₂ O ₃ +CO	-17174.772166	-17061.470814	-113.280675	-12.97

^aE_{surface} relative calculated as the difference in energies to the lowest energy surface within the selected dopant and show relative stability of the doped surfaces. First value is that of the surface optimized without CO adsorbed; second value is for the optimized surface with the CO adsorbed.