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# Mixing properties of $\text{Al}_2\text{O}_3(0001)$ -supported $\text{M}_2\text{O}_3$ and $\text{MM}'\text{O}_3$ monolayers (M, $\text{M}'=\text{Ti, V, Cr, Fe}$ )

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**Abstract.** Considering the importance of sub-monolayer transition metal oxides supported on another oxide in many industrial processes, with the help of a DFT+U approach, we provide information on the structural and electronic properties of pure  $\text{M}_2\text{O}_3$  and mixed  $\text{MM}'\text{O}_3$  3d monolayers (M,  $\text{M}' = \text{Ti, V, Cr, Fe}$ ) supported on an  $\alpha\text{-Al}_2\text{O}_3(0001)$  support. With their structure in the prolongation of the alumina corundum lattice, the monolayers have non-equivalent surface and interface cations which leads to two different cation configurations in the mixed oxides. In all cases, the interfacial charge transfer is weak, but strong cation-cation electron redistributions may take place as in  $\text{TiVO}_3$ ,  $\text{TiFeO}_3$ ,  $\text{VFeO}_3$ , and  $\text{TiCrO}_3$  in which actual redox processes lead to oxidation states different from the expected +3 value. We show that the tendency to mixing relies on the interplay between two very different driving forces. Cation-cation redox reactions, in most cases, strongly stabilise mixed configurations, but preference for a given cation position in the monolayer because of surface energy reasons may strengthen, weaken or even block the mixing tendency. By comparison with results obtained in bulk ilmenite, in free-standing monolayers and in MLs deposited on transition metal substrates, we evidence the flexibility of their electronic structure as a function of size, dimensionality and nature of support, as a lever to tune their properties for specific applications.

## 1. Introduction

Reducible transition metal (TM) sesquioxides  $\text{M}_2\text{O}_3$  of corundum structure are involved in numerous natural or industrial processes. For example, hematite  $\text{Fe}_2\text{O}_3$  is omnipresent in the natural environment where it helps fixing contaminants, and also finds applications in electrochemical water splitting. Eskolaite  $\text{Cr}_2\text{O}_3$  is an efficient catalyst and an important constituent of many ceramics. It acts as a protective layer against corrosion on iron surfaces. Apart from its role as a catalyst,  $\text{V}_2\text{O}_3$  displays a metal-insulator (MI) transition as a function of temperature which is used in energy related applications.

These properties may be tuned by doping the oxides or varying their thickness in thin film geometry.  $\text{M}_2\text{O}_3$  thin films have been synthesized on various substrates, whether metallic or insulating [1]. In the latter case, the choice of *c*-cut sapphire  $\alpha\text{-Al}_2\text{O}_3(0001)$  is especially beneficial, due to its stability, its high surface quality, and the similarity of its structure to that of the TM sesquioxides. There are numerous examples of  $\text{M}_2\text{O}_3$  thin film growth on it, for example  $\text{Ti}_2\text{O}_3$  [2],  $\text{V}_2\text{O}_3$  [3, 4],  $\text{Cr}_2\text{O}_3$  [5],  $\text{Fe}_2\text{O}_3$  [6] or sesquioxides resulting from the oxidation of stainless steel buffers intended to favour adhesion of anti-corrosive galvanic zinc coatings [7, 8]. The same is true for some mixed oxides such as  $(\text{Fe}_{1-x}\text{V}_x)_2\text{O}_3$  [9],  $(\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$  [10], or  $\text{VTiO}_3$  [11].

The incorporation of dopants in corundum oxides is also a lever to obtain new functionalities. Multicomponent oxides display flexible structural and electronic characteristics as a function of the relative concentration of their components, the particle size, the film thickness and the nature of the support on which they are synthesized [1]. Compared to their pure analogues, mixed oxides sometimes simply combine the advantages of the parent oxides, but in some cases, they may also exhibit unexpected new features. It was, for example, shown that Cr-doping changes the  $\text{V}_2\text{O}_3$  MI transition temperature [12], that Mn-doping modifies the  $\text{H}_2$  adsorption on  $\alpha\text{-Al}_2\text{O}_3$  [13], or that optical properties of  $\alpha\text{-Al}_2\text{O}_3$  are sensitive to TM atom doping [14]. Recently, we have shown that the contact between two  $\text{M}_2\text{O}_3$  oxides [15] or their mixing, whether in the bulk [16] or at the monolayer (ML) limit [17, 18, 19] may induce a change of cation oxidation states, with strong implications on their electronic and reactivity properties.

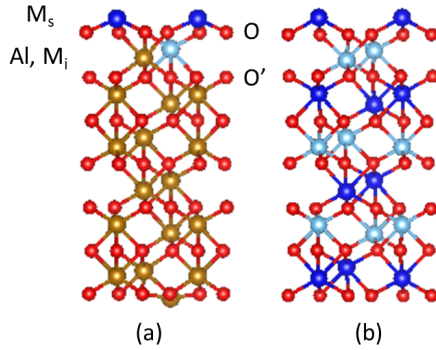
$\text{M}_2\text{O}_3$  thin films at the ultimate ML limit have been extensively studied experimentally and theoretically, whether supported on Pd(111) [20, 21], on Pt(111) [22, 23], or on Au(111) [24, 21, 18, 25, 26, 27, 28]. However, apart from MLs inserted into  $\alpha\text{-Al}_2\text{O}_3$  [29, 30], fewer works have envisioned the properties of TM sesquioxide MLs on the  $\alpha\text{-Al}_2\text{O}_3(0001)$  surface.

This is the subject of the present theoretical work, which considers both pure  $\text{M}_2\text{O}_3$  and mixed  $\text{MM}'\text{O}_3$  MLs with  $\text{M}, \text{M}' = \text{Ti}, \text{V}, \text{Cr}$  and  $\text{Fe}$ . We show that their structure, in continuation of the corundum lattice, is far from the quasi-planar geometry found on metal substrates, that the interfacial charge transfer is weak, and that segregation effects are present in the mixed MLs with preferential presence of one or the other cation at the surface. Strong electron redistributions, which can be considered as actual redox processes leading to changes of cation oxidation states, take place between the TM cations in several mixed compounds, such as in  $\text{TiVO}_3$ ,  $\text{TiFeO}_3$ ,  $\text{VFeO}_3$ , and  $\text{TiCrO}_3$ . We show that the mixing tendency, i.e. the stability of the mixed MLs with respect to their parent oxides, depends on the interplay between two physical processes, namely change of oxidation state and surface under-coordination. When comparing the present results to those obtained previously for the same mixed oxides in different morphologies or environments, we conclude that these electronic characteristics are strongly dependent on size, dimensionality and nature of support, which suggests routes to tune TM oxide ML properties for specific applications

The paper is organized as follows. After a section devoted to the computational method and set-up (Sec. 2), we report results on  $\text{Al}_2\text{O}_3$ -supported pure  $\text{M}_2\text{O}_3$  MLs (Sec. 3) and mixed  $\text{MM}'\text{O}_3$  MLs (Sec. 4). These results are then discussed in Sec. 5, before a conclusion.

## 2. Computational details

DFT calculations have been performed with the Vienna Ab-initio Simulation Package (VASP) [31, 32] using the Projector Augmented Wave (PAW) method [33, 34] to represent the electron-core interaction and a 400 eV energy cut-off in the development of Kohn-Sham orbitals on a plane-wave basis set. As in our previous studies, [16, 15, 17, 18] a dispersion-corrected (optB88-vdW) [35, 36, 37] exchange-correlation functional has been employed, within the DFT+U ap-



**Figure 1.** Profile views of the atomic structures of (a) an  $\text{Al}_2\text{O}_3$ -supported  $\text{MM}'\text{O}_3$  ML, and (b) a bulk  $\text{MM}'\text{O}_3$  oxide in the ilmenite structure. M and M' cations, oxygen atoms and Al cations are represented by light and dark blue, red, and golden balls, respectively. Subscripts  $i$  and  $s$  refer to the ML interface and surface cations, respectively.

proach proposed by Dudarev [38, 39] with  $U$  values close to those reported in the literature:  $U = 1$  eV for  $\text{Ti}_2\text{O}_3$ ,  $U = 1.7$  eV for  $\text{V}_2\text{O}_3$ ,  $U = 3$  eV for  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Moreover we have performed complementary calculations using the HSE03 hybrid approach with 1/4 of the short-range Hartree-Fock exact exchange, and range-separation parameter equal  $0.3 \text{ \AA}^{-1}$ , [40, 41] to test the sensitivity of our results to the choice of the exchange-correlation functional (Supporting Information (SI), Sections S2-S4).

All calculations are spin-polarized and the relative stability of simple non-magnetic (NM) and magnetic solutions (with either parallel (FM) or anti-parallel (AF) TM spin moments) has been systematically tested. Ionic charges are estimated with the partition scheme proposed by Bader [42, 43] and magnetic moments are obtained by integration of the spin density within the Bader's volumes. The oxide ML and alumina substrate charges are evaluated as a sum of all the respective ionic charges and the interface charge transfer is deduced from the non-neutrality of the alumina substrate. Atomic configurations are plotted with VESTA [44].

We have considered pure  $\text{M}_2\text{O}_3$  (the parents) and mixed  $\text{MM}'\text{O}_3$  monolayers (M, M' = Ti, V, Cr, and Fe), supported on  $\alpha\text{-Al}_2\text{O}_3(0001)$ , in the prolongation of the corundum structure, Figure 1a. The  $\text{Al}_2\text{O}_3$  substrate is represented by a six Al-O<sub>3</sub>-Al trilayer thick slab terminated by a single Al atom on each side (non-polar terminations), and the oxide films are deposited on one side of the support. They are modelled with a single  $\text{M}_2\text{O}_3$  or  $\text{MM}'\text{O}_3$  formula unit (f.u.) in an  $\text{Al}_2\text{O}_3(0001)$  ( $1 \times 1$ ) unit cell at the  $\text{Al}_2\text{O}_3$  bulk lattice parameter ( $4.75 \text{ \AA}$ ). The sampling of the Brillouin zone is performed with the  $\Gamma$ -centred ( $8 \times 8 \times 1$ ) Monkhorst-Pack mesh [45].

All atomic coordinates are allowed to fully relax

**Table 1.** Main structural and electronic characteristics of  $\text{Al}_2\text{O}_3$ -supported  $\text{M}_2\text{O}_3$  MLs: interplane distances  $d$  within the ML ( $\text{\AA}$ ), cation charge  $Q_M$  (e), oxygen charge in the ML  $Q_O$  (e), total substrate charge  $Q_{\text{Al}_2\text{O}_3}$  (e/surface unit cell), cation magnetic moment  $\mu_M$  ( $\mu_B$ ). Indices  $i$  and  $s$  refer to interface and surface cations of the ML, respectively.

	$\text{Ti}_2\text{O}_3$	$\text{V}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$
$d_s$	0.80	0.69	0.63	0.61
$d_i$	0.88	0.93	1.01	0.90
$Q_{Ms}$	1.54	1.55	1.58	1.52
$Q_{Mi}$	2.02	1.85	1.73	1.73
$Q_O$	-1.28	-1.23	-1.22	-1.19
$Q_{\text{Al}_2\text{O}_3}$	0.27	0.30	0.35	0.30
$\mu_{Ms}$	1.38	2.23	3.07	3.92
$\mu_{Mi}$	0.49	1.69	2.79	-3.98

until forces get lower than  $0.01 \text{ eV \AA}^{-1}$ . In the following, the atomic or electronic characteristics of these supported MLs will be compared to those of corundum  $\text{M}_2\text{O}_3$  or ilmenite  $\text{MM}'\text{O}_3$  bulk structures [16] (Figure 1b). DFT+U results for the  $\text{M}_2\text{O}_3$  bulks and free (0001) surfaces are recalled in SI, Section S1.

The mixing energies  $E_{mix}$  of the supported  $\text{MM}'\text{O}_3$  monolayers are calculated from energy differences between the supported mixed oxide  $E^{\text{MM}'\text{O}_3}$  and the average of the two corresponding supported parents  $E^{\text{M}_2\text{O}_3}$  and  $E^{\text{M}'_2\text{O}_3}$ :

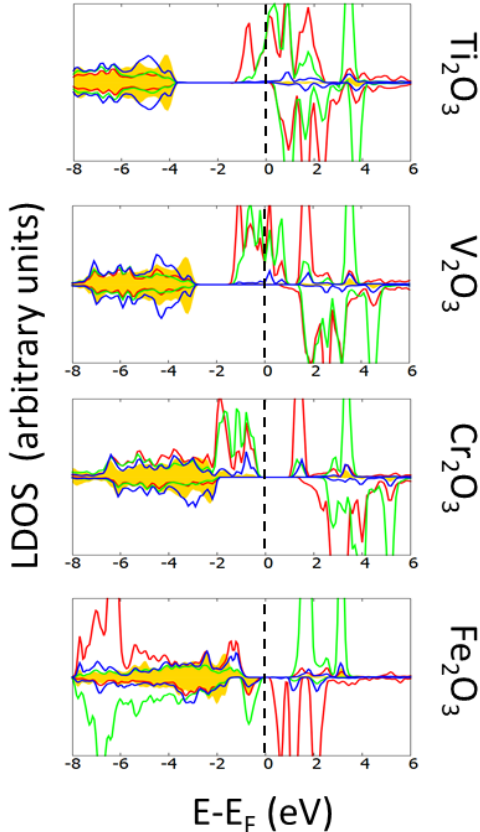
$$E_{mix}^{\text{MM}'\text{O}_3} = E^{\text{MM}'\text{O}_3} - \frac{E^{\text{M}_2\text{O}_3} + E^{\text{M}'_2\text{O}_3}}{2} \quad (1)$$

With this definition, mixing energies are negative if mixing is favoured.

### 3. Results on supported $\text{M}_2\text{O}_3$ monolayers

We first present the computational results for the  $\text{M}_2\text{O}_3$  MLs supported on  $\text{Al}_2\text{O}_3$ . Table 1 and Figure 2 report their main structural, electronic, and magnetic characteristics. Corresponding results obtained with the HSE approach are given in SI, Tab. S2 and Fig. S2.

Since, in all cases, the supported ML structure is in the continuation of the corundum lattice with interface cations in the hollow site, the two cations of the oxide layers become strongly inequivalent. The interface ones have their full octahedral environment, while the surface cations are 3-fold coordinated. As a consequence, in the ML, the interlayer distance  $d_s$  between the surface cations and the oxygen plane is strongly reduced, in line with that found at all M-terminated  $\text{M}_2\text{O}_3(0001)$  surfaces (Tab S1 in SI, and references [46, 47, 48]). The interlayer distance  $d_i$  between the interface cations and the oxygen plane, on the other hand, is of the order of that found in bulk  $\text{M}_2\text{O}_3$  along the (0001) direction (Tab S1 in SI).



**Figure 2.** Local densities of states of  $\text{Al}_2\text{O}_3$ -supported  $\text{M}_2\text{O}_3$  MLs projected on surface cations  $\text{M}_s$  (red), interface cations  $\text{M}_i$  (green), oxygen atoms O (blue), and substrate oxygen atoms (golden shading). Up and down spins are represented with positive and negative LDOS values, respectively. A broadening of 0.2 eV has been systematically applied. The vertical dashed lines indicate the positions of the Fermi levels. In the  $\text{Al}_2\text{O}_3$ -projected LDOS, the bottom of the CB, not visible at this scale, is located  $\approx 4$  eV above the VB maximum.

From an electronic point of view, in all cases, the substrate is positively charged, but the interfacial charge transfer is small, of the order of 0.3 e/ $\text{M}_2\text{O}_3$  f.u. Indeed, as shown in Figure 2, stronger electron transfers cannot take place, because the  $\text{M}_2\text{O}_3$  gap edges are sandwiched between those of  $\text{Al}_2\text{O}_3$  (type I band offset). This is qualitatively different from the much larger electron transfers which take place at the interface between the same mixed oxide MLs and some metallic substrates [19]. In the present case, the interfacial charge transfer thus merely comes from the modifications of the ionic-covalent character of interfacial bonds. In particular, the three subsurface O' atoms (Figure 1a) which have 3 Al and 1 TM neighbours have a charge which is reduced by  $\approx 0.1$  electron, with respect to that in  $\text{Al}_2\text{O}_3$ , due to the more covalent character of M-O bonds. This accounts nearly completely for the  $\text{Al}_2\text{O}_3$  positive

charging. Interestingly, in the only constituted interface involving  $\text{Al}_2\text{O}_3$  that we have previously studied, namely  $\text{Ti}_2\text{O}_3/\text{Al}_2\text{O}_3$  [15], the interfacial charge was nearly identical to that found in the present work, which confirms the very local character of this transfer.

In all cases, Fig. 2, the  $d$  states of the interface cations  $\text{M}_i$  occupy higher energy positions than those of the surface cations  $\text{M}_s$ , as a result of the larger Madelung potential generated by their octahedral environment. As a consequence, in contrast to their bulk counterparts, the Local Densities of States (LDOS) of  $\text{Ti}_2\text{O}_3$  and  $\text{V}_2\text{O}_3$  are metallic, due to an overlap of their interface and surface  $d$  states. Despite similar shifts, the LDOSs of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  remain semiconducting but with a reduced gap width.

All magnetic structures are ferromagnetic, except  $\text{Fe}_2\text{O}_3$  which is antiferromagnetic. The energy differences between the magnetic ground and excited states are 0.13 eV, 0.40 eV, 0.06 eV and 0.66 eV per unit cell in the series. The magnetic moments of interfacial and surface Cr and Fe cations are close to 3 and 4  $\mu_B$ , respectively, pointing to +3 oxidation states. The corresponding values for Ti and V depart from the respective values 1 and 2  $\mu_B$  expected for their +3 oxidation states, due to the metallic character of their band structures. This is not due to the interaction with the substrate, since the interfacial charge transfer is weak, but rather to an electron redistribution inside the ML layer, evidenced by the surface and interface LDOS overlap at the Fermi level  $E_F$ . This effect is much weaker in the HSE approach (SI Tab. S2 and Fig. S2).

#### 4. Results on supported $\text{MM}'\text{O}_3$ monolayers

DFT+U results for the main structural, electronic and magnetic characteristics of  $\text{Al}_2\text{O}_3$ -supported mixed  $\text{MM}'\text{O}_3$  MLs are given in Table 2. Figure 3 displays their LDOS in the two alternative cation configurations. Corresponding HSE results are given in SI, Table S3 and Figure S3.

Sitting in the prolongation of the  $\text{Al}_2\text{O}_3$  lattice, all  $\text{MM}'\text{O}_3$  MLs bear resemblance to an ilmenite  $\text{M-O}_3\text{-M}'(0001)$  trilayer (Fig. 1b). The two cations are not only chemically but also structurally distinct, due to their different coordination. Consequently, there are two inequivalent configurations with M at the interface and M' at the surface, or vice-versa. The preference for the location of a given cation is quantified by the energy difference  $E_2 - E_1$  between the more stable configuration (Conf. #1) and the reverse one (Conf. #2) in Table 2. In the structural ground state Conf. #1, we find that the Fe cations systematically sit at the surface, while Cr cations preferentially occupy interface

**Table 2.** Main structural and electronic characteristics of  $Al_2O_3$ -supported mixed  $MM'O_3$  monolayers in the more stable (Conf. #1) and less stable (Conf.#2) configurations: interplane distances  $d$  within the ML (Å), charges on cations  $Q_M$ ,  $Q_{M'}$  (e) and oxygen atoms  $Q_O$  (e), substrate charge  $Q_{Al_2O_3}$  (e/surface unit cell), cation magnetic moments  $\mu_M$ ,  $\mu_{M'}$  ( $\mu_B$ ), mixing energy  $E_{mix}$  and energy difference  $E_2 - E_1$  between Conf. #2 and Conf. #1 (eV/surface unit cell). The cation formal charges, as deduced from the analysis of the electronic structure are indicated. M and M' refer to the first and second cation in the chemical formula, and indices  $i$  and  $s$  to interface and surface cations, respectively.

	TiVO <sub>3</sub>	TiCrO <sub>3</sub>	TiFeO <sub>3</sub>	VCrO <sub>3</sub>	VFeO <sub>3</sub>	CrFeO <sub>3</sub>
Conf. #1						
$d_M/d_{M'}$	0.82/0.88	0.70/1.02	0.84/0.69	0.67/1.00	0.87/0.69	0.97/0.61
$Q_M/Q_{M'}$	2.13/1.33	1.69/1.73	2.14/1.30	1.62/1.72	2.02/1.31	1.74/1.53
$Q_O$	-1.24	-1.27	-1.25	-1.23	-1.21	-1.21
$Q_{Al_2O_3}$	0.27	0.39	0.30	0.34	0.31	0.36
$\mu_M/\mu_{M'}$	0.13/2.75	1.03/2.79	0.08/3.59	2.05/2.82	1.04/3.61	2.63/-3.97
$E_{mix}$	-0.59	-0.56	-1.72	-0.04	-0.76	-0.43
Conf.	Ti <sup>4+</sup> V <sup>2+</sup>	Ti <sup>3+</sup> Cr <sup>3+</sup>	Ti <sup>4+</sup> Fe <sup>2+</sup>	V <sup>3+</sup> Cr <sup>3+</sup>	V <sup>4+</sup> Fe <sup>2+</sup>	Cr <sup>3+</sup> Fe <sup>3+</sup>
Conf. #2						
$d_M/d_{M'}$	0.76/0.96	0.84/0.82	0.73/0.95	0.91/0.72	0.64/0.95	0.62/0.93
$Q_M/Q_{M'}$	1.68/1.78	2.12/1.33	1.69/1.72	1.93/1.44	1.65/1.66	1.58/1.73
$Q_O$	-1.25	-1.24	-1.24	-1.23	-1.20	-1.19
$Q_{Al_2O_3}$	0.29	0.27	0.31	0.32	0.29	0.27
$\mu_M/\mu_{M'}$	0.97/1.88	0.18/3.76	0.92/4.05	1.43/3.52	1.82/3.93	2.80/-4.06
$E_{mix}$	-0.06	-0.32	-0.01	-0.01	+0.68	+0.51
Conf.	Ti <sup>3+</sup> V <sup>3+</sup>	Ti <sup>4+</sup> Cr <sup>2+</sup>	Ti <sup>3+</sup> Fe <sup>3+</sup>	V <sup>3+</sup> Cr <sup>3+</sup>	V <sup>3+</sup> Fe <sup>3+</sup>	Cr <sup>3+</sup> Fe <sup>3+</sup>
$E_2 - E_1$	0.53	0.24	1.71	0.03	1.44	0.94

sites, as do Ti cations in TiVO<sub>3</sub>.

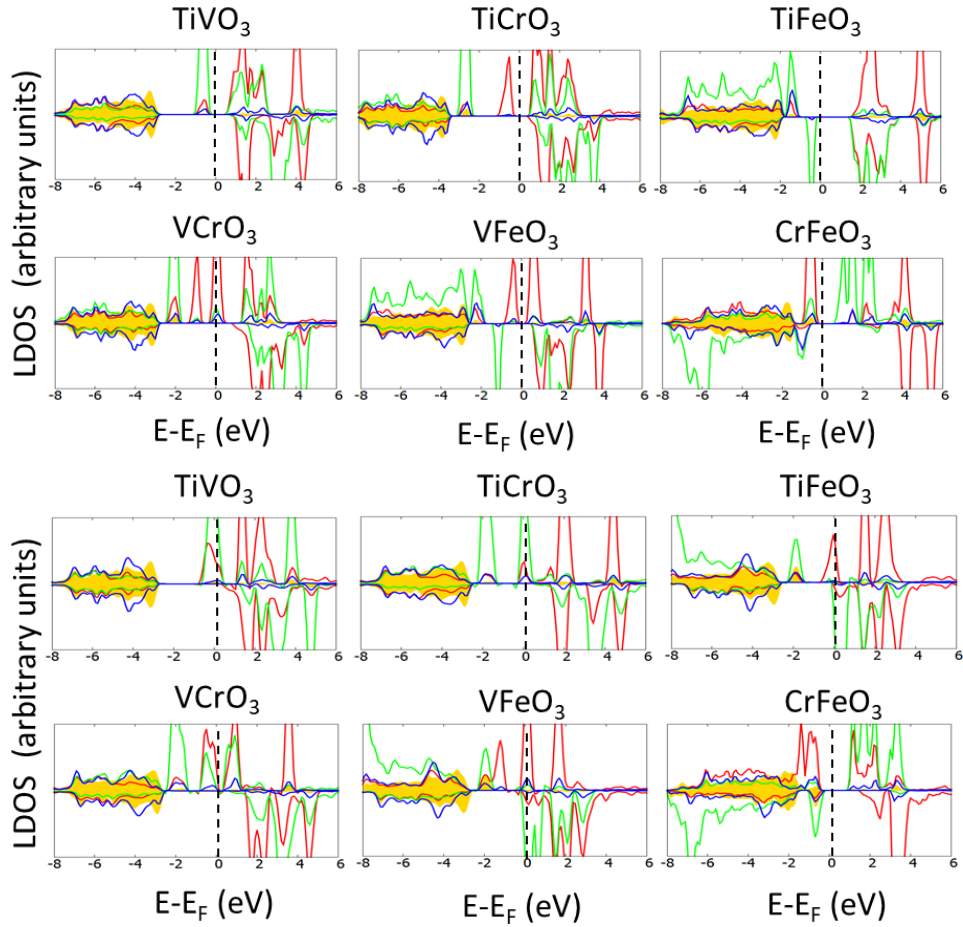
From an electronic point of view, and for the same reasons as for the  $M_2O_3$  parents (type I interface), whatever the M and M' configuration, the charge transfer to the  $Al_2O_3$  substrate is of the order of 0.3-0.4 e/surface unit cell, and due nearly entirely to the reduction of the subsurface O' charges.

In Conf. #1, all LDOSs are insulating except VCrO<sub>3</sub>. The gap widths are small, nearly vanishing in some cases, but they open in the HSE approach (SI Fig. S3). Three mixed oxides display a clear cationic change of oxidation states compared to their parents, which may be considered as resulting from an actual redox process: Ti<sup>4+</sup>V<sup>2+</sup>, Ti<sup>4+</sup>Fe<sup>2+</sup>, and V<sup>4+</sup>Fe<sup>2+</sup>. These assignments are confirmed by the concomitant observation of 1) an increased charge of the first cation and a decreased charge of the second one; 2) the values of the magnetic moments:  $\mu(Ti) \approx 0\mu_B$  characteristic of Ti<sup>4+</sup>,  $\mu(V) \approx 1\mu_B$  in VFeO<sub>3</sub> and  $\approx 3\mu_B$  in TiVO<sub>3</sub> characteristic of V<sup>4+</sup> and V<sup>2+</sup>, respectively, and  $\mu(Fe) \approx 3.6\mu_B$  characteristic of Fe<sup>2+</sup>; and finally 3) the disappearance of the Ti peak below  $E_F$ , apparition of a Fe peak below  $E_F$  and correlative shifts of the V  $d$  state. In contrast, in TiCrO<sub>3</sub>, VCrO<sub>3</sub> and CrFeO<sub>3</sub>, there is no redox reaction and the cations keep their +3 oxidation state, with magnetic moments  $\approx 1, 2, 3$ , and  $4\mu_B$  for Ti, V, Cr and Fe, respectively.

Table 2 and Figure 3 (bottom panels) also display the structural and electronic characteristics of the less stable configurations (Conf. #2) in which the two TM cations of the MLs occupy reversed positions. The two

most striking differences with respect to Conf. #1 are the absence of a redox process in TiVO<sub>3</sub>, TiFeO<sub>3</sub> and VFeO<sub>3</sub> and its occurrence in TiCrO<sub>3</sub>, as witnessed by the values of the magnetic moments and the shifts of the  $d$  states in the LDOSs (Fig. 3). The origin of these differences may be assigned to the different values of the Madelung potentials at surface and interface cationic sites, and will be further discussed in Section 5.1. The estimation of cation oxidation states is more difficult in VCrO<sub>3</sub>, because of its quasi-metallic electronic structure with strong cation-cation orbital hybridization. As a result, the magnetic moments have intermediate values between 1 and 2  $\mu_B$  for V and between 3 and 4  $\mu_B$  for Cr. Nevertheless, thanks to the noticeable gap opening which takes place within the HSE approach, the magnetic moments approach 2 and 3  $\mu_B$ , respectively, which suggest a V<sup>3+</sup>Cr<sup>3+</sup> configuration.

A favourable mixing is associated to negative values of the mixing energy  $E_{mix}$  (Equation 1). This is the case for all  $MM'O_3$  MLs in their more stable state (Conf. #1) while positive or vanishingly small values are found for most MLs in Conf. #2. The only exception in the latter case is TiCrO<sub>3</sub> in which a redox process is observed. Let us note that, whatever the relative positions of the V and Cr cations, the mixing energy is close to zero in VCrO<sub>3</sub>.



**Figure 3.** Local densities of states in  $Al_2O_3$ -supported mixed  $MM'O_3$  MLs in Conf. #1 (top panels) and #2 (bottom panels), projected on M (red),  $M'$  (green), O atoms (blue), and substrate oxygen atoms (golden shading). A broadening of 0.2 eV has been systematically applied. Vertical dashed lines indicate the position of the Fermi level. In the  $Al_2O_3$ -projected LDOS, the bottom of the CB, not visible at this scale, is located  $\approx 4$  eV above the VB maximum.

## 5. Discussion

In this section, the existence or absence of cation-cation redox processes is rationalized by the consideration of the band offsets between the supported parents. Then, the two main contributions to the mixing energy are defined and discussed. Finally, in a broader perspective, the present findings are compared to the mixing characteristics of the same oxides in other morphologies or environments.

### 5.1. Mixing effect

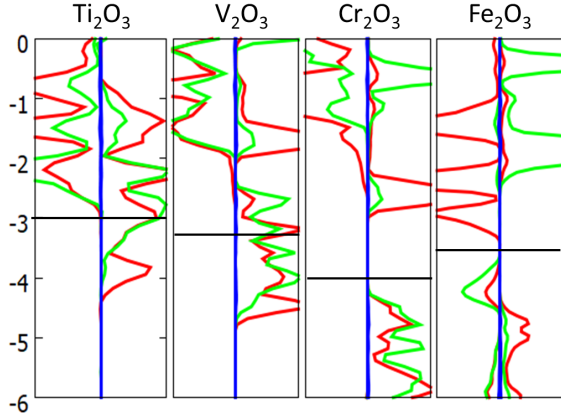
According to the results of Section 4, an electron exchange between the two cations often occurs in mixed MLs, either small when due to orbital hybridization, or, in some cases, so strong that it results in a well-defined change of the cationic oxidation states. In our past studies of bulk [16] or free-standing ML [17] mixed oxides, we have shown

that the latter effect may be qualitatively inferred from the relative positions of the parent band structures.

Figure 4 shows the cation projected LDOS of the four supported parent MLs, aligned with respect to the vacuum level (corresponding HSE result in SI Figure S4). The ordering of the Fermi levels  $E_F(Ti_2O_3) > E_F(V_2O_3) > E_F(Fe_2O_3) > E_F(Cr_2O_3)$  suggests possible cation-cation electron transfers from the left to the right in this series (approximately from the least to the most electronegative cation), provided that the relevant DOSs in the energy window between the two Fermi levels are significant.

From this last viewpoint, redox effects are expected to be markedly different in the two possible cation configurations Conf #1 and Conf #2, since the  $d$  levels of surface and interface cations occupy different positions on the energy scale—higher position at interface due to stronger Madelung potential, lower position at surface due to a reduced coordination and thus a reduced Madelung potential. This is





**Figure 4.** Local densities of states of  $\text{Al}_2\text{O}_3$ -supported  $\text{M}_2\text{O}_3$  MLs projected on cations (red for surface, green for interface) and aligned with respect to the vacuum level. A broadening of 0.2 eV has been systematically applied. The horizontal lines indicate the positions of the Fermi levels.

convincingly exemplified in Cr- and Fe-containing mixed oxides, in which, according to Figure 4, a redox reaction upon mixing with Ti or V can only take place if the Cr and Fe cations are located at the surface. Indeed three among the four mixed oxides in which a redox process takes place, namely  $\text{Ti}_i\text{Fe}_s\text{O}_3$  (Conf. #1),  $\text{V}_i\text{Fe}_s\text{O}_3$  (Conf. #1) and  $\text{Ti}_i\text{Cr}_s\text{O}_3$  (Conf. #2) have this cation configuration and no redox is found when the cation positions are reversed. In  $\text{TiVO}_3$  (Conf. #1), the band offset between the parent DOS also suggests a change of oxidation states, while in  $\text{VCrO}_3$  (Conf. #1), and  $\text{CrFeO}_3$  (Confs. #1 and #2) it correctly concludes to an absence of redox. It is quite remarkable that an argument which is still no more than a qualitative guideline allows predicting the occurrence or absence of a redox in ten among the twelve configurations under study.

### 5.2. Cation mixing and interface configurations

As a complement to the electronic properties discussed above, the value of the mixing energy  $E_{mix}$  quantifies the propensity of the two cations M and M' to mix in  $\text{Al}_2\text{O}_3$ -supported  $\text{MM}'\text{O}_3$  MLs. The  $E_{mix}$  values may be analysed by splitting them into two main contributions:

$$E_{mix} = E_{mix}^{surf} + E_{mix}^{elec} \quad (2)$$

The first one  $E_{mix}^{surf}$  is associated to the structural non-equivalence of M and M' and, thus, to the cost of bond breaking when forming a surface. Considering the definition of  $E_{mix}$  (Equation 1), it may be approximated by the difference between the surface energies  $E_{surf}$  of  $\text{M}_2\text{O}_3(0001)$  and  $\text{M}'_2\text{O}_3(0001)$  slabs, i.e.  $E_{mix}^{surf} = [E_{surf}(\text{M}_2\text{O}_3) - E_{surf}(\text{M}'_2\text{O}_3)]/2$  if M is at the surface and M' at the interface, or the

**Table 3.** Mixing energy  $E_{mix}$  in  $\text{Al}_2\text{O}_3$ -supported  $\text{MM}'\text{O}_3$  MLs and its two contributions  $E_{mix}^{surf}$  and  $E_{mix}^{elec}$  (eV/surface unit cell), in Conf. #1 (left) and Conf. #2 (right) configurations. Bold fonts are used when a redox process takes place.

	$E_{mix}$	$E_{mix}^{surf}$	$E_{mix}^{elec}$	$E_{mix}$	$E_{mix}^{surf}$	$E_{mix}^{elec}$
$\text{TiVO}_3$	-0.59	0.07	<b>-0.66</b>	-0.06	-0.07	+0.01
$\text{TiCrO}_3$	-0.56	-0.21	-0.35	-0.32	+0.21	<b>-0.53</b>
$\text{TiFeO}_3$	-1.72	-0.10	<b>-1.62</b>	-0.01	+0.10	-0.11
$\text{VCrO}_3$	-0.04	-0.14	+0.10	-0.01	+0.14	-0.15
$\text{VFeO}_3$	-0.76	-0.17	<b>-0.59</b>	+0.68	+0.17	+0.51
$\text{CrFeO}_3$	-0.43	-0.32	-0.11	+0.51	+0.32	+0.19

negative of this quantity for cations in the alternative configuration. The second contribution  $E_{mix}^{elec}$  mainly involves electronic degrees of freedom and is expected to be large and negative when a redox reaction takes place. Table 3 displays the values of  $E_{mix}$  and its two contributions for the two cation configurations.

As expected, most  $E_{mix}^{surf}$  contributions are negative in the most stable configuration Conf. #1, and positive otherwise. Since  $E_{surf}$  is equal to 2.19, 2.34, 2.62 and 2.00 eV/surface unit cell in the series from Ti to Fe (Table S1 in SI),  $E_{mix}^{surf}$  favours the location of Cr cations (the highest  $E_{surf}$ ) at the interface and of Fe cations (the lowest  $E_{surf}$ ) at the surface. This argument is in agreement with the positions of these cations in Conf. #1. Interestingly, a similar argument has been used in the literature when discussing doping effects in  $\alpha\text{-Al}_2\text{O}_3$  or TM oxides [49, 14]. The surface energy ordering  $\text{Fe}_2\text{O}_3 < \text{Ti}_2\text{O}_3 < \text{V}_2\text{O}_3 < \text{Al}_2\text{O}_3 < \text{Cr}_2\text{O}_3$  is consistent with their conclusions that Fe dopants segregate at the surface of  $\text{V}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$ , while Cr dopants sit subsurface at  $\text{Fe}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3(0001)$  surfaces. According to the same mechanism, V dopants were shown to segregate at the surface of  $\text{Cr}_2\text{O}_3$  and migrate subsurface on  $\text{Fe}_2\text{O}_3$ .

Regarding the electronic contribution to mixing, large negative values are found when a redox reaction unambiguously takes place, i.e. in  $\text{TiVO}_3$ ,  $\text{TiFeO}_3$  and  $\text{VFeO}_3$  in Conf. #1, and in  $\text{TiCrO}_3$  in Conf. #2. For eleven among the twelve mixed MLs, there is thus a definite strong correlation between the existence/absence of a cation-cation redox process and a large and negative/small or positive  $E_{mix}^{elec}$  value. It allows us to infer that, in the twelfth case (Conf. #2 of  $\text{VCrO}_3$ ) for which the analysis of the DFT+U magnetic moments and LDOS did not allow to unambiguously conclude, indeed no redox takes place, considering the low value of  $E_{mix}^{elec}$ .

This discussion shows that the stability of mixed MLs with respect to their parents (negative value of  $E_{mix}$ ) depends on the interplay between two very different driving forces, which may act concomitantly or in opposition to one another. Cation-cation redox reactions, in most cases, strongly stabilise mixed



configurations, but preference for a given cation position in the ML because of surface energy reasons may strengthen, weaken or even block the tendency to mixing. For example, in  $\text{TiCrO}_3$  and  $\text{CrFeO}_3$  (Conf. #1), in which the cations keep their +3 oxidation state, the mixing energies  $E_{mix}$  are relatively large and negative, but Table 3 shows that a large part of it is not of electronic origin but rather originates from  $E_{mix}^{surf}$ . In Conf. #2, the value of  $E_{mix}$  in  $\text{TiCrO}_3$  may seem rather weak for a compound with a change of cation oxidation states, but Table 3 proves that it is due to an unfavourable surface energy effect, while the electronic contribution is of the same order as that in the Conf. #1 of  $\text{TiVO}_3$  et  $\text{VFeO}_3$ .

### 5.3. Redox dependence on dimensionality and environment

The dependence of the mixing energy and redox properties on the cation positions evidenced in the preceding sections highlights their sensitivity to the local cation environment. To exemplify this effect more thoroughly, we now compare our present findings with results obtained previously for the same mixed oxides with different morphologies, namely the ilmenite bulk structure [16] or free-standing MLs [17]. What makes the comparison interesting is the progressive decrease of the mean cation coordination in the series from bulk (all cations are 6-fold coordinated), to  $\text{Al}_2\text{O}_3$ -supported MLs (interface and surface cations are 6- and 3- fold coordinated, respectively) and to free-standing MLs (all cations are 3-fold coordinated).

Table 4 provides a summary of the mixed oxides which display a strong mixing tendency associated to a cation redox process in these various systems. Beyond some differences between them which are related to the coordination dependence of the parent band offsets and the character of the band edges, a common bias for 6-fold coordinated Ti cations ( $\text{Ti}_i$ ) to formally become  $\text{Ti}^{4+}$  is visible, which is associated with the high position of the filled  $\text{Ti}_i$   $d$  state on the energy scale. Similarly, 3-fold coordinated Fe cations ( $\text{Fe}_s$ ) easily transform into  $\text{Fe}^{2+}$  thanks to the low position of their empty  $d$  states. The table also highlights the existence of a change of oxidation state in  $\text{TiCrO}_3$  (Conf. #2) which is specific to the  $\text{Al}_2\text{O}_3$ -supported ML.

We recall that a different mechanism is at work in MLs deposited on a metallic substrate [19]. There, we have shown that interfacial charge transfers are much larger than on  $\text{Al}_2\text{O}_3$ , so that the metal may play an active role in changes of cation oxidation states, whenever its Fermi level overlaps the oxide bands. On  $\text{Ag}(111)$ ,  $\text{Au}(111)$  and  $\text{Pt}(111)$ , this occurs in supported  $\text{Ti}_2\text{O}_3$  and  $\text{V}_2\text{O}_3$  MLs and is even increased in some mixed MLs, such as  $\text{VCrO}_3$  and  $\text{VFeO}_3$ .

**Table 4.** Mixed  $\text{MM}'\text{O}_3$  oxides displaying a strong mixing tendency associated to a change of cation oxidation states, in various morphologies: bulk,  $\text{Al}_2\text{O}_3$ -supported ML (ML/ $\text{Al}_2\text{O}_3$ ), free-standing ML (ML). The cation location is indicated by indices  $s$  and  $i$  which refer to surface and interface (or bulk), respectively.

	$\text{TiVO}_3$	$\text{TiCrO}_3$	$\text{TiFeO}_3$	$\text{VFeO}_3$
Bulk	$\text{Ti}_i\text{V}_i$	-	$\text{Ti}_i\text{Fe}_i$	-
ML/ $\text{Al}_2\text{O}_3$	$\text{Ti}_i\text{V}_s$	$\text{Ti}_i\text{Cr}_s$	$\text{Ti}_i\text{Fe}_s$	$\text{V}_i\text{Fe}_s$
ML	-	-	$\text{Ti}_s\text{Fe}_s$	$\text{V}_s\text{Fe}_s$

These significant differences in the electronic structure of a given mixed oxide according to its dimensionality and/or the substrate it is in contact with, gives an additional lever to a doping strategy, in view of various applications. For example, in vanadium oxide catalysts, it is known that the oxidation state of the vanadium atoms plays a crucial role on its reactivity. The examples given in our present and past studies show that mixing with another TM sesquioxide may favour +3, +4, or +5 oxidation states, depending on the TM partner, the morphology and dimensionality of the mixed oxide and its environment.

## 6. Conclusion

Considering the growing importance of sub-monolayer TM oxides supported on another oxide in the chemical industry, we have used a DFT+U approach to study the properties of pure  $\text{M}_2\text{O}_3$  and mixed  $\text{MM}'\text{O}_3$  3d transition metal oxide monolayers (M, M' = Ti, V, Cr, Fe) supported on an  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  support.

With their structure in the prolongation of the alumina corundum lattice, the MLs have non-equivalent surface and interface cations. Two different cation configurations thus exist in the mixed oxides. We have related the preference for one or the other to the relative values of the surface energies of the parent oxides.

In all cases, the interfacial charge transfer to the substrate is weak, but strong electron redistributions may take place between the cations in the mixed MLs, which lead to changes of cation oxidation states and can be described as actual redox processes. This is true in  $\text{TiVO}_3$ ,  $\text{TiFeO}_3$  and  $\text{VFeO}_3$  in their most stable configurations, and in  $\text{TiCrO}_3$  in the alternative configuration. We have deciphered the conditions under which redox processes occur, and shown that the band off-sets between the parent oxides are good guidelines to predict them.

The analysis of mixing energies has revealed that the stability of mixed MLs with respect to their parents depends on the interplay between two very different driving forces—tendency to a redox reaction and difference in surface energies—which may act

concomitantly or in opposition to one another.

Finally, by comparing the mixed oxide characteristics evidenced in the present study to those obtained previously in bulk ilmenite, in free-standing MLs, and in MLs deposited on transition metal substrates, we have highlighted the flexibility of their electronic structure as a function of size, dimensionality and nature of support. This suggests levers to tune TM oxide properties for specific applications.

## 7. Supporting Information Available

The Supporting Information contains:

- (i) DFT+U results for bulk  $M_2O_3$  corundum oxides and their (0001) surfaces (Tab. S1 and Fig. S1);
- (ii) HSE results for  $Al_2O_3$ -supported  $M_2O_3$  MLs and comparison with DFT+U results (Tab. S2 and Fig. S2);
- (iii) HSE results for  $Al_2O_3$ -supported mixed  $MM'O_3$  MLs in the two alternative cation configurations and comparison with DFT+U results (Tabs. S3 and Fig. S3);
- (iv) HSE band alignment of  $Al_2O_3$ -supported  $M_2O_3$  MLs and comparison with DFT+U results (Fig. S4).

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