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Jacek Goniakowski, C. Noguera. Properties of Metal-Supported Oxide Honeycomb Monolayers: M_2O_3 and $MM'O_3$ on $Me(111)$ ($M, M' = Ti, V, Cr, Fe; Me = Ag, Au, Pt$). *Journal of Physical Chemistry C*, 2020, 124 (15), pp.8186-8197. 10.1021/acs.jpcc.9b09337. hal-02875308

HAL Id: hal-02875308

<https://hal.science/hal-02875308>

Submitted on 19 Jun 2020

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Properties of Metal-Supported Oxide Honeycomb Monolayers: M_2O_3 and $MM'O_3$ on $Me(111)$ ($M, M' = Ti, V, Cr, Fe; Me = Ag, Au, Pt$)

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Abstract

With the help of a DFT+U approach, we have analyzed the characteristics of a series of pure and mixed $3d$ transition metal oxide honeycomb monolayers of M_2O_3 and $MM'O_3$ stoichiometries ($M, M' = Ti, V, Cr$ and Fe) deposited on a metal substrate ($Me = Ag, Au, Pt$). We show that the substrate-induced structural polarization, interfacial electron transfer, and oxide-metal interaction strength display general trends which are governed by the offsets between the oxide band structure and the metal Fermi level. They are the strongest for the least electronegative cations (Ti and V) deposited on supports with the largest work functions (Au, Pt), where the depletion of purely $3d$ Ti and V states provokes an increase of the cation oxidation state. Mixing generally induces electron transfers from the least (Ti and V) to the most (Cr and Fe) electronegative cations. However, the systematic delocalization of the Ti_2O_3 d valence electrons to the metal substrates limits any significant mixing-induced electronic rearrangements to the V -based compounds only. We show that these electronic effects directly impact the energetics of cationic mixing and are responsible for a dramatic destabilization of the mixed $TiFeO_3$ monolayers compared to the bulk ilmenite phase, while they stabilize ordered mixed $VFeO_3$ films which have no bulk equivalent. Our findings give general guidelines

on how oxide electronic, magnetic and reactivity characteristics can be efficiently engineered by tuning the oxide stoichiometry and the metal substrate, of direct interest for modern technologies.

1 Introduction

Aside from van der Waals two-dimensional (2D) materials such as graphene, silicene, germanene, hexagonal boron nitride, or transition metal dichalcogenides, oxide monolayers (MLs) have recently attracted more and more interest due to their promising applications in the fields of catalysis and corrosion protection and to their relevance in the process of high-temperature oxide encapsulation of noble metal catalysts. Their properties are strongly affected by their reduced size and low dimensionality, which allows a large flexibility of their stoichiometry, atomic structure and electronic characteristics, often leading to complex compounds which have no bulk equivalents.^{1,2} Moreover, the growing demand of methods for engineering the properties of such two-dimensional objects, fosters an efficient use of cation doping or mixing. Indeed, combining cations of different size, electronegativity and reducibility, may give a lever for modifying the oxide structural, electronic, and chemical reactivity characteristics.

Among the most frequently encountered oxide monolayer structures, the M_2O_3 honeycomb (HC) one, which consists of a fully-coordinated network of twelve member rings with an equal number of oxygen and metal atoms, has been extensively studied experimentally and theoretically, whether freestanding,³ or Pd(111)-,^{4,5} Pt(111)-,^{6,7} Au(111)-supported^{5,8-12} as well as sandwiched between Al_2O_3 films.¹³ Aside its occurrence in sesquioxides monolayers, oxide honeycomb films have also been observed in $Cu_3O_2/Au(111)$,¹⁴ or used as a template for a synthesis of supported ternary $Ba_xTi_2O_3/Au(111)$ compounds.¹⁵

Regarding cationic doping and mixing, we have recently shown that the low dimensionality of freestanding M_2O_3 HC MLs and their peculiar, flat atomic structure determine their specific electronic characteristics (gap width, character of gap edges) and are responsible for cation redox reactions and mixing preferences which are different from those in the corresponding three-dimensional mixed oxides.³ However, if these results provide guidelines for understanding properties of oxide films supported on very weakly interacting substrates, they are likely less relevant for the case of metal supports, which are the most widely used in practical realizations. Indeed, in another recent study, we have shown that the atomic structure of Au-supported M_2O_3 HC MLs is characterized by a large structural rumpling and that the electronic characteristics of the freestanding films are severely altered by a charge exchange with the gold substrate, which in extreme cases may result in a change of cation oxidation state.⁹

In this context, the goal of the present theoretical work is twofold. On the one hand, beyond Au-supported M_2O_3 MLs considered in our previous work,⁹ we analyze the substrate-induced characteristics of pure M_2O_3 and mixed $MM'O_3$ oxide films ($M, M' = Ti, V, Cr,$ and Fe) deposited on three metallic substrates ($Me = Ag, Au$ and Pt) of higher and higher work functions. Relying on DFT+U results on freestanding and Me-supported MLs, we identify the mechanisms responsible for the most essential structural, electronic, and energetic characteristics of these supported films. On the other

hand, at variance with mixing at weakly or non-interacting interfaces,³ we consider realistic situations by explicitly including the interaction with a metal substrate. To this goal we link the electronic and energetic characteristics of mixed $MM'O_3/Me$ compounds to those of their pure M_2O_3/Me and M'_2O_3/Me parents and we assess the roles played by the character of the latter (Mott-Hubbard or charge transfer) and by the substrate work function.

The paper is organized as follows. After a section devoted to the computational method and set-up (Sec. 2), we report the results on Me-supported pure M_2O_3 MLs (Sec. 3) and mixed $MM'O_3$ MLs (Sec. 4). These results are then discussed in Sec. 5, before a conclusion.

2 Computational details

DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP)^{16,17} using the Projector Augmented Wave (PAW) method^{18,19} 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. We have checked that an increase of the cut-off to 500 eV does not bring any noticeable modifications to the reported results. For example, for $VFeO_3$ and its parents Fe_2O_3 and V_2O_3 , regardless of the underlying metal, it changes the structural characteristics (film rumpling, anion-cation and cation-substrate bond lengths) by less than 0.01 Å, the electronic characteristics (anion, cation, and substrate charges) by less than 0.01 e/f.u. and the energetic ones (mixing energy) by less than 0.01 eV/f.u.

Dispersion-corrected (optB88-vdW)²⁰⁻²² exchange-correlation functional was employed, within the DFT+U approach proposed by Dudarev.^{23,24} As in our previous studies,^{3,9,25,26} we have used U values close to those reported in the literature: $U = 1$ eV for Ti_2O_3 , $U = 1.7$ eV for V_2O_3 , $U = 3$ eV for Cr_2O_3 and Fe_2O_3 . Moreover we have performed complementary calculations using the HSE03 hybrid approach^{27,28} to test the sensitivity of our results to the choice of the exchange-correlation

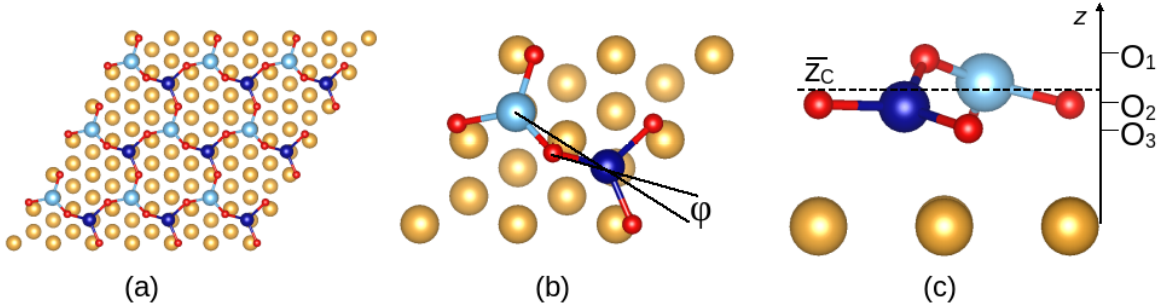


Figure 1: Atomic structures of Me-supported $MM'O_3$ oxide ML: (a) top view; (b) enlarged top view showing the rotation ϕ of the MO_3 entities; c: enlarged profile view showing the rumpling of the layer, with the two cations and the three oxygen atoms at different elevations. The dashed line represents the average cation elevation \bar{z}_c . Cations, oxygen and substrate atoms are represented by blue (dark and light), red, and golden balls, respectively.

functional (Supporting Information (SI), Sec-
 tions S2). As discussed in details in the case
 of FeO_x/Pt ,²⁹ and pointed out in studies on
 CuO_2/Au ^{14,30} and MgO/Ag ,³¹ despite the
 known difficulties of the Hartree-Fock approach
 to describe metals, the hybrid approximation
 to the DFT gives a satisfactory description of
 a metal/oxide interface and thus enables to
 account for the oxide-metal band offset.

All calculations were spin-polarized and the
 relative stability of simple non-magnetic (NM)
 and magnetic solutions (with either parallel
 (FM) or anti-parallel (AF) spin moments) was
 systematically tested. Ionic charges were es-
 timated with the partition scheme proposed
 by Bader^{32,33} and magnetic moments were ob-
 tained by integration of the spin density within
 the Bader's volumes. Atomic configurations
 were plotted with VESTA.³⁴

We have considered Me(111)-supported pure
 M_2O_3 (the parents) and mixed $MM'O_3$ mono-
 layers ($M, M' = Ti, V, Cr, \text{ and } Fe$; $Me = Ag, Au$
 and Pt) in an honeycomb structure, Figure 1.
 All of them were modelled in a (2×2) -Me(111)
 unit cell, with a single M_2O_3 or $MM'O_3$ formula
 unit per cell, at the Me experimental bulk lat-
 tice parameter (2.89 Å, 2.88 Å, and 2.765 Å
 for Ag, Au and Pt, respectively), consistently
 with experimental observations of pseudomor-
 phic growth of ML Ti_2O_3 on Au(111)¹⁰ and
 V_2O_3 on Pd(111).⁴ The sampling of the Brill-
 ouin zone was performed with the Γ -centered
 $(14 \times 14 \times 1)$ Monkhorst-Pack mesh.³⁵ The metal

substrates were represented by slabs composed
 of four (111) atomic layers. Increasing the
 metal thickness up to 6 atomic layers yields neg-
 ligible corrections on all quantities, consistently
 with marginal (less than 0.05 eV) changes of the
 metal work functions. The oxide film was de-
 posited on one side of the metal slab. Be-
 yond the symmetric film structures assumed
 in Ref.,⁹ all atomic coordinates of anions and
 cations have been allowed to fully relax until
 forces got lower than $0.01 \text{ eV}\text{\AA}^{-1}$. Atoms in
 the metal substrates were relaxed only in the
 direction normal to the surface. In the follow-
 ing, the atomic structure of supported MLs will
 be systematically quantified by the average film
 rumpling R (defined as a difference of average
 vertical positions of anions and cations $\bar{z}_O - \bar{z}_C$)
 and by the average rotation of MO_3 entities
 $\phi = \angle(M' - M - O)$ projected on the surface
 plane, Fig. 1.

Adhesion energies between the oxide mono-
 layers and the metal substrates $E_{adh}(Me)$ were
 calculated from energy differences between the
 constituted oxide/metal system $E^{oxide/Me}$ and
 its separated components (bare metal substrate
 E^{Me} and freestanding oxide ML at its equilib-
 rium lattice parameter E^{oxide}):

$$E_{adh}(Me) = E^{Me} + E^{oxide} - E^{oxide/Me} \quad (1)$$

With this definition, adhesion energies are pos-
 itive if adhesion is favored.

Formation or mixing energies E_{mix} of both

freestanding and supported $MM'O_3$ monolayers were calculated from energy differences between the mixed oxide $E^{MM'O_3}$ and the average of the two corresponding parents $(E^{M_2O_3} + E^{M'_2O_3})/2$:

$$E_{mix}^{MM'O_3} = E^{MM'O_3} - \frac{E^{M_2O_3} + E^{M'_2O_3}}{2} \quad (2)$$

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

Table 1: Main Characteristics of Freestanding and Me-supported (Me = Ag, Au and Pt) M_2O_3 MLs (M = Ti, V, Cr, and Fe): Film Rumpling R (Å), In-Plane Rotation ϕ ($^\circ$), Bader Charges on Cations Q_M (e) and Oxygen Atoms Q_O (e), Total Charge of Metal Substrate Q_{Me} (e/ M_2O_3 f.u.), and Cation Magnetic Moments μ_M (μ_B).

	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃
freestanding				
Q_M	1.78	1.69	1.62	1.64
Q_O	-1.19	-1.13	-1.08	-1.10
μ_M	0.9	2.1	3.1	3.9
Ag-supported				
R	0.60	0.41	0.09	0.09
ϕ	14	17	10	19
Q_M	1.92	1.72	1.55	1.44
Q_O	-1.06	-1.04	-1.08	-1.07
μ_M	0.0	1.4/1.5	3.0	3.8
Q_{Ag}	-0.67	-0.33	+0.15	+0.33
Au-supported				
R	0.68	0.68	0.54	0.23
ϕ	10	1	14	20
Q_M	2.00	1.83	1.65	1.53
Q_O	-1.02	-0.96	-0.96	-1.01
μ_M	0.0	1.2	2.7	3.8
Q_{Au}	-0.94	-0.77	-0.42	-0.02
Pt-supported				
R	0.70	0.75	0.47	0.29
ϕ	19	11	17	24
Q_M	2.00	1.87	1.65	1.50
Q_O	-1.01	-0.92	-0.96	-0.98
μ_M	0.0	0.5	2.5	3.8
Q_{Pt}	-0.98	-0.98	-0.44	-0.06

3 Results on supported M_2O_3 monolayers

We first present the computational results for the M_2O_3 HC monolayers (M = Ti, V, Cr, and Fe) supported on the three Me(111) substrates (Me = Ag, Au and Pt). Table 1 and Figure 2 report their main structural, electronic, and magnetic characteristics. The comprehensive set of results, is given in SI, Tabs. S1 and S2. HSE03 results for the M_2O_3 /Au system (M = Ti, V, Cr, and Fe) are given in Tab. S7 and Fig. S1. In the following, the notation Δ will refer to differences between quantities (positions, distances, charges, etc) in the supported and freestanding films

Fully relaxed freestanding oxide MLs systematically adopt a symmetric nearly planar geometry ($R \sim 0$ and $\phi \sim 0$). The only exception is the freestanding Cr_2O_3 monolayer, for which we find a non-vanishing rumpling ($R = 0.06$ Å). The interaction with the metal substrates and the in-plane compression associated to the lattice mismatch between the oxide films and metal surfaces ($a_{M_2O_3} > a_{Me}$, SI, Tab. S1) induce film distortion, which consists of in-plane rotations ϕ of the MO_3 entities and of rumpling R . We will show in the discussion that the positive sign of R (the average outward displacement of the oxygen atoms with respect to the cations), its decrease from Ti to Fe (for each substrate), and its increase from Ag to Pt (for each oxide) are principally driven by the behavior of the interface charge transfer Q_{Me} . Beyond the effect of film rumpling, the in-plane rotations ϕ of the MO_3 entities allow a further reduction of the in-plane oxide lattice parameters such that, despite substantial lattice mismatch, the cation-oxygen distances d_{M-O} remain in all cases close to the corresponding values in the freestanding MLs ($|\Delta d_{M-O}/d_{M-O}| < 2\%$, Tab. S1).

From an electronic point of view, the interaction of the oxide layers with the metallic substrates is characterized by an electron exchange between them, leading in most cases to a negative charging of the Me substrates (negative total substrate charge per M_2O_3 unit, Q_{Me}).

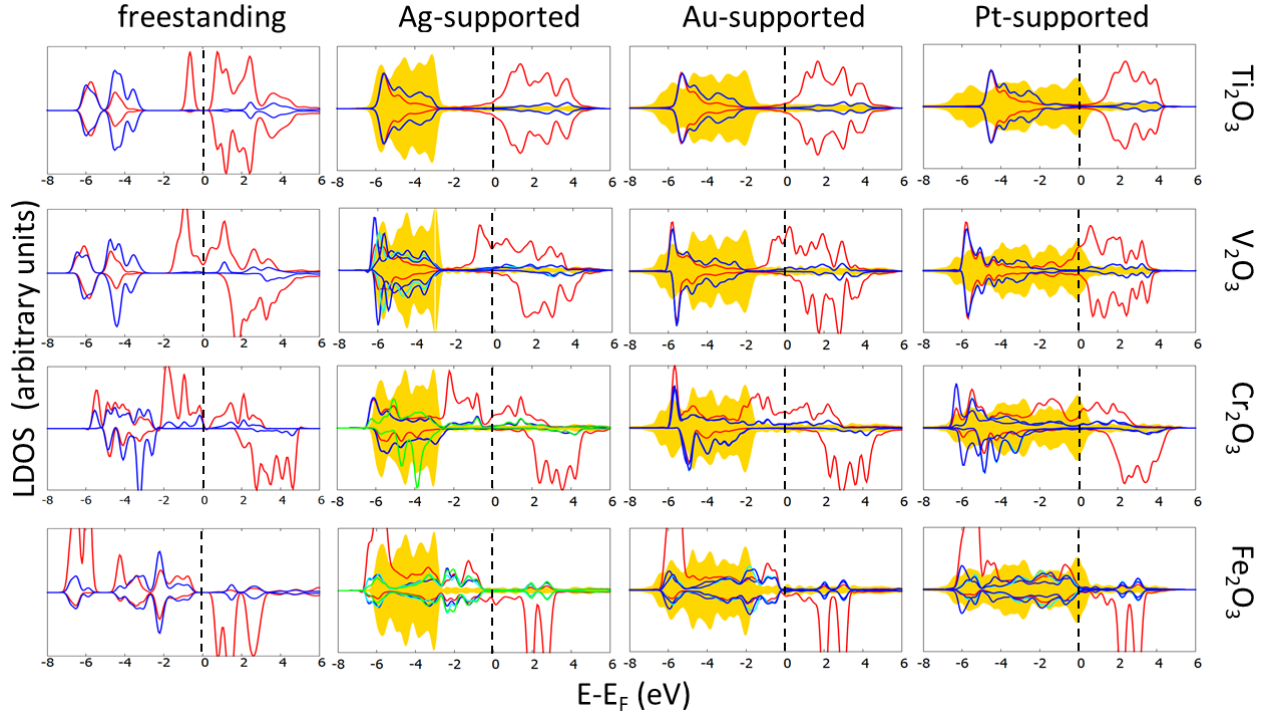


Figure 2: Local densities of states of freestanding and metal-supported M_2O_3 HC MLs ($M = \text{Ti}, \text{V}, \text{Cr}, \text{and Fe}$) projected on cations (red), oxygen atoms (blue), and substrates (golden shading). A broadening of 0.2 eV has been systematically applied. The vertical dashed lines indicate the positions of the Fermi levels.

260 Small positive Q_{Me} are found only for Cr_2O_3 284
 261 and Fe_2O_3 MLs deposited on the Ag substrate. 285
 262 In the case of Ag and Au surfaces, where the 286
 263 Fermi level is positioned relatively high in the 287
 264 valence *sp* band, the substrate *d* states con- 288
 265 tribute only little to the interfacial hybridiza- 289
 266 tion and the electrons transferred from the ox- 290
 267 ide film mainly populate the substrate *s* and 291
 268 *p* orbitals. Conversely, since the Fermi level of 292
 269 the Pt substrate falls in its 4*d* band, the Pt 293
 270 *d* states hybridize strongly with those of the ox- 294
 271 ide film and become populated by the interfa- 295
 272 cial charge transfer. Finally the Ag electrons 296
 273 transferred towards the Cr_2O_3 and Fe_2O_3 films 297
 274 populate principally the cation *d* states at the 298
 275 bottom of the oxide conduction band. As ex- 299
 276 pected, $|Q_{Me}|$ tends to decrease monotonically 300
 277 from Ti to Fe (for each substrate), following 301
 278 the increase of cation electronegativity, and in- 302
 279 creases from Ag to Pt (for each oxide), following 303
 280 the increase of the substrate surface work func- 304
 281 tions (calculated values are 4.8 eV, 5.6 eV, and 305
 282 6.1 eV for Ag, Au, and Pt, respectively). The 306
 283 negative Q_{Me} result from a cooperative effect of 307

charge modifications on the oxide cations and oxygen atoms, Q_M increasing (except Q_{Fe}) and $|Q_O|$ decreasing when in contact with a support. The relative contributions of the oxygen atoms to $|Q_{Me}|$ increase from Ti to Fe. Positive Q_{Me} are principally associated with a reduction of cation charges, the effect being particularly strong in the $\text{Fe}_2\text{O}_3/\text{Ag}$ case.

Associated to this interfacial electron transfer, the oxide local densities of states (LDOS) are substantially modified. As seen in Figure 2, whatever the substrate, the modifications are particularly strong at the beginning of the series, in the Mott-Hubbard oxides Ti_2O_3 and V_2O_3 , where filled Ti and V 3*d* states close to the Fermi level get totally or partially depleted. At variance, due to the mixed oxygen-cation character of their states at the band gap edges, the band structures of Cr_2O_3 and Fe_2O_3 are much less impacted by the interaction with the metallic substrates.⁹ For each oxide, the increase of the metal work function from Ag to Pt shifts the substrate Fermi level progressively downwards on the energy scale. As a conse-

308 quence, in Ti_2O_3 which has a nearly pure Mott- 357
 309 Hubbard character, the Fermi level E_F moves 358
 310 from the bottom of the Ti-like conduction band 359
 311 (CB) on Ag towards the oxide mid-gap on Pt. 360
 312 The single valence d electron characteristic of 361
 313 the freestanding Ti_2O_3 ML is in all cases delo- 362
 314 calized towards the underlying metal, which is 363
 315 consistent with the substantial increase of Q_{Ti} 364
 316 and the systematic quenching of μ_{Ti} , Tab. 1. 365
 317 These major modifications of the Ti_2O_3 elec- 366
 318 tronic structure suggest that a change of oxi- 367
 319 dation state takes place upon deposition. On 368
 320 general grounds, at variance with the unques- 369
 321 tionable 3+ cation valence in freestanding MLs, 370
 322 changes of oxidation states in systems with de- 371
 323 localized electrons cannot be assessed merely
 324 from Bader charges. It is the concomitant mod-
 325 ifications of the LDOS and magnetic moments 372
 326 μ_{Ti} which can be tentatively rationalized by a 373
 327 Ti 4+ oxidation state on the three substrates.

328 Similarly, in the case of the Mott-Hubbard ox- 374
 329 ide V_2O_3 , the progressive downward shift of the 375
 330 Fermi level within the majority vanadium band 376
 331 explains the increase of Q_V and the decrease of 377
 332 μ_V along the Ag, Au, Pt series. These results 378
 333 are consistent with a progressive increase of the 379
 334 vanadium oxidation state in V_2O_3 monolayer 380
 335 supported on the three metal substrates. How- 381
 336 ever, changes of V-O hybridization induced by 382
 337 film distortions and the hybridization between 383
 338 cation and substrate states (particularly strong 384
 339 in case of Pt) impede a robust and fully reli- 385
 340 able assignment of oxidation states in the three 386
 341 cases. 387

342 Finally, in Cr_2O_3 and Fe_2O_3 the shape of the 388
 343 oxide LDOS in the vicinity of the Fermi level 389
 344 is very similar on the three substrates. Consis- 390
 345 tently, changes of Q_M and μ_M with respect to 391
 346 the freestanding references are similarly small 392
 347 on the three substrates and suggest that the 393
 348 cation 3+ oxidation states are essentially not 394
 349 altered. 395

350 To summarize, the interaction with the metal 396
 351 substrates induces structural distortions of the 397
 352 oxide MLs and an electron transfer from the 398
 353 oxides towards the metal, which both increase 399
 354 from Ag to Pt and decrease from Ti to Fe. 400
 355 Only when Cr_2O_3 and Fe_2O_3 are deposited on 401
 356 Ag a small amount of electrons is transferred 402

from the substrate towards the oxide film. The
 substrate-induced change of oxide electronic
 and magnetic characteristics is particularly pro-
 nounced in Ti_2O_3 and V_2O_3 , where it can be as-
 sociated to an increase of cation oxidation state.
 If the single Ti valence electron tends to be sys-
 tematically transferred to the metal substrate,
 the cation charge of supported V_2O_3 increases
 progressively from Ag to Pt. Conversely, the
 much weaker electronic modifications found for
 Cr_2O_3 and Fe_2O_3 suggest the preservation of
 the cation 3+ oxidation state characteristic of
 the freestanding MLs. These conclusions are
 well supported by the HSE03 results (SI, Tab.
 S7).

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

DFT+U results for the main structural, elec-
 tronic and magnetic characteristics of free-
 standing and Me-supported mixed $\text{MM}'\text{O}_3$ HC
 MLs (M, M' = Ti, V, Cr, and Fe; Me = Ag,
 Au, Pt) are given in Table 2 and Figures 3 and
 4. The complete set of results can be found in
 SI, Tabs. S4 and S5, in which the symbols δ
 denote the mixing-induced differences between
 quantities (positions, distances, charges, etc) in
 the supported mixed oxides and their parents.
 HSE03 results for mixed MLs on the Au sub-
 strate are reported in SI, Tab. S8 and Fig. S2.

From a structural point of view, the metal-
 supported mixed oxide films are qualitatively
 similar to their supported parents. They
 systematically display a substantial (positive)
 rumpling and in-plane rotations of MO_3 entities
 which enable an accommodation of the inter-
 face lattice mismatch without strong modifica-
 tions of the cation-oxygen distances d_{M-O} and
 $d_{M'-O}$ ($|\Delta d_{M-O}/d_{M-O}| < 4\%$, Tab. S4). Con-
 trary to the parent systems, in the mixed films
 the two cations are systematically not coplanar.
 Cationic mixing produces a quite substantial
 rumpling enhancement ($\delta R \sim 0.15 - 0.25 \text{ \AA}$) in
 VCrO_3/Ag , VFeO_3/Pt , and CrFeO_3/Pt , but in
 TiFeO_3/Ag , TiCrO_3/Au , and VCrO_3/Au , R is
 reduced ($\delta R \sim -0.10 \text{ \AA}$), Tab. S4. We will show
 in the discussion that the positive sign and the

Table 2: Main Characteristics of Metal (Ag, Au, and Pt)-Supported Mixed MM'O₃ HC Monolayers (M, M' = Ti, V, Cr, and Fe): Film Rumpling R (Å), In-Plane Rotation ϕ (°), Bader Charges on Cations Q_M, Q'_M (e) and Oxygen Atoms Q_O (e), Metal Substrate Charge Q_{Me} (e/MM'O₃ f.u.), and Cation Magnetic Moments $\mu_M, \mu_{M'}$ (μ_B).

	TiVO ₃	TiCrO ₃	TiFeO ₃	VCrO ₃	VFeO ₃	CrFeO ₃
freestanding						
$Q_M, Q_{M'}$	1.75,1.69	1.80,1.55	2.09, 1.33	1.84, 1.47	1.87, 1.35	1.67, 1.60
Q_O	-1.15	-1.12	-1.14	-1.10	-1.08	-1.09
$\mu_M, \mu_{M'}$	1.0, 2.0	0.9, 3.2	0.1, 3.6	1.4, 3.6	1.3, 3.6	2.7, 4.0
Ag-supported						
R	0.50	0.41	0.23	0.47	0.35	0.06
ϕ	15	19	19	18	19	18
$Q_M, Q_{M'}$	1.91,1.73	1.93,1.58	1.95,1.38	1.81,1.46	1.82,1.35	1.60,1.37
Q_O	-1.05	-1.06	-1.09	-1.00	-1.01	-1.08
$\mu_M, \mu_{M'}$	0.2,1.4	0.2,2.9	0.1,3.7	0.7,3.4	0.,3.7	2.6,3.7
Q_{Ag}	-0.47	-0.33	-0.05	-0.27	-0.15	0.27
Au-supported						
R	0.69	0.52	0.45	0.49	0.50	0.35
ϕ	5	16	19	16	16	20
$Q_M, Q_{M'}$	1.99,1.86	2.01,1.67	2.01,1.54	1.93,1.51	1.94,1.42	1.69,1.51
Q_O	-0.99	-1.02	-1.03	-0.98	-0.96	-1.00
$\mu_M, \mu_{M'}$	0.1,0.9	0.1,2.8	0.1,3.9	0.5,3.4	0.0,3.7	2.2,3.9
Q_{Au}	-0.88	-0.60	-0.45	-0.50	-0.48	-0.21
Pt-supported						
R	0.74	0.61	0.52	0.68	0.67	0.62
ϕ	15	20	24	18	18	19
$Q_M, Q_{M'}$	1.97,1.91	1.98,1.69	2.00,1.55	1.94,1.62	1.96,1.49	1.75,1.47
Q_O	-0.95	-0.97	-1.00	-0.92	-0.91	-0.89
$\mu_M, \mu_{M'}$	0.0,0.0	0.1,2.3	0.1,4.0	0.3,2.8	0.1,3.9	1.3,3.9
Q_{Pt}	-1.04	-0.76	-0.54	-0.80	-0.70	-0.55

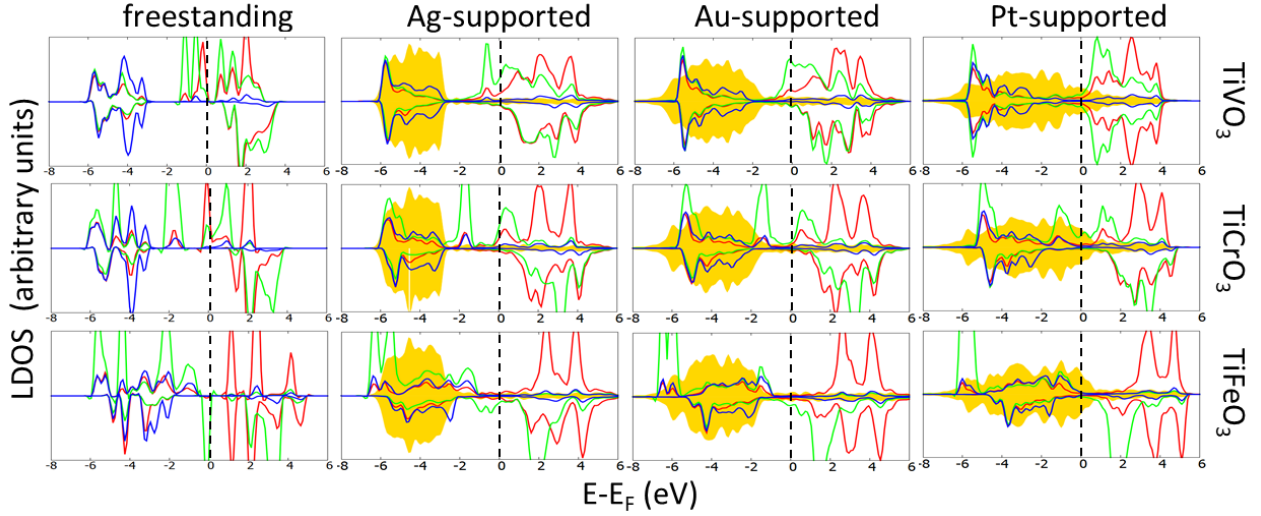


Figure 3: Local densities of states in freestanding and Me-supported mixed $\text{TiM}'\text{O}_3$ honeycomb monolayers ($M' = \text{V}, \text{Cr}, \text{Fe}$) projected on Ti (red), M' (green), O atoms (blue), and substrate atoms (gold shading). A broadening of 0.2 eV has been systematically applied. Vertical dashed lines indicate the position of the Fermi level.

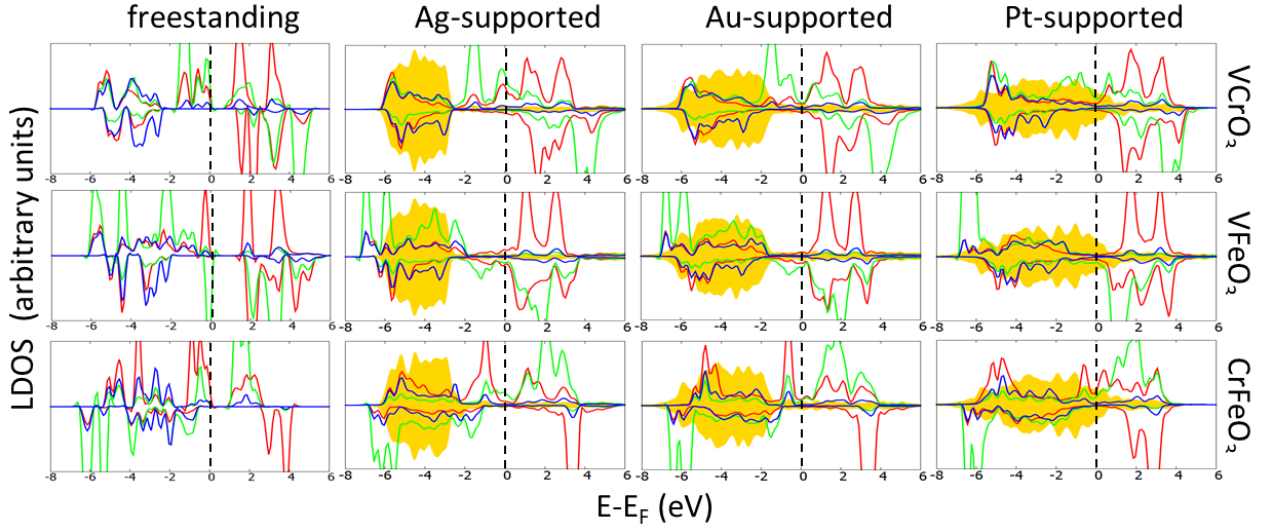


Figure 4: Local densities of states in freestanding and Me-supported mixed $\text{MM}'\text{O}_3$ honeycomb monolayers ($M = \text{V}, \text{Cr}$; $M' = \text{Cr}, \text{Fe}$) projected on M (red), M' (green), O atoms (blue), and substrate atoms (gold shading). A broadening of 0.2 eV has been systematically applied. Vertical dashed lines indicate the position of the Fermi level.

403 amplitude of R are mainly driven by the behav- 452
404 ior of the interface charge transfer Q_{Me} . 453

405 Similarly to most supported M_2O_3 parents, 454
406 the interaction of the mixed films with the 455
407 metallic substrates gives rise to a systematic 456
408 electron transfer from the oxide towards the 457
409 substrate ($Q_{Me} < 0$), but in $CrFeO_3/Ag$ where 458
410 electrons are transferred towards the oxide film 459
411 ($Q_{Me} > 0$). Both cations and anions contribute 460
412 to the interface charge transfer and the per- 461
413 centage weight of oxygen contributions progres- 462
414 sively increases along the oxide series. At each 463
415 of the three substrates $|Q_{Me}|$ decreases follow- 464
416 ing the increasing average electronegativity of 465
417 the two cations ($TiVO_3 < TiCrO_3 < VCrO_3 <$ 466
418 $TiFeO_3 < VFeO_3 < CrFeO_3$). For each oxide 467
419 it increases from Ag to Pt in line with the in- 468
420 creasing substrate work functions. As a conse- 469
421 quence, cation charges $Q_{M,M'}$ increase and oxy- 470
422 gen charges $|Q_O|$ decrease when moving from 471
423 Ag to Pt. Only Q_{Ti} values change particularly 472
424 little from one substrate to another in all sup- 473
425 ported $TiM'O_3$ compounds. 474

426 In our previous study on freestanding films,³ 475
427 we have pointed out that the electronic mod- 476
428 ifications in $TiVO_3$, $TiCrO_3$, and $CrFeO_3$ due 477
429 to mixing are small since their cationic charges 478
430 and magnetic moments are close to those in the 479
431 corresponding freestanding parents, and their 480
432 LDOS differ little from a superposition of the 481
433 parent LDOS. Conversely, in $TiFeO_3$, $VCrO_3$, 482
434 and $VFeO_3$, a well pronounced increase of Q_M 483
435 and a decrease of $Q_{M'}$, correlated with strong 484
436 modifications of cation magnetic moments and 485
437 LDOS peak positions with respect to the Fermi 486
438 level, have been rationalized in terms of mixing- 487
439 induced redox reactions, leading to $Ti^{4+}Fe^{2+}$, 488
440 $V^{4+}Cr^{2+}$, and $V^{4+}Fe^{2+}$ oxidation states, respec- 489
441 tively. 490

442 The presence of the metal substrates visibly 491
443 alters this picture. In contrast to the freestand- 492
444 ing case, supported $TiFeO_3$ displays only neg- 493
445 ligible mixing-induced electronic modifications, 494
446 regardless of the metal support (Tab. 2 and 495
447 1 and Fig. 2, 3 and 4). Moreover, while, 496
448 similarly to the freestanding films, the mixing-
449 induced changes in $VFeO_3$ and $VCrO_3$ are the
450 most pronounced, the underlying electron re-
451 distributions do not follow the same pattern

on the three substrates. Indeed, on Ag and
Au substrates, the changes mostly consist of
an electron exchange between the two cations
($\delta Q_V \approx -\delta Q_{Cr,Fe}$, Tab. S5), and are associ-
ated with opposite shifts of the V and Cr/Fe
states in the vicinity of the Fermi level (see Fig.
4). In these mixed oxides also the modifications
of oxygen charges δQ_O provide a non-negligible
contribution to δQ_{Me} . Conversely, on the Pt
substrate the largest modifications concern only
vanadium cations, which points toward an in-
crease of the vanadium oxidation state stabi-
lized by an electron transfer towards the metal
substrate δQ_{Pt} . These different behaviors illus-
trate the competition between electron trans-
fer between the two cations and from a cation
to the substrate, governed by the availability
and nature of the oxide electronic states in the
vicinity of the Fermi level. At variance with
the above, the electronic characteristics of sup-
ported $TiVO_3$ and $TiCrO_3$ films remain rela-
tively close to those of their supported parents,
as was the case for their freestanding counter-
parts. Finally, $CrFeO_3$ displays an intermediate
behavior. On Ag and Au, mixing-induced mod-
ifications are relatively weak, but on Pt, μ_{Cr} is
visibly reduced. These changes, together with
the complex DOS modifications (see Fig. 4) do
not allow a clear assignment of a change of ox-
idation state.

To summarize, the structural (R) and elec-
tronic (Q_{Me}) characteristics of the supported
pure and mixed oxide films follow qualitatively
similar trends. The electronic characteristics of
 $TiVO_3$, $TiCrO_3$, and $TiFeO_3$ correspond closely
to a superposition of those of their parents.
Conversely, in Ag- and Au- supported $VCrO_3$
and $VFeO_3$ mixing induces an electron transfer
from V to either Cr or Fe. It is much stronger
in $VFeO_3$ and can be tentatively interpreted as
a redox reaction. Interestingly, on the Pt sub-
strate, the electrons are rather transferred from
V to the metal substrate. These conclusions
are well supported by HSE03 results given in
SI, Tab. S8 and Fig. S2.

5 Discussion

498 In this section, we first discuss the mechanisms
 499 which govern the electronic and structural char-
 500 acteristics of metal-supported HC oxides upon
 501 interaction with the substrate (Section 5.1) and
 502 upon cation mixing (Section 5.2). Then we ana-
 503 lyze the evolution of the oxide adhesion (Section
 504 5.3) and mixing (Section 5.4) energies.

5.1 Electron redistribution at the oxide/metal interface

507 In our recent study on the Au-supported pure
 508 M_2O_3 monolayers,⁹ we have shown that the
 509 interfacial charge transfer Q_{Au} and its conse-
 510 quences on the electronic characteristics of the
 511 deposited oxide films may be reliably inferred
 512 from the offset between the point of zero charge
 513 of the freestanding oxide films E_{ZCP} (approx-
 514 imated by the energy at mid-gap position) with
 515 respect to the Fermi level of the bare Au sur-
 516 face $E_F(Au)$ and from the character of the oxide
 517 gap edges. We have shown that the decrease of
 518 $|Q_{Au}|$ along the series of transition metal ox-
 519 ides is due to the progressive lowering of the
 520 point of zero charge, mainly due to the increase
 521 of the cation electronegativity. This argument
 522 is generalized in Figure 5 to the parents and
 523 mixed oxide MLs deposited on the three sub-
 524 strates. Corresponding results from hybrid calcu-
 525 lations on Au-supported M_2O_3 and $MM'O_3$
 526 compounds are reported in SI, Fig. S3.

527 In agreement with the results of Ref.,⁹ we
 528 find that, for each substrate and regardless of
 529 the pure or mixed oxide character, the interface
 530 charge transfer correlates well with $E_F(Me) -$
 531 E_{ZCP} . As a consequence, Q_{Me} is systemati-
 532 cally the most negative for M_2O_3 oxides with
 533 the least electronegative cations (Ti, V), and
 534 for mixed oxides with the smallest average
 535 cation electronegativity ($TiVO_3$, $TiCrO_3$, and
 536 $VCrO_3$). Conversely, small positive Q_{Me} val-
 537 ues are found for Cr_2O_3 , Fe_2O_3 and $CrFeO_3$.
 538 Moreover, for each oxide, the substrate charge
 539 becomes more negative along the Ag, Au, and
 540 Pt series, following the increase of the work
 541 functions of the metal surfaces (4.8 eV, 5.6 eV,
 542 and 6.1 eV, respectively). Such quasi-linear be-

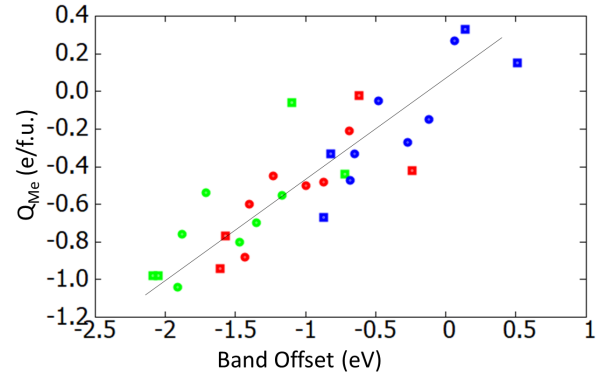


Figure 5: Interface charge transfer Q_{Me} (e/M_2O_3 or $MM'O_3$ f.u.) as a function of the offset $E_F(Me) - E_{ZCP}$ (eV) between the Fermi level of the bare metal surface and the point of zero charge of the freestanding pure (squares) and mixed (circles) oxide monolayers. Results for Ag, Au, and Pt substrates are plotted with blue, red, and green symbols, respectively. Line is drawn to guide the eye.

543 haviour of the interface charge transfer as a
 544 function of the band offset agrees well with the
 545 predictions of the Metal-Induced Gap States
 546 (MIGS) model at metal/semiconductor inter-
 547 faces.^{36,37}

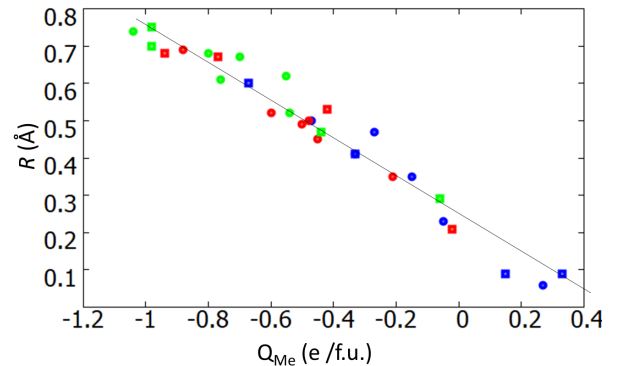


Figure 6: Average rumpling R (\AA) in supported pure M_2O_3 (squares) and mixed $MM'O_3$ (circles) MLs as a function of the electron transfer Q_{Me} (e/M_2O_3 or $MM'O_3$ f.u.) Results for $Me = Ag, Au,$ and Pt substrates are represented in blue, red, and green, respectively. Line is drawn to guide the eye.

548 Metal-supported oxide monolayers undergo
 549 structural distortions in response to the electro-
 550 static dipole produced by the interface charge

transfer Q_{Me} .^{38,39} Based on a simple electro-
static argument, a negatively charged substrate
($Q_{Me} < 0$) repels the anions and thus tends to
produce a positive rumpling ($R > 0$) whereas
a negative rumpling is expected for a positive
charging of the substrate. The induced struc-
tural dipole of the oxide film which results from
such electrostatic coupling between charge and
structure has been baptized induced polarity.³⁸
In agreement with this argument, we find that,
for each substrate and regardless of the pure
or mixed oxide character, the film rumpling R
correlates very well with the interface charge
transfer Q_{Me} . As a consequence, R is system-
atically the largest for oxides which transfer the
largest number of electrons to the metal sub-
strates (Ti_2O_3 , V_2O_3 , TiVO_3). Conversely, the
smallest film rumpling is systematically found
for Fe_2O_3 , Cr_2O_3 and CrFeO_3 . Moreover, rum-
pling of each oxide film increases when moving
from Ag to Pt, following the corresponding in-
crease of the electron transfer. We stress that
such an excellent unique $R \propto Q_{Me}$ relationship
obtained for a variety of oxide films on various
metal substrates is likely due to a negligible ef-
fect of lattice mismatch on R , the latter being
rather accommodated by in-plane rotations.

At this point it is worth noting that the mono-
tonic decrease of R is associated with more com-
plex film structure. Indeed, while large rum-
pling values (large negative Q_{Me}) are systemat-
ically associated to an outward relaxation of the
three oxygen atoms (per f.u.) with respect to
the cation planes, in Fe_2O_3 , Cr_2O_3 , and CrFeO_3
on Ag (the smallest R and positive Q_{Me} values),
although R remains positive, two oxygen atoms
are located below the average cation positions
(SI Tables S1 and S4). In case of oxides which
display the smallest negative Q_{Me} (Fe_2O_3 on Au
and Pt, TiFeO_3/Ag), only one oxygen atom is
located below the cation plane or two oxygen
atoms are nearly coplanar with the cations.

To summarize, we have shown that the elec-
tron transfer between the oxides and the metal
substrate is mainly driven by the offset between
the oxide band structure (point of zero charge)
and the substrate Fermi level. As a conse-
quence, the strongest electron redistributions
(large negative Q_{Me}) are found in oxides with

the least electronegative cations (Ti and V) de-
posited on metal substrates with the largest
work functions (Au, Pt). Moreover, we find
that the interface electron transfer determines
the behavior of the substrate-induced film po-
larization (rumpling) and is responsible for
its progressive decrease from the least (Ti_2O_3 ,
 V_2O_3 , TiVO_3) to the most (Fe_2O_3 , Cr_2O_3 , and
 CrFeO_3) electronegative compounds.

5.2 Electron redistribution upon cationic mixing

While the previous section dealt with the mod-
ifications of the oxide ML atomic and elec-
tronic structure due to their interaction with
the metallic substrates, here we focus on those
which take place upon cationic mixing.

In the past we have successfully rational-
ized the electronic characteristics of mixed bulk
 $\text{MM}'\text{O}_3$ materials,²⁵ freestanding $\text{MM}'\text{O}_3$ hon-
eycomb monolayers,³ and $\text{M}_2\text{O}_3/\text{M}'_2\text{O}_3$ inter-
faces,²⁶ from the band offsets between the cor-
responding parent M_2O_3 and $\text{M}'_2\text{O}_3$ materials. In
the present case, a similar analysis can be based
on a comparison between the LDOS of the four
metal-supported parents on an energy scale de-
fined by their common vacuum level, Fig. 7.
As a reference, the corresponding results for
the freestanding HC MLs are recalled. Corre-
sponding HSE03 results on $\text{M}_2\text{O}_3/\text{Au}$ HCs are
reported in SI, Figure S4.

The band offset between any couple of par-
ents is quantified by the difference of positions
of their Fermi levels $\Delta E_F = E_F(\text{M}_2\text{O}_3/\text{Me}) -$
 $E_F(\text{M}'_2\text{O}_3/\text{Me})$, such that positive and neg-
ative values of ΔE_F indicate an initial bias
for $\text{M}_2\text{O}_3/\text{Me} \rightarrow \text{M}'_2\text{O}_3/\text{Me}$ and $\text{M}'_2\text{O}_3/\text{Me} \rightarrow$
 $\text{M}_2\text{O}_3/\text{Me}$ electron transfers, respectively. Be-
yond the relative positions of the Fermi levels
 ΔE_F , the actual possibility of the charge trans-
fer as well as the precise origin and destination
of the transferred electrons also depend on the
character of the occupied and empty states in
the vicinity of the Fermi level.

While the ordering of Fermi level positions in
the freestanding parents was qualitatively de-
termined by the cation electronegativity differ-
ence, in the supported ones, it is rather due

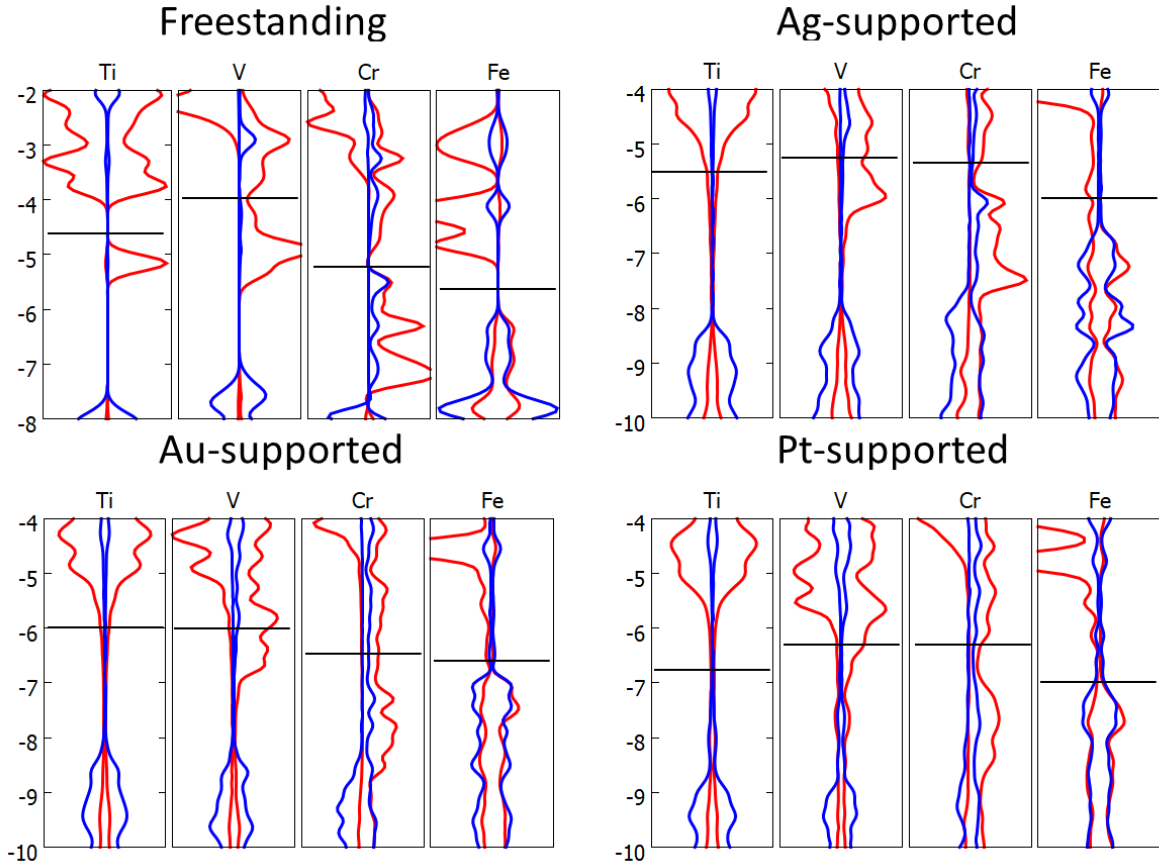


Figure 7: LDOS of the freestanding and Me-supported pure M_2O_3 monolayers ($M = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}$) in the vicinity of their Fermi level (marked by the horizontal black lines), projected on cations (red), and oxygen atoms (blue), on an energy scale obtained by alignment of the common vacuum level. A broadening of 0.2 eV has been systematically applied.

647 to the change in metal work function induced 687
 648 by the deposition of an oxide film ΔW . Cal- 688
 649 culated ΔW for the four parents are given in 689
 650 Table 3. We note that, since at each substrate 690
 651 the largest values are systematically found for 691
 652 Fe_2O_3 and the smallest ones for V_2O_3 , the re- 692
 653 sulting ordering of Fermi level positions is not 693
 654 strongly modified compared to that found in 694
 655 the freestanding films. 695

Table 3: Change of the Metal Work Function ΔW (eV) upon Deposition of Pure HC Monolayers.

	Ti_2O_3	V_2O_3	Cr_2O_3	Fe_2O_3
ΔW_{Ag}	0.62	0.38	0.45	1.15
ΔW_{Au}	0.36	0.44	0.80	0.95
ΔW_{Pt}	0.75	0.15	0.17	0.89

656 We recall that ΔW is determined by the 705
 657 dipole moment of the oxide/metal inter- 706
 658 face, which consists of three main contribu- 707
 659 tions.^{38,40,41} The first one comes from the re- 708
 660 duction of the substrate surface dipole caused 709
 661 by the compression of the spilled-out metal elec- 710
 662 trons by the deposited oxide monolayer. The 711
 663 second one is induced by the electron exchange 712
 664 Q_{Me} between the oxide film and the metallic 713
 665 substrate. The third one is due to the struc- 714
 666 tural film polarization (rumpling) R . While the 715
 667 first effect produces a negative contribution to 716
 668 ΔW , and while a positive film rumpling ($R >$ 717
 669 0) tends to increase R , the contribution due 718
 670 to electron exchange at the interface either de- 719
 671 creases (negative Q_{Me}) or increases (positive 720
 672 Q_{Me}) the substrate work function. 721

673 In the present case, the systematically pos- 722
 674 itive signs of ΔW , Tab. 3, suggest that the 723
 675 rumpling contribution is dominant, aided by 724
 676 the charge transfer term in the few cases where 725
 677 Q_{Me} is positive. However, since the largest ΔW 726
 678 values (Fe_2O_3 on the three substrates) system- 727
 679 atically correspond to the smallest rumplings 728
 680 R , the behavior of ΔW along the series of ox- 729
 681 ides is clearly not rumpling-driven. The largest 730
 682 ΔW , responsible for the most pronounced band 731
 683 offsets between parent materials, rather corre- 732
 684 spond to positive or small negative values of 733
 685 the charge transfer contribution. It should be 734
 686 noted that in-plane rotation ϕ may also play 735

a role since the largest values in Tab. 3 also correspond to the largest rotations.

Solely from the signs of ΔE_F , Fig. 7, one deduces that an electron transfer may systematically occur from $\text{Ti}_2\text{O}_3/\text{Me}$ or $\text{V}_2\text{O}_3/\text{Me}$ toward $\text{Fe}_2\text{O}_3/\text{Me}$ ($\text{Me} = \text{Ag}, \text{Au}$ and Pt) or $\text{Cr}_2\text{O}_3/\text{Au}$, and from $\text{Cr}_2\text{O}_3/\text{Me}$ toward $\text{Fe}_2\text{O}_3/\text{Me}$ ($\text{Me} = \text{Ag}$ and Pt). No electron exchange is expected between $\text{Ti}_2\text{O}_3/\text{Me}$ and $\text{V}_2\text{O}_3/\text{Me}$ except on Pt , where an electron transfer from V_2O_3 to Ti_2O_3 could be anticipated. If additionally the character and the density of states at the Fermi level are taken into account, it becomes clear that supported Ti_2O_3 is unlikely to provide electrons to Cr or Fe upon mixing because it has no available occupied cationic d states. Also the electron transfer from V_2O_3 to Ti_2O_3 on Pt is impeded by the absence of empty Ti d states in the energy range between the two Fermi levels. As a consequence, no significant mixing-induced charge redistribution is expected in all Ti -containing compounds. Conversely, since a significant number of occupied cationic states just below the Fermi level exist in $\text{V}_2\text{O}_3/\text{Me}$, an electron transfer from $\text{V}_2\text{O}_3/\text{Me}$ towards $\text{Fe}_2\text{O}_3/\text{Me}$ is systematically to be expected, as well as a transfer from $\text{V}_2\text{O}_3/\text{Au}$ towards $\text{Cr}_2\text{O}_3/\text{Au}$. We note that the absence of empty Fe_2O_3 states in the direct vicinity of the Fermi level may produce an electron transfer toward the metal substrate rather than toward the Fe cations. Finally, the limited number of occupied (empty) states at E_F in $\text{Cr}_2\text{O}_3/\text{Me}$ ($\text{Fe}_2\text{O}_3/\text{Me}$) may hinder electron redistribution in CrFeO_3/Me . These predictions correlate very well with the results of the full calculations, Sec. 4.

To summarize, the relative positions of the Fermi levels in the supported parents provide a good guide for understanding the electronic redistributions in the mixed compounds. While the ordering of Fermi levels in the series of parent oxides is not strongly modified by the metal substrate, we have pointed out that the character of the oxide states in the vicinity of the Fermi level is. For the series of supported $\text{MM}'\text{O}_3$ HC MLs, the offsets between the parent band structures and the absence of Ti d states in the the Fermi level vicinity

in supported Ti_2O_3 explain why any significant mixing-induced electronic structure modifications are limited to the VFeO_3/Me and VCrO_3/Me compounds only. The strong increase of vanadium oxidation state suggests an enhanced reactivity of the supported vanadate films, which could thus be of interest in various catalytic reactions, in the same way as the oxygen-rich V_2O_5 oxide is the most important industrial vanadium compound, used as a catalyst.

5.3 Adhesion at the HC/Me interfaces

Table 4 summarizes the adhesion energies E_{adh} (Eq. 1) of pure and mixed oxide monolayers supported on the three metal substrates as well as the misfits between the freestanding layers and metal substrate. Adhesion energies are found to be always positive (favorable to adhesion) and to span a large set of values ranging from about 1.1 eV ($\text{Cr}_2\text{O}_3/\text{Au}$ and CrFeO_3/Au) to more than 4.5 eV ($\text{Ti}_2\text{O}_3/\text{Pt}$ and TiVO_3/Pt) per formula unit. At each substrate, the adhesion of pure monolayers is systematically stronger for oxides films from the beginning of the series and, for each oxide, it tends to increase from Ag to Pt. E_{adh} of most mixed compounds are smaller than the average values of their parents ($\delta E_{adh} < 0$ in SI, Tab. S6) – the reduction being particularly large for TiFeO_3/Me –, but in the case of TiVO_3/Pt for which mixing enhances the adhesion ($\delta E_{adh} > 0$).

Since E_{adh} is calculated with respect to the corresponding freestanding oxide films at their equilibrium lattice parameters, it consists of two contributions of different nature. The first one is associated to the elastic strain of the freestanding ML necessary to match its in-plane lattice parameter with the metal substrate (Table 4) and is always unfavorable to adhesion. In the parent series, aside Cr_2O_3 which displays a non-zero rumpling when freestanding and thus a reduced lateral lattice parameter, the misfit decreases from the left to the right of the series (for a given substrate) and from Pt to Ag (for a given oxide) and ranges from about

2% ($\text{Cr}_2\text{O}_3/\text{Ag}$) to more than 15% ($\text{Ti}_2\text{O}_3/\text{Pt}$). Misfits of the mixed monolayers show a qualitatively similar behavior and do not exceed the above ranges. However, since the lattice mismatch is accommodated mainly by the in-plane rotations and film rumpling and since the involved distortions require much less energy than bondlength compression, this contribution to E_{adh} displays small variations in each oxide series (of the order of 0.2-0.3 eV/f.u.) and, for a given oxide, its maximum variation between the three substrates is of the order of 0.2 eV/f.u. (SI, Tab. S3). Thus, it is clearly not responsible for the observed large differences of adhesion energies. The second contribution is the energy gained by bringing the strained oxide film in contact with the metal substrate. It directly represents the strength of direct metal-oxide interaction at the interface. It is favorable to adhesion in all considered cases.

While trends in adhesion may not always be easy to rationalize because they involve energy terms of different origin, Figure 8 shows a clear correlation between E_{adh} and the interfacial charge transfer $|Q_{Me}|$. If, in general, a weak/strong charge exchange is indeed often associated with weak/strong interfacial interaction, the present results show the existence of a unique and nearly universal $E_{adh}(|Q_{Me}|)$ curve, which encompasses cases ranging from particularly weakly (Cr_2O_3 and Fe_2O_3 on Ag) to particularly strongly (Ti_2O_3 and V_2O_3 on Pt) interacting interfaces, regardless of the precise nature of the oxide and the metal substrate. This finding clearly demonstrates the dominant role of the direct interfacial interactions in the energetics (second contribution), driven by the cation electronegativity.

5.4 Energetics of mixing

Mixing energies E_{mix} (Eq. 2) have been calculated for the six metal-supported mixed oxide MLs as the energy difference between the mixed systems and the average of the two supported parents. Their values are reported in Table 5, together with the corresponding results for their freestanding counterparts from Ref. ³

Depending on the oxide, we find negative or

Table 4: Adhesion Energies E_{adh} (eV/f.u.) at the Interfaces Between the Oxide Monolayers and the Three Metal Substrates. Misfits (%) Between the Freestanding MLs and the Underlying Substrates Are Given for Reference.

	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	TiVO ₃	TiCrO ₃	TiFeO ₃	VCrO ₃	VFeO ₃	CrFeO ₃
Ag-supported										
E_{adh}	2.52	1.41	1.19	1.64	1.99	1.64	1.61	1.21	1.33	1.32
misfit	10.2	7.9	2.1	7.3	7.3	9.0	8.1	6.4	7.3	6.4
Au-supported										
E_{adh}	3.31	1.91	1.15	1.28	2.62	2.06	1.76	1.60	1.54	1.13
misfit	10.6	8.3	2.4	7.6	7.6	9.4	8.5	6.8	7.6	6.8
Pt-supported										
E_{adh}	4.78	3.75	2.18	2.12	4.50	3.11	2.52	2.92	2.81	1.88
misfit	15.2	12.8	6.7	12.1	12.1	13.9	13.0	11.2	12.1	11.2

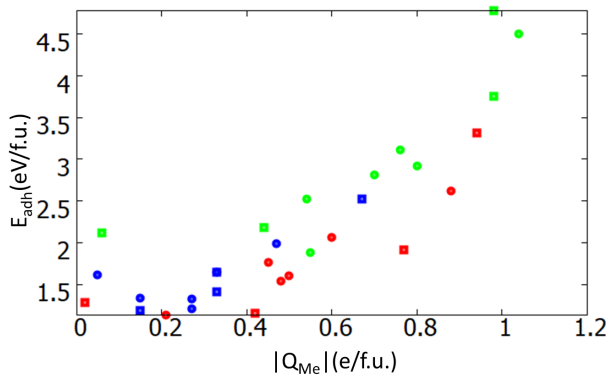


Figure 8: Adhesion energies of pure (squares) and mixed (circles) monolayers on metal substrates E_{adh} (eV/f.u.) as a function of interface charge transfer $|Q_{Me}|$ (e/M₂O₃ or MM'O₃ f.u.). Results for Ag, Au and Pt substrates are represented in blue, red and green, respectively.

830 positive mixing energies, which represent preference for cationic mixing and phase separation, respectively. If large negative $E_{mix} \sim -$ 831 0.7 eV/f.u. are found for freestanding TiFeO₃ 832 and VFeO₃ and for metal-supported VFeO₃, in 833 all other cases, the mixing energies are much 834 smaller ($|E_{mix}| < 0.4$ eV/f.u.). We find that, 835 aside few exceptions, for each mixed oxide, the 836 sign of E_{mix} is a relatively robust feature, independent of the substrate, but E_{mix} shows no 837 clear monotonic behavior along the series of oxides or metal substrates. 838

839 We recall that in the freestanding case, the 840 large negative mixing energies found for TiFeO₃ 841 and VFeO₃ have been assigned to the existence 842

845 of a mixing-induced redox reactions which produce unambiguous changes of cation oxidation states.³ The same mechanism was also shown to be at work in bulk mixed oxides²⁵ and at oxide/oxide interfaces.²⁶ For the metal-supported MLs, this correlation is somewhat less clear, partially due to the difficulty to unambiguously identify the cation oxidation states. However, the large negative E_{mix} , systematically found for VFeO₃ on the three substrates, is consistent with the enhanced oxidation of vanadium induced by the electron transfer toward the metal support and/or the Fe cation, as revealed by the features of the interface electronic structure, Sec. 4. Also, the strong reduction of $|E_{mix}|$ in all TiFeO₃/Me systems, with respect to their freestanding counterparts, correlates with the suppression of the electron transfer from Ti to Fe when metal-supported. Indeed, the electronic structure results show that the single Ti d electron is systematically transferred to the metal substrate, so that there are no occupied Ti states close to the Fermi level able to transfer electrons to the iron cations. 861

862 As to broaden the perspective, Figure 9 gives an overview of the calculated mixing energies in the same series of bulk sesquioxides, freestanding MLs, and metal-supported MLs.^{3,25} While a metal substrate enhances the preference for mixing in VCrO₃ and reduces it for the Ti-based ones, two systems clearly stand out by their strongly size and support-dependent behaviors. On the one hand, contrary to the bulk phase, the formation of ordered mixed VFeO₃ MLs is 878

Table 5: Mixing Energies E_{mix} (eV/f.u.) of the Six Freestanding³ and Metal-Supported Mixed HC MLs.

	TiVO ₃	TiCrO ₃	TiFeO ₃	VCrO ₃	VFeO ₃	CrFeO ₃
E_{mix}	+0.32	-0.16	-0.70	-0.14	-0.79	-0.16
E_{mix} (Ag)	+0.12	+0.05	-0.23	-0.22	-0.60	-0.06
E_{mix} (Au)	+0.13	+0.01	-0.17	-0.39	-0.74	-0.08
E_{mix} (Pt)	-0.09	+0.22	+0.23	-0.27	-0.67	+0.12

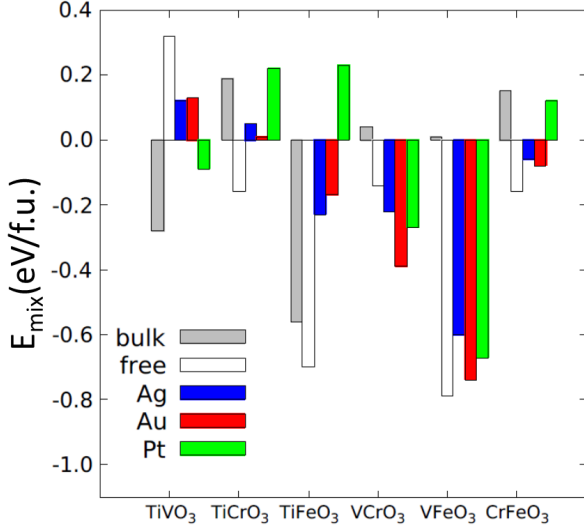


Figure 9: Mixing energies in the series of the six mixed HC oxides. Results for bulk, freestanding, Ag-, Au- and Pt-supported cases are represented in gray, white, blue, red, and green, respectively.

6 Conclusion

We have used a DFT+U approach to study how the presence of a metal substrate (Me = Ag, Au, Pt) modifies the structural, electronic and magnetic characteristics of a series of pure M_2O_3 and mixed $MM'O_3$ 3d transition metal oxide honeycomb monolayers (M, M' = Ti, V, Cr, Fe).

We have identified general trends in the substrate-induced structural film polarization, film-support electron transfer, and oxide-metal interaction strength, and we have linked them to the behavior of the offsets between the oxide band structure (point of zero charge) and the substrate Fermi level. Accordingly, the strongest interfacial effects are found in pure and mixed oxides with the least electronegative cations (Ti and V) deposited on metal substrates with the largest work functions (Au, Pt). In these cases of Mott-Hubbard oxides, the well pronounced depletion of purely 3d Ti and V states has been rationalized by an increase of the cation oxidation state with respect to the 3+ reference.

We have also shown that the relative positions of the Fermi levels in the supported pure oxides provide a good guide for understanding the electronic redistributions in the mixed compounds. However, if the ordering of Fermi levels in the series of parent oxides is only little affected by the metal substrate, the presence of a support significantly modifies the character of oxide states in the vicinity of the Fermi level. As a consequence, aside the general trend for an electron transfer from less (Ti and V) to more (Cr and Fe) electronegative cations, valid in both freestanding and supported monolayers, the metal substrates enhance electron redistributions in V-based compounds and reduce

thermodynamically favored not only when freestanding, but also when deposited on a metallic substrate. This opens a promising route for a practical synthesis of this nano-compound. On the other hand, in the perspective of tuning the oxide mixing properties and engineering novel oxide phases, our results show that mixed compounds such as $TiFeO_3$, which are stable in bulk (ilmenite) and freestanding MLs, may be dramatically destabilized by the strong interaction with the metal substrate. Such a strong dependence of mixing behavior on dimensionality and substrate should impact catalytic activity originating from the so-called SMSI (Strong Metal Support Interaction) in which, under reaction conditions, metal particles are encapsulated by an ultra-thin film of the supporting oxide.

935 them in the Ti-based ones. Indeed, the fact that 977
936 Ti_2O_3 gives all its valence electrons to the metal 978
937 substrates limits any significant mixing-induced
938 electronic rearrangements to VCrO_3/Me and 979
939 VFeO_3/Me only. Depending on the Me sub- 980
940 strate, the modifications consist of an electron
941 exchange between the two cations, or between 981
942 V and the metallic support. Due to the strong
943 modifications of their electronic structure when 982
944 deposited on metal substrates, these vanadium
945 mixed oxides are expected to display an en- 983
946 hanced reactivity, of possible interest in various 984
947 catalytic reactions. 985

948 These substrate-induced electronic effects 986
949 have direct consequences on the energetics of 987
950 cationic mixing. We have shown that, contrary 988
951 to its bulk phase, the formation of ordered 989
952 mixed VFeO_3 monolayers is thermodynamically 990
953 favored and that it is not inhibited by the pres- 991
954 ence of a metal substrate. Conversely, metal 992
955 support dramatically destabilizes monolayers of 993
956 TiFeO_3 , a mixed oxide which is stable in bulk 994
957 (ilmenite). Thus, not only our results show 995
958 that metal substrates can indeed be used for
959 engineering novel oxide phases by cationic mix- 996
960 ing, but they also provide well-founded general 997
961 guidelines on the link between support char- 998
962 acteristics, the oxide electronic structure, and 999
963 the preference for mixing or phase separation 1000
964 in the supported oxide films. 1001

965 7 Acknowledgment 1002

966 We acknowledge fruitful discussions with M. R. 1003
967 Castell, S. Wang and N. Nilius. 1004
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968 8 Supporting Information 1008

969 Available 1009

970 The Supporting Information contains: 1010
1011

- 971 • full DFT+U results for parent $\text{M}_2\text{O}_3/\text{Me}$ 1012
972 MLs (Tabs. S1-S3) and for mixed 1013
973 $\text{MM}'\text{O}_3/\text{Me}$ MLs (Tabs. S4-S6); 1014
1015
- 974 • HSE03 results for parent $\text{M}_2\text{O}_3/\text{Au}$ MLs 1016
975 (Tab. S7, Fig. S1) and for mixed 1017
976 $\text{MM}'\text{O}_3/\text{Au}$ MLs (Tab. S8, Fig. S2). 1018

Figs. S3-S4 are the HSE03 equivalents of
Figs. 5 and 7 in the main text;

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