A First-principles Study of Stability of Surface Confined Mixed Metal Oxides with Corundum Structure (Fe₂O₃, Cr₂O₃, V₂O₃)

A. S. M. Jonayat,^a Alan Kramer,^b Luca Bignardi,^c Paolo Lacovig,^c Silvano Lizzit,^c Adri C.T. van

Duin,,^{a,d} Matthias Batzill,^b Michael J. Janik,^{d,*}

^aDepartment of Mechanical and Nuclear Engineering and ^dDepartment of Chemical Engineering,

The Pennsylvania State University, University Park, Pennsylvania 16802, United States

^bDepartment of Physics, University of South Florida, Tampa, Florida 33620, United States

^cElettra-Sincrotrone Trieste S.C.p.A., Strada Statale 14 Km 163.5, I-34149 Trieste, Italy

Electronic Supplementary Information

1. Oxygen Chemical Potential at Different Relevant Pressure and Temperatures

Table S1: Oxygen chemical potential, μ_o (O atom at Oxygen molecule at 0 K as reference) at different pressures and temperatures.

Pressure (atm)	1.32E-09	1.00E+00	1.00E+05	1.00E+12	1.00E+20
Temperature (K)					
300	-0.54	-0.27	-0.12	0.08	0.32
350	-0.64	-0.33	-0.15	0.09	0.37
400	-0.73	-0.38	-0.18	0.09	0.41
450	-0.83	-0.44	-0.22	0.10	0.45
500	-0.94	-0.50	-0.25	0.10	0.50
600	-1.14	-0.61	-0.31	0.10	0.58
700	-1.35	-0.73	-0.38	0.10	0.66
800	-1.56	-0.85	-0.45	0.10	0.74
900	-1.77	-0.97	-0.53	0.10	0.81
1000	-1.98	-1.10	-0.60	0.09	0.89
1100	-2.20	-1.23	-0.68	0.08	0.96
1200	-2.41	-1.35	-0.76	0.07	1.03
1300	-2.63	-1.49	-0.84	0.06	1.09
1400	-2.85	-1.62	-0.92	0.05	1.16
1500	-3.07	-1.75	-1.01	0.04	1.23

2. Bulk Lattice Parameters for V₂O₃

For the bulk lattice parameters of V₂O₃, both PBE and PW91 functional gave similar values under DFT+U framework (Table S2). Varying U-J values slightly (3.15 vs. 3.25), very small change in the lattice parameters were observed. Negligible difference between the lattice parameters with/without spin polarization was observed. All the lattice parameters are very close to experimentally measured lattice parameters. Also, similar to previous studies by Kresse et al.¹, introducing spin polarization did not make the internal structure any better. From the results with PBE+U, it is observed with even with different magnetic alignments (FM/AF1/AF2/AF3) the lattice parameters were almost the same. AF1 and AF2 results are energetically almost similar as reported by Ezhov et al.² who reported a 5K (4.31 meV) difference between the arrangements.

				I	Lattice Parameter	`S
Method	Functional	U-J	Mag. Order	a	с	a/c
DFT+U	PBE	3.15		4.96127	14.04220	0.35331
DFT+U (Spin. Pol)	PBE	3.15	FM	5.08141	14.38223	0.35331
DFT+U (Spin. Pol)	PBE	3.15	AF1	5.07923	14.37606	0.35331
DFT+U (Spin. Pol)	PBE	3.15	AF2	5.07746	14.37105	0.35331
DFT+U (Spin. Pol)	PBE	3.15	AF3	5.07787	14.37222	0.35331
DFT	PW91	0		4.90410	13.88050	0.35331
DFT (Spin. Pol)	PW91	0	FM	4.93130	13.95740	0.35331
DFT+U	PW91	3.25		4.94780	14.00420	0.35331
DFT+U (Spin. Pol)	PW91	3.25	FM	5.07890	14.37520	0.35331
Exp 1				4.94000	13.97000	0.35361
Exp 2				4.51000	14.00200	0.32210

Table S2: Lattice parameters of optimized V₂O₃ hexagonal unit cell.

3. Effect of magnetic arrangement on surface energy of V2O3 (0001)

Table S3: Surface energies of V₂O₃ with different termination and magnetic arrangement.

Surface Termination	FM	AF1	AF2	AF3
V Termination	101.59933	85.91425	89.3825	98.27945
V=O Termination*	-31.49121	-40.63948	-39.25028	-40.43035

*at zero oxygen chemical potential

4. Effect of magnetic arrangement on surface/subsurface segregation of substituted TM in $V_2O_3\ (0001)$

4.1. 0 ML O coverage 1/3 ML Fe

Table S4: Energy difference wrt. 1/3 ML Fe on surface in TM terminated surface (very reducing environment). L1, L2 and L3 indicates atomic layers as shown in Fig 2.

Substituted Fe position	AF3	AF1	AF2
L1	0	0	0
L3	0.44763	0.40958	0.71676
L2	0.44302	0.40972	0.45891
Diff. with Most Stable Fe Top	0.44902	0.17138	0

4.2. 0 ML O coverage 1/3 ML Cr

Table S5: Energy difference wrt. 1/3 ML Cr on surface in TM terminated surface. L1, L2 and L3 indicates atomic layers as shown in Fig 2.

Substituted Cr position	AF3	AF1	AF2
L1	0	0	0
L3	0.05936	-0.12103	-0.09073
L2	-0.06283	-0.16592	-0.20691
Diff. with Most Stable Cr Top	0.14135	0	0.05484

4.3. $\frac{1}{3}$ ML O Coverage 1/3 ML Fe

Table S6: Energy difference wrt. 1/3 ML Fe on surface with 1/3 ML O coverage. L1, L2 and L3 indicates atomic layers as shown in Fig 2.

TM Positions	AF3	AF1	AF2
Fe, V, VO on surface	0	0	0
2×V, VO surface (L1), Fe subsurface (L3)	0.39920	0.41048	0.60642
2×V, VO surface (L1), Fe subsurface (L2)	0.36104	0.38438	0.47808
Diff with Most Stable Fe top	0.72651	0.31062	0

4.4. $\frac{1}{3}$ ML O Coverage 1/3 ML Cr

Table S7: Energy difference wrt. 1/3 ML Cr on surface with 1/3 ML O coverage. L1, L2 and L3 indicates atomic layers as shown in Fig 2.

TM Positions	AF3	AF1	AF2
Cr, V, VO on surface (L1)	0	0	0
$2 \times V$, VO surface (L1), Cr subsurface (L3)	0.12018	-0.05533	-0.06539
2×V, VO surface (L1), Cr subsurface (L2)	-0.02566	-0.14413	-0.14429
Diff with Most Stable Cr Top	0.20257	0.00598	0

4.5. Transition oxygen chemical potential for Fe subsurface segregation during oxidation of 2/3 ML O coverage to 1 ML O coverage

Table S8: Chemical potential for which $\Delta \varepsilon$ becomes zero for the reaction shown in Figure 9. L2 and L3 indicates atomic layers as shown in Fig 2.

	AF3	AF1	AF2
L3	-1.91943	-2.10534	-1.92397
L2	-2.01474	-2.26753	-2.09882

5. Effect U-J Value:



Figure 1: Reaction shown in Figure 9 in two steps.

The U-J values used here might introduce another uncertainty in the predicted value. To show this, the reaction in Figure 10 was broken down in to two steps. In step 1, the Fe goes from surface to the subsurface. In step 2, the V on the surface becomes oxidized (Figure S1). The $\Delta\epsilon$ of the reactions are given in Table S. The step of oxidation is dependent highly on U-J value. A 0.85 eV increase in U-J for V, increases the $\Delta\epsilon_b$ of oxidation step by 0.64 eV while the $\Delta\epsilon_b$ increases by 0.14 eV. However, at this point this uncertainty associated with U-J variation has not been quantified.

U-J	$\Delta \epsilon_{a}$	$\Delta \epsilon_b$
2.5	0.6315	-10.6207
3.15	0.7305	-10.1941
4	0.8702	-9.5524

Table S9: $\Delta \varepsilon$ *for 2 step reaction shown in Figure S1*

The uncertainty of U-J value can somewhat be solved by using hybrid functional like HSE06 or PBE0. However, this includes a choice of extent of the mixing of exact exchange.

6. Experimental Study

6.1. Methods

Two experimental analyses of corundum oxide surfaces have been conducted to verify theoretical predictions of the stability of oxidized corundum-forming transition metals at the surface of dissimilar corundum oxide substrates. The two systems, chromia/V₂O₃ (0001) and vanadia/Cr₂O₃ (0001), have been studied by scanning tunneling microscopy (STM) and synchrotron soft x-ray photoemission spectroscopy (SXPS), respectively. A short description of the methods is given in the following section.

6.1.1. STM of Chromia on V₂O₃ (0001)

STM studies were performed in an ultra-high vacuum (UHV) chamber with a base pressure in the low 10^{-10} mbar range. An ~10 nm thick V₂O₃ (0001) film was grown on a W (110) single crystal by pulsed laser deposition. A V₂O₅ ceramic target was ablated using a solid state Nd:YAG laser (430 mJ power at wavelength of 355 nm and 5 Hz repetition frequency). The film was deposited in 1×10^{-6} mbar O₂ at room temperature. We have previously shown that this procedure results in the growth of V₂O₃ films³ and may be compared to vapor deposition procedures of V₂O₃ films on various metal single crystal substrates⁴⁻⁶ including W (110).^{4,7} The V₂O₃ film grown by PLD was transferred to a UHV STM with help of a vacuum suitcase that maintained a pressure of ~10⁻⁸ mbar during transfer. Subsequently the sample was annealed at 850 K for 30 min within the UHV STM chamber. Such prepared V₂O₃ thin films are exposed to small (sub-monolayer) amounts of chromia, by vapor deposition of chromium in 7×10⁻⁸ mbar oxygen, with the sample held at room temperature. To study the surface stability of these chromia deposits the sample is subsequently annealed to 720 K and 820 K.

6.1.2. SXPS of Vanadia on Cr₂O₃(0001)

SXPS studies were performed at the Elettra-synchrotron in Italy at the SuperESCA UHVendstation.⁸ By tuning the photon energy to emit photoelectrons with a kinetic energy that falls close to the minimum of the energy-dependent inelastic mean free path length, extreme surface sensitivity can be obtained. This makes SXPS an ideal tool for characterizing the stability of atomic species at the surface.

 Cr_2O_3 films were prepared by oxidation of a Cr (110) single-crystal. The preparation procedure for formation of the Cr_2O_3 film followed the procedure previously described by Bender et al.⁹. Briefly, the Cr (110) crystal was cleaned by cycles of sputtering and annealing to 1000 K. This procedure could not remove C and N contamination completely, which are known as major contaminants in Cr-crystals. However, these contaminants did not affect the subsequent oxidation and formation of a Cr_2O_3 (0001) film. Oxidation was performed by leaking 1×10^{-6} mbar of O_2 into the UHV chamber and annealing of the sample at 800 K for 3 min. Subsequently the sample was flash-annealed to 1000 K in UHV. No metallic Cr signal was detected in XPS and the low energy electron diffraction (LEED) pattern exhibited the hexagonal structure of Cr_2O_3 (0001). The Cr-3s core-level of the Cr_2O_3 monolayer shows a peak at 74.78 eV binding energy and a satellite peak at 78.87 eV. This is consistent with previous reports¹⁰ for Cr_2O_3 . Vanadium oxide was then deposited on the Cr_2O_3 surface by vapor deposition of vanadium in 1×10^{-8} mbar O_2 with the sample at room temperature. The vanadium oxide deposition was monitored with fast SXPS by sweeping the kinetic energy corresponding to the Cr-3s and V-3s region using a photon energy of 190 eV. Subsequent annealing in 1×10^{-8} mbar O_2 was done to a temperature of 720 K to study surface stability.

Our DFT calculations, as well as the pure surface energies, predict that Cr will segregate to subsurface in V_2O_3 (0001) and V will be stable in Cr_2O_3 (0001) surface for any temperature-pressure conditions. Experimental observations of these predictions are described in this section.

6.2. Experimental Results

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6.2.1. Chromia on V₂O₃ (0001)

After annealing of a V_2O_3 film grown by PLD in UHV STM chamber, STM imaging of the sample revealed flat terraces and some deeper 'trenches' suggesting an island growth with the 'trenches' indicating grain (or island) boundaries. In this study, we focus on the morphology of the terraces. Figure (a) shows STM images of the V_2O_3 (0001) surface. The terraces exhibit a domain structure, which we attribute to areas terminated by vanadyl-oxygen and areas where the terminating oxygen has been removed. Such clustering of vanadyl-oxygen in nano-domains has been previously observed in partially reduced V_2O_3 (0001) surface by STM.^{11–17} This gives the V_2O_3 surface a characteristic appearance that helps in identifying the surface termination.



Figure S2: Scanning tunneling microscopy observations of chromia deposition on V_2O_3 (0001) thin films. The as grown V_2O_3 (0001) film is shown in (a) [scan area: (a1) 40×40 nm and (a2)20×20 nm]. STM images after chromia deposition at room temperature is shown in (b), and after annealing to 720 K in (c) [scan areas: 40×40 nm]. STM images after further annealing to 820 K are shown in (d) [scan area: (d1) 40×40 nm and (d2)20×20 nm]. Tunneling bias voltages and tunneling currents for the subfigures were: (a1) 1.0V, 1.0nA, (a2) 1.5V, 1.0nA,(b) 1.2V, 0.2nA, (c) 1.1V, 0.2nA, (d1) 1.1V, 0.15nA, (d2) 1.1V, 0.5nA.

Exposure to sub-monolayer amounts of chromia $(7 \times 10^{-8} \text{ mbar oxygen, room temperature})$ of this surface causes a disordering of the surface and formation of small clusters that are associated with chromia shown in Figure (b). After subsequent annealing to 720 K, larger clusters are formed at the surface as shown in Figure (c). It is not possible to unambiguously identify the composition of these clusters from STM images. They may consist of chromia or vanadia. The latter would form if chromium cations diffuse into the vanadia forming a solid solution. This process would require site exchange of vanadium ions with chromium ions and thus expelling vanadium cations

to the surface where they could rearrange into small vanadia ad-islands on top of the vanadia terraces. Evidence for this process becomes clearer at higher annealing temperatures of 820 K, shown in Figure (d). At this annealing temperature, the small islands aggregated into larger well-defined islands at the surface. These islands are of atomic-layer height and exhibit triangular shapes, as expected from the hexagonal structure of the corundum (0001) terraces. Importantly, the same nanostructure is observed on the islands and the lower terraces that we attributed to vanadyl-terminated domains as for the as-prepared V_2O_3 film. Atomic corrugation consistent with vanadyl termination can also be discerned which is highlighted in the inset of Figure (d). This demonstrates that this surface has the same termination as pure V_2O_3 and consequently strongly suggests that chromia has diffused subsurface, as predicted in the DFT simulations.

6.2.2. Vanadia on Cr₂O₃ (0001)

The integrated peak intensities of Cr-3s and V-3s during vanadium oxide deposition on Cr_2O_3 (0001) are plotted in Figure (a). It indicates linear decrease and increase of the peak intensity with deposition time for Cr-3s and V-3s, respectively. Linear dependence of the peak intensities indicates that the vanadia amount deposited was sub-monolayer. Subsequent annealing in 1×10^{-8} mbar O₂ shows no significant change in either the Cr-3s or the V-3s intensities up to annealing temperature of 720 K, as shown in Figure (b). This suggests that vanadia remains at the surface and there is negligible diffusion of vanadium into the subsurface region. This is further confirmed by photon-energy dependent studies. Figure (c) reports the Cr-3s and V-3s core levels after annealing, measured with 160 eV and 190 eV photon-energies. The inelastic mean free paths lengths of the corresponding photoelectrons are estimated¹⁸ to be ~0.5 and ~0.6 nm, respectively. Thus 160 eV photon energy is more surface sensitive than 190 eV. Figure (c) shows an increased V-3s/Cr-3s peak ratio at 160 eV, demonstrating that V is at the surface.

While the total peak intensity for V-3s core level does not change with annealing, the peak shape undergoes some variation with annealing, which is shown more clearly in Figure (d). In all cases the V-3s peak can be fitted with two components, whose binding energy does not vary significantly but their relative intensity changes. The low binding energy component has an energy



Figure S3: Soft x-ray photoemission spectroscopy (SXPS) investigation of vanadia deposition and thermal stability on a Cr_2O_3 thin film. a) Fast SXPS spectra (hv = 190eV) during deposition of V and total peak area of V and Cr 3s as a function of deposition time (inset). b) Monitoring of the surface composition by fast SXPS (hv = 190eV) as a function of annealing temperature. The inset shows the V-3s and Cr-3s peak area during annealing and cooling of the sample plotted as a function of temperature.

of 67.71 eV and the separation between the two components is ~ 2.3eV. This is consistent with the V-3s spectra for V_2O_3 , for which it was argued that the coupling of the spin of the 3s photo-hole with total spin of the partially filled 3d band in V_2O_3 gives rise to an exchange splitting of the 3s core-level¹⁹. The magnitude of the measured splitting is also consistent with that measured²⁰ previously for V_2O_3 . The intensity ratio of the exchange split band is given by spin states and should be 0.5 in the case of pure V_2O_3 . The ratio observed in the studies reported here diverge from that of pure V_2O_3 which may be expected for different coordination and the possible substitution of cations in the Cr_2O_3 surface. The relative intensity variations of the two components with annealing is likely an indication of local rearrangement and reordering of the V-cations at the surface. The proximity of the Cr-3s peak with the V-3s also complicates the subtraction of an appropriate background which may significantly affect the ratio of the two V-3s components. Important for this study is, however, that despite the mobility of the vanadium cations that enables local rearrangements, the vanadium remains at the surface indicating that it is the energetically favorable location. This observation is consistent with the DFT simulations that V will surface segregate to the Cr_2O_3 (0001) surface.

References

- 1 G. Kresse, S. Surnev, J. Schoiswohl and F. P. Netzer, V₂O₃(0001) surface terminations: a density functional study, *Surf. Sci.*, 2004, **555**, 118–134.
- 2 S. Y. Ezhov, V. I. Anisimov, D. I. Khomskii and G. A. Sawatzky, Orbital Occupation, Local Spin, and Exchange Interactions in V 2 O 3, *Phys. Rev. Lett.*, 1999, **83**, 4136.
- 3 A. Kramer, E. Sutter, D. Su and M. Batzill, Epitaxial corundum-VTiO₃ thin films grown on ccut sapphire, *Thin Solid Films*, 2017, **631**, 85–92.
- 4 A. C. Dupuis, M. Abu Haija, B. Richter, H. Kuhlenbeck and H. J. Freund, V₂O₃(0001) on Au(111) and W(110): growth, termination and electronic structure, *Surf. Sci.*, 2003, **539**, 99–112.
- 5 A. K. Kundua and K. S. R. Menon, in *International Conference on Condensed Matter and Applied Physics*, eds. M. S. Shekhawat, S. Bhardwaj and B. Suthar, 2016, vol. 1728.
- 6 H. Niehus, R. P. Blum and D. Ahlbehrendt, Structure of vanadium oxide (V₂O₃) grown on Cu₃Au(100), *Surf. Rev. Lett.*, 2003, **10**, 353–359.
- 7 M. Abu Haija, S. Guimond, Y. Romanyshyn, A. Uhl, H. Kuhlenbeck, T. K. Todorova, M. V. Ganduglia-Pirovano, J. Dobler, J. Sauer and H. J. Freund, Low temperature adsorption of oxygen on reduced V₂O₃(0001) surfaces, *Surf. Sci.*, 2006, **600**, 1497–1503.
- 8 W. Jark, Soft x-ray monochromator configurations for the ELETTRA undulators: A stigmatic SX700, *Rev. Sci. Instrum.*, 1992, **63**, 1241–1246.
- 9 M. Bender, D. Ehrlich, I. N. Yakovkin, F. Rohr, M. Baumer, H. Kuhlenbeck, H. J. Freund and V. Staemmler, Structural rearrangement and surface magnetism on oxide surfaces: a temperature-dependent low-energy electron diffraction-electron energy loss spectroscopy study of Cr₂O₃ (111)/Cr (110), *J. Phys.-Condens. Matter*, 1995, 7, 5289–5301.
- 10E. Agostinelli, C. Battistoni, D. Fiorani and G. Mattogno, An XPS study of the electronic structure of the Zn_xCd_{1-x}Cr₂ (X= S, Se) spinel system, *J. Phys. Chem. Solids*, 1989, **50**, 269–272.
- 11F. E. Feiten, H. Kuhlenbeck and H. J. Freund, Reducing the V₂O₃(0001) surface through electron bombardment a quantitative structure determination with I/V-LEED, *Phys. Chem. Chem. Phys.*, 2016, **18**, 3124–3130.
- 12F. Pfuner, J. Schoiswohl, M. Sock, S. Surnev, M. G. Ramsey and F. P. Netzer, The metalinsulator transition in V₂O₃(0001) thin films: surface termination effects, *J. Phys.-Condens. Matter*, 2005, **17**, 4035–4047.
- 13J. Schoiswohl, M. Sock, S. Surnev, M. G. Ramsey, F. P. Netzer, G. Kresse and J. N. Andersen, V₂O₃(0001) surface terminations: from oxygen- to vanadium-rich, *Surf. Sci.*, 2004, 555, 101–117.
- 14A. J. Window, A. Hentz, D. C. Sheppard, G. S. Parkinson, D. P. Woodruff, W. Unterberger, T. C. Q. Noakes, P. Bailey, M. V. Ganduglia-Pirovano and J. Sauer, The structure of epitaxial V₂O₃ films and their surfaces: A medium energy ion scattering study, *Surf. Sci.*, 2012, 606, 1716–1727.
- 15F. P. Leisenberger, S. Surnev, L. Vitali, M. G. Ramsey and F. P. Netzer, Nature, growth, and stability of vanadium oxides on Pd(111), *J. Vac. Sci. Technol. -Vac. Surf. Films*, 1999, **17**, 1743–1749.
- 16F. E. Feiten, H. Kuhlenbeck and H.-J. Freund, Surface Structure of V₂O₃(0001): A Combined I/V-LEED and STM Study, *J. Phys. Chem. C*, 2015, **119**, 22961–22969.

- 17F. E. Feiten, J. Seifert, J. Paier, H. Kuhlenbeck, H. Winter, J. Sauer and H.-J. Freund, Surface Structure of V₂O₃(0001) Revisited, *Phys. Rev. Lett.*, 2015, **114**, 216101.
- 18S. Tanuma, C. J. Powell and D. R. Penn, Calculations of electron inelastic mean free paths (IMFPS). IV. Evaluation of calculated IMFPs and of the predictive IMFP formula TPP-2 for electron energies between 50 and 2000 eV, *Surf. Interface Anal.*, 1993, **20**, 77–89.
- 19R. Zimmermann, R. Claessen, F. Reinert, P. Steiner and S. Hufner, Strong hybridization in vanadium oxides: evidence from photoemission and absorption spectroscopy, *J. Phys.-Condens. Matter*, 1998, **10**, 5697–5716.
- 20S. Shin, Y. Tezuka, T. Kinoshita, A. Kakizaki, T. Ishii, Y. Ueda, W. Jang, H. Takei, Y. Chiba and M. Ishigame, Observation of local magnetic moments in the Mott transition of V₂O₃ by means of 3s photoemission, *Phys. Rev. B*, 1992, **46**, 9224–9227.