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Adsorption of V on a hematite (0001) surface and its oxidation: Monolayer coverage

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Abstract

The adsorption of a monolayer of V on idealized Fe- and oxygen-terminated hematite (0001) surfaces and subsequent oxidation under atomic O adsorption are studied by density functional theory. Theoretical results are compared with X-ray surface standing wave and X-ray photoelectron spectroscopic measurements, and interpreted in the light of data on sub-monolayer coverages. Near-surface Fe reduction under V adsorption and accompanying structural relaxation are examined. These effects and subsequent response to oxidation, are found to be highly site specific. A full monolayer of oxygen leads to a V⁵⁺ state and reoxidation of subsurface Fe to the trivalent state, seen in both theory and experiment.

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1. Introduction

In a preceding paper, referred to as **I** in the following, we examined submonolayer coverage of vanadium on α -Fe₂O₃ (hematite) [1]. Experimental studies of submonolayer V adsorption on clean hematite (0001) with subsequent repeatable oxidization/reduction cycles were reported by Kim et al. [2], using atom-resolved X-ray standing wave measurements (XSW) to detect V site geometry and X-ray photoemission spectroscopy (XPS) to detect electronic structure changes. In **I** the general experimental and theoretical background was presented, and theoretical methodology was described. Theoretical studies on hematite (0001) interactions with methyl radicals and small mole-

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cules using the same methodology have been previously presented [3,4].

Experimental XSW data for submonolayer coverage were interpreted in terms of as-deposited partial occupancy of 'A' and 'C' sites, with \sim 50% of vanadium seen in XPS apparently in a disordered or incoherent state. Theoretical analysis in I verified stability of the 'chemically obvious' vacant Fe 'A' site but found the 'C' site to be strongly disfavored due to Coulomb repulsion from a subsurface lattice Fe. This leads to speculation that one or more near-surface layers may be non-stoichiometric or disordered with respect to the underlying bulk lattice used in XSW structure analysis.

The present work treats two interface structures: monolayer V/hematite, and progressive stages of oxidation $(O_x/V/hematite)$, evaluated within the framework of spinpolarized Density Functional Theory (DFT). In the first case we consider the adsorption of V on hematite (0001), with two idealized bulk-terminated surfaces, namely single-Fe terminated (Fe–O₃–Fe₂···) and oxygen-terminated

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 $(O_3$ -Fe₂- O_3 ···). Energetically favorable adsorption sites are found by starting from various scenarios and subsequently relaxing the structures. In addition to adsorption geometry and energy, we also obtain representations of the system's electronic structure including site-projected densities of states, charge distribution, magnetic moments, and core-region potential shifts. In the second part of this work, we study the interaction of atomic oxygen with monolayer V/hematite (0001). The relaxed O adsorption structure, binding energy, and the resulting oxidation state changes of V and Fe provide a starting point for understanding the interface structure between vanadium oxide and hematite and its effects on chemical and catalytic properties. By comparing with experimental XSW data for asdeposited and oxidized V/hematite, we are able to identify features common to the idealized surface models and the real surface structure. Full details of various sites analyzed appear in Refs. [4,5]. Some clear discrepancies remain to be explained, most of which are related to the assumed stoichiometric/near ideal termination of the (0001) surface. As we show in the following, the energetically disfavored 'C' site found to be occupied in I, appears to be replaced by the more plausible 'B' site under monolayer V coverage; this may give a clue to the deviations of the hematite surface structure from ideal character.

The remainder of the paper is organized as follows: Section 2 reports our results for V adsorption on both Fe- and O_3 -terminated hematite (0001) surfaces; Section 3 reports our results for oxygen adsorption on V/hematite; Section 4 contains a comparison between experiment and theory, and Section 5 gives our conclusions.

2. Results: V adsorption on hematite (0001) surface

As shown in Fig. 1 of **I**, there are several possible V adsorption sites: for single-Fe terminated hematite (0001) these include: (1) Threefold hollow B which has a subsurface Fe_B^{S-1} atom below; (2) Threefold hollow C which has a subsurface Fe_C^{S-1} atom that is higher than Fe_B^{S-1} ; (3) The bridge site between two surface O atoms; (4) Direct on top of surface Fe_A^S ; (5) Direct on top of surface O; (6) Substitution of V for Fe_A^S , while Fe_A^S displaces to other sites such as B and C. For an O₃-terminated surface, adsorption sites considered are top adsorption on O, and threefold hollow sites A, B, C plus the fourth threefold hollow site D, having no subsurface Fe.

2.1. ML V/Fe-hematite interface

2.1.1. Adsorption site, geometry and energy

We concentrate here only on the threefold hollow site configurations, as these are energetically the most interesting cases. The results of calculated adsorption energy and work function change are summarized in Table 1. Trying different configurations in which, within each unit cell two V and one Fe are distributed among hollow sites A,



Fig. 1. Atom-resolved DOS for (a) 1 ML (V_B, V_C)/Fe-hematite adsorption, (b) 1 ML (V_B, V_A)/O₃-hematite. Positive value indicates spin up electronic states while negative indicates spin down. For V and Fe, only 3d electronic states are shown and for O, 2p states are shown. Fermi energy is fixed at 0 eV. The same rule applies for the remaining DOS figures in this work.

B, C (see Fig. 1 of I), we found that the configuration (V_A, V_B, Fe_C^S) is most favorable with energy 4.98 eV, while the other two configurations (V_A, V_C, Fe_B^S) , (V_B, V_C, Fe_A^S) have their adsorption energies essentially equal, 4.56 eV and 4.57 eV. The relatively close values of E_{ads} for these three sites implies a potentially very disordered configuration when 1 ML V is deposited on a Fe-hematite surface. The work function increases for (V_A, V_B, Fe_C^S) by 0.97 eV, while dropping for the other two configurations, by 0.55 and 0.14 eV respectively. The adsorption geometries of the three configurations are listed in Table 2; the relaxed bonding geometries are similar for all three configurations. The metal atom at site A is generally the lowest in energy because of lack of repulsion from subsurface Fe. All Fe-O bonds are stretched and interlayer distances are enlarged, consistent with reduction of the cation, see below. Because of the similarity for adsorption energy and structure among the three configurations, in the subsequent discussion we choose (V_B, V_C, Fe_A) as a representative, characterized by the lowest Fe displacement.

V/O_3 -hematite, O/V	V/Fe-hematite, and $O/V/O_3$ -I	nematite
Adsorption site	E _{ads} (eV/atom)	$\Delta \Phi$ (eV)
1 ML V/Fe-hematit	е	
V _A , V _B , Fe ^S _C	4.98	0.97
V _A , V _C , Fe ^S _B	4.56	-0.55
V _B , V _C , Fe ^S _A	4.57	-0.14
1 ML V/O ₃ -hemati	te	
V _A , V _B	7.61	-4.40
V _A , V _C	6.66	-4.08
V_B, V_C	7.40	-4.95
Coverage	1 ML V/Fe-hematite	1 ML V/O ₃ -hematite
1/3 ML O	$E_{\rm ads}$ (eV)	$E_{\rm ads}~({\rm eV})$
Ob	8.07, 8.34, 8.34	_
Ot on VB	7.50	7.55
2/3 ML O		
O _b	8.02, 8.01, 7.99	7.29
1 ML 0		
O _b	9.45	6.87

Only energetically favorable threefold sites are presented for V/hematite, see text. For O/V/hematite, O_b indicates a bridging bond with metal atoms. O_t indicates adsorption directly on top of a metal. The site labels of V and Fe indicate different adsorption configurations examined, as explained in the text.

2.1.2. Electronic and bonding properties

As shown in Fig. 1, upon 1 ML V adsorption (occupied sites V_B , V_C), the DOS for the Fe_B^{S-1} and Fe_C^{S-1} subsurface sites is very similar to that found for 0.5 ML V adsorption in **I**. For Fe_A^S , however, there is a notably larger splitting between high binding energy "metal localized" and the low binding energy "covalent" regions. The low binding energy peaks move up and broaden to join with non-bonding states to form a continuous band ranging from -2.3 eV to 2.5 eV above E_f . The DOS for V_B and V_C are also similar to that of the 0.5 ML V_B case; however, the number of states in the high binding energy area is greatly reduced, while low binding area peaks move up to join with the conduction band similar to Fe_A^S . Overall the surface layers DOS is characteristic of a metal.

In Bader charge analysis for adsorption (Table 3), we can see that due to the lack of interaction of V_B , V_C with Fe_B^{S-1} and Fe_C^{S-1} respectively, the Fe subsurface atoms are only mildly reduced, while the Fe_A^S is heavily reduced, gaining 0.66 e. The two V atoms are less oxidized compared to the 0.5 ML case, with net charge of +1.13 e and +1.17 e each. In R_S volume integration we can see that the total and partial charge change pattern is quite irregular for Fe_B^{S-1} , Fe_C^{S-1} and adsorbed V atoms, comparing to clean surface and 0.5 ML cases presented in **I**. This indicates a radical change of electronic (s, p, d) charge distribution around metal atoms due to V adsorption. For configuration (V_B, V_C, Fe_A^S), the surface magnetic moments change dramatically. The two adsorbed V both have a large magnetic moment of +1.8 μ_B , while the original surface Fe's

magnetic moment decreases from $+3.4 \mu_B$ to $-0.2 \mu_B$. The subsurface Fe magnetic moments change very little, compared to 0.5 ML V.

The cluster-based electronic population analysis of 1 ML V/Fe-hematite is given in Table 4. Compared to 0.5 ML V/Fe-hematite, the adsorbed V atoms are far more reduced in both Mulliken and volume integration schemes (0.98 e, 1.11 e for Mulliken charge and 0.96 e, 1.02 e for volume charge), which is consistent with Bader analysis in the plane-wave model, but differs from $R_{\rm S}$ analysis for reasons previously discussed. The decrease in V-Fe^S_A bond length from 2.95 to 2.90 Å is accompanied by an increase of about 0.14 e in bond order, a clear indication of their direct bonding interaction. Even though the V-O bond lengths increase by about 0.2 Å compared to 0.5 ML V, their bond orders hardly change, while the V-Fe^{S-1} shared charge is considerably reduced. The bond order data thus clearly indicate the change in dominant bonding interactions, involving V and subsurface Fe as vanadium coverage increases from 0.5 ML, while the V-O covalency remains nearly constant. Core level shifts of V_B , V_C and Fe_A^S (Table 5) are all significantly negative (-0.46, -0.50, -1.42 eV)respectively): for vanadium this indicates a decrease in core-region potential relative to bulk V2O3 and a lower ionicity, consistent with our charge analyses. For surface iron, the decrease in potential relative to bulk Fe₂O₃ and also relative to the clean hematite surface (1.04 eV) clearly supports the interpretation of its partial reduction under V adsorption.

2.2. 1 ML V/O3-hematite

2.2.1. Adsorption sites, geometry and energy

Results of adsorption energy calculations for 1 ML V coverage on the O₃ terminated surface are given in Table 1; the most stable configuration (7.61 eV) corresponds to filling of the two unoccupied Fe sites, forming a (V_A, V_B) structure. The work function drops by 4.40 eV. The (V_B, V_C) configuration, at 7.40 eV, is also readily accessible. We can rationalize the reduced values of E_{ads} relative to those of 0.5 ML coverage (9.9 eV) as being largely due to V–V ionic repulsion, and competition for the limited number of surface V–O bonds. This may also be the underlying cause of the large structural changes, which we next describe.

In terms of adsorption geometry, summarized in Table 2, surface O^S atoms move upward by as much as 1 Å causing $O-Fe_B^{S-1}$ bond breaking and $O-Fe_C^{S-1}$ bond stretching. At the same time, V_B drops below the topmost O layer, forming a fourfold tetrahedral bonding with three O and the Fe_B^{S-1} below. This structure has a special character that is different from either pure $Fe_2O_3(0001)$ or $V_2O_3(0001)$ [5,6]. The $V_B-Fe_B^{S-1}$ distance is only 2.03 Å, much smaller than that found previously in the V/Fe-hematite case. Although this structure is the most stable structure we have encountered, we need to mention that the relaxed position of V_B is very sensitive to the initial position, for example,

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Table 2

Adsorption geometry of hematite, 1 ML V/Fe-hematite, 1 ML V/O3-hematite, O/1 ML V/Fe-hematite and O/1 ML V/O3-hematite

Sites	•	V_B, V_C, Fe_A^S		V _A , V _C , I	Fe _B ^S	V _A , V _B , Fe ^S _C
1 ML V/Fe-hema	tite:Inter-atomic dista	nce (Å)				
V–Fe ^S		2.90/2.90		2.89/2.95		2.90/2.90
V–O ^S		1.95/1.97		2.03/1.86		1.95/1.95
Fe ^s -O ^s		1.97		2.06		2.07
$O^{3}-Fe^{3-1}_{C}$		2.18		2.14		2.12
$O^{3}-Fe_{B}^{3-1}$		2.31		2.53		2.43
V-Fe ⁸⁻¹		2.77/2.49		2.72		2.82
Fe ^S –Fe ^{S–1}		_		3.11		2.58
Interlayer distant	e(A)	1 12/1 08		0 61/1 29		0.05/1.01
V = 0 $E_{a}^{S} = 0^{S}$		1.12/1.08		0.01/1.28		0.95/1.01
$O^{S} Ee^{S-1}$		0.92		1.21		1.24
$O = I C_C$		1.42		1.44		1.54
Fe _C –Fe _B		0.24		0.46		0.45
$Fe_B^{S-1}-O^{S-1}$		0.89		0.77		0.80
Sites		$(V_B, V_C) - O_3$		(V_A, V_C) -	O ₃	$(V_A, V_B) - O_3$
1 ML V/O ₃ -hema	tite:Inter-atomic dista	nce (Å)		1.04/1.02		1 02/1 02
$V = O^{S}$		1.80/1.81		1.84/1.92		1.83/1.82
$O^{*}-Fe_{C}^{*}$		2.42		2.04		2.15
$O^{S}-Fe_{B}^{S-1}$		5.13		2.06		3.09
$V-Fe_{B \text{ or } C}^{S-1}$		2.11, 2.68		2.43		2.03
Interlayer distant	ce (Å)	0 (0 0 0 f				
V-O ³		-0.63, 0.86		0.16, 1.12		0.57, -0.50
$O^{s}-Fe^{s-1}_{C}$		1.82		1.31		1.53
$\operatorname{Fe}_{C}^{3-1} - \operatorname{Fe}_{B}^{3-1}$		0.92		0.27		1.01
$Fe_B^{5-1}-O^{5-1}$		0.37		0.90		0.50
Coverage	O _{ads} –V	O _{ads} –Fe ^S	V–O ^S	Fe ^S –O ^S	O ^S –Fe ^{S–1}	V–Fe ^{S–1}
1/3, 2/3 and 1 M.	L O on 1 ML V/Fe-he	matite: Bond length (\AA)			
1/3 ML O	1.94	1.98	1.93/1.85	1.96	2.08/2.23/2.30	-
	1.91		2.02/1.99	2.07	2.23/2.33/2.38	2.48
			2.14/2.04	2.10		
2/3 ML O	1.88/1.94	2.12/2.08	2.05/2.02	2.01	2.13	2.65
	1.88/1.85			2.02	2.28	2.86
				2.29		
1 ML O	1 90/1 82	2.07	2 02/2 09	2.08	2.11	2.51
I ML O	1.90/1.02	2.07	2.02/2.09	2.00	2.23	2.96
~	S	S	- 5 - 5	- S - S 1	- 5 1 - 5 1	- 5 1 - 5 1
Coverage	O _{ads} –O ³	V–O ³	Fe ³ –O ³	O ³ –Fe ^{3–1}	$\mathrm{Fe}_{\mathrm{B}}^{\mathrm{S}-\mathrm{I}}-\mathrm{Fe}_{\mathrm{C}}^{\mathrm{S}-\mathrm{I}}$	$Fe^{s-1}-O^{s-1}$
Interlayer distant	xe(A)	1 17/1 14	1.00	1.24	0.41	0.02
1/3 ML O	2.18	1.1//1.14	1.06	1.34	0.41	0.82
2/3 ML O	2.15/2.11	1.25/1.20	1.10	1.55	0.30	0.87
IMLO	2.17	1.5//1.19	1.00	1.50	0.33	0.94
Coverage	0-	V	V–O ^S		O ^S -Fe ^{S-1}	V ^S -Fe ^{S-1}
1/3, 2/3 and 1 M.	L O on 1 ML V/O ₃ -he	ematite: Bond length (À	i)			
1/3 ML O	1.6	1	1.84/1.83		2.13	-
	4.0	1			3.02	2.04
2/3 ML O	1.7	7/1.75	1.92/1.86		2.30/2.01/2.04	_
	1.8	3/1.87	1.81/2.07		2.49/2.30/2.16	2.81
			2.21/1.79			
1 ML O	1.7	3	2 14/1 94		2.01	_
I ML O	1.8	9	2.1 1/ 1.9 1		2.18	2.96
<i></i>	C	0			-5.1 - 5.1	_ 0 1 _ 0 1
Coverage	O _{ads} –O ^s	V–O ^s		O ³ -Fe ³⁻¹	Fe ³⁻¹ -Fe ³⁻¹	$Fe^{s-1}-O^{s-1}$
Interlayer distant	xe(A)	·		0.02	0.20	1.61
1/3 ML O	2.31	0.71	80	0.93	0.39	1.01
2/3 ML O	2.15/2.12	1.11/0	.07 02	1.10	0.51	0.80
	2.13	1.40/1	.04	0.74	0.50	0.70

For interatomic bonding distance or interlayer distance A–B, the following rule expresses the multiple values: when A varies (for example, more than one adsorbed O atom), then "/" is used to distinguish different values, when B varies (for example, different Fe^{S-1}), then different lines are used to distinguish different values.

Site	$R_{\rm S}$ volume charge (e)	Bader charge	Magnetic moment
	Q(s, p, d)	(e)	(µ _B)
1 ML V/I	Fe		
VB	+1.43(0.24, 6.22, 3.11) ^a	+1.13	1.8
V _C	+1.43(0.24, 6.22, 3.11)	+1.17	1.8
Fe^S_A	+0.69(0.31, 0.43, 6.57)	+0.56	-0.2
$\mathrm{Fe}_{\mathrm{C}}^{\mathrm{S}-1}$	+1.19(0.34, 0.46, 6.01)	+1.52	-3.4
$\mathrm{Fe}_{\mathrm{B}}^{\mathrm{S}-1}$	+1.15(0.35, 0.48, 6.02)	+1.63	-3.5
$\mathrm{Fe}_\mathrm{A}^{\mathrm{S}-2}$	+1.12(0.36, 0.52, 6.00)	+1.77	3.5
1 ML V/0	∂ ₃		
VA	+1.28(0.29, 6.23, 3.19)	+1.52	1.9
VB	+1.08(0.34, 6.31, 3.27)	+1.46	1.1
Fe_{C}^{S-1}	+1.34(0.27, 0.32, 6.07)	+1.44	-3.4
Fe ^{S-1}	+0.26(0.53, 0.71, 6.50)	+1.19	-1.8
Fe ^{S-2}	+1.10(0.36, 0.52, 6.02)	+1.75	3.6
	1.10(0.50,0.52,0.02)	11.75	5.0
1/3 ML C) on $I ML V/Fe$	1 51	0.7
	+1.43(0.24, 0.22, 3.11) +1 43(0.24, 6.22, 3.11)	+1.31 +1.40	1.0
Fe ^S	+1.03(0.35, 0.43, 6.19)	+0.87	2.6
Fe ^{S-1}	+1.06(0.34, 0.48, 6.11)	+1.57	_3 3
Fe ^{S-1}	+1.00(0.34, 0.46, 6.06)	+1.57	3.5
I C _B	1.14(0.34, 0.40, 0.00)	11.02	-3.5
2/3 ML C	O on 1 ML V/Fe		
V _B	+1.3/(0.29, 6.30, 3.04)	+1./1	-0.4
V _C	+1.45(0.28, 6.29, 2.98)	+1./8	0.4
Fe _A	+1.13(0.33, 0.40, 6.14)	+1.18	2.9
Fe ^{S-1}	+1.11(0.34, 0.49, 6.06)	+1.60	-3.4
$\mathrm{Fe}^{\mathrm{S-1}}_{\mathrm{B}}$	+1.21(0.34, 0.45, 5.99)	+1.65	-3.6
1 ML 0 a	on 1 ML V/Fe		
VB	+1.27(0.33, 6.37, 3.03)	+2.08	0.4
V _C	+1.28(0.30, 6.35, 3.07)	+1.95	0.9
Fe _A	+0.99(0.31, 0.44, 6.26)	+1.54	3.0
Fe_C^{S-1}	+1.10(0.35, 0.50, 6.05)	+1.62	-3.4
$\mathrm{Fe}_\mathrm{B}^{\mathrm{S}-1}$	+1.24(0.34, 0.46, 5.97)	+1.69	-3.6
1/3 ML C	O on 1 ML V/O3		
V_A	+1.00(0.36, 6.40, 3.25)	+2.08	0.5
V_B	+1.11(0.34, 6.31, 3.24)	+1.55	1.0
$\mathrm{Fe}_{\mathrm{C}}^{\mathrm{S-1}}$	+1.29(0.28, 0.36, 6.08)	+1.49	-3.3
$\mathrm{Fe}_{\mathrm{B}}^{\mathrm{S}-1}$	+0.32(0.52, 0.69, 6.48)	+1.17	-1.9
2/3 ML C	O on 1 ML V/O3		
VA	+1.26(0.33, 6.36, 3.05)	+2.02	0.6
VB	+1.14(0.35, 6.38, 3.14)	+2.00	0.7
Fe_C^{S-1}	+1.22(0.31, 0.42, 6.05)	+1.59	-3.4
Fe _B ^{S-1}	+1.06(0.36, 0.5, 6.08)	+1.63	-3.4
1 MI O	on $1 ML V/O_2$		
V _A	+1.46(0.32, 6.39, 2.83)	+2.21	0.0
VB	+1.15(0.36, 6.42, 3.07)	+2.21	0.2
Fe ^{S-1}	+1.26(0.33, 0.45, 5.95)	+1.74	-3.6
Fe ^{S-1}	+1.10(0.37, 0.53, 6.00)	+1.73	-3.6
D			

The numbers in brackets for volume charge indicate s, p, d angular character.

^a V 3p 'shallow-core' levels were included in the variational space, in order to use a compact pseudopotential core region. The more contracted Fe 3p states were kept within the PAW pseudopotential. Further computational parameters are described in Ref. [1].

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Analytic Mulliken	charge,	volume	integrated	charge,	and	bond	orders
derived from embed	dded-clu	ster calc	ulations				

	Mulliken charge	Volume charge	Bond order	
	(e)	(e)	(e)	
1 ML	V/Fe-hematite			
VB	+0.98	+0.96	$V_B - Fe_A^S$	0.17
V _C	+1.11	+1.02	$V_C - Fe^S_A$	0.16
Fe ^S _A	+1.98	+1.70	$V_B - O^S$	0.07 *3
Fe ^{S-1} _B	+2.34	+2.01	$V_C - O^S$	0.09 *3
Fe _C ^{S-1}	+2.30	+1.98	$\begin{array}{l} V_C \!\!-\!\! F e_C^{S-1} \\ V_B \!\!-\!\! F e_B^{S-1} \end{array}$	0.07 0.02
1 ML	V/O ₃ -hematite			
VA	+2.49	+1.83	$V_{A}\!\!-\!\!O^{S}$	0.15 *3
VB	+1.93	+1.45	$V_{B} - O^{S}$	0.10 *3
Fe ^{S-1}	+1.49	+1.66	$V_B - Fe_B^{S-1}$	0.79
Fe _C ^{S-1}	+2.48	+2.06		

Notation *3 denotes three	equivalent	bonds of	f the given	bond	order
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Table 5

Core level shift ΔE for	1 ML V/Fe-hematite and	1 ML V/O ₃ -hematite
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Configuration		Cor	e level shift (eV)
1 ML V/Fe			
VB		-0.4	46
V _C		-0.3	50
Fe ^S _A		-1.4	42
Fe ^{S-1}		-0.3	31
Fe ^{S-1}		-0.0	02
$\mathrm{Fe}_\mathrm{A}^{\mathrm{S}-2}$		0.1	30
1 ML VIO2-hematite			
V _A		-0.4	19
V _B		-0.0)7
$\mathrm{Fe}_{C}^{\mathrm{S}-1}$		-0.1	58
Fe ^{S-1}		-0.1	33
Fe ^{S-2}		0.	14
1 ML V/Fe-hematite	1/3 ML O	2/3 ML O	1 ML O
V _B	-0.21	0.36	0.40
V _C	0.00	0.53	0.95
Fe ^S _A	-0.82	-0.69	-0.54
Fe ^{S-1}	-0.24	-0.26	-0.21
Fe ^{S-1}	0.04	0.05	0.09
Fe_A^{S-2}	0.35	0.34	0.26
1 ML V/O ₃ -hematite	1/3 ML O	2/3 ML O	1 ML O
V _A	0.50	0.65	1.14
VB	0.03	0.67	0.82
$\operatorname{Fe}_{C}^{S-1}$	-0.26	-0.29	-0.24
$\mathrm{Fe}_B^{\mathrm{S}-1}$	0.04	0.05	0.08
$\mathrm{Fe}_A^{\mathrm{S}-2}$	0.13	0.12	0.04

The reference value for Fe is the same site before V adsorption, the reference state for V is V^{3+} in V_2O_3 . The calculation is done within the initial state approximation.

when it is initially put high above the topmost O layer, it will not sink down, even though the resulting metastable structure is less stable.

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2.2.2. Electronic structure and bonding analysis

The DOS (Fig. 1) for (V_A, V_B) occupancy shows distinct splitting at -3 eV between high binding energy and low binding energy bands for $\text{Fe}_{\text{C}}^{\text{S}-1}$. For $\text{Fe}_{\text{B}}^{\text{S}-1}$, since its bonding with O is broken, there are two 3d spin up peaks showing up at about -2.5 eV. The occupied conduction band portion for adsorbed V is greatly increased; one can say that the V overlayer is metallic.

For the (V_A, V_B) configuration the Bader charges for Fe_C^{S-1} and Fe_B^{S-1} are 1.44 e and 1.19 e, see Table 3. The former is fairly close to the Fe^{2+} reference state while the latter is even more reduced because of the direct electron contribution from V_B. In the $R_{\rm S}$ volume integration, Fe^{S-1}_B s, p, d populations dramatically increase to yield a charge of only 0.26 e, the largest increase (\sim 0.5 e) being in d orbitals, which implies donation of electrons from V_B to Fe_B^{S-1} . Note that while Bader and R_S charges sample space differently, they are in clear agreement on the special role of Fe_B^{S-1} . The (V_A, V_B) magnetic moments of are 1.9 and 1.1 μ_B , considerably larger than for the 0.5 ML case. The magnetic moment of Fe_C^{S-1} changes from $-1.7 \mu_B$ (clean surface) to a bulk-like $-3.4\,\mu_B$ while the moment of Fe_B^{S-1} is little changed, at $-1.8\,\mu_B$. The smaller Fe_B^{S-1} magnetic moment is due to its interaction with VB as discussed above. Mulliken atomic charges and volume charges for V/O3-hematite embedded cluster models (Table 4) show considerably highly V ionicity compared to the 1 MLV/Fe overlayer structure. Fe_B^{S-1} is again seen to be greatly perturbed compared to Fe_C^{S-1} , and in V/Fe.

Looking at the core level shifts shown in Table 5, we can see that though V_A and V_B have similar Bader charge, V_A has a higher negative core level shift (-0.61 eV) than V_B (-0.20 eV), despite the larger charge perturbation just discussed. Fe^{S-1}_C and Fe^{S-1}_B also show significant negative binding energy shifts upon V adsorption, which is contrary to their presumed reduction (supported by Bader charges).

3. Atomic oxygen adsorption on monolayer V/hematite

Here we study atomic oxygen adsorption on representative 1 ML V/hematite model surfaces. We assume that O adsorption will take on 1×1 supercell symmetry without any longer-ranged reconstruction or disorder, and that O only adsorbs on top of the surface instead of penetrating to subsurface sites. We expect that this simple model can bring insight about the resulting geometric and electronic properties changes upon O adsorption on V/hematite (0001) necessary for understanding the certainly more complicated actual oxidization process. In modeling atomic O adsorption, we study three types of coverage, 1/3 ML, 2/3 ML and 1 ML, following the notation of Czekaj et al. [5] where the atomic density of an ideal oxygen plane along (0001) is referred to as 1 ML. Two pre-adsorbed 1 ML V/ hematite surfaces are chosen from representative energyfavorable configurations obtained from our previous calculations: (V_B, V_C, Fe_A^S) and (V_A, V_B) . For configurations that have only one metal atom at the surface, we found that O will adsorb on top of the metal to form a Me=O double bond (Me = Fe, V). For configurations that have more than one surface metal atom, we found that O prefers binding at Me-Me bridge sites to form a Me-O-Me group. A previous study of O adsorption on the V₂O₃(0001) surface also concluded that for a multi-metal terminated surface such bridge site adsorption can give the most stable adsorbate-substrate complex [5].

3.1. O adsorption on 1 ML V/Fe-hematite

3.1.1. Adsorption sites, geometry and energy

As shown in Table 1 and Fig. 2, for the 1 ML V/Fehematite surface, for 1/3, 2/3, and 1 ML O coverage, the "bulk O" sites which can form three stable bonds with surface metal atoms (V_B , V_C , Fe_A^S) are favored. The affinity of 1 ML O to 1 ML V/Fe-hematite substrate is clearly larger than that of 0.5 ML V/Fe with an increase of E_{ads} from 3.4 eV/atom to 9.45 eV/atom, the most obvious reason being the additional number of V–O bonds formed. Adsorption energy for partial O coverage is lower than that of the 'saturated' 1 ML: 8.02 eV/atom for 2/3 ML vs 8.34 eV/atom for 1/3 ML, as previously noted for 0.5 ML V/Fe-hematite. Thus some additional binding energy is gained from forming a saturated oxygen-surface adsorbate band.

For O–1 ML V/Fe-hematite, the O_{ads} –V bond length decreases as coverage goes up, suggesting a stronger bonding affinity for the metallic overlayer. As the O_{ads} –V bond becomes shorter, O–Fe bond lengths become longer with increasing coverage, see Table 2. In reference to the surface O^{S} plane average height, the adsorbed O is 2.18 Å higher



Fig. 2. Models for O adsorption on V/Fe-hematite. (a) 1/3 ML O on 0.5 ML V_A; (b) 1 ML O on 0.5 ML V_A; (c) 1/3 ML O on 1 ML (V_A, V_B); (d) 1 ML O adsorption on 1 ML (V_A, V_B).

for 1/3 ML, 2.15/2.11 Å for 2/3 ML, 2.17 Å for 1 ML. The V atom height increases somewhat with increasing O coverage from 1.17/1.14 Å (1/3 ML) to 1.37/1.19 Å (1 ML). The substrate is screened very well by the metal layer, so that structural effects on hematite layers due to O adsorption become very minor.

3.1.2. Electronic and bonding properties

The DOS are shown in Fig. 3 for 1/3 ML and 1 ML O coverage. For all coverages of O–1 ML V/Fe-hematite, the overall shapes of V and Fe 3d orbital distributions are similar to those in O–0.5 ML V/Fe-hematite. Consistent with partial reduction found with increased V coverage (Table 3), some portion of the V conduction band is seen to be shifted to below $E_{\rm f}$. With three metal atoms at the surface, the adsorbed O have higher coordination number than their counterparts in 0.5 ML V/Fe-hematite; therefore the O_b 2p orbital density is shifted toward greater binding and is more aligned with surface O^S atoms. The O_b bandwidth increases with coverage as expected, due to O–O interactions.

For O-1 ML V/Fe-hematite, results collected in the Bader analysis (Table 3) imply that Fe and V lose electrons as



Fig. 3. Atom-resolved DOS for oxygen adsorbed on 1 ML (V_B,V_C)/Fehematite. (a) 1/3 ML O, (b) 1 ML O.

O coverage increases, as expected. For 1 ML O adsorption, the Fe^S_A atoms (1.54 e) are not fully reoxidized to the 3+ state (1.79 e). However, the V atoms (1.95/2.08 e) are very close to the 5+ state discussed above. The $R_{\rm S}$ volume charge change is irregular, similar to that on 0.5 ML V/ Fe-hematite, again due to the rehybridization among metal s, p, d electrons which move electronic distributions across the integration sphere boundaries. For oxygen adsorption on 1 ML V/Fe-hematite, the Fe^S_A magnetic moment dramatically increases from $-0.2 \mu_{\rm B}$ (0 ML) to $2.6 \mu_{\rm B}$ (1/ 3 ML), $2.9 \mu_{\rm B}$ (2/3 ML) and $3.0 \mu_{\rm B}$ (1 ML). The two V moments show a very irregular variation with O coverage, but the absolute value is much smaller ($-0.4 \leq M \leq 1.0 \mu_{\rm B}$) compared to that before oxidization, of $1.8 \mu_{\rm B}$.

3.2. O adsorption on 1 ML V/O_3 -hematite

3.2.1. Adsorption sites, geometry and energy

For 1 ML V/O₃-hematite, as V_B sinks below the topmost O plane, at 1/3 ML O adsorption, the most preferred adsorption site is on top of the higher V with formation of a vanadyl bond V=O_t, with binding energy of 7.55 eV/ atom (Table 1). Here the anionic potential barrier prevents the adsorbed O from bonding with both V atoms and no stable O_b sites are found. When the coverage increases to 2/3 ML, the relaxed structure shows that the extra adsorbed O atoms can pull the sunken V back above the topmost O plane, forming a V–O_b–V bridging bond structure, with adsorption energy of 7.29 eV/atom. 1 ML O adsorption coverage further decreases the adsorption energy to 6.87 eV/atom, due to O–O repulsion. The geometry for 1/3 ML and 1 ML O adsorption can be seen in Fig. 4.



Fig. 4. Models for O adsorption on V/O_3 -hematite. (a) 1/3 ML O on 0.5 ML V; (b) 1/3 ML O on 1 ML V; (c) 1 ML O on 1 ML V.

The V–O_t bond length for 1/3 ML coverage is 1.61 Å, the same as V=O on 0.5 ML V/O₃ hematite (Table 2). The V_A -O^S interlayer distance of 1.84/1.83 Å is increased by only 0.01 Å compared to clean 1 ML V/O₃ and the region below is also barely changed. For 2/3 ML O coverage, V shifts above O^S, the two O_b positions are distorted from bulk O sites, both forming asymmetric bonds with underlying V atoms, of length 1.77 Å, 1.83 Å and 1.75, 1.87 Å. With 1 ML O coverage an ordered structure forms very similar to an O₃-terminated hematite surface with V replacing Fe atoms at the subsurface layer. Relative to the O^S plane, the original (higher) V atom shifts steadily upward by 0.18 Å (1/3 ML), 0.54 Å (2/3 ML), 0.89 Å (1 ML) with O coverage. The second (lower) V atom moves even more dramatically, from 0.5 Å below the O₃ plane before oxidization to 1.02 Å higher under 1 ML O adsorption, see Table 2.

3.2.2. Electronic structure and bonding properties

Fig. 5 gives the atom-resolved DOS for 1/3 ML O and 1 ML O adsorption on 1 ML V/O₃-hematite. For 1/3 ML O, as the vanadyl V=O_t bond is formed, the DOS for O_t and V_A is very similar to that for adsorption on 0.5 ML V. However, because of the presence of another V atom,



Fig. 5. Atom-resolved DOS for oxygen absorbed on 1 ML (V_A , V_B)/O₃-hematite: (a) 1/3 ML, (b) 1 ML O.

 V_A has not completely reached the 5+ state; therefore the conduction band density is non-zero at E_f . For 1 ML O adsorption, the V_A , V_B conduction bands lie completely above the Fermi level, indicating that V atoms are all in the 5+ state, which is similar to the subsurface oxidization state for $V_2O_3(0001)$ [5]. Fe^{S-1} and Fe^{S-1} show broad 3d valence bands that strongly hybridize with O^S 2p, a clear sign of reoxidization, and again the surface O band broadens with coverage.

As shown in Table 3, the Bader analysis implies that for 1/3 ML and 2/3 ML O adsorption, V is not completely oxidized, yet for 1 ML O, with charge of 2.21 e, V now is in the 5+ state. The Fe_C^{S-1} , Fe_B^{S-1} are reoxidized upon O adsorption: at 1 ML they are clearly oxidized to the 3+ state with Bader charge of 1.73 and 1.74 e. The $R_{\rm S}$ volume integration once again does not give a clear trend of the metal atoms' charge changes due to significant electronic redistribution in the diffuse region outside $R_{\rm S}$. One interesting phenomenon is that in 1/3 ML O adsorption, although V_A, V_B have different O coordination numbers, their d orbital population is the same, as has been mentioned in Kresse et al. [6]. This again emphasizes the rather stable valence-region rearrangements which accompany redox events. The vanadium magnetic moment decreases as the coverage O increases, from $0.5/1.0 \,\mu_B$ for $1/3 \,ML$ O to $\sim 0 \mu_B$ for 1 ML. The only notable Fe moment suppression occurs for a neighboring Fe_B^{S-1} (1.9 μ_B) in 1/3 ML coverage.

4. Comparison of experiment with theory

Fig. 6 shows the angle θ dependence of the V K α X-ray fluorescence yield in the vicinity of the substrate (0006) Bragg reflection. Also shown is a ball-and-stick model depicting the average V height (relative to bulk-like substrate lattice and unit cell) inferred for 1 ML vanadium coverage, as-deposited and after oxidation. The XSW model-independent analysis [7,8] of these data produces the (0006) unitary geometrical structure factor (Fourier component) for the V atomic distribution relative to the substrate unit cell. These measured Fourier component amplitudes and phases are listed in Table 6 for the two surface conditions studied and for the three different hkil Bragg reflections used. As a point of reference the unit cell origin chosen in this analysis (See Fig. 6) has a $P_{006} = 0$ phase for the (0006) Fourier component of the bulk-like Fe sublattice The as-deposited value of $P_{006} = 0.60$ for the V distribution (Table 6) can be interpreted as the average relative *d*-spacing V position, only if the V distribution profile is less than half the width of the 0006 d-spacing of c/12 = 1.1 Å. In which case the average height would be $0.6 * d_{006} = 1.38 \text{ Å} above \text{ or } 0.4 * d_{006} = 0.92 \text{ Å} below the}$ average bulk-like Fe height. The large change of P_{006} to 0.88 upon oxidation could be interpreted as a major change in V vertical position; however, a different interpretation is quite plausible, since there are probably two or more sites, and multiple surface domains. Therefore these data require

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Fig. 6. Normalized reflectivity and V K α yield versus angle, about (0006) Bragg reflection for 1 ML V coverage. Left: as-deposited, right: after oxidation. Blue dots represent average V position relative to bulk inferred from these data. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 6 XSW analyses of Fourier amplitude f and phase P for as-deposited and air-exposed oxidized 1 ML VO₃/ α -Fe₂O₃(0001) surfaces

(hkil)	As-deposite	As-deposited		-air meas.)
	f	Р	f	Р
(0006)	0.30(1)	0.60(1)	0.36(2)	0.88(1)
$(10\bar{1}4)$	0.27(1)	0.21(1)	0.35(1)	0.46(1)
$(01\bar{1}2)$	_	_	0.12(1)	0.49(2)

further interpretation. For this purpose, we applied the model-independent XSW imaging method [8–12] where the 3D atom distribution is generated from the summation of the XSW measured Fourier components.

The oxidized surface was removed from the UHV chamber and the XSW measurements were performed from the air-exposed and consequently hydrated surface. It should be noted that the oxidized 1 ML V surface is stable against hydration as evidenced by our observing no measurable changes in the 0006 f and P values after moving the sample from UHV to air.

Side view cuts through the XSW measured 3D V map are displayed in Fig. 7, where we can see that the 1 ML oxidized V distribution is similar to the 0.5 ML reported case [2], except that the B/A relative site occupation fraction ratio is higher for 1 ML. Interpreting these results further: the A-site (closer to underlying oxygen layer) appears stable with respect to the coverage change, existing in both 0.5 ML and 1 ML as-deposited surfaces. However, the C-site occupied in 0.5 ML disappears in the 1 ML asdeposited surface. Further deposition of V to the 0.5 ML



Fig. 7. $(\bar{1}\bar{1}20)$ 2D cuts of 3D vanadium atom density maps of asdeposited and oxidized 1 ML V/hematite, constructed using (0006) and (1014) XSW data listed in Table 6. The ($\bar{1}\bar{1}20$) projection of bulk-like Fe (red) and oxygen (purple) sites are drawn in to aid in the visualization of the experimentally measured V distribution. High symmetry surface sites are labeled as A, B, and C directly above each site. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

surface may cause V to migrate from C- to B-sites, and oxidation may move some of the V from B- to A-sites.

5. Summary and conclusions

In this work we investigated geometric and electronic properties of two systems:

1 ML V adsorption on an ideal hematite (0001) surface with two idealized bulk cut terminations, and atomic O adsorption on the 1 ML V/Hematite system. In the first models, we calculated the energy and relaxed structure of V adsorbed onto a hematite (0001) surface, studying its electronic structure using both plane-wave projected density of states and cluster analysis. We found that threefold bonding of (V_A, V_B) on O₃-hematite with surface O^S at a position where no Fe is directly below is the most stable configuration, followed closely by (V_B, V_C) . In the second set of models, we studied atomic O adsorption on the 1 ML V/Hematite system under different coverage, finding that O forms strong bonds with surface Fe or V, causing them to be further oxidized. Adsorption of O also induced large surface structural changes.

Interatomic distances and interlayer spacings are found to be rather sensitive to adsorption sites; e.g., the V-Fe nearest neighbor distance varies from 2.90 Å on V/Fehematite to 2.03 Å on the (V_A, V_B) –O₃ interface, the latter indicating a direct M-M bonding interaction contributing to the low energy state. Calculated V-O^S interlayer spacings show the large site-dependent variations in V vertical position: 0.61/1.28 Å for (V_A, V_C)-Fe metal-on-metal adsorption versus -0.63/0.86 Å for (VB,VC)-O3 metalon-oxygen adsorption. The latter displacements actually lead to O-Fe_B^{S-1} bond breaking and O-Fe_C^{S-1} bond stretching, and formation of a $(V_B Fe_B^{S-1}O_2^S)$ tetrahedral unit which might be regarded as a precursor to some major reconstruction. Upon sequential oxidation steps from 1/3, 2/3, to 1 ML O the V-O^S spacing is seen to recover gradually from ~ 0.7 Å to ~ 1.4 –1.5 Å as a indicator of formation of something like a 'normal' V₂O₃ surface overlayer.

Using four different measures of atomic charge distributions (band structure: R_S volume and Bader charge, embedded cluster: Mulliken charge and volume integration) we are able to understand in detail not only the experimentally observed reduction of Fe upon V adsorption and subsequent reoxidation upon treatment with atomic oxygen, but also to measure the more complex interplay between s, p, and d-electron states on the metal atoms. The detailed charge distribution of 1 ML adsorbed V was also traced, starting with a net Bader charge of ~ 1.1 e, less ionic than the 1/2 ML case previously studied, and its evolution with addition of 1/3, 2/3, and 1 ML O toward \sim 2.2 e characteristic of the formally fully oxidized V⁵⁺ state. Oxidation states of Fe and V are found here (full V monolayer) and in I (1/2 V monolayer) to be largely determined by short range chemical effects; i.e., the number of coordinated oxygens and the competition for M-O bonds among nearby metal sites. To be sure, there are some direct metal-metal interactions, as in V_B -Fe^{S-1}_B pairs encountered in several settings; however, the general picture is of rapidly diminishing perturbations of both charge state and magnetization with depth into S-1, S-2... subsurface layers.

The DOS results demonstrate details of perturbations to the surface layer Fe_A^S energy levels due to formation of a metallic/near-metallic 1 ML V overlayer, while only slightly modifying Fe^{S-1} , consistent with charge density analyses. The DOS for 1/3, 2/3, and 1 ML oxygen coverage

on V/Fe-hematite record the initial formation of a fairly narrow ($\sim 2 \text{ eV}$) oxygen adsorbate band, which broadens with increasing coverage to become very similar to the \boldsymbol{O}^{S} previous surface band. More subtle shifts of V and Fe^S_A bands are also visible, accompanying the gradual metal oxidation process. A very similar picture emerges for gradual formation of an oxygen overlayer on the (V_A, V_B) -O₃ interface, with the ensuing metal shifts and band reshaping accompanying complete V and Fe oxidation being more dramatic. Calculated V and Fe 2p core level shifts, which in the simplest model should track oxidation state changes, reveal a site-dependent complexity which is hidden within the rather broad experimental XPS spectral bands. This complexity is due primarily to the fact that the level shifts measure the local potential, which is a superposition of local charge state and long distance Coulomb potentials due to lattice relaxation and distant lattice charges. Future angular-resolved and polarization-selected photoelectron spectra might be able to provide a better determination of the various possible surface structures. Similarly, in principle, future measurements of X-ray magnetic circular dichroism around the V 2p resonances could resolve the predicted surface magnetic moments. At present, such measurements would be extremely difficult to perform.

By comparing our results with experimental interpretations, we find agreement with the "chemically obvious" metal V_A site, for both as-deposited and oxidized states. While experiment suggests that the V_C site is occupied for 0.5 ML V and vacant for 1 ML V, the 1 × 1 surface cell calculations lead to a different model. Calculations predict that V_C is unfavored in low coverage due to repulsion from the underlying Fe, while for 1 ML V the disadvantage is largely overcome and a mixture of all possible (V_i, V_i) configurations is expected. The predicted coverage- and sitedependent surface relaxation makes direct comparison and interpretation in terms of a simple displacement with respect to bulk Fe sites problematical. Further research is needed, particularly to discover the disposition of the "amorphous" half of deposited V, and the geometry of reconstructed surface-region hematite layers.

It would be very interesting to carry out statistical thermodynamic studies of composition and stability of mixed V_nO_m/hematite with terminations other than the Fe- and O₃ interfaces considered in this work. Bergermayer et al. [13] examined the thermodynamics of O_2 :hematite(0001), obtaining very plausible results using electronic structure methods similar to those employed here. However, the best experimental data so far available [10] suggest that the actual (0001) surfaces may be more complex, with significant biphase and defect composition. Theoretical studies of epitactic V_2O_3 monolayers and V_nO_m terminations on the well-understood isostructural α -Al₂O₃(0001) surface [14,15] and oxygen stabilization of the $V_2O_3(0001)$ surface [5] suggest that adequate theoretical tools are available, when the hematite parameter space can be better specified by experiment.

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