Supporting Information for

Electronic and Geometric Features Controlling the Reactivity of Mg-vanadate and V₂O₅ Surfaces toward the Initial C–H Activation of C₁–C₃ Alkanes – a DFT+U Study Hansel Montalvo-Castro¹, Álvaro Loaiza-Orduz², Randall J Meyer³, Craig Plaisance², and David Hibbitts^{1*}

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S1. Bulk Structures and Optimizations

Bulk optimizations were performed with varying *k*-point mesh for V_2O_5 and Mg-vanadate bulk structures. In general, the larger the *k*-point mesh, the more accurate the DFT calculation becomes. This accuracy, however, occurs at the concurrent expense of increasing computational time and resources. Thus, it is necessary to determine an optimal *k*-point mesh to perform DFT calculations; not too small to lose accuracy, but not too high to introduce unnecessary computational expense. **Figure S1** shows the results for bulk optimizations as a function of *k*-point mesh. We show that the k-point selection alters the converged energy by not more than 0.25 eV. Given that the largest *k*-point mesh will result in the most accurate DFT calculation, surfaces were cleaved from the bulk structures that were optimized with the largest *k*-point mesh. During bulk optimization, both the atoms and unit cell parameters were allowed to relax (ISIF = 3). Given that these materials are expected to be semiconductors, we used conventional oxide settings (ISMEAR = 0) during bulk optimization. Moreover, a +U Hubbard correction was also included (U = 3.0 eV).



Figure S1. K-point mesh screening during the bulk structure optimization of a) V_2O_5 , b) MgV_2O_6 , c) tri- $Mg_2V_2O_7$, d) mono- $Mg_2V_2O_7$, and e) $Mg_3V_2O_8$.

S2. Surface Structures and Termination Screening

Surfaces were cut from the largest k-point mesh bulk calculations. A total of 5 low Miller-index surfaces were systematically explored to account for all their terminations. Surfaces were initially optimized as singular unit cells, while relaxing all atomic positions. Surface formation energies (SFE) were calculated according to Equation 1 from the main text. The corresponding SFE values for all surfaces and their respective terminations (127 total) are summarized in Table S1. SFE values in green indicate that surfaces were kept for further exploration of C–H activation barriers and descriptors.

Bulk structures for V₂O₅ and Mg-vanadates have no unpaired electrons and therefore, those should exhibit a net magnetic dipole equal to zero. DFT+U methodology features an output that informs about the oxidation state of the atom being corrected (in this case V-atoms), allowing to assess the net magnetic dipole moment of a given surface. As such, surfaces that resulted in reduced V-atoms were also excluded from investigation, so that not all of the selected surfaces correspond to the lowest SFE values. For example, Mg₃V₂O₈ (001) surface has an SFE = 8.15 kJ mol⁻¹ Å⁻², however, it exhibited reduced V-atoms. In addition to SFE and the oxidation state of V-atoms upon surface optimization, we also considered including surfaces exhibiting structural diversity to build a wide configurational space of O-atom coordinations and environments, which is crucial to demonstrate descriptor transferability.

		, 0				
Surface	Tl	<i>T2</i>	Т3	T4	T5	<i>T6</i>
V ₂ O ₅ 001	3.25	10.98	15.76	_	_	_
V ₂ O ₅ 010	0.03	27.31	_	_	_	_
V ₂ O ₅ 011	1.37	10.39	11.39	_	_	_
V ₂ O ₅ 100	2.84	_	_	_	_	_
V ₂ O ₅ 101	3.24	8.04	10.55	_	_	_
V ₂ O ₅ 110	2.49	_	_	_	_	_
V ₂ O ₅ 111	3.44	6.32	_	_	_	_
V ₂ O ₅ 201	221.3	_	_	_	_	_
V ₂ O ₅ 221	345.11	—	_	_	_	_
MgV_2O_6 001	2.10	8.38	15.13	21.18	22.54	_
MgV_2O_6010	4.18	_	_	_	_	_
MgV_2O_6011	5.23	—	_	_	-	_
MgV_2O_6012	926.60	_	_	_	_	_
MgV_2O_6021	4.67	—	_	_	-	_
$MgV_2O_6 10\overline{1}$	2.42	9.48	18.85	_	_	_
$MgV_2O_6 10\overline{2}$	456.87	_	_	_	_	_
MgV ₂ O ₆ 100	3.77	11.31	14.52	22.07		_
MgV ₂ O ₆ 101	7.15	19.90	_	_	_	_
MgV ₂ O ₆ 102	525.08	_	_	_	_	_
$MgV_2O_611\overline{1}$	6.43	9.41	14.46	_	_	_
$MgV_2O_611\overline{2}$	4.76	13.80	_	_	_	_
MgV ₂ O ₆ 110	3.80	11.38	_	_	_	_
MgV ₂ O ₆ 111	2.91	4.79	_	_	_	_
MgV ₂ O ₆ 112	4.70	12.54	_	_	_	_
$MgV_2O_620\overline{1}$	3.59	4.87	11.14	25.26		_
MgV ₂ O ₆ 201	6.33	11.27	14.10	_	_	_
$MgV_2O_621\overline{1}$	5.32	8.47	_	_	_	_
$MgV_2O_621\overline{2}$	11.15	_	_	_	_	_
MgV_2O_6210	13.60	_	_	_	_	_
MgV ₂ O ₆ 211	13.51	_	_	_	_	_
MgV ₂ O ₆ 221	5.60	12.23	_	_	_	_
t-Mg ₂ V ₂ O ₇ 001	583.01	584.38	597.94	604.20	605.57	632.05
$t-Mg_2V_2O_701\overline{1}$	430.26	706.60	747.13	824.97	_	_
$t-Mg_2V_2O_701\overline{2}$	7.09	608.27	_	_	_	_
$t-Mg_2V_2O_7010$	6.27	290.67	751.29	783.73	_	_
$t-Mg_2V_2O_7011$	782.15	786.40	417.11	_	_	_
$t-Mg_2V_2O_7012$	417.10	563.94	776.89	_	_	_
$t-Mg_2V_2O_702\overline{1}$	542.55	754.48	_	_	_	_
$t-Mg_2V_2O_7021$	783.36	_	_	_	_	_
$t-Mg_2V_2O_70\overline{1}0$	17.56	19.87	_	_	_	_
$t-Mg_2V_2O_70\overline{1}1$	15.18	15.79	_	_	_	_
$t-Mg_2V_2O_7 10\overline{1}$	8.91	8.96	9.77	_	_	_
t-Mg ₂ V ₂ O ₇ 100	8.31	8.43	8.77	_	_	_
t-Mg ₂ V ₂ O ₇ 101	5.98	6.85	7.12	7.54	_	_
$t-Mg_2V_2O_7 11\overline{1}$	4.62	4.69	_	_	_	_
$t-Mg_2V_2O_7 110$	3.37	4.04	4.06	_	_	_
$t - Mg_2 V_2 O_7 111$	2.75	3 03	_	_	_	_
$t - M\sigma_2 V_2 O_7 2\overline{10}$	12.91	_	_	_	_	_
$t_{-M\sigma_{2}V_{2}O_{7}} \sqrt{210}$	11.04	_	_	_	_	_
· 1152 · 207211	11.04	_				

Table S1. Initial Screening of Surface Formation Energies (SFE, kJ mol⁻¹ Å⁻²) across V_2O_5 and Mg-vanadate surfaces of varying Miller index.

$t-Mg_2V_2O_7212$	9.99	10.79	_	_	_	—
$t\text{-}Mg_2V_2O_72\overline{2}1$	15.89	_	_	_	_	_
$t\text{-}Mg_2V_2O_720\overline{1}$	8.83	_	_	_	_	_
t-Mg ₂ V ₂ O ₇ 201	8.08	_	_	_	_	_
$t-Mg_2V_2O_721\overline{1}$	5.31	_	_	_	_	_
$t-Mg_2V_2O_721\overline{2}$	5.51	_	_	_	_	_
$t-Mg_2V_2O_7210$	5.06	_	_	_	_	_
t-Mg ₂ V ₂ O ₇ 211	4.99	_	_	_	_	_
$t-Mg_2V_2O_7212$	4.75	_	_	_	_	_
$t-Mg_2V_2O_722\overline{1}$	4.29	_	_	_	_	_
$t-Mg_2V_2O_7221$	3.06	_	_	_	_	_
m-Mg ₂ V ₂ O ₇ 001	7.13	9.60	12.51	12.58	_	_
$m-Mg_2V_2O_7010$	8.86	14.26	16.76	_	_	_
m-Mg ₂ V ₂ O ₇ 011	4.80	11.13	13.91	_	_	_
$m-Mg_2V_2O_7021$	14.06	_	_	_	_	_
$m-Mg_2V_2O_710\overline{1}$	14.87	_	_	_	_	_
$m-Mg_2V_2O_7100$	5.05	7.73	12.83	13.83	14.00	_
m-Mg ₂ V ₂ O ₇ 101	10.47	12.04	15.13	_	_	_
$m-Mg_2V_2O_711\overline{1}$	888.71	_	_	_	_	_
$m-Mg_2V_2O_711\overline{2}$	467.91	_	_	_	_	_
$m-Mg_2V_2O_7110$	12.22	13.02	_	_	_	_
$m-Mg_2V_2O_7111$	777.97	_	_	_	_	_
m-Mg ₂ V ₂ O ₇ 112	404.52	_	_	_	_	_
$m-Mg_2V_2O_7201$	363.97	_	_	_	_	_
Mg ₃ V ₂ O ₈ 001	10.67	17.19	_	_	_	_
$Mg_{3}V_{2}O_{8}010$	3.36	11.48	_	_	_	_
$Mg_{3}V_{2}O_{8}010$	13.22	14.22	_	_	_	_
$Mg_{3}V_{2}O_{8}012$	483.54	_	_	_	_	_
$Mg_{3}V_{2}O_{8}021$	14.31	1780	33.65	_	_	_
Mg ₃ V ₂ O ₈ 100	12.09	_	_	_	_	_
Mg ₃ V ₂ O ₈ 101	_	_	_	_	_	_
$Mg_{3}V_{2}O_{8}111$	_	_	_	_	_	_
Mg ₃ V ₂ O ₈ 102	642.96	_	_	_	_	_
$Mg_{3}V_{2}O_{8}110$	6.48	8.68	_	_	_	_
Mg ₃ V ₂ O ₈ 111	5.82	10.81	11.02	13.55	_	_
$Mg_{3}V_{2}O_{8}112$	7.50	9.48	10.23	_	_	_
$Mg_{3}V_{2}O_{8}120$	784.38	_	_	_	_	_
Mg ₃ V ₂ O ₈ 121	940.47	_	_	_	_	_
$Mg_{3}V_{2}O_{8}122$	473.13	_	_	_	_	_
M. M.O. 201	11.88	709.06	_	_	_	_
$Mg_{3}V_{2}O_{8}201$	11.00					
$Mg_{3}V_{2}O_{8}201$ $Mg_{3}V_{2}O_{8}211$	355.18	_	_	_	_	

			0								
Surface	Tl	<i>T2</i>	Т3	Τ4	T5	Т6	<i>T7</i>	Τ8	Т9	<i>T10</i>	T11
V ₂ O ₅ 010	0.11	9.43	22.24	11.24	_	_	_	_	_	_	_
V ₂ O ₅ 011	4.57	16.67	15.97	4.57	3.94	_	_	_	_	_	_
V ₂ O ₅ 100	9.32	3.84	9.54	21.81	_	_	_	_	_	_	_
V ₂ O ₅ 101	10.13	11.48	4.97	10.06	10.00	_	_	_	_	_	_
V ₂ O ₅ 110	11.40	7.18	1.55	11.75	20.05	_	_	_	_	_	_
MgV ₂ O ₆ 001	12.84	12.85	14.06	22.46	22.75	2.30	22.88	25.61	12.57	_	_
MgV_2O_6100	7.65	7.65	9.85	16.95	16.63	7.66	_	_	_	_	_
$MgV_2O_6 10\overline{1}$	21.55	21.57	18.35	2.89	10.76	18.45	21.70	15.22	_	_	_
MgV ₂ O ₆ 111	16.80	16.81	26.03	5.27	22.73	8.03	_	_	_	_	_
$MgV_2O_620\overline{1}$	8.50	20.46	12.54	10.53	12.54	12.25	_	_	_	_	_
$t-Mg_2V_2O_7001$	8.37	12.93	_	_	_	_	_	_	_	_	_
$t-Mg_2V_2O_7100$	4.62	9.90	4.05	_	_	_	_	_	_	_	_
$t-Mg_2V_2O_7210$	3.81	7.58	—	—	_	_	_	_	_	_	_
$t-Mg_2V_2O_7211$	9.68	13.37	6.48	15.43	—	—	_	—	_	_	_
$m-Mg_2V_2O_7001$	15.15	14.27	10.89	9.20	13.55	9.05	4.88	_	—	_	_
$m-Mg_2V_2O_7010$	12.25	14.88	14.27	13.68	13.68	7.51	_	_	_	_	_
$m-Mg_2V_2O_7011$	14.02	11.71	10.24	13.86	11.85	5.05	_	_	_	_	_
$m-Mg_2V_2O_7100$	12.22	9.60	14.44	15.57	11.31	10.00	9.45	9.45	_	_	_
$m-Mg_2V_2O_7110$	15.67	18.22	16.03	11.84	16.23	9.82	16.93	8.08	7.82	_	_
$Mg_{3}V_{2}O_{8}001$	8.15	14.80	12.46	12.46	14.14	_	_	_	_	_	_
$Mg_{3}V_{2}O_{8}010$	18.96	12.11	16.11	16.11	12.05	9.30	_	_	_	_	_
$Mg_{3}V_{2}O_{8}110$	14.46	12.10	12.13	12.36	12.74	12.73	13.97	7.70	6.64	13.62	_
$Mg_{3}V_{2}O_{8}111$	8.59	10.49	14.39	13.35	17.19	17.19	13.35	13.36	10.68	8.59	12.38
$Mg_{3}V_{2}O_{8}112$	13.52	12.14	9.43	16.21	15.05	15.11	11.16	10.24	7.90	10.29	

Table S2. Termination Screening of Surface Formation Energies (SFE, kJ mol⁻¹ Å⁻²) across V₂O₅ and Mg-vanadate surfaces selected from the initial screening. ^a

^a Surfaces with grey values were excluded from further examination.

Surfaces were initially optimized as single unit cells to explore a wide surface space. The corresponding optimized unit-cell parameters are given in Table S2. Following the single-unit cell optimization, supercell models were generated for surfaces that were not large enough to accommodate adsorbates and transition states. The corresponding optimized supercell parameters are also given in Table S2. The SFE values are between single-unit cells and their corresponding supercell are consistent within 6%; as such, we proceeded to perform all the descriptors and transition state calculations in this work over the supercell surfaces marked in green. These surfaces are summarized in Figure S2, which shows both the top and side views of optimized slab-models. For spacing purposes, side-views are truncated along the z-axis, but their corresponding cell parameters are summarized in Table S2.



Figure S2. Top and side-views of slab-structure models of V_2O_5 (vanadium pentoxide), MgV_2O_6 (metavanadate, monoclinic), $Mg_2V_2O_7$ (pyrovanadate, triclinic), $Mg_2V_2O_7$ (pyrovanadate, monoclinic), and $Mg_3V_2O_8$ (orthovanadate, orthorhombic).

S3. Effect of Mg: V Ratio on C-H Activation Energies for CH₄ and C₃H₈

Section 3.2 (from main text) discusses the role of Mg:V ratio on alkane activation energies. Consistent with the results shown for C₂H₆ (Fig. 3), each V₂O₅ and Mg-vanadate surface exhibits very different reactivity across different active sites (O-atoms) for CH₄ (Fig. S3) and C₃H₈ (Fig. S4-S5). These data suggest that the reactivity of these materials toward alkane C–H activation is governed by oxygen-specific properties, rather than surface specific properties. In general, barriers increase with increasing Mg:V ratios. For example, the lowest C–H activation energies for CH₄, α -C₃H₈, and β -C₃H₈ are, respectively, 128, 118, and 102 kJ mol⁻¹ on V₂O₅, whereas being 187, 162, and 145 kJ mol⁻¹ on Mg₃V₂O₈. These barriers trend with the corresponding alkane C–H bond dissociation energy (CH₄ > C₂H₆ > α -C₃H₈ > β -C₃H₈).



Figure S3. Initial C–H activation energy for CH₄ as a function of relative surface formation energies (SFE) across the selected surfaces for a) V_2O_5 , b) MgV₂O₆, c) triclinic Mg₂V₂O₇, d) monoclinic Mg₂V₂O₇, and e) Mg₃V₂O₈. Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom. Values in red indicate the lowest C–H activation barrier for each bulk, irrespective of surface. Two distinct terminations (one Mg-rich and the other V-rich) are shown for tri-M₂V₂O₇ (100) surface.



Figure S4. Initial C–H activation energy for C_3H_8 at the terminal position as a function of relative surface formation energies (SFE) across the selected surfaces for a) V_2O_5 , b) MgV₂O₆, c) triclinic Mg₂V₂O₇, d) monoclinic Mg₂V₂O₇, and e) Mg₃V₂O₈. Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom. Values in red indicate the lowest C–H activation barrier for each bulk, irrespective of surface. Two distinct terminations (one Mg-rich and the other V-rich) are shown for tri-M₂V₂O₇ (100) surface.



Figure S5. Initial C–H activation energy for C_3H_8 at the central position as a function of relative surface formation energies (SFE) across the selected surfaces for a) V_2O_5 , b) MgV₂O₆, c) triclinic Mg₂V₂O₇, d) monoclinic Mg₂V₂O₇, and e) Mg₃V₂O₈. Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom. Values in red indicate the lowest C–H activation barrier for each bulk, irrespective of surface. Two distinct terminations (one Mg-rich and the other V-rich) are shown for tri-M₂V₂O₇ (100) surface.

The spread in oxygen reactivity across each surface then motivates exploring oxygen-specific features, for example O atom environment and coordination. Lattice surface O atoms can exhibit distinct environments (e.g., atop vs. bridged) and neighbors (Mg-V vs. V-V). Barriers generally trend with atom coordination with atop being most reactive and 3-fold being least reactive (Figs. S6-S8). When contrasting among bridged and 3-fold O-atoms, reactivity decreases with increasing Mg:V ratio.



Surface Oxygen Coordination and Environment

Figure S6. Initial C–H activation energy for CH₄ as a function of surface oxygen coordination and environment classified a) per bulk and b) per coordination across all the selected surfaces for V_2O_5 (red), b) MgV₂O₆ (green), triclinic Mg₂V₂O₇ (blue) d) monoclinic Mg₂V₂O₇ (pink), and Mg₃V₂O₈ (orange). Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom. Average values and total number of O-atoms per type are also provided in panel (b).



Surface Oxygen Coordination and Environment

Figure S7. Initial C–H activation energy for C_3H_8 at the terminal position as a function of surface oxygen coordination and environment classified a) per bulk and b) per coordination across all the selected surfaces for V_2O_5 (red), b) MgV_2O_6 (green), triclinic Mg₂V₂O₇ (blue) d) monoclinic Mg₂V₂O₇ (pink), and Mg₃V₂O₈ (orange). Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom. Average values and total number of O-atoms per type are also provided in panel (b).



Surface Oxygen Coordination and Environment

Figure S8. Initial C–H activation energy for C_3H_8 at the central position as a function of surface oxygen coordination and environment classified a) per bulk and b) per coordination across all the selected surfaces for V_2O_5 (red), b) MgV₂O₆ (green), triclinic Mg₂V₂O₇ (blue) d) monoclinic Mg₂V₂O₇ (pink), and Mg₃V₂O₈ (orange). Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom. Average values and total number of O-atoms per type are also provided in panel (b).

S4. Methyl-Addition Energies (MAE) across V₂O₅ and Mg-vanadates

Figure S9 shows the corresponding methyl-addition energy (MAE) values across the fourteen models explored in this work. Similar to the hydrogen addition energy (HAE) values, MAE values generally increase with increasing Mg:V ratios, suggesting that surfaces become less reactive from VO_x isolation.



Figure S9. Methyl-addition energies (VFE) as a function of relative surface formation energies (SFE) across examined surfaces for a) V_2O_5 , b) MgV₂O₆, c) triclinic Mg₂V₂O₇, d) monoclinic Mg₂V₂O₇, and e) Mg₃V₂O₈. Lattice planes are labeled by surface Miller index. Each data point corresponds to a unique O lattice atom.

S5. Partial Density of States

Partial density of states for both O-atoms and V-atoms was considered as a proxy for surface reducibility. For the case of O atoms, the partial density of states of *p*-orbitals is considered, whereas for V-atoms, the *d*-orbitals are considered as these are the relevant orbitals during surface reduction (O $1s^22s^22p^4$; V [Ar]3d^34s^2). Figure S10 shows the corresponding *p*-PDOS for two unique O surface atoms in V₂O₅ 010 and the corresponding *d*-PDOS of the V-atoms that undergo reduction upon H-addition (or CH₃-addition). The PDOS spectrum resembles that of a semiconductor, with an existing bandgap between the valance and the conduction band. Moreover, O-atoms have higher PDOS at the valance shell than in the conduction shell, whereas V-atoms have higher PDOS at the conduction band. The second moment of the valance band of O-atoms. The rationale of taking the difference between these two energies is that it serves as proxy for V-O pair reducibility, according to Equation 12 from the main text. While the O-atom accepts H-atom during the C–H activation, the V-atom gets reduced. This PDOS is typical of a semi-conductor material, and both the valence and conduction bands are shown for *p*-orbital and *d*-orbital for O and V, respectively.



Figure S10. DFT-computed partial density of states for two V–O pairs in V_2O_5 (010) involved in alkane C–H activation.