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The Dual-Phase Mechanism for the Catalytic Conversion of *n*-Butane to Maleic Anhydride by the Vanadyl Pyrophosphate Heterogeneous Catalyst

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Abstract

Industrial production of maleic anhydride (MA) from *n*-butane relies on the vanadyl pyrophosphate (VPO) catalyst. Improving VPO's selectivity and activity could have enormous economic and environmental impact, but efforts have been impeded by uncertainties regarding the active phases and atomistic mechanism of the VPO catalyst. We report here a plausible 15 step mechanism taking *n*-butane to MA with energetics computed using hybrid density functional theory calculations on periodic models of the surface layers. We find that the P=O group on the X1 phase is solely responsible for butane activation. The P=O group is made active by the reduction of a nearby vanadium atom, a so-called *reduction-coupled oxo-activation*. However, we show that a catalyst consisting only of the X1 phase would not be selective due to several highly exothermic steps. Instead, we show that the more stable α_1 phase can catalyze the formation of MA after initial activation, thus proposing and validating a dual-phase mechanism that takes butane to MA. Our new mechanism inspires the development of a more selective VPO catalyst containing small X1 regions highly separated by α_1 surfaces.

1. Introduction

Vanadium pyrophosphate (VPO) is a unique heterogeneous catalyst that converts *n*-butane to maleic anhydride (MA) with high selectivity (60-70%)¹. VPO is of great industrial importance, producing 500 ktonne of MA annually², and consequently many empirical efforts have been made to improve its selectivity and activity. We believe that these efforts have been seriously impeded by the lack of a plausible reaction mechanism explaining VPO's remarkable selectivity.

VPO catalysts operate at high temperatures (>300°C) on a gas feedstock of butane and oxygen. Butane is oxidized and functionalized to MA, while gaseous oxygen reoxidizes the catalyst. The most basic mystery surrounding VPO's mechanism concerns which phases are responsible for the reaction. The VPO reduced phase, (VO)₂P₂O₇, is often assumed to be active, though VPO possesses five additional oxidized phases – β-, δ-, α₁-, α₂-, and X1-VOPO₄ – that could play a role. Among the oxidized phases, the sensible candidates are α₁-, α₂-, and X1-VOPO₄, since they form layered structures and possess stable surfaces.

The reduced and oxidized candidate phases consist of 8-membered rings of alternating vanadium and phosphorus atoms linked by oxygen atoms. However, each phase possesses different surface motifs on which reactions could take place, such as V=O, P=O, and bridging oxygens (V-O-P). Diagrams of the candidate phases, along with their surface motifs, are presented in figure 1.

Figure 1. Candidate active surfaces of VPO with labeled surface motifs. Oxygen atoms are red, vanadium atoms are silver, and phosphorus atoms are purple. For clarity, we exclude the second layer of $(\text{VO})_2\text{P}_2\text{O}_7$.

Without a doubt, the first step of VPO's mechanism is butane activation: a hydrogen is abstracted from *n*-butane to form a highly reactive butyl radical. A long-standing puzzle was how a surface site could be active enough to break the strong butane C-H bond. Our previous two studies, denoted in this paper as CG^{2,3}, used the Perdew-Burke-Ernzerhof⁴ (PBE) flavor of density functional theory (DFT) with periodic boundary conditions (PBC) to investigate butane activation on $(\text{VO})_2\text{P}_2\text{O}_7$ and on α_1 -, α_2 -, and X1-VOPO₄. CG found that only the P=O motif on

the X1 phase could activate butane with a low activation barrier, $E_a = 13.6$ kcal/mol. Moreover, CG showed that this highly reactive P=O group of the X1 phase could drive subsequent reactions to form MA with low reaction barriers.

CG explained this very surprising finding, that a P=O bond could activate strong alkane C-H bonds, in terms of a completely new reaction mechanism, the *reduction-coupled oxo-activation* (ROA) mechanism. In ROA, as the abstracted hydrogen atom converts P=O to P-OH, a new P=O bond simultaneously points at a neighboring vanadium atom, causing it to be reduced from the +5 to the +4 oxidation state. That is, $O=P-O-V^{+5}$ is transformed into $HO-P=O \cdots V^{+4}$. Effectively the proton of the C-H bond “transfers” to the P=O bond while an unpaired electron arrives at the V^{+5} , decoupling the oxidation and reduction processes.

The ROA mechanism is not unique to VPO. In another study, Cheng and Goddard found that ROA enabled the ammoxidation of propane to acrylonitrile by the MoVNbTeO_x mixed metal oxide catalyst⁵. In fact, we believe that ROA is relevant to many mixed metal oxide catalysts, particularly those that catalyze difficult oxidation reactions.

CG’s calculations used the PBE functional (without London dispersion corrections) and a plane wave basis set (with a 30 Ry energy cutoff). This is the most popular flavor of DFT for PBC calculations and is implemented in many mainstream electronic structure codes. However, our general experience in DFT calculations on organometallic catalysts involving localized spins, is that the Becke-three-parameter-Lee-Yang-Parr (B3LYP) hybrid functional⁶⁻⁹ gives higher quality reaction energies, barriers, and mechanisms than the PBE non-hybrid approach. Accounting for London dispersion adds additional accuracy. Unfortunately, B3LYP is extremely difficult to apply to periodic solids, requiring the use of Gaussian basis sets rather than plane

waves. Undeterred, we decided to use B3LYP to reexamine the catalysis of butane to MA on VPO.

2. Computational Details

Applying hybrid DFT to periodic systems is not straightforward; evaluating the exact exchange interactions with plane waves leads to slow convergence, increasing the computational cost by a factor of 100-2000 times. In contrast, evaluating the exact exchange interactions with Gaussian basis sets increases the cost by only a factor of three compared to PBE. However, using Gaussian basis sets required an understanding of what level of Gaussian basis sets are consistent with the plane wave basis sets used in CG. To achieve this end, we first tested the performance of various basis sets on small, finite $V_xP_{4-x}O_{10}$ clusters. We used these results to select a suitable hybrid functional and used that functional to revise CG's mechanism for the conversion of *n*-butane to MA.

We performed cluster DFT calculations using the PBE, M06¹⁰, and B3LYP functionals as implemented in the Jaguar electronic structure package¹¹, which is suitable for non-periodic calculations. For all functionals, we included the Grimme D3 London dispersion correction¹². In our PBE and M06 calculations, we used the Pople 6-31G** basis set¹³⁻¹⁶ for light atoms and the angular-momentum-projected^{17,18} LANL2TZ effective core potential basis set^{19,20} for vanadium atoms (denoted LACVP** within Jaguar). We performed B3LYP calculations using three different basis sets:

- 1) LACVP**
- 2) A modified LACVP** basis set, with diffuse Gaussian functions removed (denoted mod-LACVP** within this paper)
- 3) The Pople 6-311G** basis set²¹ for light atoms and the LANL2TZ effective core potential

basis set for vanadium atoms (denoted LACV3P within Jaguar)

We performed DFT calculations on bulk (3D) and single-layered (2D) VOPO_4 and $(\text{VO})_2\text{P}_2\text{O}_7$ using the PBE and B3LYP functionals as implemented in the CRYSTAL14 electronic structure package²² which, unlike Jaguar, implements periodic boundary conditions. We included the Grimme D2 London dispersion correction²³ in these calculations (D3 is not implemented in CRYSTAL14). For both functionals, we used the mod-LACVP** basis set. This is because including the most diffuse Gaussian functions of LACVP** (with exponents less than 0.06) led to wild divergences in CRYSTAL14 due to linear dependencies.

We first optimized the atom positions and cell parameters for the five bulk 3D structures. We then formed periodic slabs by slicing these fully optimized bulk structures while ensuring that no covalent bonds were broken. Subsequent optimizations of the slabs were made holding the periodic cell parameters constant, to mimic the true bulk surface. For the α_1 and α_2 layered oxidized phases of VPO, slicing without breaking covalent bonds was straightforward. However, the layers of $(\text{VO})_2\text{P}_2\text{O}_7$ are held together with pyrophosphate bonds in the z-direction. To form the $(\text{VO})_2\text{P}_2\text{O}_7$ slabs, we sliced such that two layers of $(\text{VO})_2\text{P}_2\text{O}_7$ remained intact and then capped the newly broken pyrophosphate bonds with hydrogen to form surface hydroxides. This maintained the oxidation states of the phosphorus and vanadium atoms.

We calculated reaction intermediate energies through energy minimizations; we verified intermediates by ensuring all calculated vibrational frequencies were real. We calculated transition state (TS) energies through a two-step process, made necessary by the inefficient TS optimization processes in CRYSTAL14. We first determined approximate TS bond lengths through relaxed coordinate scans on finite VPO clusters. We then performed optimizations on periodic slabs while keeping these bond lengths constrained, to obtain TS energies. We are

confident that the TS energies calculated are good approximations of the true barriers.

For bulk α_1 - and α_2 -VOPO₄, we sampled the Brillouin zone with a 3x3x4 Monkhorst-Pack k-point grid (MPKG)²⁴. For bulk X1-VOPO₄ and (VO)₂P₂O₇, we used a 2x2x2 MPKG instead. For single layer α_1 - and α_2 -VOPO₄ slabs, we sampled the Brillouin zone with a 3x3x1 MPKG. For single layer X1-VOPO₄ and (VO)₂P₂O₇ slabs, we used a 2x2x1 MPKG. In all calculations, we smeared the Fermi surface with a width of 0.005 Ha. These computational parameters are identical to those used in CG.

3. Results

3.1 Finite Cluster O-H Bond Energies According to Multiple Functionals and Basis Sets

We calculated O-H bond energies on V_xP_{4-x}O₁₀ clusters since these clusters mimic the phases of VPO. The clusters and the periodic systems both contain V^V atoms, V=O groups, P=O groups, and bridging oxygen atoms.

We calculated O-H bond energies by subtracting the ground state energy of the protonated cluster from the ground state energies of the cluster and the hydrogen atom in vacuum:

$$D_{OH} = h_{\text{Cluster}} + h_H - h_{\text{Cluster-H}} \quad (1)$$

We examined the ROA effect for the four relevant clusters on which hydrogen was bonded to the P=O group. We varied the number of adjacent vanadium atoms and calculated the ROA effect by comparing the cluster's O-H bond energy to that of P₄O₁₀, the base case:

$$ROA = D_{\text{Cluster-H}} - D_{\text{P}_4\text{O}_{10}\text{-H}} \quad (2)$$

Our results, diagramed in figure 2, illuminate inconsistencies between methods while demonstrating little deviation between calculations made with different basis sets. Since all

cluster calculations included identical London dispersion corrections, the inconsistencies are caused by the functionals themselves.

All three functionals captured the ROA effect; vanadium atoms coupled through adjacent bridging oxygens significantly increasing the PO-H bond strength. Here, M06 and B3LYP predict a more significant ROA effect than PBE, probably because hybrid methods are more accurate for localized electron states. Furthermore, PBE predicts substantially lower bond energies than B3LYP, while M06 predicts intermediate energies.

Functional	O-H Bond Energies (kcal/mol)					ROA Effect (kcal/mol)		
	PBE	M06	B3LYP			PBE	M06	B3LYP
Basis Set	LACVP**		LACV3P**	mod-LACVP**		LACVP**		
a. POH	24.4	20.6	24.5	25.3	24.5	0	0	0
b. POH	61.1	73.7	81.5	84.5	80.8	36.7	53.1	57.0
c. POH	65.7	76.7	84.3	86.5	83.4	41.3	56.1	59.8
d. POH	73.1	80.0	86.4	87.8	85.1	48.7	59.4	61.9
e. VOH	72.2	72.4	77.8	79.2	77.9			
f. VOH	57.1	65.9	75.3	78.1	76.7			
g. V-OH-P	50.8	60.6	69.8	73.1	68.3			
h. P-OH-P	27.0	24.6	30.2	21.8	30.2			

Figure 2. Finite clusters, modelling VPO, with O-H bond energies calculated using various functionals and basis sets. The bond energies were changed little by the larger (LACV3P**) and modified (mod-LACVP**) basis sets, justifying use of the modified basis set in CRYSTAL14 calculations. All methods find an ROA effect, but the magnitudes differ.

We expect that the bond energies calculated using B3LYP are superior to those calculated using PBE because every case possesses localized singly occupied orbitals. Informed by previous organometallic calculations, we suspect that B3LYP best represents localized orbitals. Indeed, B3LYP calculations placed the unpaired spin on a single vanadium atom, while PBE delocalized the unpaired electron onto all present vanadium atoms. Thus, we used only B3LYP in the remainder of our calculations.

With B3LYP, we evaluated several basis sets (results in figure 2). Calculations using LACVP** and LACV3P** were reasonably consistent, with bond energies using LACV3P** less than 5% higher than those predicted with LACVP**. Thus, we conclude that the smaller LACVP** basis set is adequate for VPO systems. The bond energies predicted for the clusters using the LACVP** basis set and our modified mod-LACVP** basis set (with diffuse functions removed) were within 2.1% of each other. These results validated our use of mod-LACVP** in the VPO calculations discussed in the next section.

3.2 VPO Surface O-H Bond Energies and the Consequences for Butane Activation

Table 1. Calculated B3LYP O-H bond strengths, alongside with those reported by CG, on $(\text{VO})_2\text{P}_2\text{O}_7$ and VOPO_4 slabs for the motifs introduced in figure 1.

Phase	Motif	PBE – from CG ^{2,3} (kcal/mol)	B3LYP (kcal/mol)
$(\text{VO})_2\text{P}_2\text{O}_7$	VOH	58.2	76.3
	V-OH-P	17.0	29.3
$\alpha_2\text{-VOPO}_4$	VOH	52.1	75.0
	V-OH-P	45.2	72.7
$\alpha_1\text{-VOPO}_4$	VOH	49.2	71.8
	V-OH-P	48.5	73.9
X1- VOPO_4	VOH	59.6	94.7
	V-O(1)H-P	51.6	74.6
	V-O(2)H-P	62.8	81.4
	POH	84.3	107.6

We used DFT to determine O-H bond strengths on $(\text{VO})_2\text{P}_2\text{O}_7$ and VOPO_4 slabs, reported

in table 1 for the motifs labelled in figure 1. Bond strengths for slabs were computed in the same fashion as for clusters (equation 1). In our experience, butane activation occurs through a linear surface-H-butyl transition state with a typical barrier around 10 kcal/mol above the endothermicity. B3LYP predicts the *n*-butane central C-H bond energy to be 107.9 kcal/mol, so we can estimate the minimum activation barrier to be

$$E_a = 107.9 + 10 - \Delta h_{OH} \text{ (in kcal/mol)}. \quad (3)$$

Seeking a barrier of <30 kcal/mol, we therefore searched for O-H bond energies, Δh_{OH} , greater than 88 kcal/mol.

We found that neither $(VO)_2P_2O_7$ nor the α_1 or α_2 -VOPO₄ phases could activate butane, since all the possible oxygen sites on these phases formed O-H bonds with energies significantly less than 88 kcal/mol. For X1-VOPO₄, however, our calculated O-H bond energies on the V=O and P=O sites were sufficient to activate butane.

3.2.1 The reduced phase, $(VO)_2P_2O_7$

The reduced form of VPO, $(VO)_2P_2O_7$, contains V=O groups and bridging oxygen sites (V-OH-P), as well as pyrophosphate bonds in the z-direction. In addition, the reduced phase is special in that each vanadium possesses an unpaired spin such that each vanadium atom is antiferromagnetically coupled to its neighbors along the chain²⁵.

For $(VO)_2P_2O_7$, we determined $D_{VOH} = 76.3$ kcal/mol and $D_{V-OH-P} = 29.3$ kcal/mol, both higher than calculated by CG ($D_{VOH} = 58.2$ kcal/mol and $D_{V-OH-P} = 17.0$ kcal/mol). **Neither site can activate butane**, since the O-H bond energies are much less than the required threshold of 88 kcal/mol.

Mulliken population analysis offered insight into the extremely inactive bridging oxygens

of $(\text{VO})_2\text{P}_2\text{O}_7$. Although a nearby vanadium accommodated the unpaired electron, there was no stabilization due to ROA. We think this was because the vanadium is reduced from V^{+4} to V^{+3} , resulting in much less stabilization than the V^{+5} to V^{+4} transformation central to the ROA effect.

3.2.2 The α_1 and α_2 phases of the oxidized phase, VOPO_4

The α_1 and α_2 phases contain $\text{V}=\text{O}$ groups, but no $\text{P}=\text{O}$ groups, so that the active sites of the two phases are either $\text{V}=\text{O}$ or bridging oxygen sites.

For α_1 - VOPO_4 , we determined $D_{\text{VOH}} = 71.8$ kcal/mol and $D_{\text{V-OH-P}} = 73.9$ kcal/mol. These bond energies are considerably higher than the PBE results from CG of $D_{\text{VOH}} = 49.2$ kcal/mol and $D_{\text{V-OH-P}} = 48.5$ kcal/mol, but still too small to activate butane.

For α_2 - VOPO_4 , we determined $D_{\text{VOH}} = 75.0$ kcal/mol and $D_{\text{V-OH-P}} = 72.7$ kcal/mol, again considerably higher than determined by PBE: $D_{\text{VOH}} = 52.1$ kcal/mol and $D_{\text{V-OH-P}} = 45.2$ kcal/mol.

Unlike in $(\text{VO})_2\text{P}_2\text{O}_7$, we found the α_1 and α_2 bridging oxygen sites to be surprisingly active. Indeed, Mulliken analyses revealed a neighboring V^{V} to V^{IV} reduction, which resulted in significant stabilization, an ROA-like effect. However, using B3LYP, neither site can be responsible for the observed activation of butane since the activation barriers would be at least 34 kcal/mol. Thus, we conclude that the α_1 and α_2 phases play no part in the initial activation of butane.

3.2.3 The X1 phase of the oxidized phase, VOPO_4

The X1 phase contains both $\text{V}=\text{O}$ and $\text{P}=\text{O}$ groups, opening new possibilities for reactivity. Using B3LYP, we calculated

$D_{\text{VOH}} = 94.7$ kcal/mol (compare to 59.6 kcal/mol for PBE),

$D_{\text{POH}} = 107.6$ kcal/mol (compare to 84.3 kcal/mol for PBE),

$D_{V-O(1)H-P} = 74.6$ kcal/mol (compare to 51.6 kcal/mol for PBE), and

$D_{V-O(2)H-P} = 81.4$ kcal/mol (compare to 62.8 kcal/mol for PBE).

Thus the bridging oxygen sites cannot be responsible for butane activation. Also, the P=O group is extremely active, providing an estimated $E_a \approx 10$ kcal/mol.

According to the criterion established in equation 3, both the P=O and V=O groups can activate butane. Even so, by the Arrhenius rate equation, the rate for activation by P=O versus V=O should be greater by $O(10^4)$ at the operating temperature ($>300^\circ\text{C}$) for catalysis.

Mulliken charges reveal the ROA effect is responsible for this extremely active P=O motif. When H reacts with V=O (VOH case), the unpaired electron remains on the active site vanadium, leading to no extra stabilization. In contrast, when H reacts with P=O (POH case), the entire unpaired electron is localized on a neighboring vanadium, dramatically stabilizing the system and forming a very strong PO-H bond. As observed in the finite cluster calculations, B3LYP predicts that the unpaired electron spin is localized on the slab. This contrasts with CG's PBE calculations that predicted unpaired electron delocalization across multiple neighboring vanadium atoms.

Summarizing, our new B3LYP calculations corroborate CG's most significant qualitative conclusion: due to ROA, the P=O group on the X1 phase is the only site capable of activating *n*-butane. However, we find that B3LYP predicts much higher bond energies than PBE, which we now argue has a dramatic effect on the subsequent reaction steps. Our inclusion of London dispersion corrections explains only a small portion of the discrepancy, < 5 kcal/mol. Similarly, we assert that our use of Gaussian basis sets (rather than plane waves) did not significantly affect results, as validated through cluster calculations. The only possible explanation for the higher

bond energies is our use of the hybrid B3LYP DFT functional over PBE.

Next, we examine the mechanism for the remaining 14 steps of the *n*-butane to MA conversion.

Figure 3. The dual-phase mechanism for the gas phase conversion of *n*-butane to MA by the

VPO catalyst with energies (Δh) and barriers (E_a) reported in kcal/mol. Diagrams of the X1 and

α_1 surfaces illustrate relevant motifs. Selected TS and intermediate structures are presented below mechanism.

3.3 Demonstration of a Viable Mechanism for the Conversion from Butane to Maleic Anhydride

Figure S1 presents the reaction energetics for the reaction surface for the pathway proposed by CG for the gas phase conversion of *n*-butane to MA on X1-VOPO₄. We calculated an approximate transition state barrier of $E_a = 11.7$ kcal/mol for the initial butane activation by the P=O of the X1 phase, in agreement with the value of 13.5 reported by CG. However, we found several subsequent steps to be extremely exothermic (up to -85.3 kcal/mol). Such large energy changes would likely most lead to low catalytic selectivity since the excess energy can fuel side reactions. We consider such highly exothermic steps to be incompatible with the high selectivity observed for VPO. In addition, some desorption steps are now far too endothermic (up to 50 kcal/mol) to occur under catalytic conditions. We concluded that **the X1 phase, although necessary for butane activation, cannot be the phase responsible for selectively catalyzing the remainder of the reaction.**

Next we considered the remaining steps of the CG mechanism on either α_1 -VOPO₄ or α_2 -VOPO₄. We determined that, relative to reduced VPO, bulk α_1 and α_2 were significantly more stable than bulk X1 (stabilized by -98.5 kcal/mol and -115.4 kcal/mol respectively, while X1 is stabilized by only -27.9 kcal/mol). Thus, we can expect that the oxidized surface of a VPO catalyst contains significant amounts of α phases, in agreement with ion scattering experiments²⁶. From geometric considerations, we expect that the surface α_1 phase is more likely formed from the starting VPO phase than the surface α_2 phase. This is because α_1 has coplanar vanadium and phosphorus atoms, making this phase nearly isomorphic with reduced VPO and X1 whereas α_2 , which does not have coplanar vanadium and phosphorus atoms, is quite different. Therefore, we

computed the reaction energies (Δh) and reaction barriers (E_a) on α_1 -VOPO₄ as shown in Figure 3. We arrived at a dual-phase mechanism, in which **all steps are carried out by the α_1 phase except initial butane activation, which is done by the X1 phase**. In these calculations, we assume that desorbed intermediates can move freely over the surface between sites and phases. This dual-phase mechanism, corresponding to the numbering in figure 3, is as follows:

- *Step 1-2* Activate secondary C-H bond of gas phase butane with a P=O site of X1. $\Delta h = -1.4$ kcal/mol and $E_a = 11.7$ kcal/mol, in agreement with CG (compare to -0.6 kcal/mol and 13.6 kcal/mol).
- *Step 2-3* Activate the other secondary C-H bond of gas phase butane radical with α_1 bridging oxygen to form 2-butene. $\Delta h = -27.2$ kcal/mol.
- *Step 3-4* Activate terminal C-H bond of gas phase 2-butene with α_1 bridging oxygen. $\Delta h = 14.6$ kcal/mol and $E_a = 19.0$ kcal/mol.
- *Step 4-5* Activate terminal C-H bond of gas phase 2-butene radical with α_1 bridging oxygen, forming butadiene. $\Delta h = -17.3$ kcal/mol.
- *Step 5-6* Adsorb butadiene onto a V=O site of α_1 . $\Delta h = 0.0$ kcal/mol.
- *Step 6-7* Form adsorbed 2,5-dihydrofuran through ring formation. $\Delta h = -19.1$ kcal/mol.
- *Step 7-8* Desorb 2,5-dihydrofuran. $\Delta h = E_a = 26.4$ kcal/mol, including a correction involving the second layer. We assumed a V=O group belonging to a second layer attacks the surface V^{III} site left behind from desorption, forming a V^{IV}-O-V^{IV} linkage. We calculated that this interlayer bond stabilizes the system by 5.9 kcal/mol.
- *Step 8-9* Activate primary C-H bond of gas phase 2,5-dihydrofuran with α_1 bridging oxygen. $\Delta h = 10.2$ kcal/mol.
- *Step 9-10* Adsorb 2,5-dihydrofuran radical onto a V=O site of the α_1 phase. $\Delta h = -40.7$

kcal/mol.

- *Step 10-11* Abstract hydrogen closest to V with by a bridging oxygen of the α_1 phase, forming adsorbed 2,5-dihydrofuran-2-one. $\Delta h = -27.0$ kcal/mol.
- *Step 11-12* Desorb 2,5-dihydrofuran-2-one. $\Delta h = E_a = 25.7$ kcal/mol, including 5.9 kcal/mol two-layer correction.
- *Step 12-13* Activate gas phase 2,5-dihydrofuran-2-one with α_1 bridging oxygen. $\Delta h = 10.1$ kcal/mol.
- *Step 13-14* Adsorb 2,5-dihydrofuran-2-one radical onto α_1 V=O. $\Delta h = -40.1$ kcal/mol.
- *Step 14-15* Activate hydrogen closest to V with α_1 bridging oxygen. $\Delta h = -18.0$ kcal/mol.
- *Step 15-16* Desorb MA. $\Delta h = E_a = 30.8$ kcal/mol, including a 5.9 kcal/mol second-layer correction as in step 7.

Our new dual-phase mechanism involving both the X1 and α_1 phases leads to much more reasonable energetics than the X1 based mechanism. Adsorption steps are only moderately exothermic (enough to overcome the unfavorable $-T\Delta S$), while desorption steps are only moderately endothermic (which is aided by the favorable $-T\Delta S$), and the most troublesome steps lead to modest activation energies. The mechanistic steps are identical to those proposed by CG, apart from steps one through four. Here CG considered that transformation of butane into butadiene involved adsorption steps, while we consider intermediates in the gas phase. These gas phase activations are equally favorable and likely faster, due to fewer barriers. Indeed, the stable gas phase intermediates (butene and butadiene) were observed in TAP reactor experiments on VPO²⁷.

Our B3LYP-derived dual-phase mechanism considers the VPO catalyst to be bi-functional. Both phases must be present to perform the full conversion, but only a small amount

of X1 phase is required. In fact, we expect that excess X1 phase lowers selectivity due to highly exothermic reactions. Thus, we predict that an optimal catalyst consists of small regions of X1 phase surrounded by large swaths of the α_1 phase. Here we imagine that gas-phase butane molecules diffuse across the VPO surface until they find a small X1 region. After activation, the activated butane product likely encounters only α_1 sites, on which it is selectively converted into MA. This conclusion, diagrammed in figure 4, is validated by ion-scattering experiments that find the working catalyst to be mainly α phases²⁶.

Figure 4. Overall schematic of the dual-phase mechanism. Butane is activated on an X1 region before diffusing an α_1 region to be converted to MA. Overall, the surfaces gain eight hydrogens and lose three oxygens.

Our new dual-phase mechanism is reminiscent of the mechanism observed for the MoVNbTeO_x multicomponent propane ammoxidation catalyst⁵, where it is widely believed that the optimum structure contains small regions of highly active M1 (that converts propane to propene) surrounded by the M2 phase that can only convert propene to acrylonitrile (AN) (but cannot activate propane). Recently we proposed how to synthesize a new single phase M1-based catalyst in which the surface is mainly a matrix of MoNbTeO_x (which cannot activate propane but can convert propene into AN) on which are deposited nanodots of Te₂V₅O_x (which can activate propane to form propene). Similar synthetic techniques could be developed for VPO. Formation of the α_1 phase could be completed by over-oxidizing reduced VPO, followed by V⁺

ion implantation or other processing to form nm-scale X1 inclusions.

4. Conclusions and Outlook

4.1 VPO Catalysis

Using the B3LYP hybrid DFT functional, we obtain the same key conclusions as our previous non-hybrid PBE DFT study: **The X1 phase is essential to activate butane.** However, B3LYP predicts the X1 phase to be far too reactive to selectively convert the butyl radical product into maleic anhydride. We solve this problem with our new **dual-phase mechanism that evokes the less active α_1 phase to maintain selectivity in the 14 subsequent steps to form MA.** Thus, we expect that the selectivity of a VPO catalyst could be optimized by synthesizing a surface that is predominantly α_1 phase but contains small nm-size islands of the X1 phase. Indeed, it is possible that the complex processing involved in successful commercial VPO catalysts may already lead to a similar structure.

However, bearing in mind the complex dynamics of surface catalysis and reoxidation, we expect that regions of X1-like and α_1 -like regions are in dynamic equilibrium. If this is the case, the locations of active sites on the catalyst surface are continually changing due to reduction (to form MA) and oxidation (by O_2). Therefore, the true dynamic mechanism of VPO catalysts is likely very complicated.

The next step in our mechanistic investigations will be to carry out reactive molecular dynamics (RMD) to follow all reaction steps simultaneously, including re-oxidation. Clearly the POH and under-coordinated V sites of the reduced catalyst must be re-oxidized to complete the VPO catalytic cycle.

However, a comprehensive study on re-oxidation likely involves complex structures and

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2
3 reactions, making a molecular dynamic study preferable to a mechanistic study. We plan to use
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5 the QM results reported here to train a ReaxFF²⁸ reactive force field suitable for reaction
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7 dynamics on this catalyst, as the time and length scales involved are too large for QM dynamics
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9 to be practical. Using ReaxFF reactive molecular dynamics (RMD), we plan to simulate the
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11 conversion of *n*-butane to MA on the catalyst surface at operating temperature. Previous ReaxFF
12
13 RMD reported for BiMoO₃²⁹ and Mo₃VOx³⁰ provided new insight into catalytic cycles. After
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15 performing a similar study on VPO, we will be in position to develop strategies to further
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17 improve the selectivity and activity of VPO.
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22 *4.2 DFT Methods for Studying Metal-Oxide Catalysts*

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25 It is relatively straightforward to carry out PBE DFT calculations on periodic surfaces
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27 using plane-wave basis sets. Consequently, PBE has become ubiquitous in studies of reactions
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29 and catalysis on periodic systems, with many successes in calculating activation energies. Thus,
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31 it is quite alarming that PBE produces results so disparate from B3LYP on these VPO systems,
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33 even after accounting for differing basis sets and London dispersion corrections. Of course, it is
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35 well known that PBE has trouble with localized open shell electronic states; however, we were
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37 shocked by the energetic errors. Thus, it would be prudent to consider applying hybrid-DFT to
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39 re-examine other heterogeneous catalysts studied using PBE. Additionally, our findings motivate
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41 further development of more accurate doubly hybrid functionals (such as XYG3³¹ and XYGJ-
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43 OS^{32,33}).
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49 **Supporting Information**

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52 Specification of mod-LACVP** basis set. X1-based mechanism and enthalpies. Atomic
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54 coordinates and ground state energies of finite clusters, slabs, gas phase species, intermediate
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56 slabs, transition state finite clusters, and transition state slabs.
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Table of Contents Image