Implications of sterically constrained n-butane oxidation reactions on the reaction mechanism and selectivity to 1-butanol

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Abstract

Density functional theory (DFT) is used to analyze the reaction network in n-butane oxidation to 1-butanol over a Ag/Pd alloy catalyst under steric constraints, and the implications on the ability to produce 1-butanol selectively using MOF-encapsulated catalysts are discussed. MOFs are porous crystalline solids comprised of metal nodes linked by organic molecules. Recently, they

have been successfully grown around metal nanoparticle catalysts. The resulting porous networks have been shown to promote regioselective chemistry, i.e., hydrogenation of *trans*-1,3-hexadiene to 3-hexene, presumably by forcing the linear alkene to stand “upright” on the catalyst surface and allowing only the terminal C-H bonds to be activated. In this work, we extend this concept to alkane oxidation. **Our goal is to determine if a MOF-encapsulated catalyst could be used to selectively produce 1-butanol.** Reaction energies and activation barriers are presented for more than 40 reactions in the pathway for n-butane oxidation. We find that C-H bond activation proceeds through an oxygen-assisted pathway and that butanal and 1-butanol are some of the possible products.

Keywords: C-H bond activation, oxidation, regioselectivity, metal-organic framework, encapsulated catalysts, computational catalysis

1. INTRODUCTION

Achieving high selectivity is one of the grand challenges faced by the chemical industry as it moves toward more cost- and energy-efficient synthesis processes. However, achieving selectivity toward a given product can be challenging if other products are more stable. Consider, for instance, the oxidation of methane with O_2 , where methanol or carbon monoxide are desired and valuable products,[1] but where undesired and non-valuable carbon dioxide and water are more stable. A number of catalysts have been tested for selective methane oxidation,[2-5] but they present a variety of issues [2; 6] such as low turnover frequencies, small yields, high temperature requirements, and deactivation. These issues arise due to symmetric and strong C-H bonds.[2] Similar problems are encountered in, for instance, the oxidation of alkanes to their corresponding primary alcohols. The secondary alcohols are more stable,[7; 8] and an aggressive oxidation process capable of oxidizing primary C-H bonds could also oxidize the secondary C-H bonds, possibly even preferentially. In the case of butanol, 2-butanol is more stable than 1-butanol by 16 kJ/mol. Thus, achieving a high selectivity toward 1-butanol requires a catalyst that selectively targets the primary carbons.

In principle, one way to prevent the oxidation of the secondary C-H bonds could be to prevent these bonds from contacting the catalyst surface through steric restrictions. Notably, Stephenson *et al.*[9] demonstrated how to provide these kinds of steric restrictions by encapsulating ca. 3.0 nm Pt nanoparticles with the porous material ZIF-8. In their experiments, Stephenson *et al.* hydrogenated 1,3-hexene and achieved 95% selectivity to 3-hexene. Without ZIF-8, n-hexane is preferentially formed at 80% selectivity,[9] suggesting that the porous structure of ZIF-8 imposes steric constraints at the Pt/ZIF-8 interface that prevent the internal

double bond from contacting the Pt surface. ZIF-8 belongs to the class of porous materials known as metal-organic frameworks (MOFs),[10-12] and systems where nanoparticles (NPs) are encapsulated by MOFs are known as NP@MOF systems.[9; 13] These systems can be synthesized such that the metal nanoparticles are encapsulated by the MOF, and it is possible to encapsulate nanoparticles of larger diameter than the largest cavity diameter of the encapsulating MOF.[13] For instance, Lu *et al.*[13] encapsulated 160 nm Ag nanoparticles in ZIF-8, even though the largest cavity diameter of ZIF-8 is ca. 1.2 nm. Similarly, Figure 1a, shows a TEM image of ca. 5 nm Pt nanoparticles encapsulated by ZIF-8. Indeed, with the method of Lu *et al.*[13] and variations used by others,[9; 14] the MOF grows around the nanoparticle, presumably giving rise to a NP/MOF interface somewhat akin to that of MOF films on metal substrates,[15-17] but whose atomistic details are yet unknown (Figure 1b).

Figure 1. a) TEM image of NP@MOF system: Pt nanoparticles (ca. 5 nm) encapsulated in ZIF-8, whose largest cavity is 1.2 nm. b) The Pt/ZIF-8 interface is plausibly akin to NP/MOF interfaces in MOF films on metal substrates, but atomistic details of the interface are unknown.

A number of examples of NP@MOF catalysts have been reported in the literature, but the development of such catalysts has thus far relied on experimental work.[13; 18-26] This is partly due to the computationally prohibitive size of fully atomistic models of the NP/MOF interface for density functional theory (DFT) calculations, and partly due to the unknown structural details

of the interface. With the goal of using DFT calculations to help develop NP@MOF catalysts, but aiming to circumvent the unknown details of the NP/MOF interface, Gomez-Gualdron *et al.*[8] introduced a simplified approach where steric constraints near the catalyst surface are provided by a “surrogate” pore formed by chemically inert atoms. While ignoring effects such as potential electronic modifications on the catalyst engendered by the MOF, this approach focuses on the generalized effect of steric constraints that relatively non-polar MOF pore windows could provide. For instance, Gomez-Gualdron *et al.*[8] studied the thermodynamics of the selective oxidation of n-butane to 1-butanol (a reaction and product relevant in the pharmaceuticals and specialty chemicals industries[27]) and showed that steric constraints on a Pd catalyst may facilitate the C-H activation of n-butane due to the different relative destabilization of n-butane and 1-butyl.

In this work, we use the surrogate pore approach to investigate whether the imposition of steric constraints is a sufficient condition to achieve the selective oxidation of n-butane to 1-butanol on a MOF@NP catalyst. We present computational insights about the thermodynamics and kinetics of sterically constrained reaction pathways for n-butane oxidation. The resulting reaction network is comprised of 39 reactions including the desired formation of 1-butanol and competing undesired formation of 1-butanal and 1-butene oxide, which represent the first steps in over-dehydrogenation of the primary and secondary carbons, respectively. **We show that 1-butanol and 1-butanal could both be competitive products, so to further push the selectivity toward 1-butanol will require tuning of the catalyst and/or careful selection of reaction conditions.**

2. COMPUTATIONAL METHODS

Sterically constrained catalyst model. We selected Ag₃Pd(111) to model a potential catalyst for the selective oxidation of n-butane. Based on the typical nanoparticle sizes encapsulated in MOFs by the Liu *et al.*[13] NP@MOF synthesis method, we chose the (111) facet for our model, which is representative of large nanoparticles (>5 nm).[28] Although both metal and metal oxide catalysts could be encapsulated in NP@MOF systems,[13] we opted for a transition metal catalyst motivated by the reported examples of catalytically active MOF-encapsulated catalysts.[9; 13] Since Pd has been used for alkane combustion,[29] whereas Ag is relatively inactive for C-H bond activation, we hypothesized that an Ag₃Pd alloy could potentially engender the necessary oxidative strength to partially oxidize n-butane. We used a perfectly mixed model of Ag₃Pd, which resembles more closely the ideal scenario where a monometallic catalyst constituted by an element with 75% and 25% of the electronic character of Ag and Pd is investigated. **While our model is homogeneous in composition, under actual oxidative conditions, the Pd atoms in an actual Ag₃Pd alloy may migrate to surface to minimize surface energy,[30] or the catalyst could convert to an oxide. We have chosen to avoid these complexities in our analysis, since** in this phase of the project, we are interested in identifying information about the reaction steps involved in n-butane activation, oxidation, and over-dehydrogenation on a *metal* nanoparticle catalyst encapsulated by a MOF. We will use the insights garnered in this work in future work aimed at catalyst screening for optimized and more realistic catalyst materials.

Steric constraints on the Ag₃Pd surface are provided by the surrogate pore approach, which has been introduced, described, and validated in detail by Gomez-Gualdron *et al.*[8] The surrogate pore limits the way C₄ species can interact with catalyst surface, while imparting only

weak dispersion interactions. It is composed of chemically inert helium atoms (Figure 2), the positions of which remain fixed during the simulations. The helium atoms form two rings, each composed of nine helium atoms. The distance between neighbor He atoms in a ring, as well as the distance between rings, is 3.0 Å. The distance between the bottom ring and the metal surface was tested in the 2.7 - 3.5 Å range, and reaction and activation energies are reported at the 3.5 Å height. We note that defects in the NP and/or MOF, chemical interactions between the NP and MOF, and other phenomena could influence catalyst surface energetics in a way that is not being captured by the surrogate pore approach. However, the surrogate pore approach does provide insights into how sterics influence the catalysis, which is what we have chosen to focus on in this phase of the project, since prior experimental results by Stephenson *et al.*[9] provide compelling evidence that the MOF influences the sterics at the interface.

Figure 2. a) Top view of $\text{Ag}_3\text{Pd}(111)$ catalyst model surface with a p(2x2)-O overlayer. b) Top view of $\text{Ag}_3\text{Pd}(111)$ model surface with a p(2x2)-O overlayer and surrogate pore. c) Side view of system shown in panel b. Ag = pink, Pd = blue, O = red, He = white. Unit cell born out in yellow.

As an example of a MOF that could be used for the encapsulation, the steric constraints invoked by the surrogate pore are somewhat similar to those that the pore windows of a MOF such as **UiO-66**[31] (Figure 3) could provide. **UiO-66** is a good candidate MOF to encapsulate

catalysts[25] due to its stability (decomposition temperature > 773 K).[32] **UiO-66** has **fcu** pore topology with “large” octahedral cages (ca. 1.2 nm) and “small” tetrahedral cages (ca. 0.75 nm), all interconnected by triangular pore windows. Although atomistic details of a **UiO-66** interface with relatively large nanoparticles (> 5 nm) are unknown, one can anticipate the pore windows to play a significant role in providing steric constraints. In regard to the interaction of C₄ species with the surrogate pore, a test calculation shows that the adsorption energy of n-butane on Pd(111) is similar (ca. 50 kJ/mol) for steric constraints provided either by the surrogate pore or by three ethylene molecules (whose atomic positions are fixed) crudely mimicking the chemical lining of a **UiO-66** pore window (Figure S4).

Figure 3. a) Pore structure of UiO-66. Octahedral cages (ca. 1.2 nm) denoted by purple spheres, tetrahedral cages (ca. 0.75 nm) denoted by yellow spheres. b) How potentially the pore windows (outlined by white circles) of **UiO-66** could provide steric constraints on a Ag_3Pd catalyst. The UiO-66 corresponds to the UiO-66(111) crystallographic plane. Zr: Pale blue, H: white, C: gray, O: red, Pd: blue, Ag: Pink.

Oxygen coverages and configurations. The surface coverage of oxygen atoms ($\theta_{\text{O}} = N_{\text{O}} \div N_{\text{M}}$, where N_{M} is the number of metal atoms on the catalyst surface) relevant to the oxidizing conditions under consideration (i.e., equilibrium with O_2 (g) at a pressure of 1 bar and temperature in the 298 K to 498 K range) was estimated using the method of first principles thermodynamics (FPT).[33] In this method, the catalyst surface energy $\gamma^{(1)}$ is calculated as the first Legendre transform of the Helmholtz free energy divided by the surface area, i.e., $\gamma^{(1)} = \gamma^{(1)}_{\text{Ag}_3\text{Pd}, \text{O}} - \gamma^{(1)}_{\text{Ag}_3\text{Pd}, \text{O}-\text{O}_2}$, [34] which allows for estimation of the surface coverage of oxygen atoms in equilibrium with an oxygen source. Hence, $\theta_{\text{O}} = 12 \gamma^{(1)}_{\text{O}_2} / \Delta G_{\text{O}_2}$, where $12 \gamma^{(1)}_{\text{O}_2}$ is calculated as in previous work.[34] **FPT analysis was performed on $\text{Ag}_3\text{Pd}(111)$ surfaces in the presence of the surrogate pore. We have previously reported that the surrogate pore model has no impact on the electronic structure of the metal surface, and that it has only little influence on the binding energies of the “small” adsorbates O^* , H^* , and OH^* , [8] so we do not expect the surrogate pore to have a significant effect on the calculated surface energies.** Approximating F as the electronic energy of the slab calculated in DFT (i.e., ignoring vibrational contributions[34]), we find that the $\text{p}(2 \times 2)$ oxygen overlayer structure (corresponding to $\theta_{\text{O}} = 0.25$ ML) is the most stable under the oxygen pressures of interest. The most stable oxygen overlayer structure has all O atoms occupying threefold hollow fcc sites and touching one of the Pd in the topmost surface layer (Figure 2). **All O atoms in the $\text{p}(2 \times 2)$ lattice have six 3rd nearest neighbor (3NN) O atoms and zero 1NN and 2NN.**[34] (1NN, 2NN, and 3NN configurations are defined in the Supporting Information, Figure S2.) **Our reaction energy and activation barrier calculations (discussed below) indicate that the $\text{p}(2 \times 2)$ -O structure is inactive for some of the steps that we considered, likely because adsorbates on this structure necessarily**

interact with two O atoms in 1NN positions, which creates a significant energy penalty (see Tables 1 and 2). Hence, we have additionally considered Ag₃Pd(111) catalyst models with 1) coverages < 0.25 ML, and 2) coverages ≥ 0.25 ML but with configurations that leave one of the sites in the p(2×2) lattice open (e.g., see the “triangle” configuration in Figure S1e). The oxygen coverage and configuration models that we have used for this study are described in detail in the Supporting Information.

Simulation details. Density functional theory (DFT) calculations were performed with the VASP code,[35; 36] which utilizes periodic boundary conditions and plane wave basis sets. Valence electron exchange and correlation were calculated with the PBE functional,[37; 38] while core electrons were simulated with PAW pseudopotentials [39; 40] to an energy cut-off of 400 eV. In principle, an energy cutoff of 500 eV is needed to accurately model the electronic structure of the surrogate pore (helium atoms), but test calculations show that identical reaction energies and activation barriers are obtained with either energy cutoff. Reaction energies and activation barriers were calculated by subtracting the energies of the reactants from the energy of the products (ΔE_{rxn}) or transition state complexes (ΔE_{a}), respectively, for each reaction. For example, for the dissociation of O₂*, i.e., O₂* + * → 2O*, where * denotes a catalyst site:

$$\Delta E_{\text{rxn}} = E_{2\text{O}^*} - E_{(\text{O}_2^* + *)} \quad \text{eq (1)}$$

$$\Delta E_{\text{a}} = E_{(\text{O}-\text{O})^*\ddagger} - E_{\text{O}_2^*} \quad \text{eq (2)}$$

where E 's are the electronic energies calculated in DFT, and (O-O)[‡] is the transition state complex for the reaction. During geometry optimizations, used to identify local minima on the potential energy surface (PES), electronic structures were converged self consistently until the energy difference between subsequent steps was less than 10⁻⁶ eV. On the other hand, during transition state (TS) searches, the energy tolerance for the electronic energies was set to 10⁻⁷ eV.

The D2 method of Grimme [41] was employed in all calculations to improve the modeling of dispersion interactions.

The $\text{Ag}_3\text{Pd}(111)$ catalyst surface was modeled by cutting a 4-layer (111) surface from the bulk L_{12} structure of Ag_3Pd , [30] which has a calculated lattice parameter of 4.104 Å, in agreement with a prior computational study. [30] $4 \times 4 \times 1$ supercells that included 13.5 Å of vacuum space between vertical images were used for the simulations. We find that the reaction energies are converged to within 0.01 eV using this vacuum spacing. The atoms in the bottommost layer of the metal slabs were held fixed in their calculated bulk positions, while the atoms in the top three layers were allowed to relax. Supercell calculations were performed non-spin-polarized, and energies were converged until the magnitudes of all the forces on all the non-fixed atoms were less than 0.03 eV/Å. Gamma-centered $\mathbf{k}$ -point meshes of $7 \times 7 \times 1$ were used to sample the first Brillouin zones.

Gas phase molecules were modeled in a $13 \times 14 \times 16$ Å rhomboid box. Calculations were performed at the Gamma point, and spin polarization was included when appropriate.

Transition states (TSs) were located with a combination of the Climbing Image Nudged Elastic Band (CI-NEB) [42; 43] and dimer methods. [44] First, discrete images along the proposed reaction coordinate were relaxed until the forces perpendicular to the reaction coordinate fell below 0.50 eV/Å. The **number of images used was typically taken as the total distance between the reactant and product images divided by 1 Å and rounded to the nearest integer**. Second, a dimer calculation was formed from the partially converged pathway, and it was then converged until the forces on the central image fell below 0.03 eV/Å. **In some circumstances, transition states located for one reaction were used as starting points for other reactions, without re-performing the NEB simulations. An example is the transition**

state for reaction 32, which used the transition state from reaction 7, which is the same reaction but at a lower coverage of O (see Figure 4 and Table 1), as a starting point.

Vibrational modes were calculated using finite differences in the DFT-calculated gradients for all TSs to verify that only one imaginary frequency in the correct degree of freedom was found. Most TSs fulfilled this criterion, although a few TSs have two imaginary modes, where the second one corresponds to a very low energy rotational vibration. An example of such a mode is animated in the Supporting Information (Figure S3). We do not expect the second vibrational modes to have any significant influence on the calculated transition barriers or the conclusions obtained in this work.

2. RESULTS

The reaction network for n-butane (C_4H_{10}) oxidation is shown in Figure 4, whereas corresponding energetic details are shown in Table 1. The connection between Figure 4 and Table 1 can be readily made through the reaction numbers. **The energetics of all reactions have been calculated at multiple oxygen coverages moderately above and moderately below the calculated equilibrium coverage of 0.25 ML, since in the absence of microkinetic modeling results, we cannot know exactly what the operating O coverage will be.** The reaction network can be divided into four regions (Figure 4, regions A – D) based on the typical oxygen coverage in each region (see details in SI). Region C represents surfaces where the minimum O coverage is 0.25 ML, due to O_2 (g) adsorption and dissociation, and Region B represents surfaces where 0.25 ML O is the maximum coverage, due to surface O^* being depleted by reacting with C_4H_{10} before O_2 (g) has an opportunity to adsorb and dissociate. The specific O configurations that were used to model the different coverages are stated in Table 1 and shown in the SI. We note that most configurations have been published previously.[34] As expected, we find that the

energetics of most of the reactions in the reaction network in Figure 4 are sensitive to the oxygen coverage. Since dependence on oxygen coverage is due primarily to 1NN interactions of reactants with O*, we have presented the number of 1NN interactions for each configuration in Table 1. We have also calculated the 1NN interaction energies between the adsorbates considered in this work and surface O*, and these are presented in Table 2. For example, the 1NN interaction energy between an overlayer O* and an adsorbate B* is calculated using the formula

$$\Delta E_{\text{interaction}} = E_{(\text{O}^*+\text{B}^*)} + E^* - E_{\text{O}^*} - E_{\text{B}^*} \quad \text{eq (3)}$$

where $E_{(\text{O}^*+\text{B}^*)}$ is the DFT-calculated energy of the interacting system with O* and B* in 1NN positions, E^* is the energy of the clean surface, and E_{O^*} and E_{B^*} are the energies of the isolated adsorbates.

Figure 4. Reaction network for sterically constrained n-butane oxidation on $\text{Ag}_3\text{Pd}(111)$. The numbers on the arrows are the same reaction numbers as in Table 1. The surface structure is represented by circles (pink = surface Ag, blue = surface Pd, red = overlayer oxygen (O^*)). Adsorbed species have the “*” suffix. C_4H_{10} = n-butane, $\text{C}_4\text{H}_9\text{O}$ = 1-butoxy, $\text{C}_4\text{H}_9\text{OH}$ = 1-butanol, $\text{C}_4\text{H}_8\text{O}(\text{al})$ = 1-butanal, $\text{C}_4\text{H}_8\text{O}(\text{ep})$ = 1-butene oxide, O_2 = molecular oxygen, OH = hydroxyl. Red reaction numbers are used for over-dehydrogenation reactions. Regions A through D are characterized by different oxygen coverages (see SI). Energies are given in units of eV.

Table 1. Reaction energies ΔE_{rxn} and activation barriers ΔE_a for reactions in the n-butane oxidation reaction network grouped by analogous reactions only differing in oxygen coverage. Nomenclature for chemical species as in Figure 4.

Rxn #		Starting O configuration ^[a] (O coverage, ML / # of 1NN ^[b] interactions)	Ending O configuration ^[a] (O coverage, ML / # of 1NN ^[b] interactions)	ΔE_{rxn} (eV)	ΔE_a (eV)
30	$\text{O}_2(\text{g}) + * \rightarrow \text{O}_2^*$	p(4×4)-3O (0.19 / 0)	p(4×4)-3O (0.19 / 0)	-0.52	N/A
3		triangle (0.25 / 2)	triangle (0.25 / 3)	-0.35	N/A
5		p(2×2)-O (0.25 / 0)	p(2×2)-O (0.25 / 2)	+0.00	N/A
1	$\text{O}_2^* + * \rightarrow 2\text{O}^*$	p(2×4)-O (0.12 / 0)	triangle (0.25 / 2)	-0.39	+0.66
27		p(4×4)-3O (0.19 / 0)	X (0.31 / 2)	-0.39	+0.60
6		triangle (0.25 / 4)	K (0.38 / 5)	-0.18	+0.71
14 ^[c]		p(2×2)-O (0.25 / 2)	V (0.38 / 5)	+0.67	+1.26
15 ^[c]		p(2×2)-O (0.25 / 2)	K (0.38 / 5)	+0.14	+1.50
24	$\text{O}_2^* + \text{C}_4\text{H}_{10}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + \text{O}^*$	p(2×2)-O (0.25 / 2)	X (0.31 / 2)	-2.00	+1.55
41 ^[d]	$\text{C}_4\text{H}_{10}^* + * \rightarrow \text{C}_4\text{H}_9^* + \text{H}^*$	p(4×4)-3O (0.19 / 0)	p(4×4)-3O (0.19 / 0)	+0.66	+0.77
7	$\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{H}^*$	p(2×2)-O (0.25 / 0)	p(4×4)-3O (0.19 / 0)	-0.18	+1.14
32		X (0.31 / 2)	triangle (0.25 / 2)	-0.05	+1.27
17		V (0.38 / 5)	V-0.3125 (0.31 / 5)	+0.65	+1.40
8	$\text{C}_4\text{H}_{10}^* + \text{O}^* + * \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^*$	p(2×2)-O (0.25 / 0)	p(4×4)-3O (0.19 / 0)	-0.34	+0.92
31		X (0.31 / 2)	p(2×2)-O (0.25 / 2)	-0.38	+0.91
18		K (0.38 / 5)	K-0.3125 (0.31 / 5)	-0.06	+0.80
9	$\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$	p(2×2)-O (0.25 / 0)	p(4×4)-3O (0.19 / 0)	-1.10	+1.22
33		X (0.31 / 2)	p(2×2)-O (0.25 / 0)	-1.85	+0.59
25		K (0.38 / 5)	X (0.31 / 2)	-1.78	+0.47
42 ^[d]	$\text{C}_4\text{H}_{10}^* + 2\text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{OH}^*$	X (0.31 / 2)	p(4×4)-3O (0.19 / 2)	-1.77	N/A ^[e]
43 ^[d]		K (0.38 / 5)	p(2×2)-O (0.25 / 5)	-2.21	N/A ^[e]
10	$\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^*(\text{ep}) + \text{OH}^*$	p(4×4)-3O (0.19 / 2)	p(2×4)-O (0.12 / 0)	-0.55	+0.75
37		triangle (0.25 / 4)	p(4×4)-3O (0.19 / 2)	-0.86	+0.58
20		V-0.3125 (0.31 / 5)	triangle (0.25 / 4)	-1.16	+0.11
11	$\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^*(\text{al}) + \text{OH}^*$	p(4×4)-3O (0.19 / 2)	p(2×4)-O (0.12 / 2)	-1.23	+0.20
36		triangle (0.25 / 4)	p(4×4)-3O (0.19 / 2)	-2.26	+0.32
19		V-0.3125 (0.31 / 5)	triangle (0.25 / 4)	-2.34	+0.39^[f]
12	$\text{C}_4\text{H}_9\text{O}^* + \text{H}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$	p(4×4)-3O (0.19 / 1)	p(4×4)-3O (0.19 / 0)	-0.95	+0.43
35		triangle (0.25 / 4)	triangle (0.25 / 2)	-1.15	+0.33

21		V-0.3125 (0.31 / 5)	V-0.3125 (0.31 / 5)	-1.23	+0.19
13	$C_4H_9^* + OH^* \rightarrow C_4H_9OH^* + ^*$	p(4×4)-3O (0.19 / 0)	p(4×4)-3O (0.19 / 0)	-1.36	+0.75
34		triangle (0.25 / 2)	triangle (0.25 / 2)	-0.99	+0.89
22		K-0.3125 (0.31 / 4)	K-0.3125 (0.31 / 4)	-1.05	+0.60
44 ^[d]	$C_4H_9O^* + OH^* \rightarrow C_4H_9OH^* + O^*$	p(2×4)-O (0.25 / 1)	p(4×4)-3O (0.25 / 0)	-0.14	+0.14
45 ^[d]		line (0.19 / 4)	triangle (0.25 / 2)	-0.38	+0.25
46 ^[d]		triangle (0.25 / 4)	X (0.31 / 2)	-0.40	+0.21
4	$C_4H_{10} + ^* \rightarrow C_4H_{10}^*$	p(2×2)-O (0.25 / 0)	p(2×2)-O (0.25 / 0)	-0.47	N/A
23		p(2×2)-O (0.25 / 0)	p(2×2)-O (0.25 / 0)	-0.29 ^[g]	N/A
29		X (0.31 / 2)	X (0.31 / 2)	-0.29	N/A
16		K (0.38 / 5)	K (0.38 / 5)	-0.40	N/A
26	$C_4H_9OH^* \rightarrow C_4H_9OH + ^*$	p(4×4)-3O (0.19 / 0)	p(4×4)-3O (0.19 / 0)	+0.79	N/A
39		triangle (0.25 / 2)	triangle (0.25 / 2)	+0.86	N/A
38		p(2×2)-O (0.25 / 0)	p(2×2)-O (0.25 / 0)	+0.86	N/A
28		X (0.31 / 2)	X (0.31 / 2)	+0.97	N/A
2	O* diffusion	triangle (0.25 / 2)	p(2×2)-O (0.25 / 0)	-0.66	+0.35

^[a]O configurations are described in the Supporting Information.

^[b]A first nearest neighbor (1NN) interaction occurs when two molecules bind in adjacent FCC sites, or to any of the three surface metal atoms that make up two adjacent FCC sites. They are depicted in the Supporting Information. The following surface intermediates are not counted in the 1NN tally, since they do not have strong effects on adsorbate binding energies (See Table 2): H, C₄H₁₀, C₄H₉, C₄H₈O(ep), C₄H₈O(al), C₄H₉OH. Numbers given are per 16 surface metal atoms.

^[c]We considered O₂ dissociation on the p(2×2)-O configurations into two product O configurations, “K” (Figure S1f), and “V” (Figure S1g). The former gives a lower reaction barrier, while the latter gives a lower reaction energy.

^[d]Not included in Figure 4.

^[e]We did not locate a transition state for this reaction. The closest transition state that we found was for C₄H₁₀* + O* → C₄H₉OH* + *.

^[f]Forces are higher than 0.03 eV/Å.

^[g]In the presence of O₂*

Table 2. Energies of 1NN interactions ($\Delta E_{\text{interaction}}$) in eV with chemisorbed O*. Nomenclature for chemical species as in Figure 4.

O	OH	H	O ₂	C ₄ H ₁₀	C ₄ H ₈ O(ep)	C ₄ H ₈ O(al)	C ₄ H ₉	C ₄ H ₉ OH	C ₄ H ₉ O
+0.37	+0.19	+0.09	+0.22	+0.01	-0.03	-0.12	+0.04	-0.02	+0.19

n-butane adsorption and 1-butanol desorption. Adsorption geometries for n-butane and 1-butanol are shown in Figure 5. The adsorption of butane, $\text{C}_4\text{H}_{10}(\text{g}) + * \rightarrow \text{C}_4\text{H}_{10}^*$ (reactions 4, 16, 23, and 29) is exothermic by 0.29 – 0.47 eV, which is in line with the literature.[45] The desorption of 1-butanol, $\text{C}_4\text{H}_9\text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}(\text{g}) + *$ (reactions 26, 28, 38, 39) is endothermic by 0.79 – 0.97 eV. The interaction of 1-butanol with the Ag₃Pd surface is in some cases strengthened by the formation of a hydrogen bond between the terminal hydroxyl and chemisorbed oxygen (Figure 5). We note that these energies only reflect the interaction between butane/butanol and the Ag₃Pd(111) surface, since interactions between butane/butanol and the surrogate pore are small (0.005 eV/0.017 eV, respectively).

Figure 5. a) Top view of adsorbed n-butane on the p(2x2)-O overlayer configuration. b) Side view of the system shown in panel a. c) Top view of adsorbed 1-butanol on the triangle overlayer configuration. d) Side view of the system shown in panel d (hydrogen bond shown in blue). Ag = pink, Pd = blue, O = red, C = grey, H = small white, He = big white. For clarity, no pore atoms are shown in side views.

O₂ adsorption and dissociation. Associative O₂ adsorption, $\text{O}_2 + * \rightarrow \text{O}_2^*$ (reactions 3, 5, and 30) depends strongly on the local coverage of oxygen atoms.[46][47] This process is exothermic for $\theta_{\text{O}} < 0.25$ ML, but thermoneutral on the p(2×2)-O surface ($\theta_{\text{O}} = 0.25$ ML). Similarly, direct O₂ dissociation, $\text{O}_2^* + * \rightarrow 2\text{O}^*$ (reactions 1, 6, 14, 15, and 27) is strongly dependent on the O coverage/configuration.[46; 48] The dissociation is exothermic (−0.39 eV) with a relatively low barrier (0.66 eV) on the triangle configuration ($\theta_{\text{O}} = 0.25$ ML) due to the availability of a “free” fcc site, **i.e., a vacancy in the p(2×2)-O lattice due to one O atom in that lattice being out of place**. Such a configuration provides a local coverage environment that avoids dramatic

increases in the number of 1NN oxygen interactions with the TS (Figure S5). Similarly, O₂ direct dissociation is exothermic by 0.39 eV with more modest barriers (0.60 – 0.71 eV) at low oxygen coverages ($\theta_{\text{O}} < 0.25$ ML).

The dissociation process is endothermic by 0.14 – 0.67 eV with very high activation barriers (1.26 – 1.50 eV) on the p(2×2)-O surface, due to an increase of three 1NN interactions going from reactants to products. Thus, we expect O₂ direct dissociation is not possible on the p(2×2)-O surface. Therefore, we explored the possibility of an “n-butane-assisted” dissociation route on this surface, $\text{O}_2^* + \text{C}_4\text{H}_{10}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + \text{O}^*$ (reaction 24). **The transition state for this step is analogous to the “rebound step,”[49] proposed as the mechanism for C-H bond hydroxylation on cytochrome P450. The n-butane-assisted dissociation route is shown in Figure S7. We find that this reaction is highly exothermic (by 2.00 eV); however, the activation barrier is quite high (1.55 eV), likely due to the transition state being comprised of a C₄H₉ radical. Thus, we can conclude that n-butane-assisted O₂ dissociation is kinetically inhibited on the p(2×2)-O surface. Since O₂ dissociation is a necessary step in n-butane oxidation, this suggests that the Ag₃Pd(111) catalyst operates at a coverage ≤ 0.25 ML O and/or that a configuration of O atoms such as the triangle configuration, which comprises a free fcc site (i.e., with a “local” coverage < 0.25 ML), plays a significant role in the mechanism.**

C-H bond dissociation. In agreement with prior research,[8; 50-52] we find that C-H bond activation/dissociation assisted by chemisorbed oxygen (O*) is more thermodynamically favorable than direct C-H bond dissociation. In fact, we calculate that direct dissociation, $\text{C}_4\text{H}_{10}^* + * \rightarrow \text{C}_4\text{H}_9^* + \text{H}^*$ (reaction 41) is endothermic by nearly 0.7 eV. The O*-assisted pathways that we investigated here are:

- C-H bond dissociation assisted by O₂ ($\text{O}_2^* + \text{C}_4\text{H}_{10}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + \text{O}^*$, reaction 24)

- C-H bond dissociation assisted by 2O* 1NN, ($\text{C}_4\text{H}_{10}^* + 2\text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{OH}^* + *$, reactions 42 and 43)
- C-H bond dissociation assisted by O* ($\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{H}^*$, reactions 7, 17, and 32; $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^*$, reactions 8, 18, and 31; and $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$, reactions 9, 25, 33)

Reactions 42/43 and 9/25/33 are highly exothermic by more than 1.0 eV on all the O coverages considered. However, in our CI-NEB calculations, we found that reaction 42/43 cedes to reaction 9/25/33, suggesting that reaction 42/43 is unlikely. In these reactions, the n-butane rebounds with a surface O*, forming a C₄H₉ radical and a surface OH* at the TS. It is more energetically favorable for the radical to react with the OH* (forming 1-butanol) than with another surface O* (forming 1-butoxy). Additionally, the reaction coordinate (i.e., the distance going from reactants $\rightarrow$ transition state $\rightarrow$ products) for $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ is shorter than for $\text{C}_4\text{H}_{10}^* + 2\text{O}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{OH}^* + *$. Hence, we conclude that $\text{C}_4\text{H}_{10}^* + 2\text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{OH}^* + *$ is unlikely.^[53] Therefore, reactions 42/43 are not included in Figure 4. **The activation barrier for $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ decreases with increasing oxygen coverage, going from +1.22 eV at low coverage to +0.48 eV on the 0.375 ML “K” configuration. On the other hand, the energetics of $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^*$ remain relatively consistent with coverage, while the energetics of $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{H}^*$ worsen. Hence, which C-H bond activation path is followed depends on the local coverage of O*. $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^*$ is the most likely at low coverage, while $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ is the most likely at high coverage. $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{H}^*$ is possible at low coverage, but not at high coverage. Oxygen-assisted C-H bond activation pathways are shown in Figures 6-8.**

Reactant

Transition State

Product

Figure 6. Reaction 7: $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^* + \text{H}^*$ on the p(2x2)-O configuration. $\Delta E_{\text{rxn}} = -0.18 \text{ eV}$ $\Delta E_{\text{a}} = 1.14 \text{ eV}$. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue and green.

Reactant

Transition State

Product

Figure 7. Reaction 8: $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^*$ on the p(2x2)-O configuration. $\Delta E_{\text{rxn}} = -0.34 \text{ eV}$ $\Delta E_{\text{a}} = 0.92 \text{ eV}$. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue and green.

Reactant

Transition State

Product

Figure 8. Reaction 9: $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ on the p(2x2)-O configuration. $\Delta E_{\text{rxn}} = -1.10$ eV, $\Delta E_{\text{a}} = 1.22$ eV. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue, cyan and green.

1-Butanol Formation/Decomposition. We considered two 1-butanol formation reactions starting from a 1-butoxy intermediate, $\text{C}_4\text{H}_9\text{O}^* + \text{H}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ (reactions 12, 21, and 35) and $\text{C}_4\text{H}_9\text{O}^* + \text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + \text{O}^*$ (reactions 44 – 46), as well as one reaction starting from a 1-butyl intermediate, $\text{C}_4\text{H}_9^* + \text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ (reactions 13, 22, and 34). For the oxygen overlayer configurations considered in this work, we find that the reactions originating from $\text{C}_4\text{H}_9\text{O}^*$ are exothermic (by 0.14 – 1.15 eV) with small barriers (0.14 – 0.43). **The reaction energies for $\text{C}_4\text{H}_9\text{O}^* + \text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + \text{O}^*$ are more modestly exothermic (0.14 – 0.40 eV), suggesting that these reactions could proceed in the forward or reverse directions. Hence, it is possible that 1-butanol formed via reactions 13, 22, or 34 could decompose on the catalyst after being formed. Thus, even if the $\text{C}_4\text{H}_9\text{O}^*$ intermediate is not produced in C-H bond activation, as is expected at high O^* coverage, it could still be formed via decomposition of 1-butanol.** The reaction originating from C_4H_9^* is exothermic (by 0.99 – 1.36 eV), but the barrier is relatively higher (0.60 – 0.75 eV) than the barriers leading to 1-butanol from 1-butoxy.[54] **The pathways to 1-butanol formation are shown in Figures 9 – 11.**

Reactant

Transition State

Product

Figure 9. Reaction 12: $\text{C}_4\text{H}_9\text{O}^* + \text{H}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ on the p(4x4)-3O configuration. $\Delta E_{\text{rxn}} = -0.95 \text{ eV}$, $\Delta E_{\text{a}} = 0.43 \text{ eV}$. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue and green.

Reactant

Transition State

Product

Figure 10. Reaction 44: $\text{C}_4\text{H}_9\text{O}^* + \text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + \text{O}^*$ on the p(4x4)-3O configuration. $\Delta E_{\text{rxn}} = -0.14$ eV $\Delta E_{\text{a}} = 0.14$ eV. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue and green.

Reactant

Transition State

Product

Figure 11. Reaction 13: $\text{C}_4\text{H}_9^* + \text{OH}^* \rightarrow \text{C}_4\text{H}_9\text{OH}^* + *$ on the p(4x4)-3O configuration. $\Delta E_{\text{rxn}} = -1.36$ eV, $\Delta E_{\text{a}} = 0.75$ eV. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue and green.

Reactions that lead to over-dehydrogenation. We have examined two potential pathways that lead to undesired products; both involving dissociation of a second C-H bond. Both pathways

initiate from the $\text{C}_4\text{H}_9\text{O}^*$ (1-butoxy) intermediate. (We find that the reaction C_4H_9^* (1-butyl) + $\text{O}^* \rightarrow \text{C}_4\text{H}_8^*$ (1-butenyl) + OH^* is endothermic by 0.17 eV, in agreement with the results on Pd(111) that we published previously,[8] and C_4H_9^* (1-butyl) + $\text{O}^* \rightarrow \text{C}_4\text{H}_8^*$ (2-butenyl) + OH^* is endothermic by 1.1 eV. These reactions are not included in Table 1 or Figure 4.) Specifically, when a hydrogen atom is abstracted from the primary carbon, 1-butanol is formed, $\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^*$ (al) + OH^* (reactions 11, 19, and 36), whereas when a hydrogen atom is abstracted from the secondary carbon, 1-butene oxide is formed, $\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^*$ (ep) + OH^* (reactions 10, 20, and 37). The formation of butanol is exothermic (by 1.23 – 2.26 eV) with a low barrier (0.20 – 0.32 eV). The formation of 1-butene oxide is also exothermic (by 0.55 – 1.16 eV), although not by as much. This reaction has more modest barriers (0.58 – 0.75 eV) at low coverage that decrease to just 0.1 eV on the 0.375 ML “V” configuration. The comparison of 1-butanol and 1-butene oxide formation reactions shows that the formation of 1-butanol is relatively more favorable at low O coverage, but both reactions are favorable at high O^* coverage. The 1-butanol and 1-butene oxide reactions are illustrated in Figures 12 and 13.

The top row in Figure 13 shows the reactants, transition state, and products in formation of 1-butene oxide in van der Waals representation. These pictures show that with the surrogate pore used here, which offers a similar steric environment that a MOF such as UiO-66 would provide, oxidation of the secondary carbon is not prevented entirely. Note that in all three structures (reactant, transition state, and product), the C_4 molecule contorts in such a way so as to just touch against the van der Waals surface of the MOF pore. The 1-butoxy species is able to lean over just enough to deposit a hydrogen atom from its secondary carbon onto the chemisorbed oxygen (O^*), producing 1-butene oxide and a hydroxyl group (OH^*). Indeed, the

presence of chemisorbed O* is what facilitates the formation of 1-butene oxide by i) favoring the thermodynamics of C-H bond dissociation via O*-assisted hydrogen abstraction, and ii) lifting off the surface (by ~ 0.5 Å) to accept the abstracted hydrogen, effectively decreasing the extent to which the 1-butoxy species must lean over and thus partially counteracting the steric restraints imposed by the pore. These results indicate that even in the presence of the surrogate pore, oxidation of the secondary carbon is not prevented. At low O* coverage, however, energetic arguments indicate that formation of 1-butanal and 1-butanol will be preferred over 1-butene oxide.

Reactant

Transition State

Product

Figure 12. Reaction 11: $\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^*(\text{al}) + \text{OH}^*$ on the p(4x4)-3O configuration. $\Delta E_{\text{rxn}} = -1.23 \text{ eV}$, $\Delta E_{\text{a}} = 0.20 \text{ eV}$. Ag = pink, Pd = blue, O = red, C = grey, H = white. For clarity, no pore atoms are shown. Select distances in blue and green.

Figure 13. Reaction 10: $\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^*(\text{ep}) + \text{OH}^*$ on the p(4x4)-3O configuration. $\Delta E_{\text{rxn}} = -0.55 \text{ eV}$, $\Delta E_{\text{a}} = 0.75 \text{ eV}$. Ag = pink, Pd = blue, O = red, C = grey, H = small white, He = big white. For clarity, no pore atoms are shown. Select distances in blue and green. Side view in bottom row. Top view in top row. Atoms in top view shown in CPK representation.

Activation of the secondary carbon. Finally, we have investigated the possibility of n-butane reacting with surface O^* at the secondary carbon to form either $\text{C}_4\text{H}_9\text{O}^*$ (2-butoxy) + H^* or C_4H_9^* (2-butyl) + OH^* . (These reactions are not listed in Table 1 or Figure 4.) Both calculations were performed at low O coverage ($\leq 0.25 \text{ ML}$). We modeled both reactions in the presence and absence of the surrogate pore, and found essentially the same results. The former reaction is exothermic by 0.82 eV, where as the latter is strongly endothermic (by more than 1 eV). We have not been able to locate a transition state for the reaction $\text{C}_4\text{H}_{10}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_9\text{O}^*$ (2-butoxy) + H^* . All of our attempts have resulted in structures with activation barriers greater than 2 eV, suggesting that this reaction is

kinetically prevented. That these results are the same in the presence and absence of the surrogate pore indicates that steric constraints are not responsible for the unfavorabilities of these reactions.

3. DISCUSSION

Even in the absence of the microkinetic modeling results, the calculations performed in this work allow us to derive implications about the reaction pathway for sterically-constrained n-butane oxidation. For one, since O₂ dissociation is kinetically inhibited on the p(2×2)-O surface, the catalyst operates at a coverage ≤ 0.25 ML O and/or involves a configuration of O atoms with a free fcc site (such as the triangle configuration). Thus, the dominant reaction pathway either starts in Region B in Figure 4 and goes to Region D, or it starts in Region A and goes to Region C through the triangle configuration (reaction 6). Activation of the first C-H bond of n-butane occurs via an O*-assisted route, since direct activation is strongly endothermic. If the dominant reaction pathway goes from Region B to Region D, the most likely route is to form a C₄H₉* + OH* product (reaction 8), although the energetics to forming C₄H₉O* + H* (reaction 7) are competitive. If the dominant reaction pathway starts in Region A and goes to Region C via the triangle configuration, then the most likely C-H bond activation route is to form 1-butanol directly through reaction 25.

If C₄H₉* is formed, as is expected at low O coverage, then it could react with OH* to form C₄H₉OH* (1-butanol; e.g., through reaction 13), or it could react with H* to form C₄H₁₀* (n-butane; e.g., through the reverse of reaction 41). If C₄H₉O* is formed, it could react with either H* or OH* to form 1-butanol or 1-butanol + O* (e.g., via reactions 12 and 44, respectively). However, C₄H₉O* can also react with O* to form C₄H₈O* (1-butanal;

e.g., via reaction 11). This process poses strong competition to 1-butanol formation because it has a low barrier (0.20 – 0.32 eV) comparable with the lowest barriers for 1-butanol formation (i.e. via reaction 44) and is more exothermic.

Once 1-butanol is formed, it could either desorb or decompose on the surface to form $\text{C}_4\text{H}_9\text{O}^* + \text{OH}^*$ (via the reverse of reactions 44/45/46). Thus, even at high coverages, where oxygen-assisted C-H bond activation to form $\text{C}_4\text{H}_9\text{O}^* + \text{H}^*$ is energetically prevented, over-dehydrogenation to 1-butanal or 1-butene oxide is still possible, since the $\text{C}_4\text{H}_9\text{O}^*$ intermediate needed to initiate these processes can be formed from 1-butanol decomposition. Desorption of 1-butanol is endothermic by 0.79 – 0.97 eV, which is larger in magnitude than the activation barriers for the most favorable intermediate reactions leading to 1-butanol formation. Nevertheless, entropic contributions not considered here may facilitate the desorption of 1-butanol and other intermediates.

One of the questions that we set out to answer in this work was if the steric constraints imposed by the MOF pore restrict the catalysis to the terminal carbon. Our results indicate that activation of the secondary carbon on n-butane is energetically prevented, since n-butane reacting to form 2-butyl is highly endothermic, and n-butane reacting to form 2-butoxy has an activation barrier > 2 eV. However, these things are true even in the absence of the surrogate pore, and thus they are unfavorable for reasons other than steric constraint.

Another way for the secondary carbon to be activated occurs when the $\text{C}_4\text{H}_9\text{O}^*$ 1-butoxy intermediate reacts to form $\text{C}_4\text{H}_8\text{O}^*$ 1-butene oxide. At low O^* coverage, the barrier in going from 1-butoxy to 1-butene oxide is significantly larger than the barriers going from 1-butoxy to 1-butanol and 1-butanal, which are both terminally oxidized

products. While it is expected that the transition state leading to 1-butene oxide will be lower than that leading to 1-butanal, since 1-butene oxide (g) is thermodynamically less stable than 1-butanal (g) (by 0.84 eV, according to the DFT-calculated isomerization energy), we do find that the barrier to 1-butene oxide formation is influenced by the steric constraints imposed by the MOF pore. We have calculated the barrier for reaction 10, i.e., $\text{C}_4\text{H}_9\text{O}^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8\text{O}^* (\text{ep}) + \text{OH}^*$, in the absence of the pore to be 0.16 eV smaller than the barrier in the presence of the pore, i.e., removing the pore decreases the barrier of reaction 10 from 0.75 eV to 0.59 eV. Thus, the surrogate pore hinders the kinetics of reaction 10. At high O^* coverages, formation of 1-butene oxide is much more energetically favorable (i.e., through reaction 20). Thus, we do not expect chemistry to be restricted to the terminal carbon at high coverages of O^* .

4. CONCLUSIONS

We have demonstrated the use of DFT calculations and a surrogate pore model to construct a reaction network for sterically constrained n-butane oxidation on an Ag_3Pd catalyst and discussed the implications of our findings on the design of novel MOF-encapsulated catalysts.

Through this exercise, we find that

1. **n-butane oxidation on $\text{Ag}_3\text{Pd}(111)$ must occur at low O coverages (≤ 0.25 ML) or on metastable O configurations, where $\text{O}=\text{O}$ activation is thermodynamically and kinetically favorable.**
2. **Activation of n-butane proceeds through an oxygen-assisted route, where either a 1-butyl or a 1-butoxy intermediate is formed (low coverages), or where 1-butanol is formed directly (high coverages). The relative probabilities of these processes**

depend on the local coverage environments and their relative populations on the surface.[55]

3. If the 1-butoxy intermediate is formed, it can further react to form 1-butanol (low coverage) or 1-butanol and 1-butene oxide (high coverage), affecting the ability of the catalyst to achieve a high selectivity toward 1-butanol. Formation of $C_4H_9O^*$ from $C_4H_{10}^* + O^*$ is energetically prevented at high coverages; however, $C_4H_9O^*$ could still form at such coverages from the decomposition of 1-butanol, i.e., through $C_4H_9OH^* + O^* \rightarrow C_4H_9O^* + OH^*$.
4. Activation of the secondary carbon is hindered on the sterically constrained $Ag_3Pd(111)$ surface, since the surrogate pore increases the activation barrier for $C_4H_9O^* + O^* \rightarrow C_4H_8O^* (ep) + OH^*$ by 0.16 eV. Activation of the secondary C-H bond of n-butane was found to be kinetically inhibited, but this inhibition is not caused by the surrogate pore.
5. Reaction conditions that result in low coverages of O^* should be pursued in order to maximize regioselective activation of the terminal carbon. Such coverages are inhibitive to $C_4H_9O^* + O^* \rightarrow C_4H_8O^* (ep) + OH^*$ and should suppress the decomposition of 1-butanol on the catalyst through reactions 44-46.

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7. REFERENCES

- [1] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell, P.D.F. Vernon, *Nature* 344 (1990) 319-321.
- [2] C. Hammond, S. Conrad, I. Hermans, *ChemSusChem* 5 (2012) 1668-1686.
- [3] M.H. Ab Rahim, et al., *Angew. Chem. Int. Ed.* 125 (2012) 1318-1322.
- [4] M.H. Groothaert, P.J. Smeets, B.F. Sels, P.A. Jacobs, R.A. Schoonheydt, *Journal of the American Chemical Society* 127 (2005) 1394-1395.
- [5] R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* 280 (1998) 560-564.
- [6] S. Albonetti, F. Cavani, F. Trifiro, *Catalysis Reviews: Science and Engineering* 38 (1996) 413-438.
- [7] J.A. Labinger, J.E. Bercaw, *Nature* 417 (2002) 507-514.
- [8] D.A. Gomez-Gualdron, S.T. Dix, R.B. Getman, R.Q. Snurr, *Phys. Chem. Chem. Phys.* 17 (2015) 27596-27608.
- [9] C.J. Stephenson, J.T. Hupp, O.K. Farha, *Inorg. Chem. Front.* 2 (2015) 448-452.
- [10] S.L. James, *Chem. Soc. Rev.* 32 (2003) 276-288.
- [11] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature* 402 (1999) 276-279.
- [12] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, *Science* 341 (2013) 1230444.
- [13] G. Lu, et al., *Nature Chem.* 4 (2012) 310-316.

- [14] C. Rosler, R.A. Fischer, *CrystEngComm* 17 (2015) 199-217.
- [15] O. Skekhah, J. Liu, R.A. Fischer, C. Woll, *Chem. Soc. Rev.* 40 (2011) 1081-1106.
- [16] M.C. So, M.H. Beyzavi, R. Sawhney, O. Shekhah, M. Eddaoudi, S.S. Al-Juaied, J.T. Hupp, O.K. Farha, *Chem. Comm.* 51 (2015) 85-88.
- [17] D. Zacher, O. Shekhah, C. Woll, R.A. Fischer, *Chem. Soc. Rev.* 38 (2009) 1418-1429.
- [18] M.H. Alkordi, Y. Liu, R.W. Larsen, J.F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* 130 (2008) 12639-12641.
- [19] Y.K. Hwang, D.-Y. Hong, J.-S. Chang, S.H. Jung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Ferey, *Angew. Chem. Int. Ed.* 47 (2008) 4144-4148.
- [20] Y. Zhang, V. Degirmenci, C. Li, E.J.M. Hensen, *ChemSusChem* 4 (2011) 59-64.
- [21] Y. Huang, Z. Lin, R. Cao, *Chem. Eur. J.* 17 (2011) 12706-12712.
- [22] J. Juan-Alcaniz, J. Gascon, F. Kapteijn, *J. Mater. Chem.* 22 (2012) 10102-10118.
- [23] R.W. Larsen, L. Wojtas, J. Perman, R.L. Musselman, M.J. Zaworotko, C.M. Vetromile, *J. Am. Chem. Soc.* 133 (2011) 10356-10359.
- [24] L.-G. Qui, A.-J. Xie, L.-D. Zhang, *Adv. Mater.* 17 (2005) 689-692.
- [25] X. Li, T.-W. Goh, L. Li, C. Xiao, Z. Guo, X.C. Zeng, W. Huang, *ACS Catalysis* (2016) available online.
- [26] C.J. Stephenson, C.L. Whitford, P.C. Stair, O.K. Farha, J.T. Hupp, *ChemCatChem* 8 (2016) 855-860.
- [27] M. Hartmann, S. Ernst, *Angewandte Chemie International Edition* 39 (2000) 888-890.
- [28] A.D. Smeltz, W.N. Delgass, F.H. Ribeiro, *Langmuir* 26 (2010) 16578-16588.
- [29] Y.-H.C. Chin, E. Iglesia, *J. Phys. Chem. C* 115 (2011) 17845-17855.
- [30] J.R. Kitchin, K. Reuter, M. Scheffler, *Phys. Rev. B* 77 (2008) 075437.
- [31] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K.P. Lillerud, *J. Am. Chem. Soc.* 130 (2008) 13850-13851.
- [32] M. Kandiah, M.H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E.A. Quadrelli, F. Bonino, K.P. Lillerud, *Chemistry of Materials* 22 (2010) 6632-6640.

- [33] K. Reuter, C. Stampfl, M. Scheffler, in: S. Yip (Ed.), *Handbook of Materials Modeling*, Springer, the Netherlands, 2005, pp. 149-194.
- [34] R.B. Getman, Y. Xu, W.F. Schneider, *J. Phys. Chem. C* 112 (2008) 9559-9572.
- [35] G. Kresse, J. Furthmuller, *Comput. Mat. Sci.* 6 (1996) 15-50.
- [36] G. Kresse, J. Furthmuller, *Phys. Rev. B* 54 (1996) 11169-11186.
- [37] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865-3868.
- [38] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 78 (1997) 1396.
- [39] P.E. Blochl, *Phys. Rev. B* 50 (1994) 17953-17979.
- [40] G. Kresse, D. Joubert, *Phys. Rev. B* 59 (1999) 1758-1775.
- [41] S. Grimme, *J. Comput. Chem.* 27 (2006) 1787-1799.
- [42] G. Henkelman, H. Jonsson, *J. Chem. Phys.* 113 (2000) 9901-9904.
- [43] G. Henkelman, H. Jonsson, *J. Chem. Phys.* 113 (2000) 9978-9985.
- [44] G. Henkelman, H. Jonsson, *J. Chem. Phys.* 111 (1999) 7010-7022.
- [45] A. Antony, C. Hakanoglu, A. Asthagiri, J.F. Weaver, *J. Chem. Phys.* 136 (2012) 054702.
- [46] R.B. Getman, W.F. Schneider, *ChemCatChem* 2 (2010) 1450-1460.
- [47] We have performed all direct O₂* dissociation calculations on both sterically constrained and unconstrained Ag₃Pd(111), and the reaction energies and activation barriers are within 0.02 eV. This is in agreement with our prior work, which indicates that the surrogate pore model only exhibits small influences on the adsorption energies of “small” adsorbates.[8]
- [48] R.B. Getman, W.F. Schneider, A.D. Smeltz, W.N. Delgass, F.H. Ribeiro, *Phys. Rev. Lett.* 102 (2009) 076101.
- [49] S. Shaik, S. Cohen, S.P.d. Visser, P.K. Sharma, D. Kumar, S. Kozuch, F. Ogliaro, D. Danovich, *Eur. J. Inorg. Chem.* (2004) 207-226.
- [50] Y.-H.C. Chin, C. Buda, M. Neurock, E. Iglesia, *J. Am. Chem. Soc.* 135 (2013) 15425-15442.
- [51] Y.-H.C. Chin, C. Buda, M. Neurock, E. Iglesia, *J. Am. Chem. Soc.* 133 (2011) 15958-15978.
- [52] Y.-H.C. Chin, C. Buda, M. Neurock, E. Iglesia, *J. Catal.* 283 (2011) 10-24.

[53] Prior work by Chin, Buda, Neurock, and Iglesia on O-assisted C-H bond activation of methane over Pt(111) indicates that the reaction $\text{CH}_4 + 2\text{O}^* \rightarrow \text{CH}_3\text{O}^* + \text{OH}^*$ is feasible.[50] We hypothesize that this could be due to the smaller lattice parameter of Pt (4 Å) versus Ag_3Pd (4.1 Å).

[54] Reactions 44 – 46 are not included in Figure 4, since there is no natural place to put them within the network. However, how the catalysis plays out will depend on the surface coverages, and thus, these reactions may be relevant, which is why we present them in Table 1 and discuss them in the text.

[55] C. Wu, D.J. Schmidt, C. Wolverton, W.F. Schneider, *J. Catal.* 286 (2012) 88-94.