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A modelling approach for MOF-encapsulated metal catalysts and application to n-butane oxidation†

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Metal nanoparticles (NP) encapsulated by metal-organic frameworks (MOFs) are novel composite materials that have shown promise as regioselective catalysts. The regioselectivity in these materials arises from steric constraints imposed by the porous MOF structure, which limit the way molecules approach and interact with the metal surface. Here we introduce a computationally simple DFT approach to model reactions under such steric constraints. This approach is computationally efficient and accounts for the steric constraints imposed by a MOF pore in a general way. The adsorption of reactants, intermediates, and products associated with oxidation of n-butane to 1-butanol (and 2-butanol) on clean and oxygen-covered palladium surfaces is investigated with (and without) the constraints of a pore. Reaction energies are calculated, and we find that the thermodynamic favorability of the intermediate reactions is affected by the presence of steric constraints, oxygen coverage, and the exposed crystal surface of the metal. Based on these results, the Pd(111) surface with 0.25 ML oxygen coverage and steric constraints (which could be provided by a suitable MOF) seems promising to favor the desired sequence of reactions that would lead to the conversion of n-butane to 1-butanol.

Introduction

Designing catalysts that are highly selective is one of the grand challenges in catalysis, and it is becoming increasingly important in the chemical industry, playing a key role in the development of “green” and economic processes for the production of commodity chemicals. 1-3 Highly selective processes reduce chemical waste and costly, energy-intensive separation processes associated with the formation of undesired products. A common strategy to improve the selectivity of heterogeneous catalysts has been to use strategically alloyed or doped versions of parent catalysts. 4-9 and theoretical methods such as density functional theory (DFT) have helped to identify promising compositions for reactions of interest. 4,10,11 However, alloying or doping by itself is often not sufficient to achieve the required selectivity.

Nature, in the form of enzymes, presents another working principle for highly selective reactions by controlling the orientation of reactants as they reach the (catalyst) active sites thus allowing only specific reactant regions to undergo catalytic conversion. 12 Although applying this principle in designing new heterogeneous catalysts remains a challenge, an interesting proposition is to surround catalyst particles with a porous shell 13,16 that could impart the desired orientation control. Metal-organic frameworks (MOFs) are attractive candidates for the porous shell material, because they have uniform, highly tunable pore structures. MOF tunability originates from their modular structure, where different combinations of organic and inorganic “building units” can be assembled into different MOFs. 17-20 Indeed, the combinatorial possibilities are virtually unlimited, motivating the study of MOFs for applications such as gas storage, 21,22 separations, 23 and catalysis. 24

In recent promising work, Lu et al. 16 developed a strategy for surrounding nanoparticles (NP) with a MOF to create so-called NP@MOF systems. Lu et al. 16 showed that a Pt@ZIF-8 system could hydrogenate n-hexene, but not the bulkier cyclooctene, due to the size-selective nature of the surrounding MOF. More recently, Stephenson et al. 25 demonstrated that a Pt@ZIF-8 system could regioselectively hydrogenate trans-1,3-hexadiene to 3-hexene. Here the terminal double bond was hydrogenated while the internal double bond was not, presumably because it could not access the metal catalyst surface due to steric constraints. Other recent examples of catalysis with NP@MOFs have been reported elsewhere. 26-35

In light of these findings, an intriguing question is whether these NP@MOF systems can carry out more complex reactions. We are interested in designing a NP@MOF system to carry out the partial oxidation of a long alkane to its corresponding primary alcohol. This would allow, for instance, the production of 1-butanol—which is a widely used solvent and feedstock—through the partial oxidation of n-butane rather than through the hydroformylation of propylene (a more expensive and scarce feedstock). The primary challenge is preventing the oxidation of the secondary carbon, whose C-H bonds are less stable than those of the primary carbon, 17 and the eventual formation of 2-butanol, which is
calculated to be 16 kJ/mol more stable than 1-butanol.\textsuperscript{38} Additionally, overoxidation to CO\textsubscript{2} needs to be avoided.\textsuperscript{39}

To address the above challenges, the structure of the surrounding n-butane MOF should be tuned so that only the terminal carbon of n-butane can contact the NP surface at the MOF/NP interface, while the composition of the NP surface—and consequently, its electronic structure—should be tuned so that only the desired sequence of reactions occurs on the contacting carbon. Identifying the ideal NP@MOF system, however, can be difficult due to the large number of possible MOF structures and NP compositions\textsuperscript{41}—not to mention the combinatorial explosion of their combinations. Therefore, insights obtained from DFT calculations can be highly valuable to begin to understand NP@MOF systems and help with their rational design.

One of the unusual aspects of utilizing NP@MOF systems for n-butane oxidation is that the catalysis would occur under steric constraints, creating a reaction scenario that has been largely unexplored for metal surfaces. Challenges in modelling n-butane oxidation (or other reactions) at the catalytically relevant NP/MOF interface include the computationally prohibitive large number of atoms involved in a fully atomistic model of the NP surface and MOF pores.\textsuperscript{37-40} Although this could be alleviated using QM/MM models,\textsuperscript{42-45} these methods often require specialized codes and are not straightforward to use. In addition, the exact structure of the NP/MOF interface (which would change with the MOF) in these novel NP@MOF systems is not well characterized. To address these challenges, we propose a simple approach to explore—in a general way—the chemistry of metal catalyst surfaces under sterically constrained conditions using standard DFT programs.

In this approach we use a surrogate pore on top of a slab catalyst model to mimic the steric constraints that would arise from a given MOF pore. In this study, the surrogate pore is made of chemically inert atoms, whereas the slab is made of catalytically active palladium atoms. Note that this surrogate pore model focuses on steric effects and does not provide electrostatic interactions that may be important, for instance, in MOFs whose linkers have strongly polarized functional groups. Moreover, while the NP/MOF interface might include true NP/MOF chemical bonds that may alter the electronic structure of the NP, the surrogate pore model introduced here leaves the electronic structure of the metal surface essentially intact. The selection of palladium as the potential NP component was motivated by prior theoretical\textsuperscript{46-49} and experimental\textsuperscript{47,49-51} investigations of palladium and oxidized palladium for the oxidation of alkanes. After demonstrating the suitability of the surrogate pore to sterically constrain the interaction of reactants, intermediates and products on clean and oxygen-covered palladium surfaces, we sought to understand these interactions and their consequences on the reaction energies relevant to the catalytic oxidation of n-butane. Specifically, we focused on differences arising due to the presence or absence of the pore (i.e. presence or absence of steric constraints), the oxygen-coverage conditions, and the crystallographic structure of the palladium surface. We used this information as a first assessment of the potential suitability of Pd@MOF catalysts to regioselectively oxidize n-butane to 1-butanol.

### Computational methods

Plane-wave density functional theory (PW-DFT) calculations were performed using the VASP code.\textsuperscript{52-55} The electron exchange and correlation were described using the GGA Purdie-Burke-Ernzerhof (PBE)\textsuperscript{56} functional, and core electrons were described using the projector-augmented wave method.\textsuperscript{57,58} The D2 method of Grimme\textsuperscript{59} was used to improve the modelling of dispersion interactions. An energy cutoff of 500 eV was used for Bloch waves to construct the solutions to the Kohn-Sham equations. All simulations used spin polarization. Gaussian smearing\textsuperscript{60} was used to accelerate energy convergence with respect to the k-mesh density, but a smearing parameter of 0.03 was necessary to reduce T*S from the smearing to less than 0.001 eV/atom. Based on test runs, the electronic structure of a given geometry was considered solved when the energy difference between consecutive, self-consistent electronic steps was less than 10\textsuperscript{-5} eV. A geometry optimization was considered complete when the energy difference between consecutive geometries was less than 10\textsuperscript{-6} eV/Å.

The optimal lattice constant of bulk fcc palladium was calculated to be 3.959 Å, which is within 2% of the experimental value of 3.889 Å.\textsuperscript{61} These calculations used a Gamma-centred 1x1x1 k-point mesh (energy converged within 10\textsuperscript{-6} eV/atom). From the DFT-optimized palladium fcc unit cell, we constructed 4-layered slabs of the Pd(111) and Pd(100) surfaces using the Surface Builder module of Materials Studio.\textsuperscript{62} Both Pd(111) and Pd(100) were represented by a 4x4x1 simulation supercell, which was large enough to accommodate the surrogate pore. The simulation supercell included a 15 Å vacuum space between slabs along the z direction. The Crystal Builder module of Materials Studio\textsuperscript{62} was used to place the pore and construct the simulation models in general. In all slab calculations, the supercell, the surrogate pore, and the two bottommost layers remained fixed, and a 4x4x1 k-point mesh was used (energy converged within 5x10\textsuperscript{-6} eV/atom). In select optimized geometries, we used the tetrahedron smearing method with Blochl corrections to compute the electron density.\textsuperscript{63} This electron density was used with the Bader electron density splitting formalism to obtain atomic charges\textsuperscript{64,65} and/or used in an additional non-self-consistent calculation using an 8x8x1 k-point mesh to obtain the electronic density of states. Optimizations of gas phase molecules and other isolated chemical species were done at the Γ point using a 15 Å x 15 Å x 20 Å orthogonal supercell.

Adsortion and interaction energies (E\textsubscript{ads}) were calculated as follows. Note that we use the two terms interchangeably. A negative energy of E\textsubscript{ads} denotes a favourable interaction. The interaction energy of a chemical species “x” with a palladium surface slab without the pore is calculated in standard fashion as

\[
E_{\text{ads}} = E_{\text{slab+x}} - E_{\text{slab}} - E_{x}
\]

where the three right-hand terms correspond to the total energies of the “slab + x” system and the slab and species x on their own. Similarly, for the interaction energy of chemical species “x” on the palladium surfaces with the pore we use
\[ E_{\text{ads}} = E_{\text{slab-pore-x}} - E_{\text{slab-pore}} - E_x \]

where the three right-hand terms correspond to the total energies of the “slab + pore + x” and “slab + pore” systems and species x on their own. Note that if species “x” refers to O, H, or OH, \( E_x \) corresponds to half the total energy of an isolated oxygen, hydrogen, or hydrogen peroxide molecule, respectively. Also note that since we include oxygen-covered surfaces in our study, the “slab” term can also refer to an oxygen-covered surface.

To quantify the thermodynamic favourability of a given reaction we calculated reaction energies, \( E_{\text{rxn}} \). If a reaction on the palladium surface slab without the pore involves the adsorbed species \( x^* \), \( y^* \), \( xy^* \) so

\[ x^* + y^* \rightarrow xy^* + * \]

then the reaction energy is calculated as

\[ E_{\text{rxn}} = E_{\text{slab+xy*}} - E_{\text{slab}} - E_{\text{xy*}} \]

where the right-hand terms are the total energies of the “slab + xy” (\( xy^* \)), “slab” (*), “slab + x” (\( x^* \)) and “slab + y” (\( y^* \)) systems. Similarly, if reaction 3 occurs on the palladium surface slab with the pore, the reaction energy is calculated instead as

\[ E_{\text{rxn}} = E_{\text{slab+pore-xy*}} - E_{\text{slab+pore}} - E_{\text{slab+pore-xy*}} \]

where the right-hand terms are the total energies of the “slab + pore + xy” (\( xy^* \)), “slab + pore” (*), “slab + pore + x” (\( x^* \)) and “slab + pore + y” (\( y^* \)) systems. As with interactions energies, the “slab” term in eq. 4 and 5 can refer to clean or oxygen-covered surfaces.

To understand the role of dispersion forces on interactions and reactions, we obtained approximate estimations of the contribution of dispersion interactions—modeled with the Grimme term—to adsorption and reaction energies by applying equations 1 through 5 using only the contributions of the Grimme term to the respective total energies instead of the total energies themselves.

**Surrogate pore model**

We illustrate the type of system that we aim to model in Figure 1a, which shows an all-atom model of a region of a NP@MOF composite. The figure shows a truncated octahedral palladium nanoparticle surrounded by the porous structure of the prototypical zeolitic imidazolate framework (ZIF) ZIF-8. In this MOF, 2-methylimidazole linkers connect Zn(II) ions to form a 4-connected network of sodalite (sod) topology. ZIF-8 has often been used in NP@MOF composites and demonstrated to engender regioselective catalysis, as previously mentioned. Nanoparticle sizes that have been employed in ZIF-8-based composites have reached sizes up to 100 nm. The model in Figure 1a shows a 3 nm nanoparticle (Figure 1b), as used in several works. A particle of this size cannot be embedded within a defect-free ZIF-8 structure, because the ZIF-8 cavities (Figure 1c) are less than 1.2 nm in diameter. Thus, conceptually, one can imagine that cavities of ~3 nm must be “carved” within the perfect ZIF-8 crystal to host 3 nm nanoparticles. However, so far, the characterization of NP@MOF composites leaves the exact structure of the host cavities and the NP/MOF interface unknown.

ZIF-8 has two types of windows corresponding to four- and six-membered rings, which are outlined in purple and black, respectively, in Figure 1c. Only the six-membered ring is believed to allow the passage of molecules such as alkanes and alcohols from one cavity to another. Based on the experimental evidence of regioselectivity in NP@ZIF-8 composites, one can hypothesize that in some regions of the NP/ZIF-8 interface there are six-membered rings on top of the nanoparticle facets such as Pd(111) (Figure 1d) and Pd(100) (Figure 1e). The NP/ZIF-8 interface is shown in Figure 1d,e with the ZIF Zn(II) ions closest to the Pd surfaces, but whether the Zn(II) ions or the 2-methylimidazole linkers are closest to the metal surface is not known. However, what seems certain from catalysis experiments is that steric constraints on molecules are imposed by the MOF at the NP/MOF boundary.

It is important to note that although the MOF plays a role by imposing steric constraints, it is the nanoparticle that ultimately brings the catalytic functionality to NP@MOF composites, and thus the nanoparticle structure and composition warrant careful analysis and design. On these grounds, we used a surrogate pore model (shown in Figure 1f) sterically constraining the adsorption of n-butane on Pd(111)) that allows us to focus on the chemistry occurring on the surface of the sterically constrained catalyst. This pore is constructed here using chemically inert helium atoms, which with
only two valence electrons are expected to only moderately increase the computational costs of the DFT calculations. Note that the inert character of the surrogate pore is expected to chemically affect neither the catalyst surface nor the adsorbed species.

**Results and discussion**

**Validation of the surrogate pore model**

**Surrogate pore geometric description.** The surrogate pore was used on Pd(111) and Pd(100) surfaces centred at either a hollow or atop position. Figure 2a shows the simulation supercell for a Pd(111) surface with an atop-centred pore. The top and bottom rings of the surrogate pore are separated by 2.8 Å, and the bottom ring and topmost palladium layer are separated by 3.5 Å (|z₂-z₀| in Figure 2a). These distances and all others reported on this work are based on center-to-center distances. Each pore ring is composed of nine helium atoms evenly distributed along the circumference of an 8.8 Å diameter circle (He-He distance equal to 3.0 Å). As a reference for the sizes of the surrogate pore atoms, note that σₐ₉ = 2.63 Å.⁷⁰

The goal of the pore design is to i) prevent repulsive interactions between pore atoms that would sharply increase the energy of the system, ii) minimize the number of atoms required to make the surrogate pore, iii) preclude any chemical species from being able to pass between pore atoms, iv) minimize effects of the surrogate pore on the electronic structure of the catalyst surface, and v) leave all surface sites available for the chemisorption of small chemical species, i.e. O, H, and OH. The following subsections show that the design goals were achieved.

**Surrogate pore interaction with the catalyst.** We determined whether the interaction between the surrogate pore and a palladium surface would affect the electronic structure of the latter through electronic structure analysis. Figure 2b shows the contribution of pore and catalyst atoms to the partial density of states (PDOS) for the system in Figure 2a. Note that occupied states (PDOS) for the system in Figure 2a. Note that occupied electron density mapped on different horizontal slices cut at the heights indicated in panel a. Atoms coloured as in Fig. 1.

**Surrogate pore interaction with molecules.** Due to the tetragonal and trigonal shapes of the Pd(100) and Pd(111) surfaces, with hollow- and atop-centred pores (Table 1), which are essentially unaffected by the centring of the pore. Note that 76-95% of the interaction energy—depending on the surface—originates from the van der Waals term. The slightly stronger interactions of the pore with Pd(111) are likely due to the higher surface density of Pd(111) compared to Pd(100).

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configuration has a slightly stronger interaction energy \((-10 \text{ kJ/mol})\), with almost 90% corresponding to dispersion interactions (Table 2). This suggests no significant charge transfer or other electronic effects occurring during pore/Butane interactions, as confirmed by Bader atomic charge analysis (Figure 3b). Note that the inclusion of Butane in the pore only changes the charge of the pore atoms from (essentially) zero to \(-0.005\) at most. With these calculations we show that the surrogate pore sterically constrains molecular species, such as n-Butane, while remaining chemically inert.

**Surrogate pore influence on surface accessibility.** Our final test is to determine whether, as intended in the design of the pore, all catalyst sites can be accessed by small species such as O, H, and OH without impact on the adsorption energies. Table 3 shows that within 1 kJ/mol O and H adsorption on different surface sites was equal with and without the pore, and the adsorption trends agree with reported adsorption energies\(^{21-25}\) and preferred adsorption sites observed experimentally.\(^{76,77}\) O, H and OH accessibility to the catalyst surface in the presence of the pore was evaluated by adsorbing O, H and OH adsorption on fourteen Pd(111) hollow fcc sites (Figure 4a) with the pore present. Figure 4b-d shows O, H and OH adsorbed directly below a pore atom. Within a 1 kJ/mol tolerance, the adsorption energies of O, H, and OH on all sites were \(-134, -62\) and \(-129 \text{ kJ/mol}\), respectively. Furthermore, Bader charge analysis shows that there are not significant differences in the atomic charges of a given adsorbate or between different surface sites independently of whether the pore is present (Table 4).

**Exploration of n-Butane oxidation.** In the previous subsections we demonstrated that the only expected effect of the surrogate pore is to sterically constrain the adsorption of long molecular species such as n-Butane in the manner that would occur in a suitable NP@MOF system. On the other hand, all surface sites remained accessible for small species such as O, H and OH. We now proceed to use the surrogate pore to investigate n-Butane oxidation under sterically constrained conditions.

**Catalyst conditions and reactions.** Here we focus on the catalyst surfaces and coverages shown in Figure 5, which include the catalyst surface without the pore and with the hollow-centred and atop-centred pore. The centring of the pore was varied to see whether the exact location of the pore relative to the surface affects the adsorption energies and, in turn, the reaction energies. The atop- and hollow-centring were chosen because adsorption on atop and hollow sites are typically markedly different (Table 3). The "pore-free" surfaces were chosen to compare between sterically-constrained and unconstrained n-Butane oxidation. Clean and oxygen-covered Pd(111) and Pd(100) surfaces were studied. Oxygen-covered surfaces were included because pre-adsorbed oxygen has been shown to affect reactions in other oxidation systems,\(^{49,78,79}\) although here we only considered moderate oxygen coverages (0.25 ML). At this coverage both Pd(111) and Pd(100) present a 4 to 1 Pd to O ratio at the surface, making them suitable for direct comparison. This comparison is not possible at higher oxygen coverages because, as also reported experimentally,\(^{80}\) higher oxygen content leads to the deformation of Pd(100), which hints to the susceptibility of palladium to oxidize to palladium oxide via this facet.\(^{81-83}\)
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Fig. 6. Most favourable adsorption (interaction) configurations of (from left to right) n-butane (C\textsubscript{4}H\textsubscript{10}), 1-butyl (C\textsubscript{4}H\textsubscript{11}), 1-butanol (C\textsubscript{4}H\textsubscript{11}OH), 1-butoxy (C\textsubscript{4}H\textsubscript{11}O), and 1-butenyl (C\textsubscript{4}H\textsubscript{11}CH\textsubscript{2}) on a) Pd(111) with no pore, b) Pd(111) with the atop-centred pore, c) Pd(100) with no pore, and d) Pd(100) with the atop-centred pore. Adsorption (interaction) energies, \(E_{\text{ads}}\), are given in kJ/mol and calculated using eq.1 (a and c) or eq.2 (b and d). Values in parentheses are estimates of the contribution of dispersion interactions to the adsorption energies. Pore atoms in b and d are not shown for clarity.

We focus on the following reactions

\[ \text{O}^* + \text{H}^* \rightarrow \text{HO}^* + \ast \]  
\[ \text{C}_4\text{H}_{10}^* + \ast \rightarrow \text{C}_4\text{H}_9^* + \text{H}^* \]  
\[ \text{C}_4\text{H}_9^* + \text{O}^* \rightarrow \text{C}_4\text{H}_8^* + \text{HO}^* \]  
\[ \text{C}_4\text{H}_8^* + \ast \rightarrow \text{C}_4\text{H}_7^* + \text{H}^* \]  
\[ \text{C}_4\text{H}_7^* + \text{O}^* \rightarrow \text{C}_4\text{H}_6^* + \text{HO}^* \]  
\[ \text{C}_4\text{H}_6^* + \text{O}^* \rightarrow \text{C}_4\text{H}_5^* + \ast \]  
\[ \text{C}_4\text{H}_5^* + \text{O}^* \rightarrow \text{C}_4\text{H}_4^* + \ast \]  
\[ \text{C}_4\text{H}_4^* + \text{O}^* \rightarrow \text{C}_4\text{H}_3^* + \ast \]  
\[ \text{C}_4\text{H}_3^* + \text{O}^* \rightarrow \text{C}_4\text{H}_2^* + \ast \]  
\[ \text{C}_4\text{H}_2^* + \text{O}^* \rightarrow \text{C}_4\text{H}_1^* + \ast \]  
\[ \text{C}_4\text{H}_1^* + \text{O}^* \rightarrow \text{C}_4\text{H}_0^* + \ast \]  

where the C\textsubscript{4} species correspond to n-butane (C\textsubscript{4}H\textsubscript{10}), 1-butyl or 2-butyl (C\textsubscript{4}H\textsubscript{11}), 1-butenyl or 2-butenyl (C\textsubscript{4}H\textsubscript{11}CH\textsubscript{2}), and 1-butanol or 2-butanol (C\textsubscript{4}H\textsubscript{11}OH). We postulate that a possible route for 1-butanol formation is the sequence n-butane\(\rightarrow\)1-butyl\(\rightarrow\)1-butoxy\(\rightarrow\)1-butanol (i.e. reaction 7 or 8)\(\rightarrow\)reaction 11\(\rightarrow\)reaction 12 (or 13)), and here we calculate whether that sequence is thermodynamically favoured in any of the systems studied instead of the sequence n-butane\(\rightarrow\)1-butyl\(\rightarrow\)1-butenyl (i.e. reaction 7 or 8)\(\rightarrow\)reaction 9 (or 10)), which leads to further dehydrogenated products. Note that without the pore, the “n-butane\(\rightarrow\)2-butyl\(\rightarrow\)2-butoxy\(\rightarrow\)2-butanol” and “n-butane\(\rightarrow\)2-butyl\(\rightarrow\)2-butenyl” sequences are also possible and are, thus, explored.

Adsorption of C\textsubscript{4} species. We first calculated the most stable adsorption configurations and energies of all species mentioned above to understand their interactions with the palladium surfaces with and without pre-adsorbed oxygen and with and without steric constraints. The most stable adsorption configurations and corresponding adsorption energies are shown in Figure 6 (clean palladium) and Figure 7 (oxygen-covered palladium) for the linear (“1”) C\textsubscript{4} species without and with the atop-centred pore (detailed adsorption configuration for all species on all systems are shown in Table 5 and Table 6 additionally show adsorption energies for n-butane, probably due to the more significant role of dispersion interactions on n-butane than 1-butyl.

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Figures S5-S10. Table 5 and Table 6 additionally show adsorption energies for n-butane, probably due to the more significant role of dispersion interactions on n-butane than 1-butyl.
and Pd(100) (>60 kJ/mol), which are not so pronounced on the accentuates differences between 1-butenyl adsorption of Pd(111) oxygen weakens the adsorption of 1-butenyl by more than 40 the pore is present. For instance, on Pd(111), the pre-adsorbed bigger impact on the adsorption of 1-butenyl radicals than whether the surface conditions. In fact, surface conditions seem to have a clean surfaces (< 25 kJ/mol) (Figure S15). 46,48

In general, the way the dehydrogenated carbons of butyl and butenyl radicals coordinate to surface palladium atoms agrees with the coordination of C₄ radicals reported in DFT studies of methane dehydrogenation on palladium. Trends in interaction energies agree as well, with Trincher et al., for instance, reporting a -167 kJ/mol adsorption energy for the CH₂ radical and -399 kJ/ml for the CH₃ radical.

The oxygenated species 1- and 2-butoxy adsorb on clean surfaces by placing their oxygen atom either at a bridge position forming two 2.1 Å Pd-O bonds (for clean surfaces) or at a hollow position forming three longer Pd-O bonds (for oxygen-covered surfaces). However, in light of the adsorption energy magnitudes (>300 kJ/mol), these bonds are not as strong as the Pd-C bonds formed during the adsorption of butenyl radicals. Therefore, the relative contribution of dispersion interactions to the adsorption energy is higher for 1- and 2-butoxy than for the butenyl radicals, and differences in adsorption strengths with and without the pore are also higher for the former (Figure S13). As with previous species, without the pore, 1- and 2-butoxy adsorb horizontally, whereas with the pore n-butoxy sits roughly perpendicular, although less so than any of the other C₄ species (Figure S7). For butoxy adsorption on O-covered surfaces (Figure 7), the butoxy oxygen is assumed to have come from one of the surface oxygens from the configurations in Figure 5. Thus if 1- or 2-butoxy desorbs, the surface is left with one oxygen “vacancy.” We use the surfaces with vacancies to calculate the adsorption energy of butoxy on O-covered surfaces. According to our calculations, the adsorption energy of 1- and 2-butoxy is higher in magnitude on the oxygen-covered surfaces than on the clean surfaces. Also, when there is pre-adsorbed oxygen, 1- and 2-butoxy orient to interact with Pd atoms instead of O atoms.

The adsorption energies of 1- and 2-butanol are calculated in a similar fashion as for 1- and 2-butoxy. However, the adsorption of 1- and 2-butanol is more similar to that of n-butane, although somewhat stronger. Dispersion interactions dominate the adsorption, which occurs horizontally and vertically without and with the pore, respectively, leading to a weakening of the adsorption energy by 30-52 kJ/mol depending on the surface coverage. In general, 1- and 2-butanol adsorb with the hydroxyl oxygen (almost) atop of a palladium atom with a ~2.4 Å Pd-O distance (Figure 6, Figure 7 and Figure S10). Similar to n-butane, differences in adsorption energies on Pd(111) and Pd(100) are minimal.

Interestingly, the position of the pore on the surface does not seem to affect the interaction energy of C₄ species as much as we had anticipated. Indeed, the largest differences in interaction energies between atop-centred and hollow-centred pores were 5 kJ/mol on Pd(111) and 10 kJ/mol on Pd(100) (Figure S14). Thus, for clarity, from this point on we will focus our discussion only on the atop-centred pore.

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**Table 6. Calculated adsorption energies in kJ/mol for different C₄ species on Pd(111) and Pd(100) surfaces with oxygen coverage.**

<table>
<thead>
<tr>
<th>Species</th>
<th>No pore</th>
<th>Atop-centred pore</th>
<th>Hollow-centred pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>butane</td>
<td>-73</td>
<td>-88</td>
<td>-56</td>
</tr>
<tr>
<td>1-butyl</td>
<td>-231</td>
<td>-227</td>
<td>-217</td>
</tr>
<tr>
<td>2-butyl</td>
<td>-217</td>
<td>-222</td>
<td>-217</td>
</tr>
<tr>
<td>1-butenyl</td>
<td>-370</td>
<td>-367</td>
<td>-417</td>
</tr>
<tr>
<td>2-butenyl</td>
<td>-382</td>
<td>-414</td>
<td>-370</td>
</tr>
<tr>
<td>1-butoxy</td>
<td>-280</td>
<td>-220</td>
<td>-221</td>
</tr>
<tr>
<td>2-butoxy</td>
<td>-296</td>
<td>-298</td>
<td>-221</td>
</tr>
<tr>
<td>1-butanol</td>
<td>-127</td>
<td>-127</td>
<td>-83</td>
</tr>
<tr>
<td>2-butanol</td>
<td>-131</td>
<td>-125</td>
<td>-86</td>
</tr>
</tbody>
</table>

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butenyl; reactions 9 and 10), and c) 1-butoxy hydrogenation (1-butoxy → 1-butanol; reactions 12 and 13). Suffix "p" added for surfaces with the atop-centred pore, "o" added for 0.25 ML oxygen-covered surfaces.

Fig. 8. Reaction energies for different catalyst surfaces and conditions for (a) C-H activation (n-butane → 1-buty1; reactions 7 and 8), (b) Second dehydrogenation (1-buty1 → 1-butene1; reactions 9 and 10), and (c) 1-butoxy hydrogenation (1-butoxy → 1-butanol; reactions 12 and 13). Suffix "p" added for surfaces with the atop-centred pore, "o" added for 0.25 ML oxygen-covered surfaces.

Fig. 9. Generalized schematic of how steric constraints from the pore increase the favourability of C-H activation by weakening n-butane adsorption. ΔE_ads indicates the change in adsorption energy upon adding the pore. The dashed line indicates energies without the pore, and the solid line indicates energies with the pore.

Implications of adsorption strengths on reaction energies. With the energies for the lowest-energy adsorption configurations on the clean and oxygen-covered surfaces, we calculated the reaction energies for reactions 6 through 13 using Equations 4 and 5 (all reaction energies are reported in Table S2). We find that reaction 6 is unaffected by the presence of the pore and more favourable on Pd(100) than on Pd(111). Combining adsorbed H and O to form OH is exothermic only by 4 kJ/mol on clean Pd(111), but by 46 kJ/mol on clean Pd(100). This marked difference is reduced, however, with oxygen coverage where hydroxyl formation is exothermic by 28 kJ/mol on Pd(111) and by 33 kJ/mol on Pd(100) when they have 0.25 ML of pre-adsorbed oxygen. Since hydroxyl formation is favourable for all studied surfaces and conditions, the activation of the primary C-H bond of n-butane is more favourable when it is O-assisted (reaction 8) than when it is direct (reaction 7) (Figure 8a). This favourability is slight on clean Pd(111) and more pronounced for all other cases.

Notably, whether O-assisted or direct, C-H activation is more favourable in the presence of the pore (compare the surface and surface-p cases in Figure 8a). Since H adsorption and hydroxyl formation are unaffected by the pore, the changes in favourability must arise from the effects of the pore on n-butane and 1-buty1 adsorption. Recall from the previous subsection that weakening of n-butane adsorption is more pronounced upon adding the pore than the corresponding weakening for 1-buty1 adsorption.

Therefore, although palladium or pre-adsorbed oxygen binds the hydrogen extracted from the n-butane equally strong with and without the pore, it is relatively more favourable to have 1-buty1 adsorbed than n-butane when the pore is present (Figure 9). The favourability of C-H activation due to the pore, however, is less marked for Pd(111) when there is pre-adsorbed oxygen ("Pd(111)-o-p" vs. "Pd(111)-o" in Figure 8a).

The second dehydrogenation of the activated carbon of 1-buty1 (reactions 9 and 10) is also more favourable O-assisted than direct and also significantly more favoured on Pd(100) than on Pd(111) at any surface conditions (Figure 8b). When the surfaces are clean (blue bars), this is primarily due to Pd(100) being more favourable than Pd(111) toward hydroxyl formation; when the surfaces have pre-adsorbed oxygen (red bars) this is primarily due to Pd(100) binding more strongly than Pd(111) 1-buty1 and 1-butoxy. Remarkably, with the pore, the second dehydrogenation seems to be relatively unfavourable (>20 kJ/mol endothermic) for Pd(111) with 0.25 ML oxygen coverage ("Pd(111)-o-p" in Figure 8b), mainly due to the considerable weakening of 1-butenyl adsorption caused by the pre-adsorbed oxygen.

As shown in Figure 8c, at all surface conditions, hydrogenating 1-butoxy to form 1-butanol through reaction 13 is less favourable on Pd(100) (endothermic) than on Pd(111) (exothermic). This is partly due to (again) the favourability of Pd(100) to form hydroxyls—which makes it less favourable to break the adsorbed OH to transfer the H to 1-butoxy—and partly due to the stronger adsorption of butoxy on Pd(100) than Pd(111). The hydrogenation of 1-butoxy to 1-butanol is only slightly affected by the presence of the pore when the surfaces are clean. However, when there is pre-adsorbed oxygen the pore makes the reaction even less favourable on Pd(100) ("Pd(100)-o-p" versus "Pd(100)-o" in Figure 8c), but notably it makes it more favourable on Pd(111) ("Pd(111)-o-p" versus "Pd(111)-o" in Figure 8c).

The formation of 1-butoxy (reaction 11) is exothermic in all cases except for Pd(111) when the pore is present, in which the reaction is slightly endothermic (10 kJ/mol) (Figure 10 red bars). Comparing the red and gray bars in Figure 10, we see that in most cases the reaction energies are similar or lower (more favourable) for 1-butenyl formation (O-assisted) compared to 1-butoxy formation. Notably the exception is Pd(111) with 0.25 ML oxygen coverage, in
which case the 1-butoxy formation is clearly favoured over that of 1-butenyl.

Fig. 10. Comparison of reactions energies for the O-assisted second dehydrogenation (reaction 10) and for the formation of 1-butoxy (reaction 11) for different catalyst surfaces and conditions. Suffix "-p" added for surfaces with the pore, "-o" added for 0.25 ML oxygen-covered surfaces.

Without the pore, reactions on the secondary carbon of n-butane can also occur, and thus we also calculated the corresponding reaction energies (Table S2). Briefly, the trends discussed so far for the reactions on the primary carbon are also applicable for those on the secondary carbon (Figure S16), only that the reactions leading to the formation of 2-butoxy are overall slightly more favourable than those leading to 1-butoxy. However, the hydrogenation of 1-butoxy to 1-butanol is somewhat more favourable than that of 2-butoxy to 2-butanol, except on the case of clean Pd(100). Thus, without the pore, the overall sequence of reaction energies indicates that 2-butanol is equally or more favoured than 1-butanol on palladium.

With the pore, one promising system favouring 1-butoxy formation over 1-butenyl is Pd(111) with 0.25 ML oxygen coverage. Therefore, in Figure 11b we illustrate the complete set of reactions for this system. Figure 11 also shows some analogous systems for comparison purposes. (Note that the energies shown are the reaction energies and not reaction barriers. Searching for transition states and determining reaction barriers are planned for the future.) In “Pd(111)-o” (without pore; Figure 11a), activation of the secondary carbon is slightly more facile than the primary one (−9 versus −6 kJ/mol). For either butyl radical, the second dehydrogenation is slightly endothermic, because as previously noted O-coverage weakens the adsorption of butenyl radicals. Butoxy formation is thus preferred, although with the formation of 2-butoxy being more favourable than the formation of 1-butoxy (−62 versus −37 kJ/mol), 2-butanol formation may be favoured overall. On “Pd(100)-o” (without pore; Figure 11c), 2-butanol formation may also be favoured. Note, however, that both the C-H activation and second dehydrogenation are more favourable than for “Pd(111)-o”, even if butoxy formation is still preferred to the second dehydrogenation. Also note that the (1- or 2-)butoxy conversion to (1- or 2-butanol) is less favourable than for “Pd(111)-o”.

For “Pd(111)-o-p” (with pore; Figure 11b) the combination of oxygen coverage (making reaction 11 more favourable than reaction 10) and the presence of the pore (making reactions on the secondary carbon not possible) favours the targeted sequence of reactions (with only one slightly endothermic step) that could form the desired 1-butanol. Note that the presence of the pore is a necessary but not sufficient condition to make the targeted sequence of reactions favourable. Consider the analogous system “Pd(100)-o-p” (with pore; Figure 11d) where although the reactions on the secondary carbon are eliminated, the formation of 1-butenyl is slightly favoured over the formation of 1-butoxy. Furthermore, note that if 1-butoxy is formed, its hydrogenation to 1-butanol in this case is endothermic by 56 kJ/mol.

Fig. 11. Reaction energies on a) Pd(111) with 0.25 ML oxygen coverage and without the pore, b) Pd(111) with a 0.25 ML oxygen coverage and with the pore, c) Pd(100) with 0.25 ML oxygen coverage and without the pore, and d) Pd(100) with 0.25 ML oxygen coverage and with the pore. All reaction energies are in kJ/mol. The reaction numbers are in parentheses. The coloured lines indicate the favoured path according to the reaction energies.
We should note that the surface conditions studied here correspond to relatively low oxygen coverage, which as previously mentioned was done to facilitate comparison of the behaviour of the Pd(111) and Pd(100) facets. However, we also performed additional calculations on Pd(111) saturated with oxygen, i.e. 1 ML, which is a coverage unrealized on single crystal flat surfaces, but possible on nanoparticles. With no available metal sites, all C₄ species adsorb on O atoms, and only O-assisted dehydrogenation is possible. This dehydrogenation is highly exothermic on both the primary carbon (-242 kJ/mol with the pore, -227 kJ/mol without the pore) and secondary carbon (-249 kJ/mol without the pore) forming directly 1-butoxy or 2-butoxy. However, the issue is that the dehydrogenation of the 1- or 2-butoxy is also exothermic by more than 200 kJ/mol, and thus significantly more favourable than the hydrogenation to form 1- or 2-butanol (less than 50 kJ/mol exothermic). Therefore, based on all tested conditions, palladium nanoparticles exposing (111) facets with moderate oxygen coverage (0.25 ML) and steric constraints provided by a suitable MOF shell may be a promising candidate for the selective oxidation of n-butane to 1-butanol.

Conclusions

We introduced a simple DFT modelling approach for MOF-encapsulated metal catalysts (NP@MOFs), where a surrogate pore composed of chemically inert atoms mimics the steric constraints imposed by the MOF. The surrogate pore is composed of inert helium atoms, which were chosen for computational efficiency. Different tests showed that the only expected effect of the pore is to sterically constrain the adsorption of C₄ species on the studied palladium surfaces. We carried out DFT calculations of the adsorption of species relevant to n-butane oxidation on different surfaces and conditions to discern the effects of surface structure, oxygen coverage, and the presence or absence of steric constraints. We showed that steric constraints cause the C₄ species to adsorb roughly perpendicular to the surface, weakening the adsorption compared to their horizontal configurations when there are no steric constraints. Overall, the weakening was more pronounced for n-butane and 1-butanol, whose adsorption is dominated by dispersion interactions, and less pronounced for 1-butyln, 1-butenyl, and 1-butoxy, whose adsorption is dominated by chemical interactions. Also, we found that oxygen coverage tended to weaken the adsorption of the oxygen-free C₄ species and strengthen the adsorption of oxygen-containing C₄ species.

Based on calculated reaction energies, we showed that the activation of the primary n-butane C-H bond was more favourable when assisted by O than when catalysed directly by the Pd surface, and more favourable on Pd(100) than on Pd(111), partly due to higher favourability of hydroxyl formation on the former surface. This, however, also makes the hydrogenation of 1-butoxy less favourable on Pd(100). We also showed that the presence of the pore increases the favourability of C-H activation by weakening n-butane adsorption relative to 1-butyln adsorption. In most palladium systems, further dehydrogenation of 1-butyln is equally or more favourable than 1-butoxy formation, with the exception of Pd(111) with 0.25 ML oxygen-coverage. This was shown to be due to the weakening of n-butenyl adsorption due to the presence of pre-adsorbed oxygen. If this effect on Pd(111) is combined with the imposition of steric constraints, the targeted sequence of reactions to produce 1-butanol is favoured. This result may provide a design for NP@MOF catalysts for selective oxidation of normal alkanes to primary alcohols. Future work will include the calculation of kinetic energy barriers using the pore modelling approach demonstrated here and microkinetic modelling for catalytic surfaces such as palladium and palladium alloys.

Acknowledgements

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Notes

† The large difference (26 kJ/mol) of n-butenyl adsorption on 0.25 ML oxygen-covered Pd(100) depending on whether the pore is atop-centred or hollow-centred arose because for the latter one of the pre-adsorbed oxygen atoms moved out of its original position.

‡ The large difference (26 kJ/mol) of n-butenyl adsorption on 0.25 ML oxygen-covered Pd(100) depending on whether the pore is atop-centred or hollow-centred arose because for the latter one of the pre-adsorbed oxygen atoms moved out of its original position.

§ We use the term “clean” surface although one pre-adsorbed oxygen needs to be present to carry out reactions 6, 8, and 10, 11 and 13. One pre-adsorbed oxygen on a 4x4 supercell corresponds to a 0.0625 ML oxygen coverage.

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on Pd(111), Re(0001), ReML/Re(0001), ReML/Pd(111)
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