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

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A B S T R A C T

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.

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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 and 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, Fig. 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 (Fig. 1b).

A number of examples of NP@MOF catalysts have been reported in the literature, but the development of such catalysts has thus far relied

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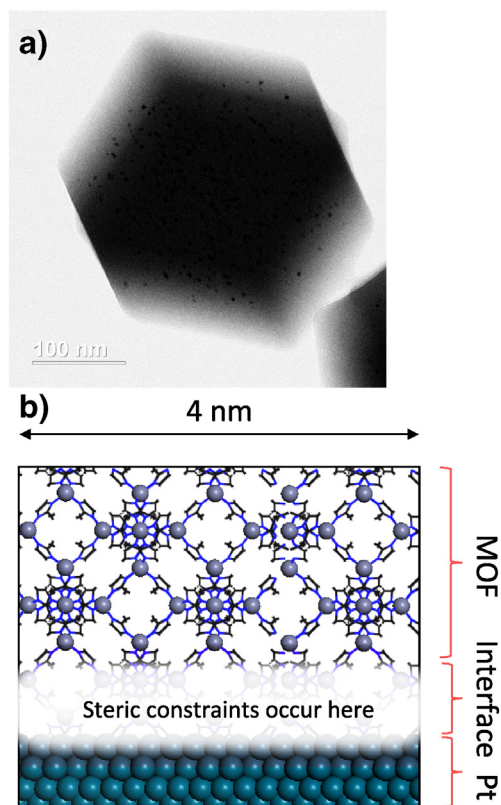E-mail address: rgetman@clemson.edu (R.B. Getman).

Fig. 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.

2. Computational methods

2.1. Sterically constrained catalyst model

We selected $Ag_3Pd(111)$ 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 a Ag_3Pd alloy could potentially engender the necessary oxidative strength to partially oxidize n-butane. We used a perfectly mixed model of Ag_3Pd, 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 Ag_3Pd 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 Ag_3Pd surface are provided by the surrogate pore approach, which has been introduced, described, and validated in detail by Gómez-Gualdrón et al. [8]. The surrogate pore limits the way C_4 species can interact with catalyst surface, while imparting only weak dispersion interactions. It is composed of chemically inert helium atoms (Fig. 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.

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] (Fig. 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 C_4 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 (Fig. S4).

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, Gómez-Gualdrón 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, Gómez-Gualdrón 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 destabilizations 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.