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DFT investigation of hydroperoxide decomposition over copper and cobalt sites within metal-organic frameworks

Patrick Ryan, Ivan Konstantinov, Randall Q. Snurr *, Linda J. Broadbelt *

Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, United States

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ABSTRACT

Experimental results in the literature show that two metal-organic frameworks (MOFs) containing copper and cobalt nodes are active for hydroperoxide decomposition, which is an important reaction in autooxidation processes. Density functional theory (DFT) calculations reported here for these systems suggest that the metal sites in the interior of these MOFs are not the active sites for this type of reaction due to the steric effects of the adjacent linkers. This implies that the experimental catalysis observed may occur on the exterior surface of the MOF crystals. Additional calculations with a copper paddlewheel node show that, despite being able to form complexes with hydroperoxides, the metal sites in copper paddlewheels do not catalyze hydroperoxide decomposition. Preliminary calculations involving undercoordinated metal atoms as a model for metal sites on the MOF exterior crystal surface suggest that these sites could be catalytically active.

1. Introduction

Metal-organic frameworks [1–5], or MOFs, are a new class of nanoporous materials composed of metal cations connected by organic linkers. These materials are synthesized in a self-assembly process yielding stable, porous, and crystalline frameworks. Large surface areas, open pores, low densities, and high thermal stabilities are a few of their attractive properties. The ability to tailor the pore environment with different linkers and maintain ordered, periodic pores has attracted much interest in MOFs for hydrogen storage [6–8], gas separation [9,10], and more recently catalysis [11–15].

There are four distinct ways in which MOFs can be used for catalysis [16], as shown in Fig. 1. The first is to use unsaturated metal sites that are sometimes present at the nodes or corners of these materials; for example, Schlichte et al. [17] showed that unsaturated square planar copper sites in HKUST-1 could catalyze a cyanosilylation reaction with coordinated benzaldehyde. Choomwattana et al. [18] used hybrid quantum/classical computational methods to predict that a concerted, single-step reaction between formaldehyde and propylene could be catalyzed over copper node sites in MOF-11. Another strategy is to incorporate active sites within the organic linkers. Cho et al. [13] immobilized an active Mn-salen catalyst as an organic linker within a mixed-ligand MOF and found that it catalyzes enantioselective epoxidation of an olefin substrate. Whereas homogeneous salen catalysts are prone to deactivation due to formation of μ-oxo dimers, the salen MOF catalyst exhibited close to constant reactivity over the course of the experiment and could be reused for subsequent reactions. Gascon et al. [19] recently used amine-functionalized MOFs, namely IRMOF-3 and amino-functionalized MIL-53, to catalyze Knoevenagel condensation reactions. The third strategy is to use linkers or metal sites within MOFs as attachment points for catalysts. Banerjee et al. [20] post-synthetically modified the MIL-101 MOF [21] by coordinating chiral organic catalysts to unsaturated metal nodes and noticed these heterogenized catalysts resulted in much higher enantiomeric excess of aldol reaction products relative to the homogeneous chiral catalyst in solution. Finally, MOFs can be used for the encapsulation of other active catalysts; for example, Sun et al. [22] recently incorporated polyoxometalate species within HKUST-1 and found that these species selectively occupied one of the larger type pores within the structure. They discovered that the hybrid catalyst was active for ethyl acetate hydrolysis and that its activity compared well with other common catalysts for this reaction. Alkordi et al. [23] incorporated porphyrins within the pores of a zeolite-like MOF and demonstrated the catalytic activity of the encapsulated porphyrins for cyclohexane oxidation.

Capitalizing on the idea of using open metal sites in MOFs for catalysis, Llabrés i Xamena et al. [24] demonstrated that two copper- or cobalt-containing MOFs were active for tetralin oxidation to ketone and alcohol derivatives, as shown in Fig. 2. The basic free radical mechanism underlying this chemistry is well understood, where hydrocarbons are initially oxidized to hydroperoxides. It was proposed that the MOFs catalyze the hydroperoxide decomposition reactions, following the Haber–Weiss cycle. In this cycle, metal

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* Corresponding authors. Fax: +1 847 491 3728.
E-mail addresses: snurr@northwestern.edu (R.Q. Snurr), broadbelt@northwestern.edu (L.J. Broadbelt).

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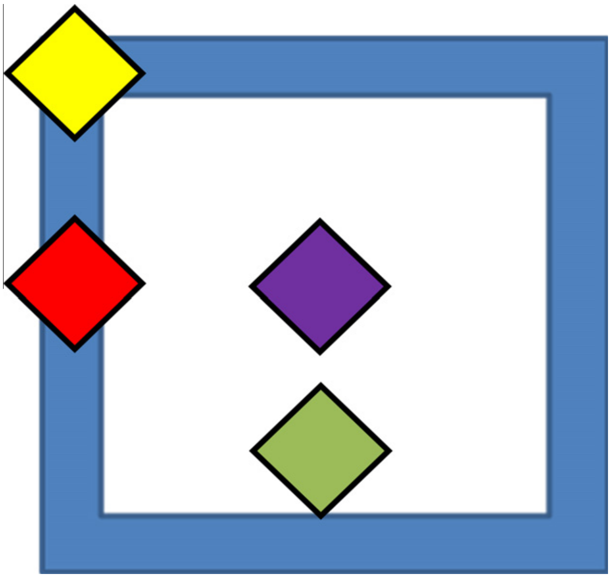

Fig. 1. Catalytic sites can be introduced into MOFs in four distinct ways: unsaturated metal sites at the nodes (yellow), homogeneous catalysts incorporated as part of the framework (red), catalysts attached to either nodes or linkers (green), and supported or encapsulated catalysts (purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cations undergo oxidation and reduction to decompose hydroperoxides into alkoxy and peroxy radical species, respectively:

$$\mathrm{ROOH} + \mathrm{M}^{n+} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{OH}^{-} + \mathrm{M}^{(n+1)+}$$
$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \rightarrow \mathrm{ROO}^{\cdot} + \mathrm{H}^{+} + \mathrm{M}^{n+}$$

The presence of the MOF prevented buildup of the intermediate hydroperoxide, in contrast to the reaction in the absence of the MOF [24]. However, the exact role of the MOF and its interaction with reactive intermediates are yet to be fully understood.

In related chemistry, Moden et al. [25] suggested that radical species during cyclohexane auto-oxidation over a MnAlPO-5 catalyst remained bound as adsorbed intermediates and that ROOH decomposition over Mn^{2+} sites was a kinetically-relevant step. Gomez-Hortiguela et al. [26] noted the importance of redox activity and coordinative unsaturation of MnAlPO-5 sites for oxidation of both hydrocarbons and hydroperoxide species. For homogeneous systems, Zabarnick and Phelps [27] also proposed that $^{\cdot}$OH radicals could remain bound to metal cations after oxygen–oxygen bond cleavage during hydroperoxide decomposition. Turra et al. [28] used quantum mechanics to map a Haber–Weiss reaction cycle over the homogeneous catalyst cobalt(II) acetylacetonate. By analogy, the open metal sites in the MOFs could play similar roles. While commercial processes for auto-oxidation have used copper and cobalt salts for some time, only a few examples exist in which researchers used computational methods to investigate oxidation reactions over these metal salts [27–29].

In this article, we investigate the decomposition of hydroperoxides over the two MOFs studied by Llabrés i Xamena et al. using quantum chemical calculations. The cobalt-containing MOF (denoted here simply as Co-MOF), composed of Co^{2+} cations and anionic phenylimidazolate linkers, has a sodalite-type structure and is also known as zeolitic imidazolate framework 9 (ZIF-9) developed by the Yaghi group [30]. The cobalt atoms in this MOF are coordinated in a tetrahedral geometry with the adjacent linkers. The copper-containing MOF (Cu-MOF) [31] is composed of Cu^{2+} cations and 2-hydroxypyrimidinolate linkers in a 1:2 molar ratio. Copper sites are in a near-square planar configuration, which leaves them coordinatively unsaturated and able to interact with guest molecules. Additionally, we investigate the copper paddle-wheel structure, which is a common structural motif in several MOFs, including HKUST-1 [32] and the NOTT series [33].

2. Computational methods

In this study, representative clusters were extracted from the MOF crystal structures around the active sites. For Co-MOF, one cobalt atom with four surrounding linkers was chosen as the model, but to reduce the computational cost, smaller imidazolate linkers were used instead of the phenylimidazolate linkers, as shown in Fig. 3a. For Cu-MOF, one copper atom and four 2-hydroxypyrimidinolate linkers were modeled (Fig. 3b). In the periodic MOF, the linkers of both MOFs are anionic and bound at both ends by metal cations. In our cluster models, the four boundary atoms of the cluster (where the next metal atom would occur in the periodic structure) were saturated with protons. This choice renders the metal–nitrogen bonds between all four linkers and the central metal atom equivalent and gives each cluster a charge of 2+. The copper paddlewheel model was composed of two copper atoms coordinated to four acetate groups, yielding a charge neutral cluster. See Fig. 3. 1-Phenylethylhydroperoxide, the hydroperoxide of ethylbenzene, was studied as the reactant. Given the presence of a benzylic carbon, it is a suitable model of tetralin, which should undergo similar auto-oxidation and decomposition reactions.

Density functional theory (DFT) calculations with Becke's three-parameter hybrid exchange functional (B3) [34] and the correlation functional of Lee, Yang, and Parr (LYP) [35] were performed. To select a basis set, calculated bond energies using several methods for

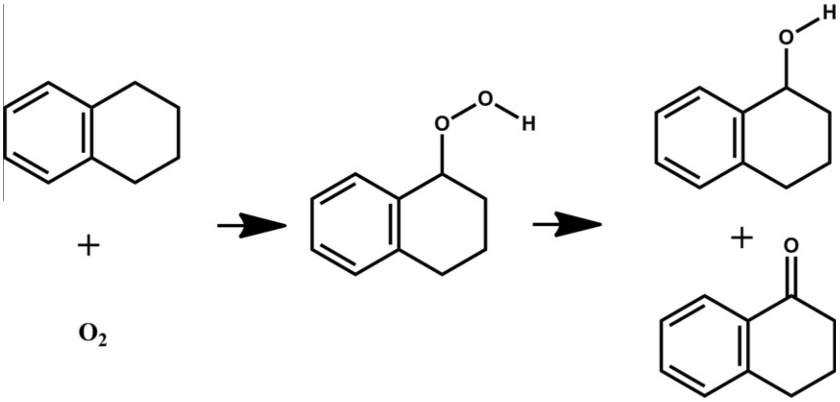

Fig. 2. Auto-oxidation reaction scheme of tetralin in the presence of dioxygen to alcohol and ketone derivatives.