

METAL-ORGANIC FRAMEWORKS AS OXIDATION CATALYSTS: ARE METALS IN THE FRAMEWORK CATALYTICALLY ACTIVE?

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Summary

Experimental results in the literature show that some metal-organic frameworks (MOFs) are active for hydroperoxide decomposition, which is an important reaction in autooxidation processes. Using density functional theory (DFT), we suggest that the metal sites in the interior of these MOFs are not the active sites for this type of reaction. Instead, we hypothesize the experimental catalysis observed may occur on the surface of the MOF crystals, which could contain undercoordinated metal sites.

Keywords

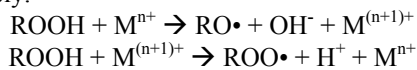
Rational Design of Catalysts, Computational Catalysis

Introduction

Metal-organic frameworks,¹ or MOFs, are a new class of nanoporous materials composed of metal cations connected by organic linkers. These materials self-assemble in solution to yield stable, porous, 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 for MOFs in hydrogen storage, gas separation, and more recently catalysis.²

MOFs can be catalytically active in three distinct ways. The first is to use unsaturated metal sites, which often appear at the nodes or corners of these materials. Another strategy is to utilize active sites within organic linkers. Finally, MOFs can be used as supports for other active catalysts.

Using the first method described above, Llabres i Xamena et al.³ demonstrated that certain copper- and cobalt-containing MOFs are active for tetralin oxidation to ketone and alcohol derivatives. This radical chemistry is well understood, where hydroperoxide builds up in an autocatalytic cycle. The MOFs in this case appear to catalyze hydroperoxide decomposition reactions, which follow the Haber-Weiss cycle. In this cycle, metal cations undergo oxidation and reduction to decompose hydroperoxides into alkoxy and peroxy radical species, respectively:



As demonstrated in their paper, the presence of the MOF is necessary to prevent a buildup of the intermediate hydroperoxide. However, the exact cycle is not fully understood. Moden et al.⁴ suggest that radical species during cyclohexane autooxidation over a MnAlPO-5 catalyst remain bound as adsorbed intermediates and that ROOH decomposition over Mn²⁺ sites is a kinetically relevant step. Zabarnick et al.⁵ also propose that •OH radical can remain bound to metal cations after oxygen-oxygen bond cleavage.

In this work, we investigate these decomposition reactions over the MOFs studied by Llabres i Xamena et al.³ using quantum chemical calculations. The cobalt-containing MOF (Co-MOF), composed of Co²⁺ cations and anionic phenylimidazolate linkers, has a sodalite type structure and is also known as zeolite imidazolate framework 9 (ZIF-9) developed by the Yaghi group.⁶ The copper-containing MOF⁷ (Cu-MOF) is composed of Cu²⁺ cations and 2-hydroxypyrimidinolate linkers also in a 1:2 molar ratio.

Computational Methods

We performed density functional theory (DFT) calculations with the B3LYP functional and the 6-31G(d,p) basis set for all atoms except the metal atoms, for which a TZVP basis set was used. Metal clusters that are representative of each active site were taken directly from the crystal structures of both MOFs, as shown in Figure 1. Since the linkers in each MOF are anionic, we saturated boundary atoms of the cluster with protons, making each

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ligand neutral and leaving the cluster with an overall +2 charge. Additionally 1-phenylethylhydroperoxide was the reactant as a model for the larger hydroperoxide of tetralin.

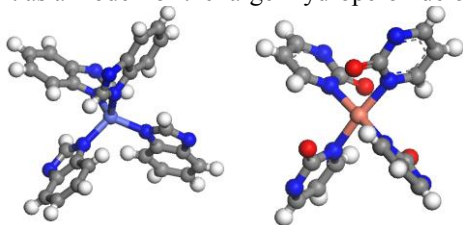


Figure 1. Representative clusters taken from Co-MOF (left) and Cu-MOF (right). Carbon, hydrogen, nitrogen, and oxygen atoms are gray, white, blue, and red, respectively.

Results

Our DFT results suggest that the tetrahedral cobalt site in Co-MOF is not active for catalysis due to the constraints of the framework. Optimization of the hydroperoxide in the presence of a fixed tetrahedral cobalt cluster resulted in the hydroperoxide leaving the active site, suggesting the metal site is too sterically protected to interact with guest molecules. Additionally, if we allow the cluster to fully relax, the cobalt atom can interact with an oxygen atom of the hydroperoxide but with substantial geometric rearrangement. The cobalt reorganizes into a trigonal bipyramidal structure, which is not compatible with the extended MOF structure. Calculations with more extended structures are underway, but the results to date suggest that catalysis by metal atoms inside the pores is not feasible in the Co-MOF. In addition, the cavity size of 4.31 Å⁶ indicates that the pores are too small to accommodate tetralin. Nonetheless, we cannot definitively rule out the catalytic activity of tetrahedral cobalt sites, since it could be possible for a similar rearrangement in another MOF or support. This type of rearrangement might be similar to titanium in TS-1, which changes from 4- to 5-coordinate during catalysis.

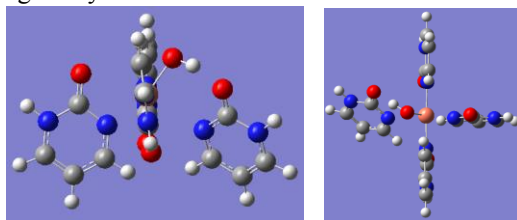


Figure 2. Side (left) and top (right) views of •OH radical coordinating to the copper cluster. The •OH radical forces a loss of coordination to the organic linker, suggesting these copper sites cannot be active for hydroperoxide decomposition.

While Cu-MOF has a pore size of 8.1 Å and cavities of 14 Å, suggesting that the copper sites are accessible to tetralin, our initial DFT calculations suggest these copper sites are not active for hydroperoxide decomposition. Whenever a radical substrate (e.g., •OH radical) was introduced to the copper site, the cluster rearranged to form a square planar complex, with the •OH radical displacing one of the original coordinated organic linkers (Figure 2). This result was particularly interesting, since catalytically active sites need to accommodate some

radical species (whether RO• or •OH) after homolytic cleavage of the oxygen-oxygen bond in hydroperoxides. We were able to find stable complexes of the copper cluster with water and simple ketones such as formaldehyde, suggesting that the copper sites can accommodate other guest molecules.

Conclusion

Recent experiments have demonstrated that MOFs can be catalytically active materials; however, our computational results suggest that metal sites within the Co- and Cu-MOFs studied by Llabres i Xamena et al.³ for oxidation chemistry are limited in their catalytic potential. Specifically, steric effects around metal sites may prevent direct interaction with metal centers. Small pore sizes, as in Co-MOF, can prevent diffusion of guest molecules and should be considered before selecting MOFs as candidate catalysts. Additionally, metals with particular oxidation states exist in predetermined geometries (e.g., Cu²⁺ prefers being square planar), and any oxidation or reduction of that metal has the potential to disrupt the local structure and possibly degrade the MOF. Our results suggest the possibility that surface catalysis may be dominant in these systems.

References

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