Flexible and Responsive Nature of 2D Layered Conductive Metal-organic Frameworks Determine their Catalytic Activity in Oxidative Dehydrogenation of Propane

Mohammad R. Momeni*, Zeyu Zhang, and Farnaz A. Shakib*
Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark 07102, NJ United States
Received September 7, 2020; E-mail: momeni@njit.edu, shakib@njit.edu

Abstract: A combined quantum mechanics and classical molecular dynamics approach is used to unravel the effects of structural deformations and heterogeneity on catalytic activity of the 2D π-stacked layered Co₃(HTTP)₂, HTTP=hexathiatriphenylene, metal-organic framework. A newly developed ab initio force field captures the flexible nature of this material and unravels a complex array of catalytically active sites. Using an ensemble approach and oxygen bond formation energy, as an excellent probe, we investigate the catalytic activity of Co₃(HTTP)₂ down to the single active site level. This study is one step forward in reaching a predictive modeling strategy needed for studying highly flexible materials such as 2D π-stacked layered MOFs.

Recently introduced 2D π-stacked layered conductive M₃(H(H,I,T)TP)₂ metal-organic frameworks (MOFs), where M = Co²⁺, Cu²⁺, and Ni²⁺ and HTTP=hexahydroxytriphenylene, HITP=hexaiminotriphenylene, and HTTP=hexathiatriphenylene, offer record breaking electrical conductivity along with high surface area and structurally tuneable bandgap.¹⁻⁴ Combined with their low dimensionality for compact device implementation, they have inspired development of MOF-based batteries and supercapacitors⁵⁻¹² as well as potentiometric and chemiresistive sensors.¹³⁻¹⁵ Having 1-D channels with ∼ 20 Å diameters, they allow penetration of targeted analytes making them perfect choices for adsorption, separation and catalysis (Figure 1). In spite of all their merits, device engineering based on these highly flexible materials remains a pressing challenge due to limited fundamental understanding of the intrinsic MOF structure and dynamics, as well as limited knowledge of host-guest interactions and water dynamics at the interface and within the confined spaces of their 1D channels. The flexible nature of these materials and the complex dynamics of confined water renders the conventional static electronic structure calculations or short-time ab initio molecular dynamics (AIMD) simulations inadequate at their best.

Herein, we employ a combined quantum mechanics / molecular dynamics approach to bridge the gap between the intrinsic and guest(water) induced structural transformations and flexibility of 2D MOFs and their catalytic activity. We focus on Co₃(HTTP)₂, as a representative of 2D layered conductive MOFs, as well as the results are transferable to similar layered systems. Our simulations illustrate different levels of heterogeneity and disorder in equilibrated 2D MOFs, painting a realistic picture of catalytic activity of Co₃(HTTP)₂ compared to pristine structures obtained from static electronic structure calculations. We show that cobalt-oxygen bond formation energy can be used as an excellent probe of temperature and water induced heterogeneity and disorder in this material. To the best of our knowledge, this is the first study illustrating the intrinsic and water-induced framework deformations and dynamics as well as catalytic activity of 2D layered conductive MOFs.

Figure 1. Conductive 2D π-stacked layered Co₃(HTTP)₂ MOF. Schematic representation of (a) tetra-coordinated metal node creating (b) an extended layer via tri-topic HTTP linkers, and (c) crystal structure of the tetra-layered 2 × 2 × 2 extended supercell highlighting the hexagonal array of the 1D channels.

Figure 2. Final snapshots of the MD equilibrated hydrated Co₃(HTTP)₂ MOF with (a) 48, (b) 96, (c) 144 and (d) 192 H₂O molecules at 293 K in the NPT ensemble. Calculated (e) Co-Co and (f) Co-Ow (oxygen of water) RDFs are also given.

Periodic electronic structure and classical MD simulations were performed on an extended 2 × 2 × 2 model of Co₃(HTTP)₂ MOF. MD simulations were run based on our newly-developed ab initio force field (FF) parameterized against highly accurateωB97M-v/def2-TZVP¹⁶ density functional. This FF allows nanosecond scale simulations, far beyond capabilities of AIMD simulations while reproducing similar accuracy in capturing the intra- and inter-layer framework deformation and heterogeneity. Details of developing and validating the force field against experimental and ab initio data, and the complete list of bonded and non-bonded parameters are reported in the Supporting Information (SI) (section S2, Figure S1 and Tables S1-S5). The 0 K PBE-D3/DZVP-MOLOPT optimized and the 293
K MD equilibrated extended $2 \times 2 \times 2$ Co$_3$(HTTP)$_2$ frameworks show layers that are slipped relative to each other along the “a” and “b” vectors. The Co-Co-Co-Co dihedral angle, $\angle da$, passing through four layers of the MOF within the supercell, was found to be a good geometrical descriptor to quantify the degree of slipping disorder. There are 12 such angles within the cell. While $\angle da$ of the 0 K optimized MOF has a very narrow range of $179.4^\circ - 180.0^\circ$, the calculated range of $\angle da$ for MD equilibrated MOF at 293 K is $170.0^\circ - 177.2^\circ$ showing a higher degree of deformation. This observation is in agreement with previous studies where slipping of layers, mostly to form an AB slipped-parallel stacking pattern, has been confirmed in various 2D MOFs including Co$_3$(HTTP)$_2$.\textsuperscript{4,14,17-20} Figures 2a–2d illustrate the final MD snapshots of Co$_3$(HTTP)$_2$ bearing 48, 96, 144 and 192 water molecules. At the beginning of the simulation, water molecules are placed at the center of the 1D channel in a sphere with as small of a radius as possible. As the simulation progresses, they relocate themselves towards the interface with the framework in response to two opposing forces. Water molecules are drawn to the surface of framework because of either chemisorption to the coordinatively unsaturated Co centers or forming hydrogen bonds (H-bond) with the exposed S atoms of the linkers. On the other hand, the hydrogen bond network between water molecules prevent their free movement towards the surface. For systems with 48 (48@MOF) and 96 (96@MOF) water molecules, one can recognize that the latter is more important which keeps a cluster of water molecules inside the 1D channel, Figures 2a and 2b. Adsorption of water molecules by the surface become more apparent in systems with 144 (144@MOF) and 192 (192@MOF) water molecules to the degree that water molecules diffuse to the interlayer space, Figures 2c and 2d. Figure 2e illustrates the calculated RDFs for Co-Co distances in dry and hydrated Co$_3$(HTTP)$_2$ MOF at 293 K demonstrating the existence of a long-range order along the stacking direction which can also serve as an estimate of interlayer distances. The Co-Co RDF of the dry MOF is centered at ~4.2 Å, so are the RDFs of 48@MOF and 96@MOF. Noticeable chemisorption of water molecules to the Co centers in 144@MOF and 192@MOF leads to broadening of the prominent Co-Co RDF peak. In case of 192@MOF, the center of the peak slightly shifts to 4.3 Å (Figure 2e). The calculated Co-O$_w$ (oxygen of water) RDF peaks of occasional chemisorbed water molecules in both 48@MOF and 96@MOF systems are centered around 1.89 Å. Addition of water molecules in 144@MOF and 192@MOF systems, which create a H-bond network around chemisorbed water molecules, leads to a shift of Co-O$_w$ RDF peaks to 1.93 Å (Figure 2h). In short, the layers are distanced from each other to accommodate the incoming water molecules. The calculated range of $\angle da$ is also found to increase in the presence of water, with the largest range of 148.7$^\circ$ - 179.7$^\circ$ observed for the 192@MOF system, showing more vivid movement of layers in the ab plane in the presence of water.

Analysis of the 5 ns MD trajectories of hydrated Co$_3$(HTTP)$_2$, Figure 3a, shows five different types of water molecules including those that are coordinated to one (1W$_{Co}$) and two (2W$_{Co}$) open Co$^{2+}$ sites, those that are H-bonded to one (1W$_{HB}$) and two (2W$_{HB}$) S atoms of the linkers as well as free water molecules (W$_f$).

First, regardless of water concentration, the majority of water molecules tend to stay together and move freely along the main 1D channels. Second, analysis of our MD trajectories shows that adsorption of water molecules on the framework’s surface is first governed by formation of H-bonds with the S atoms of the organic linkers which brings the water molecules closer to the open-metal sites and allows the following chemisorption. Figure 3a shows that increase of 1W$_{HB}$ from 48@MOF to 144@MOF is accompanied by the increase of 1W$_{Co}$. Chemisorbed water molecules to Co centers create nucleation sites pulling the rest of the water molecules towards interlayer distance and the nearby channels. In 192@MOF, interlayer water molecules enter the neighboring 1D channels hence increasing the number of free water molecules compared to 144@MOF. The calculated RDF peak for the Co–S bonds, see SI Figure S3, shows that coordination of more than one water molecule to the same metal site in the case of 144@MOF and 192@MOF leads to the weakening, and in some cases breakage, of some of the Co-S bonds. As highlighted in Figure 3b, in spite of some broken Co-S bonds in these nucleation sites, the framework is able to preserve its structural integrity thanks to a continuum H-bond network of the chemisorbed water molecules, free water molecules and S atoms of the linkers.

Single-atom Co-deposited MOFs are shown to be excellent heterogeneous catalysts in catalytic conversion of propane to value-added chemicals under mild conditions.\textsuperscript{21-22} Herein, oxidative dehydrogenation (ODH) of propane using N$_2$O as oxidizing agent\textsuperscript{23,24} is adopted for studying the effect of structural deformations on catalytic activity of the coordinatively unsaturated Co sites in Co$_3$(HTTP)$_2$. We have shown in our previous studies that presence of such open-metal sites are crucial in achieving catalytic activity in MOFs’ secondary building units.\textsuperscript{25-29} Barona et al have suggested a 4-step mechanistic cycle for N$_2$O–assisted ODH of propane on PCN-250 which starts with binding of the oxidizing agent N$_2$O to the open-metal sites resulting in formation of a metal-oxo bond and N$_2$ liberation (step 1, rate-determining step).\textsuperscript{23,24} It is then followed by C-H bond activation of the secondary hydrogen of propane (step 2) resulting in either

![Figure 3](image-url)
formation of propanol or another C-H activation to form terminal water and propene, see SI Figure S6. Having found a strong correlation ($R^2 = 0.98$) between the $N_2O$ activation energy barriers and the metal-oxygen bond formation energies, they used metal-oxygen bond formation energies to predict the catalytic activity of different metal nodes. Here, we first perform quantum mechanical calculations to test the applicability of such predictive descriptor in 0 K optimized 2D MOFs and then the 293 K equilibrated systems. To be able to provide a general picture, we cut cluster models from 0 K optimized structures of both $M_3$(HTTP)$_2$ and $M_4$(HTTP)$_2$ MOFs (with $M = \text{Co and Cu}$) with truncating the organic linkers to dithiophenolates (DTP) and catecholates (CAT), respectively. Metal-oxo bond formation energies ($\Delta E_O$) were calculated relative to the bare node ($E_M$) and an isolated $N_2O$ molecule ($E_{N_2O}$) using the following formula: $\Delta E_O = E_{M-O} + E_{N_2} - E_M - E_{N_2O}$. The $N_2O$ activation energy barriers vs. the oxygen bond formation energies for these four cluster models are plotted in SI Figure S8 which show a very good correlation with $R^2 = 0.98$, validating the predictive tool suggested by Barona et al. in these systems. Notably, Co(DTP)$_2$ forms the most stable metal-oxo bond ($\Delta H_O = -62.6$ kcal/mol) and shows the lowest $N_2O$ activation enthalpy of 30.4 kcal/mol.

Now, we look into utilizing the computed $\Delta E_O$s as an energy descriptor to illustrate the degree of deformation and heterogeneity in 2D MOFs and also to explore if the correlation found between $N_2O$ activation energy barriers and the $\Delta E_O$s still holds. We take an ensemble approach by computing $\Delta E_O$s for all 48 different catalytically active Co sites present in the extended $2\times2\times2$ supercell with many local minima being surveyed for the framework. To account for both temperature and water-induced structural transformations/deformations, these calculations are performed on the dry MOF after removing 192 water molecules from the framework and subsequently equilibrating the system ($192_{\text{dry}}@\text{MOF}$). We repeated similar calculations for the 0 K optimized dry MOF for comparison.

![Figure 4](image-url)  
**Figure 4.** Top: six different isomers found for oxygen interacting with the layered Co$_3$(HTTP)$_2$ framework where “int” stands for oxygen forming interlayer bonds and “d” stands for oxygen bonding to the defect sites present in the framework. Bottom: a, b, and c depict PBE-D3 optimized Co$_{284}$-S(int), Co$_{64}$-S(d), and Co$_{63}$-Co$_{825}$ (int) isomers, respectively.

Bonding of one oxygen atom to different open Co sites of the Co$_3$(HTTP)$_2$ framework leads to formation of six different isomers which are shown in Figure 4. In the case of the 0 K optimized MOF, only four distinct isomers were identified, namely Co, S, Co-S, and Co-Co(int). The two additional isomers in 192$_{\text{dry}}@\text{MOF}$, namely Co-S(int) and Co-S(d) are only formed due to the slipping of the layers as a result of the incorporation of temperature and humidity effects into account. Starting from optimized MOF, Co isomer was found to be the highest energy isomer with $\Delta E_O = 16.1$ kcal/mol followed by Co-Co(int), Co-S and S isomers ($\Delta E_O = +1.3$, -20.0, and -34.0 kcal/mol, respectively). This difference in $\Delta E_O$s is likely due to changes in formal oxidation of Co upon binding to the oxygen atom from +2 to +4. In contrast, in the more stable Co-S and S isomers, due to the participation of the redox-active HTTP linkers, formal oxidation of Co increases only from +2 to +3 in the former and stays as +2 in the latter. Nevertheless, we classify the S isomers as off-cycle species that would not play a role on the reaction mechanism as depicted in SI Figure S6.

As can be seen from Figure 4b, incorporating temperature and solvent into the simulations leads to creation of certain defect sites with a pseudo-tetrahedral Co center coordinated to three HTTP linkers as opposed to its normal square planar geometry formed when it is bonded to two HTTP linkers (i.e. (a) and (b) in Figure 4). Out of the 24 Co sites present inside the main 1D channel of the studied $2\times2\times2$ supercell, 8 sites fall into the category of defect sites which were found to be amongst the most favorable sites for bonding to the oxygen ($\Delta E_O = -47.1$ kcal/mol compared to -23.1 kcal/mol for the rest, SI Table S7). RESP charges were computed and showed defect sites are more positively charged compared to the rest, an average of +0.473 e vs. +0.264 e (SI Table S7). The computed $\Delta E_O$s values for the Co, Co-Co(int), and S isomers in 192$_{\text{dry}}@\text{MOF}$ are 29.1, 22.4, and 5.7 kcal/mol, compared to the same isomers in the 0 K optimized MOF. When averaged over all 48 open-Co$^{2+}$ sites, this value is found to be 26.1 kcal/mol lower than the corresponding value for the optimized system (~27.0 kcal/mol vs. ~0.9 kcal/mol) indicating likely higher catalytic activity than what would be presumed based on static electronic structure calculations. These results highlight the importance of incorporating the temperature and solvent effects which lead to structural deformation when studying catalysis in these fluxional materials.

Finally, we examined the four step mechanistic scheme, as outlined in SI Figure S6, for three representative isomers namely Co$_{63}$-Co$_{825}$(int), Co$_{64}$-S$_{123}$(d) and Co$_{284}$-S$_{534}$(int) (Figure 5). These Co centers experience different electronic environments and as such are expected to show different catalytic activities. The Co$_{64}$-S$_{123}$(d), a Co center present at the defect sites, shows the highest $\Delta E_O$ as well as the lowest activation free energy ($\Delta G^*$) of 29.2 kcal/mol for step 1. However, opposite to what was
seen for cluster models and what is reported in the literature.  

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Supporting Information Available  

Details of our flexible ab initio force field, results of our classical MD simulations, details of the periodic and cluster electronic structure calculations as well as XYZ coordinates of all systems.

References


