

Metal Organic Frameworks; their Stability and Computational Modelling

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Abstract

Metal Organic Frameworks possess many desirable properties. This has been a driving factor that has led to their application in a diverse range of fields. However, their stability need to be improved if they are to be synthesisable on an industrial scale. This can be achieved through an improved understanding of their structure, provided by transmission electron microscopy. Computational modelling offers many insights into the processes that take place during imaging, and can help us better understand how to decrease beam damage and improve image interpretation.

1. Introduction

More than 20,000 different metal organic frameworks (MOFs) have appeared in the literature in the past decade.¹ This is due to the family of compounds having a range of different geometries, sizes, and functionalities, making them very versatile in application. Their diverse usage is in large part due to their desirable properties such as permanent porosity, open framework, high surface area, and pore volume, which give MOFs their commercial appeal.²⁻⁵ These properties are what has led to the diversity in areas of research in which MOFs are now being applied in, ranging from gas adsorption and storage, drug delivery, antimicrobial properties, medical imaging and luminescent applications.^{1,2,6,7}

However, it is due to the MOF's high surface area to scaffold ratio that they are relatively fragile and prone to collapse during desolvation, leading to defects in products.^{8,9} This issue in stability must be addressed if MOFs are ever to be synthesisable on an industrial scale and reach commercial viability.

Due to this, there has been a focus in recent years to design MOFs that have increased resilience and stability. In order to do this, a detailed structural analysis of the MOFs needs to be obtained, so as to determine what functionalities are more resilient than others.

2. Metal Organic Frameworks

2.1 Structure

MOFs are crystalline porous materials made by connecting inorganic metal ions to organic ligands.¹⁰ This is achieved by coordination, which leads to the open framework that MOFs enjoy. They often demonstrate permanent porosity due to their long organic linkers which provide large open pores within the MOF structure. These pores act as large storage spaces that contain numerous absorption sites within MOFs.² There are a large variety of MOF structures attainable due to

the range of coordination geometries of the metal ion centres. This allows MOF structures to be tailored to purpose,¹¹ and can be seen in the literature with the array of 1-, 2-, and 3-D MOFs that have been identified.⁴

2.2 Synthesis

There are a variety of routes that have been developed to synthesise MOFs, ranging from solvo/hydro thermal methods, slow diffusion, conventional heating, slow evaporation, mechano-chemical, and sonochemical.¹²⁻¹⁶ In general, all synthetic routes can be categorised as one-pot synthesis or post-synthesis modification. One-pot approaches offer simplicity and few step syntheses, but suffer from a lack of control over the final metal distribution. Post-synthesis routes such as transmetalation reactions can access metal-organic formations not accessible in one-pot synthesis that arise from constraints due to metal ion reactivity.¹⁷

When specifically targeting 2D MOFs, there are two methods that are used in the literature.¹⁸

Top-down methods require the exfoliation of layered bulk MOFs, with techniques such as sonication exfoliation that break the interlayer bonds within a 3D MOF structure to generate 2D sheets.^{19,20}

Bottom-up methods involve the direct synthesis of 2D MOF nanosheets, where crystal growth is restricted to one dimension to achieve a 2D sheet. Techniques to do this include interfacial synthesis^{21,22} and small molecule blocking groups^{23,24}.

2.3 Stability

MOFs in general suffer from a lack of stability. This causes them to be susceptible to thermal decomposition²⁵, desolvation collapse²⁶, and dissociation during imaging²⁷. However, there has been work in recent years to alter functionalities to synthesise more resilient MOFs.²⁸

The stability of a MOF is primarily determined by its metal-

ligand coordination bond strength.^{28–30} This strength is dependent on the metal ion within the MOF, and the functionalities present within the ligand.

Healy *et al.*²⁵ demonstrates that functionalities affect thermal stability. In general, activating functionalities such as BDC, NDC, amino and methyl groups increase thermal stability, and deactivating functionalities such as bromo, nitro, and chloro groups decrease thermal stability.

During desolvation, the structural support that solvents provide is removed, and can lead to structural collapse within the MOFs. James²⁶ states that framework stability can be maximised by ensuring good hard-hard or soft-soft matching between the MOF ligand and metal, and Abrahams *et al.*³¹ suggest maximising the chelate effect to increase desolvation stability.

While there are no systematic studies comparing MOF functionalities to electron beam resilience, Wiktor *et al.*²⁷ state that the metal centre of a MOF is crucial in determining its electron beam stability, with Cu and Ru ions in MOFs frequently being reduced by the beam to form nanoparticles within the MOF matrix. They further go on to say that the organic linkers have less of an effect, however, the lighter atoms that they introduce can be completely removed by inelastic scattering, leaving highly reactive species.

3. Electron Beam Irradiation Damage

3.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) has been of particular interest to achieve a structural understanding of MOFs, as it offers atomic scale resolutions which provide the most detailed images for analysis.^{32–34} However, TEM hasn't yet reached large scale success as the electron beams used are of considerably high energy.

This poses an issue as this energy can be transferred to the MOFs being imaged, and further destabilise their already fragile structure, resulting in fragmentation or a complete structural decomposition.^{35,36} This damage can be seen in the electron diffraction pattern of the imaged sample, where the peaks of electron intensity fade or become blurred as the regular atomic arrangement is disrupted.³⁷

3.2 Damage Mechanisms

There are two mechanisms with which electrons are scattered by atoms, elastic scattering and inelastic scattering.³⁸ Both mechanisms contribute to the overall sample degradation during TEM imaging.³⁹

Elastic scattering transfers energy from an electron to a nucleus equal to

$$E = E_{max} \cdot \sin^2 \left(\frac{\theta}{2} \right) \quad (1)$$

where θ is the scattering angle and E_{max} is the energy loss for 180° scattering.³⁷ Most elastic scattering involves angles below 1°, corresponding to an electron energy loss of about

1 eV. This low angle scattering is responsible for the electron diffraction pattern observed in TEM. However, the small fraction of electrons that scatter through large angles experience a considerable energy loss, on the scale of several hundred keV. This can cause the corresponding nucleus to eject from the sample if the energy delivered exceeds a threshold energy E_d , the ejection energy threshold. This process removes atoms from the imaged sample, and can lead to a loss of structural order or a complete decomposition of the sample, resulting in information to be lost from the observed diffraction pattern.^{37,40}

Inelastic scattering occurs when the electron energy losses are on the scale of a few eV to tens or hundreds of eV. This causes excitation of electrons in the corresponding nucleus, and can result in permanent breakage of chemical bonds and a change in the molecular structure of the sample.^{41,42} This process can also cause cross-linking, resulting in the generation of new functionalities not found in the original sample.⁴³ This process has the result of altering the atomic connectivity of the imaged sample, causing the observed diffraction pattern to be unrepresentative of the original sample structure.

Damage during imaging is measured by the electron dose required to destroy the sample. That is, the number of electron incident on the sample to cause the observed diffraction pattern to disappear.^{38,44–46} This metric is proportional to the energy delivered to the sample during imaging, so is also a measure of stability. However, electron dose can only be obtained from experimental measurement on MOFs that have already been synthesised. To measure stability theoretically, to improve MOF structures before they are developed, a metric known as cross section is used.

3.3 Cross Section for Species Dissociation

Cross section is the probability that a species dissociates from the sample being imaged. It is calculated using the formula:⁴⁷

$$\sigma_d = 4\pi \left(\frac{z \cdot e^2}{4\pi\epsilon_0 \cdot 2m_e c^2} \right)^2 \cdot \frac{1 - \beta^2}{\beta} \left\{ \frac{T_{max}}{E_d} - 1 - \beta^2 \cdot \ln \left(\frac{T_{max}}{E_d} \right) + \pi \frac{z \cdot e^2}{\hbar \cdot c} \beta \left[2 \left(\frac{T_{max}}{E_d} \right)^{\frac{1}{2}} - \ln \left(\frac{T_{max}}{E_d} \right) - 2 \right] \right\} \quad (2)$$

where z is the nuclear charge, $\beta = \frac{v_e}{c}$ is the ratio of electron velocity v_e to the speed of light, c , m_e is the mass of an electron and T_{max} is the maximum kinetic energy that an electron can confer to an atom. It is calculated by:⁴⁸

$$T_{max} = \frac{2ME \cdot (E + m_e c^2)}{(M + m_e)^2 + 2ME} \quad (3)$$

where M is the mass of the atom, and E is the electron kinetic energy. This equation for T_{max} applies to stationary atoms. An alternative approach that considers the effect of velocity

distributions on T_{max} is:⁴⁹

$$T_{max} = \frac{1}{2M} \left(r \left(r + \frac{2t}{c} \right) + \left(\frac{t}{c} \right)^2 \right) \quad (4)$$

$$r = \frac{1}{c} \sqrt{E(E + 2mc^2) + MV_n} \quad (5)$$

$$t = \sqrt{(E + E_n)(E + 2mc^2 + E_n)} \quad (6)$$

where V_n is the initial velocity of the atoms parallel to the electron beam and E_n is the initial kinetic energy of the atom.

The term E_d in Eq. (2) is the ejection energy threshold. It is the minimum energy that the atom requires to dissociate and must be obtained analytically through computational methods. E_d captures the bond strength between the atom and the total imaged species, and is therefore greater for more stable species. If T_{max} is less than E_d then there isn't sufficient energy to break the bonds and no dissociation takes place. However, if T_{max} is greater than E_d then dissociation of the atom is possible.³⁷ The probability that the atom rejoins the molecule is dependent on its kinetic energy after dissociation and so cross section, σ_d , is dependent on the ratio of these two terms.

4. Modelling of Electron Beam Irradiation Damage

The atomic scale resolutions reached by TEM offer unmatched imaged detail, but interpretation of the quantum picture that they provide is by no means intuitive.^{34,50} Computational analysis can provide an understanding of the molecule's likely fragmentation patterns and imaging damage that has taken place. This can aid in the characterisation of a molecule from the diffraction pattern obtained, as it allowing for a more informed perspective when assigning structure, as well as provide an understanding of the effects of structure on resilience properties. This can be achieved through molecular dynamics.

4.1 Molecular Dynamics

Molecular dynamics (MD) are simulations that deploy numerical methods to study many-particle systems. It involves solving Newton's equations of motion for each individual particle in the system and then adjusting that particle's dynamics. This process is iterated over a time scale to provide a dynamic simulation of the system as a whole.⁵¹

The motion of each atom is modelled classically, however, the electrostatic interactions that generate the force they experience are a quantum mechanical problem. There are two ways to model this potential, either classical MD or ab-initio MD (AIMD). In a classical MD simulation interactions are approximated by classical model potentials which have been derived from and fitted to experimental results. As such they are empirical potentials. AIMD simulations perform a full quantum calculation of the electronic structure at every time step.⁵²

Classical potentials are ideal for nonreactive interactions, such as angle-strain, dispersion, and Coulombic interactions.

However, such models often fail at capturing changes in atom connectivity. More recent approaches overcome this by including a bond-order formalism into potentials, allowing them to capture reaction chemistry more accurately without explicit quantum mechanical considerations.⁵³ Quantum calculations consider these quantum effect, and are therefore more accurate, however, they scale much more rapidly and can become too expensive to perform. It is therefore important to consider what level of accuracy is necessary, to find the best cost-accuracy compromise.⁵⁴

4.2 Irradiation Damage Modelling Applications

Yasuda *et al.*⁵⁵ conducted a MD simulation of electron irradiation targeted at single-walled carbon nanotubes. Their model consisted of a combination of empirical potentials: Tersoff-Brenner^{56–58} at short range and Lennard-Jones⁵⁹ at long-range. The Tersoff-Brenner potential captured all many-body effects and correctly predicts trends relating energy barrier height and position to reaction exothermicity. However, it fails in its description of weak non-bonding interactions. Yasuda *et al.* succeeded in capturing most physical properties that were experimentally observed accurately, such as electron sputtering, bending deformation, and dislocation. However, they failed to capture the mechanism for plastic deformation correctly.

Asayama *et al.*⁶⁰ also conducted MD simulation of an electron irradiation process using the same combination of empirical potentials, however they were interested in interactions with graphene. They were able to successfully capture the formation of three-dimensional structures from bilayer graphene, driven by electron irradiation. Their work also demonstrated the dynamics that occurs in single-layer graphene during beam cutting and single-chain formation.

Yasuda *et al.*⁶¹ further applied this potential model to study carbon nanotube-based oscillators and bearings under electron irradiation. They found that irradiation effected the period of oscillation, and could lead to malfunctions due to the formation of cross-links.

Jang *et al.*⁶² modelled carbon nanotube welding under electron beam irradiation using the many-body, reactive empirical bond-order (REBO)^{59,63,64} potential. Rebo extends the Tersoff potential to provide a more accurate treatment of the energetic, elastic, and vibrational properties of solid carbon and small hydrocarbons. Jang *et al.* predicted a significant degree of covalent joining but not complete merging of the crossed carbon nanotubes. They suggest that their model is a better representation of real electron-welded junctions, rather than models of 'ideal, epitaxial' junctions. Mechanical behaviour was also successfully captured.

Zhu *et al.*⁶⁵ modelled graphene nanoribbons under low-voltage electron irradiation. The interatomic forces were modelled using the many-body, adaptive intermolecular reactive empirical bond-order (AIREBO)⁶⁶ potential. This potential further includes an adaptive treatment of the nonbonding and dihedral-angle interactions, which still allows for covalent

bonding interactions. The group were able to capture the zigzag structures on the graphene nanotube edges which have been observed experimentally. They demonstrated that these are dynamically stable, and make electron irradiation an attractive technique for fabrication.

Rahnamoun *et al.*⁶⁷ modelled Kapton polyimide damage by electron beam irradiation. The interatomic forces were modelled using the reactive force-field (ReaxFF) potential.⁶⁸ ReaxFF employs a bond-order formalism in conjunction with polarisable charge descriptions to describe both reactive and non-reactive interactions between atoms, allowing it to accurately model both covalent and electrostatic interactions. Rahnamoun *et al.* demonstrated the experimentally observed behaviours of cross-linking, rearrangements, ring rupture, and radical formation. They further analysed mechanical properties which were in agreement with dynamic mechanical analysis.

Algara-Siller *et al.*⁶⁹ modelled electron beam engineering of singled-walled carbon nanotubes from bilayer graphene. They employed the bond-order Brenner empirical potential.⁵⁸ and were able to demonstrate the formation of alternate stacking pattern near bilayer edges that have been experimentally observed.

5. Future Outlook

There are a variety of electron beam modelling approaches within the literature, all looking at an array of different compounds and applications. However, it is still relatively unusual to see MOFs being the focus of such analysis. As such, their dynamics during electron beam irradiation is unknown and leaves a gap in both the literature, and the knowledge that experimentalists have at their disposal when addressing MOF resilience. Molecular dynamical modelling is key in progressing this field of research.

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