Circumventing Wear and Tear of Adaptive Porous Materials

Stefano Canossa,* Zhe Ji,* and Stefan Wuttke*

Dr. Stefano Canossa: EMAT, Department of Physics, University of Antwerp Groenenborgenlaan 171, B-2020 Antwerp, Belgium
e-mail: *stefano.canossa@uantwerpen.be*

Dr. Zhe Ji: Department of Chemistry, University of California–Berkeley Berkeley, CA 94720, USA
e-mail: *zheji@berkeley.edu*

Prof. Dr. Stefan Wuttke: Basque Center for Materials UPV/EHU Science Park, 48940 Leioa, Spain
e-mail: *stefan.wuttke@bcmaterials.net*

ABSTRACT: The assessment of the architectural stability of molecular porous materials is not yet a common practice, but critical to their understanding and development. The conformational adaptation of porous materials to guest binding and other chemical dynamics poses a risk of architectural damage, leading to performance deterioration during their prolonged usage. The deformation of the framework backbone and the disconnection of building units are driven by chemical, mechanical, and thermal perturbations, and can be quantitatively described by the term connection completeness. Analytical means that can be used to measure this parameter are presented in order to provide a standard, practical protocol for evaluating architectural damage made to framework materials. Preventive and remedial strategies are proposed for enhancing the architectural integrity of frameworks without compromising their functional mechanisms, paving the way to the design of robust yet adaptive materials. In this way, the discussion on architectural stability is initiated, and readers are encouraged to carefully characterize molecular porous materials for a better understanding of their structure-property relationship.

1. Introduction

Porous materials possess extensive interior for carrying out a wide variety of chemical processes in confined space. These include adsorption,[1–3] catalysis,[4–6] and ion transport,[7–9] during which the formation of new chemical bonds and the variation of intermolecular interactions constantly perturb the structure of the cavity itself. It is therefore necessary for the porous host to be adaptive to the structural stress present during these processes in order to function for multiple times. Being adaptive, however, requires the structure to become flexible enough to transform back-and-forth through multiple states of guest binding. This flexibility requirement typically compromises the robustness of the porous structure, e.g. catalytic pockets of enzymes cannot endure high temperature and can only work under a narrow window of conditions.[10,11] Structural failure is also to be expected when artificial pores made of polymers and supramolecular assemblies are subjected to repeated dynamics.

> **Adaptive porous materials** *are crystalline solids that can adapt to the changing chemical environment of their interior pores through structural rearrangement, which ranges from subtle structural distortion to substantial conformational change. The adaptiveness lies in their capability of adopting a stabilizing conformation upon internal chemical changes, without losing the overall connectivity between their building blocks.*

Reticular chemistry —stitching molecular building units into extended frameworks using strong bonds— has been creating a unique landscape of materials comprising metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), where robustness and adaptiveness synergize:[12–14]

the rigid backbone enables the dynamics of guests and tethered functionalities within the pore, with retention of frameworks' architectural stability and therefore permanent porosity.[15]

The architectural stability of framework materials, however, cannot always be simply presumed especially when large amplitude motion is involved and thus the structural stress imposed by the dynamic processes exceeds the limit of backbone stabilization energy. In fact, crystals of MOFs have been observed cracked and broken into smaller pieces, accompanied by a decrease in their performances (e.g., gas uptake in adsorption–desorption cycles), even under those conditions that the MOF structures are supposed to be chemically inert and thermally stable.[16,17] This type of structure damage has long been overlooked, might related to the lack of established characterization protocols, as opposed to chemical and thermal stability, which is examined almost every time a new structure is discovered. Another overlooked aspect is the ubiquity of structure distortion and adaptation, which are responsive to even subtle changes in pore environment, making architectural damage a common cause of material deterioration in prolonged use. To better evaluate and quantify this structural feature, here we define architectural damage as the loss in the number of connections between building units and introduce a parameter — connection completeness — for describing to what extent connection is removed from the ideal, fully linked structure. Such connection breakage between building units can have multiple origins. a) When the pores' chemical environment is altered by the introduction of a foreign species or an ongoing chemical reaction, the backbone enclosing this pore is then subjected to a continuous conformational change guided by the formation of new chemical bonds and interactions within the pore. b) Heat generated from neighboring regions can drive the dissociation of building-unit molecules before dissipating into the bulk media. c) Mechanical stress either applied externally or built up in a pore can be relaxed through bond breaking and further reduce mechanical resistance before reaching the point of collapse of the whole crystal. In all cases, the consequence of architectural damage can be displayed on the molecular level when the disconnection between building units is accumulated in specific regions (wear), which can propagate, overcome lattice forces, and cause macroscopic fractures (tear). In this contribution, we bring to the attention of the material science community the importance of evaluating architectural damage made to porous materials in their prolonged usage.

In the following sections, we present an overview of chemical, mechanical, and thermal origins of architectural damage and provide general guidelines for its thorough assessment, prevention, and remediation, in order to inform the design of robust and durable porous materials.

2. Origins of Usage-Induced Architectural Damage

At the atomic level, architectural damage consists of the breakage of chemical bonds connecting the building units of a material and the subsequent chemical or structural rearrangement. This process can be initiated by chemical, mechanical, and thermal causes, despite their expression on the final chemical stage being the same: local lattice deformation and distorted bond geometries favoring a consequent disconnection on the backbone. The chemical origin involves the formation of new bonds or intermolecular interactions which perturb backbone structure, either in a static state or through reversible, dynamic cycles. The mechanical stress breaks bonds by using entropic energy in releasing guests from a high pressure to a low-pressure region. Localized heat transfer in addition provides a thermal driving force to break the backbone.

2.1. Defective Adaptation to Guest Species

The internal pore surface of molecular porous frameworks forms a microscopic interface with guest molecules, giving rise to the macroscopic properties used in industrial applications.[18–22] The interaction exerted by the guest with the adsorption site perturbs the local environment of the host, leading to its instantaneous structural adaptation. This usually does not undermine the integrity of the guest, since its relative free motion allowed within the pore does not constrain the structural adaptation to its new states. On the other hand, the host material can have its internal bonds weakened by these interactions and their accumulation during the usage of the material can be architecturally destructive. There are three general scenarios in which a guest molecule can weaken or disrupt the backbone of its

host. In the first scenario, the guest replaces a building unit without fulfilling all its connectivity (Figure 1.1a). This is common to framework materials made of reversible linkage chemistry, where ligand substitution reactions or dynamic covalent chemistry can take place, as exemplified by replacing tetratopic carboxylate linker in PCN-521 by a tritopic linker, leaving an unconnected site.[23] Other than permanent disconnection, dynamic dissociation of building units can take place, facilitated by the temporary bonding of foreign ligands. It was revealed that the Zn^{2+} ions in MOF-5 bind solvent molecules, thereby increasing their coordination number and dynamically dissociating from the framework even at low temperatures.[24] Such dynamic behavior of building units inevitably exposes frameworks to a high risk of permanent damage. The second possible threat to frameworks' architectural integrity arises from the steric hindrance between guest and framework backbone (Figure 1.1b). When bulky molecules are incorporated into a pore through either adsorption or covalent attachment, the pore scaffold deforms accordingly and creates a disconnection when the original architecture cannot withstand the increase of local hindrance. This was observed in the case of replacing linkers in UiO-67 with those bearing a bulky fluorescein moiety, which barely fits into the octahedral pore.[25] The introduction of hindrance indeed led to a corresponding increase in the number of local defects, as revealed by fluorescence lifetime imaging. Steric repulsion induced architectural damage requires the energy debt in disconnection to be compensated by the gain in the adsorption of guest, if it is not prepaid by the covalent attachment of the bulky moiety to the scaffold in the first place. This type of architectural damage becomes more likely when the guest species lie in proximity to connection sites. The third cause for architectural damage is the conformational change of building units in response to framework–guest interactions (Figure 1.1c). This effect involves electron density redistribution within building units, as a result of parts of their structures being stabilized by guests through weak interactions (Van der Waals, π-stacking, hydrogen bonds, halogen bonds, etc.). The study of MOF structures using single-crystal X-ray diffraction (XRD) shed light to this effect. It was found that framework-solvent interactions, prominent at low temperature, lead to the bending of benzene rings within the linkers and thereby introduce disorder to the framework backbone.[26] Although the structural distortion can be relaxed at high temperatures in the studied system, a higher susceptibility of frameworks to architectural damage should be considered when stronger framework-guest interactions are engaged.

2.2. Irreversible Adaptation to Guest Dynamics

In above scenarios, we have discussed the impact of framework-guest interaction in a single step of guest binding (Figure 1.2). Most applications of porous materials, however, require the interconversion of the system between multiple binding states (e.g., in adsorption and desorption cycles), thus imposing a dynamic stress to the pore scaffold. Structures that are rigid enough to withstand any distortion by guests in a single event may not survive a continuum of changing stress, which can partially explain why some porous materials deteriorate in gas uptake upon prolonged cycling. These dynamic processes often entail a drastic change of pore environment in a short period of time, during which a complete structure adaptation is not fast enough to take place. As such, the resulting partial conformation change of pore scaffold provides a transient force to break connections in specific regions. It has been observed that applying abrupt pressure drop for activating porous materials (removal of interior solvent) can lead to structure collapse.[27–29]
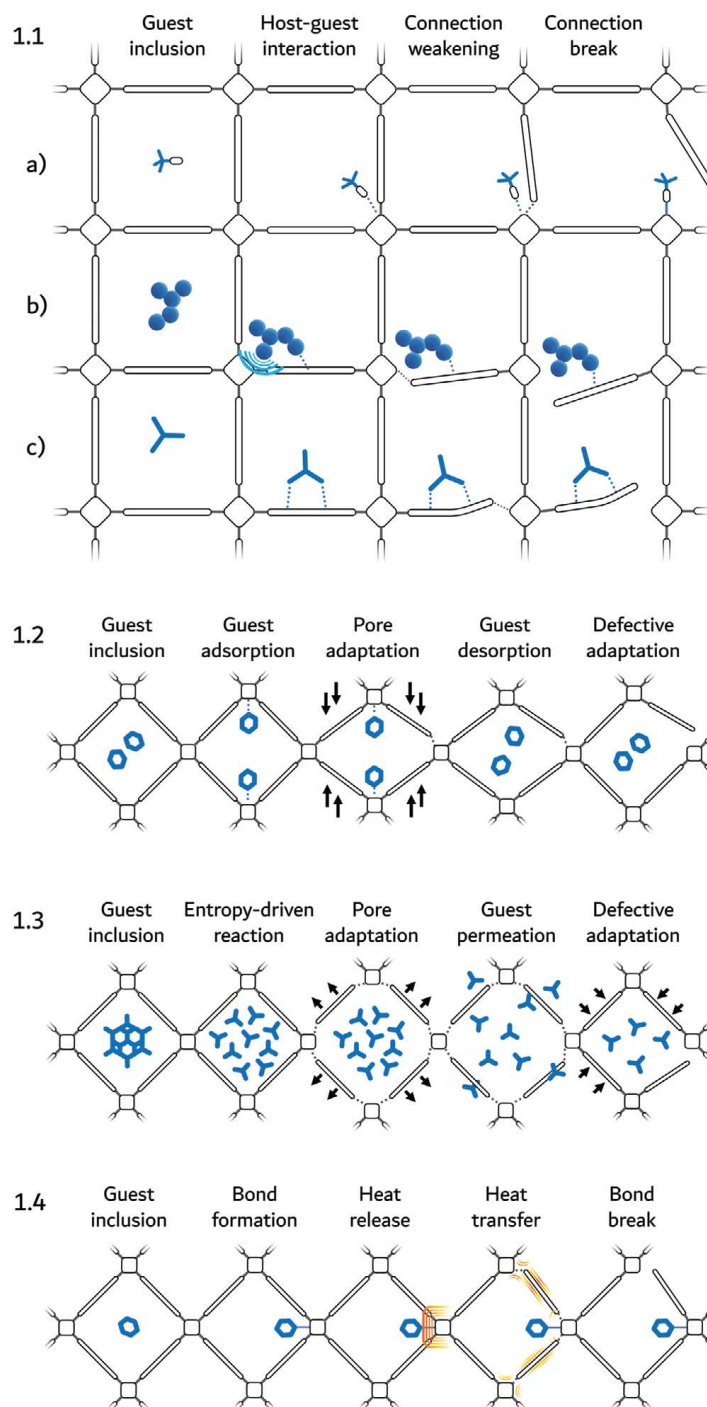
Figure 1. 1.1a–c) The origin of architectural damage formed in adaptive frameworks: defective adaptation to guest species, 1.2) irreversible adaptation to guest dynamics, 1.3) destructive relaxation upon pore pressure increase, and 1.4) localized thermal deterioration.

Connection completeness (κ) *describes the degree of architectural integrity of a framework structure in terms of the number of connections present for linking building units. This parameter is expressed as:*

$$\kappa = C/C_{max} \qquad (1)$$

where C is the experimentally determined number of connections (surface included) and C_{max} is the maximal number of connections the same type of structure can possibly have, when all the building units according to the perfect crystal structure are present and fully connected.

2.3. Destructive Relaxation Upon Pore Pressure Increase

A rapid change in diffusion pressure within pores, possibly as a result of an entropy-driven chemical reaction, requires fast mass transport across pore windows for instantly balancing any pressure difference between the pores. When the transport of guest molecules is sterically hindered or kinetically sluggish, pore "explosion" occurs, breaking backbone connections with the energy released from such entropy-driven processes (Figure 1.3). Accordingly, catalytically active sites with high turnover frequency should be considered as a potential threat to the architectural integrity of its pore scaffold. The collapse of such pores can in turn lead to low turnover numbers, even though the catalytic reaction itself is not chemically destructive.

2.4. Localized Thermal Deterioration

Heat generated from exothermic processes taking place within the pore can be transferred to local regions before fully dissipating into the bulk media. As such, chemical bonds, especially those involved in the linking of building units, are activated for dissociation, leading to partial disconnection of framework backbone even at temperatures well below the decomposition point. Therefore, a heat-releasing post-synthetic modification conducted to porous materials can cause architectural damage without being chemically incompatible (Figure 1.4). As of now the thermodynamics of MOFs has been widely explored and even resulted in the discovery of remarkable polymorphism phenomena, which were observed for the zeolitic imidazolate framework family.[30] However, to the best of our knowledge the adverse effect of thermal perturbation on the framework architectural integrity has not been addressed so far, thus remaining a speculative yet potentially important topic for future studies.

3. Aging Assessment: Experimental Tools for Analyzing Architectural Damage

In order to assess the evolution of architectural damage in adaptive porous materials, it is crucial to define a unique parameter which can be used as an indicator. All the categories of damage discussed above have one common trait: a decrease in the total number of connections between the building units of the framework architecture. These connections are considered part of the architecture only if they are in the interior or taking part in the building of its surface, whose contour forms a closed loop without missing connections (Figure 2). In this way, any connections belonging to a dangling linker on the surface is not considered and is not contributing to the calculation of architectural damage. For a given structure, the morphology and size of a framework single crystal define uniquely the maximum possible number of connections present between its building blocks, assuming no missing-unit defects or disconnections. In order to describe a given framework crystal with a specific number of defects, we introduce the concept of connection completeness. The decrease in crystal size of a polycrystalline powder is a special instance in which, for every crystal that breaks in two fragments, two shape-complementary surfaces are created, thus causing many building units to have fewer connections as they stop being part of the internal connection network of the material.

Since a polycrystalline powder can be affected by a high internal variability in crystallite size, morphology, and surface roughness, the quantification of the surface building units can be a real analytical challenge. For this reason, it may be advantageous to define the aforementioned connection completeness as absolute connection completeness and to complement its use with the more analytically available relative connection completeness (κR), expressed as the percentage ratio between the number of connections that exist in the material at a certain stage of its use and the number of connections at its first use.

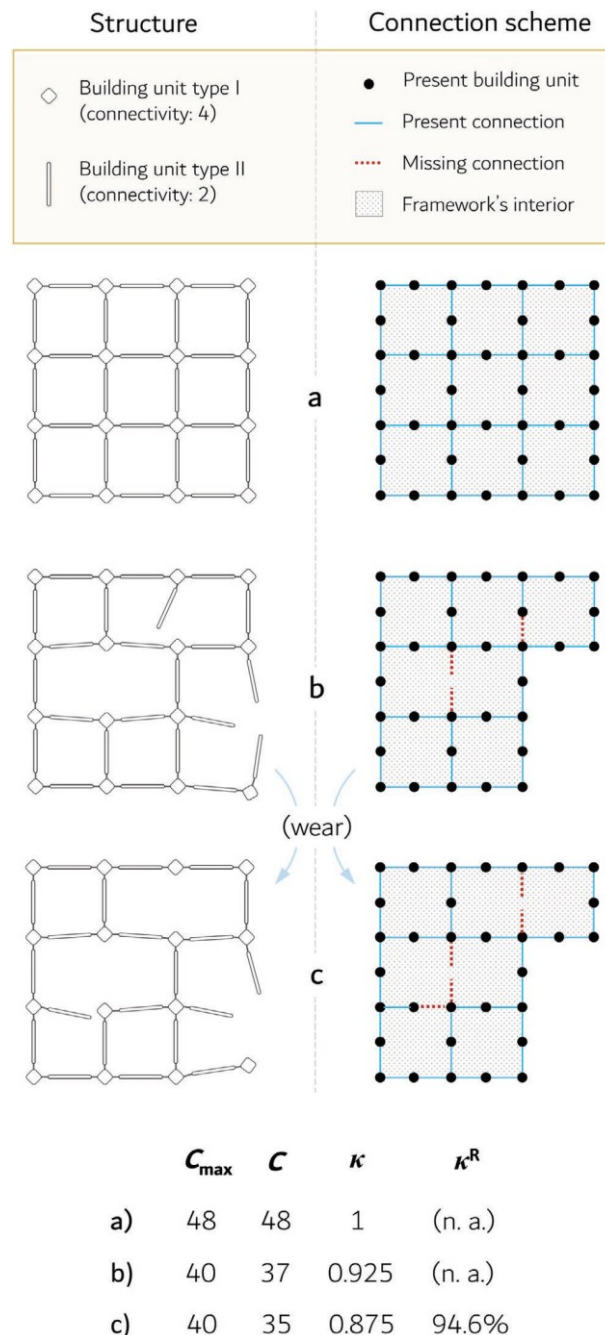|	C_{max}	C	κ	κ^R
a)	48	48	1	(n. a.)
b)	40	37	0.925	(n. a.)
c)	40	35	0.875	94.6%

Figure 2. Graphical representation of different scenarios in calculating connection completeness of a 2D framework: a) a perfect structure with no missing connection, b) a similar structure with three missing connections, and c) its situation after further deterioration. Below, the main values relative to connection completeness are displayed for each case. In b,c), the type I building unit at the bottom right corner is

considered as dangling pieces, excluded from the connection network, as it is not a part of the closed contour.

In general, the determination of κ requires well-planned analytical steps whose complementarity in terms of acquired information is crucial. In the following paragraph, we provide a general overview of how these analyses can be organized to obtain the two main values needed to determine κ: C_{max} and C (Figure 3). The identification of the first value requires the knowledge of the ideal complete structure of the material and the volume of the crystals. The first piece of information can be easily obtained by diffraction techniques such as XRD,[31] neutron diffraction (ND),[32] and electron diffraction (ED),[33] which are able to provide the average structure of crystalline materials with high precision. Once the crystal structure is obtained, the unit cell volume and the number of connections per unit cell can be easily derived and used to obtain the theoretical connection density ρC (number of connections per volume) of the ideally perfect crystal phase, as illustrated in the case of MOF-5 in Figure 3. As the next step, scanning and transmission electron microscopy[34,35] can be employed to obtain fine details about crystal size, morphology, and their distributions, while a combination of small angle X-ray scattering[36] and powder XRD (PXRD) can add valuable information to confirm the reliability of the outcomes of electron microscopy techniques. Once size and morphology have been determined, the volume can be readily calculated and all the values defining C_{max} are available. The identification of the actual, present connections, on the other hand, is a more delicate practice where the use of complementary analysis is particularly necessary. Two categories of analyses should be used at this stage: those that acquire information on the number of building units and those investigating the number of connections. The first set of analyses can be made using techniques that provide reliable compositional information such as inductively coupled plasma-optical emission spectroscopy or mass spectrometry,[37] elemental analysis, energy-dispersive X-ray spectroscopy,[34,38] X-ray fluorescence,[39] and nuclear magnetic resonance spectroscopy. Thermogravimetric analyses can also provide useful insight into the ratio between organic and inorganic building blocks, which can be compared with the other techniques. Structural analyses such as pair distribution function analysis (PDF)[40] and extended X-ray absorption fine structure analysis[41] can be an useful addition to the crystallographic model achieved by diffraction techniques (XRD, ED, and ND), as it can highlight cases where certain components are partially present or disordered in a mixed bonded/unbonded condition or provide information on the spatial correlations of the defects (PDF). As for the analysis of connections themselves, the most direct information can be obtained by using techniques that directly detect the presence of chemical bonds, such as vibrational spectroscopy techniques (IR, Raman). It is also possible to use digestion titration to quantify the number of bonds in the bulk material by breaking them and acquiring chemical information on the number of these chemical events—the number of consumed acid or competitive ligand corresponds to the number of existing connections in MOFs.[42] Since the occurrence of damage is directly related to the availability of specific chemical sites, another interesting quantification approach is defect-site titration. In this method, chemical species capable of reacting with defective sites can progressively react with the system until all the sites of interest are consumed (the equivalence point) and a specific optical or electrical response is triggered and detected. Another defective-site quantification method is to use chemical probes with strong affinity and precise response to their interactions with defective sites, which can be quantified by spectroscopic methods (fluorescence, UV–vis, and IR). In addition, when the evolution of damage is associated with a variation of the catalytic performance of the material, this can be used as an indirect tool for defect quantification. This approach consists of monitoring the yield of a certain catalytic conversion, which is directly affected, either positively or negatively, by the disconnection present in the framework.[43] One last parameter that can be investigated to understand the connection completeness of a real sample is crystal density. This value quantifies the absolute number of building units in a given amount of crystal volume, complementing the information regarding their relative amounts obtained from other characterization methods. For this purpose, the best available analyses are gas pycnometry,[44,45] mercury porosimetry,[46] and mass correlation spectroscopy.[47,48] So far, we have outlined a comprehensive

albeit not necessarily complete list of analytical techniques and stressed the importance of their complementarity in gathering different types of information. However, another important aspect to be considered is the representativeness of the acquired data. Indeed, highly accurate information can be obtained from samples with scarce statistical weight with respect to the bulk material, whereas bulk analysis often provides a view of the samples' overall status although lacking in the level of details. As an example, total-scattering single-crystal XRD affords an unparalleled precision for structure determination, but the transferability of the acquired information to all the other crystals in the material is unrealistic. Therefore, the use of PXRD is vital to compensate this drawback and to avoid drawing false conclusions regarding the structure of the bulk material. In conclusion, as information complementarity should always be the strategy of choice for scientific thoroughness, both precision and significance must be pursued especially when investigating complex aspects of materials such as connection completeness.
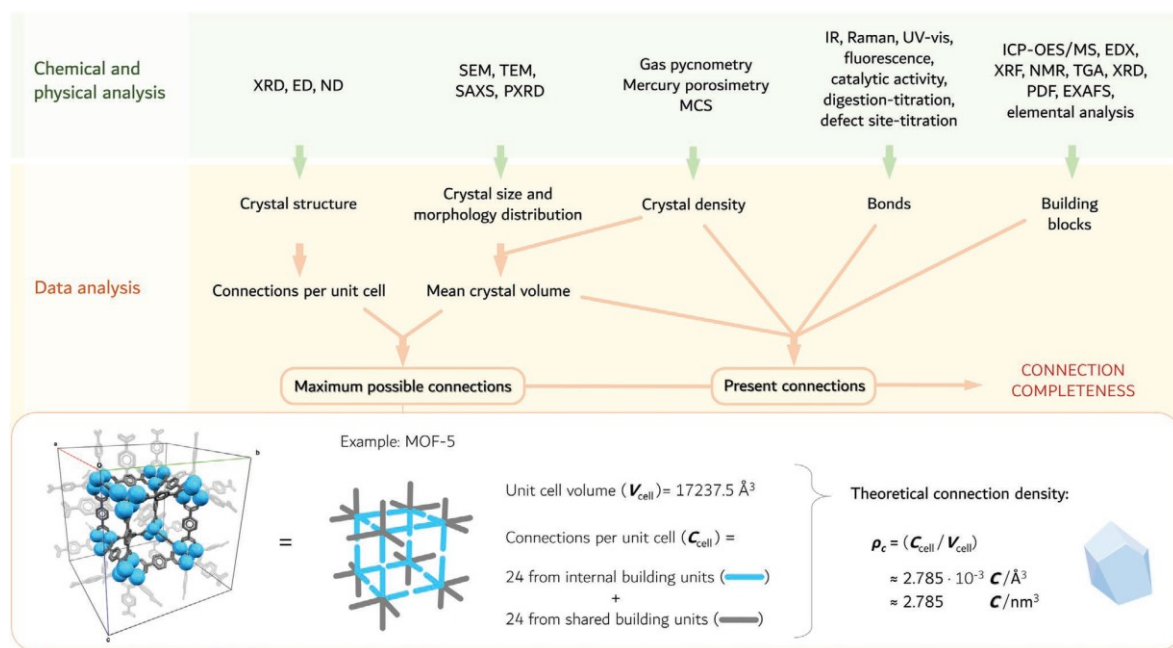

Figure 3. Analytical pathway to the determination of connection completeness. MOF-5[49] is used as an example to show how material's theoretical connection density can be derived as a simple ratio between the connections present in the unit cell and the cell volume.

4. Circumventing Wear and Tear

As more accurate analytical techniques are developed, we hope that our understanding of how damage in adaptive porous materials originates and evolves will improve as well. These advances will facilitate the identification of each material's structural weakness and foster new strategies to enhance post-wear structural resistance to further damage at the pore level. In this context, we define three main strategies for circumventing wear and tear in adaptive porous materials: prevention, self-maintenance, and correction. Deep, atomic understanding of damage in materials is critical to discern the origin of mechanical weakness and the development of new materials with improved mechanical stability, so that the formation of damage itself is disfavored. Since flexibility is a functional aspect of adaptive porous materials, the use of this preventive strategy requires careful evaluation of the trade-off between susceptibility to adaptation-induced damage and functional adaptiveness. For instance, the flexibility in the coordination number of a metal node can allow a very effective chemisorption of coordinating

guests but can also cause significant structural re-arrangement of the linkers that may induce harmful mechanical stress in the pore.[50] In such cases, it is useful to tailor the metal-linker combination in order to mitigate the distortion of the coordination geometry resulting from the change in the number of ligands.[51] Caution should be taken in this process to avoid undermining functional adaptiveness. For instance, the choice of a different metal can be advantageous for the above-mentioned remedy, but a lower guest-metal affinity would obviously lower the guest trapping performance. On the other hand, a decrease in the linker rigidity can improve the framework resistance to damage by enhancing its structural adaptiveness, but at the same time hampers the size-selectivity of the pores by making their opening more dependent on the chemical and physical conditions they are exposed to. Since the occurrence of damage cannot be completely prevented, it is important to consider also strategies to counteract or reverse its effects. To this end, it is desirable to create materials with self-maintenance mechanisms encoded in their functionalities. One strategy to create such a mechanism would be to introduce species capable of performing framework-specific "healing" reactions in the pores without compromising the function of the material. For instance, a linker molecule can be designed to react to its disconnection from the framework by adopting a configuration that favors the restoration of the broken connection. To create self-healing materials is undoubtedly a challenge, especially when considering that their functional behavior should be as unaltered as possible. Therefore, it is necessary to take corrective actions after the damage has been created. The analytical component in this strategy is crucial since not only the amount, but also the type and distribution of all connection faults need to be known in order to undertake appropriate corrective treatments. Once the overall structural damage of the material is assessed, the corrective treatment re-establishes the missing connections either chemically or thermally. In the first case, compounds are introduced to the cavities for structure healing. For example, adding extra linker molecules into the working solution of MOFs can bridge between unconnected metal clusters and thereby restore the lost connection.[52] Thermal stimuli, on the other hand, can be used when the framework is sufficiently stable to allow rearrangement of its components towards a higher connection completeness. As thermal energy can also damage the connections in the material, it is important to assess the trade-off between providing sufficient energy for the building units to re-arrange and reach their connection-favorable positions and preventing the heat from overcoming the bonding energy and leading to the framework deterioration. As the bonding between building units are typically reversible in MOFs, this energy input can enable the framework system to overcome kinetic barrier and arrives the thermodynamic minimum (fully connected). Given the advantages and challenges of these strategies, the ideal way to combat the formation and the presence of damage is to use a combination of preventive, self-maintenance, and corrective strategies that are compatible with each material.

5. Concluding Remarks

While the research of adaptive porous materials moves fast towards its future breakthroughs, wear and tear remain a constant and natural presence which defines their performance and limits their durability. The key to enabling disruptive real world applications of porous materials is to have a good understanding and description of their structural complexity and its consequences on their properties.[53] For this reason, we defined architectural damage, discuss its origin in the use of adaptive frameworks, and introduce connection completeness as a parameter for characterizing architectural damage during its evolution. After outlining the analytical pathway to the determination of connection completeness and its practical use, we categorize the strategies that can be employed to circumvent wear and tear in order to limit their occurrence. Thereby, with this essay we aim to provide material scientists with the awareness and methodology necessary to use these strategies for designing robust functional materials in a variety of applications. Most importantly, we foster the emergence of a widespread and meticulous attention to the analysis and remediation of architectural damage, which will lead to an improved understanding of the underlying mechanisms and to better methods for its treatment.

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