Virtual Networks for Mechanically Robust MOFs

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A new way to assess and predict the mechanical stability of metal–organic frameworks by incorporating virtual networks is reported.

One of the prerequisites for the development of materials for practical applications is their mechanical stability. Now a molecular simulation group led by Berend Smit reports the rationalization of metal–organic frameworks (MOFs) with the focus on their mechanical stability. This work establishes a possible correlation between the macroscopic properties of MOFs, their bonding topology, and functional groups, which gives an insight into the assessment and prediction of mechanical stability of MOFs based on their crystal structure.

Marked by the measurement of the first gas adsorption isotherm that revealed their extensive internal surface area, MOFs emerged as a promising class of porous crystalline materials. In the last two decades, the number of developed MOF structures has grown to over 20 thousand, reflecting the expanding variety of available organic linkers and functional groups and a large number of topologies, including those that have not been achieved in zeolites and other porous crystals.

MOFs are extremely efficient in storing and separating gases such as methane, hydrogen, and carbon dioxide, resulting in their commercialization and mass production at the multiton scale. However, their mechanical stability remains a long-standing challenge in their design and application. Unlike the frequently discussed and assessed chemical stability of MOFs, studies on the mechanical stability of MOFs (e.g., how hard it is to deform them) are relatively rare. This gap could be due to the lack of general correlation between the microscopic structure of MOF crystals and their macroscopic-level mechanical properties.

Smit and co-workers used computer simulations to generate MOF structures with various functional groups and compared their calculated mechanical stability (Figure 1). Although these functional groups do not form the backbone of the frameworks, the proper introduction of these functional groups forms a “virtual” secondary network with nonbonded interactions in the framework structure, leading to increased mechanical stability of the entire structure. The presence of methyl and nitro groups at the C(2) position in imidazole linkers drastically improves the stability of MOFs against shear forces. The contribution from the virtual network is more substantial than that from the primary network in both bulk modulus and shear modulus of these MOFs. The impact of topologies is also important: a change in topology leads to a more than 3-fold increase in Young’s modulus (the ability to tolerate stretching). The virtual network mimics the pillars and caryatids in the ancient Greek architecture that provide additional support for the pediment (Figure 1).

Published: June 20, 2018

First Reactions

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For the first time, the role of the functional groups, rather than the backbone of MOFs, was revealed and discussed, which provides insight into the future design of MOFs with better mechanical properties. Systematic studies screening all possible functional groups will provide a more accurate assessment of, or reveal more details about, the correlation between molecular structures and the macroscopic properties of MOFs. In the specific case of zeolitic imidazolate MOFs, the distance between the functional groups is short, and thus the effect of functional groups is more noticeable. Therefore, it would be interesting to show possible correlations and applicability of similar simulation methods for MOFs based on carboxylate linkages.

Another aspect that could be further explored involves the recent introduction of multiple functional groups into one single crystal to generate multivariate MOFs. Due to the synergy between the functional groups, these new MOFs showed enhanced gas separation efficiencies and catalytic performances. In addition, because there are several scenarios in the spatial arrangements of these functional groups, their arrangement is critical for the enhancement of both physical and chemical properties of these MOFs. Theoretically, each scenario will produce a unique “virtual” network with different mechanical stability. These MOFs with multiple functional groups stand as good platforms for the illustration of the power of these “virtual networks”.

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