

Gas Absorption and Pore Breathing of Metal-Organic Frameworks Studied Using *in situ* Environmental Transmission Electron Microscopy (ETEM)

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Metal-organic frameworks (MOFs), a class of periodic mesoporous nanomaterials, exhibit promising small molecule adsorption properties for gas storage/separation, comparable to those of zeolites [1]. However, little is currently known about the fundamental mechanisms involved in functional gas absorption/release (“pore breathing”) behavior of these nanostructures, which limits our ability to controllably design and bulk-produce MOFs that are optimized for specific gas storage or separation applications. The bulk gas-storage capacity and kinetics of uptake/release of porous materials, including MOFs, are routinely screened using bulk gas adsorption analysis, such as breakthrough analysis and dynamic loading, supported by (bulk) powder X-ray diffraction (PXRD) [2,3]. However, these techniques cannot reveal the underlying molecular-scale mechanisms that give rise to the observed bulk gas storage properties. At the fundamental level, gas adsorption(/release) into a mesoporous nanostructure is a molecular transport and lattice rearrangement phenomenon, and must be studied at this length scale (angstrom/nano-scale). *In situ* Environmental (E)TEM studies, which monitor and characterize nanostructures in gas/vapor environments, can provide unprecedented insight into the fundamental molecular transport and structural transformation processes directly related to bulk properties of gas-storage/release.

In this work [4], we have used *in situ* ETEM characterization (TEM imaging and diffraction) to study a prototypical breathing MOF, MIL-53(Cr), which is known to store-and-release H₂O molecules when cyclically heated and cooled in a water-vapor environment, but where the details of this breathing process, or the extent of storage-and-release, are not known. By acquiring *in situ* ETEM diffraction patterns and low-dose images of a single-crystalline MIL-53(Cr) nanoparticle during heating-cooling in water-vapor (Figure 1), and correlating these experimental data with molecular dynamics (MD) simulations of the MIL-53(Cr) lattice at the same environmental conditions, we were able to precisely determine the number of water molecules adsorbed-desorbed during reversible breathing cycles, and identify the mechanism of activation of the structure that occurs during the first heating (calcination) step. The MIL-53(Cr) breathing process (in H₂O-vapor) is initially primed by the removal of H₂bdc (residual solvent from the synthesis) from the MOF’s pore channels when lightly irradiated by the e⁻ beam in UH-vacuum (Figure 1a), with no lattice change or gas absorption following the introduction of H₂O vapor at room temperature (Figure 1b). When the MOF is heated to 300 °C (Figure 1c), 1 H₂O molecule per unit cell is adsorbed into the pore channels (change in lattice structure and diffraction pattern), and when cooled back to 27 °C (Figure 1d), an additional 24 H₂O molecules (per unit cell) are adsorbed in the pores (further change in lattice structure and diffraction pattern). This breathing transition between 1 and 25 H₂O molecules is reversible by heating-cooling cycling. Adsorption of a single water molecule per unit cell during the first heating step to 300 °C activates the breathing effect, transitioning the lattice to accommodate up to 25 H₂O molecules when subsequently cooled and cycled (heating-cooling). The ETEM-MD approach that we have

employed in this study establishes an experimental method to precisely characterize the gas absorption-release in individual nanostructures at the nanoscale, and should serve as the foundation for additional studies of other MOF systems and nanoporous materials using a similar approach (*in situ* ETEM correlated with MD simulation) [5].

References:

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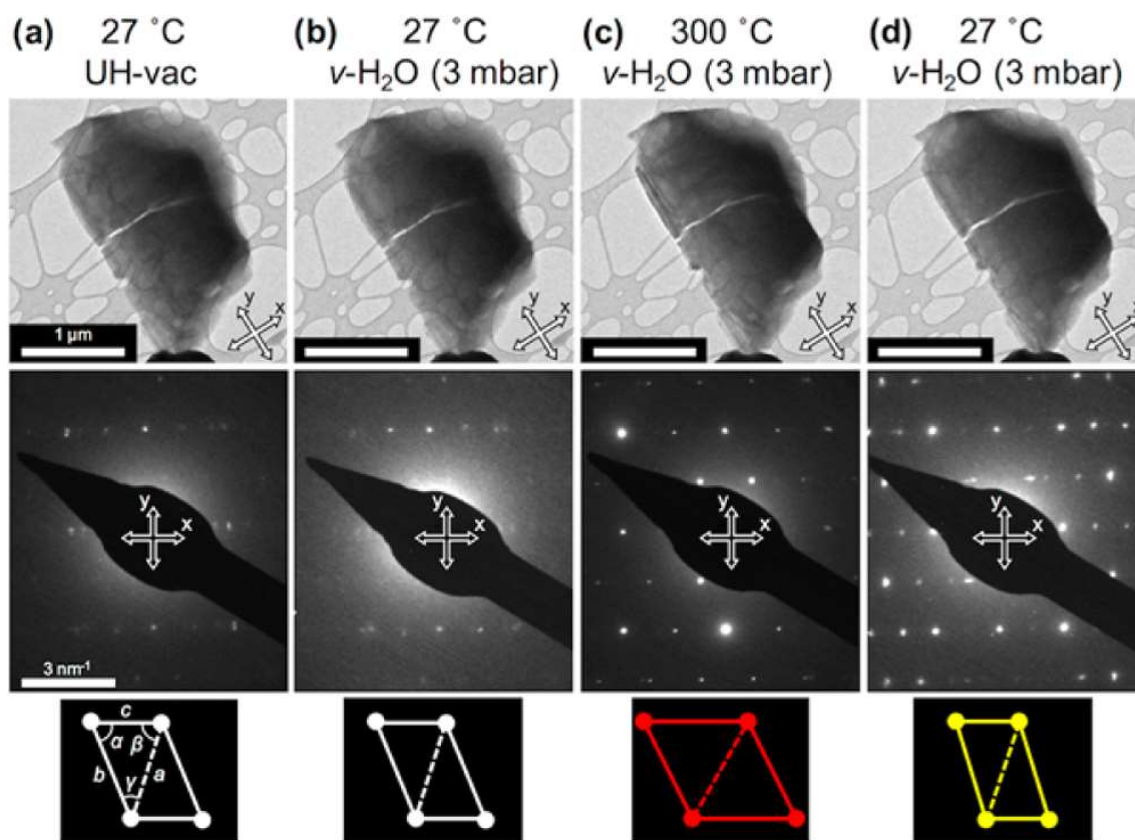


Figure 1. *In situ* ETEM images (top row) and diffraction patterns (middle row) of one MIL-53(Cr) nanocrystal on the [322] zone axis at four different environmental conditions during breathing; (a) 27 °C and UH- vacuum, (b) 27 °C and water vapor (“pre-activation”), (c) 300 °C and water vapor (“calcinated”), and (d) 27 °C and water vapor (“post-calcination”). The bottom row illustrates the MOF’s lattice transions in diffraction space viewed on the [322] zone axis. (Figure reproduced from ref. [4])