Unveiling adsorption distribution in a metal–organic framework crystal with 3D XAFS-CT mapping

Metal-organic frameworks (MOFs) are crystalline solids with nanosized pores, formed by infinite linkages between metal ions and organic ligands. Their design flexibility, ease of synthesis, and periodic structures make them ideal adsorbents. Understanding MOF adsorption behavior is crucial for developing new functionalities. While X-ray diffraction (XRD) has clarified molecular-level behaviors within unit cells, meso- and macro-scale properties in MOF crystals remain unresolved. Meanwhile, studying transient states during adsorption, including surface adsorption, diffusion, and pore filling, is particularly challenging as XRD averages spatial and temporal information, making it unsuitable for capturing local heterogeneities.

Recent advances in hard X-ray imaging, such as XAFS-CT, enable 3D visualization of mesoscale behaviors and local chemical states, revealing defect structures in MOFs [1]. However, studies so far have focused on static heterogeneities, failing to capture dynamic adsorption processes. Here, we use 3D XAFS-CT imaging to visualize adsorption distribution across entire single MOF-74-Co crystals [2].

For XAFS-CT measurements, MOF-74-Co, featuring hexagonal one-dimensional pores and exposed metal sites, was selected (Fig. 1(a)) [3]. Pillar-shaped single crystals were prepared, treated with methanol, and desolvated under vacuum. Bulk crystallinity and porosity were confirmed by powder XRD and nitrogen adsorption isotherms at 77 K. The water adsorption isotherm at 298 K showed a stepwise profile, with a saturated capacity of 4.85 H_2O molecules per Co ion, consistent with reported structures (Fig. 1(b)). Isosteric heat of adsorption indicated strong host–guest interactions for up to one H_2O molecule per Co ion. Co *K*-edge XAFS spectra, sensitive to hydration, revealed a significant increase in white-line height at 7717 eV during hydration (Fig. 1(c)).

In situ XAFS-CT measurements were conducted under controlled water vapor pressures at SPring-8 **BL36XU** (Fig. 2). Crystals in a glass capillary connected to a vacuum/vapor control line were scanned around the Co *K*-edge. 2D transmission images were captured at 181 angles in 1° increments. Original 2048 × 2048 pixel images were binned to 512 × 512 to enhance the signal-to-noise ratio. XAFS spectra were analyzed via linear combination fitting (LCF) using dehydrated and hydrated Co spectra as references. Reconstructed 3D images provided voxel-level Co density and hydration ratio (hydrated Co/all Co) information with a voxel resolution of 0.995 μm³ (Fig. 3).

Co density, proportional to the number of Co ions per voxel, remained constant regardless of vapor pressure, but inhomogeneity was observed at the tapered edges, linked to micro-displacements during adsorption/desorption. This inhomogeneity corresponded to local crystallinity disorders.

Figure 3(c) shows 3D maps of Co hydration ratio across the particle. At low vapor pressure, the crystal

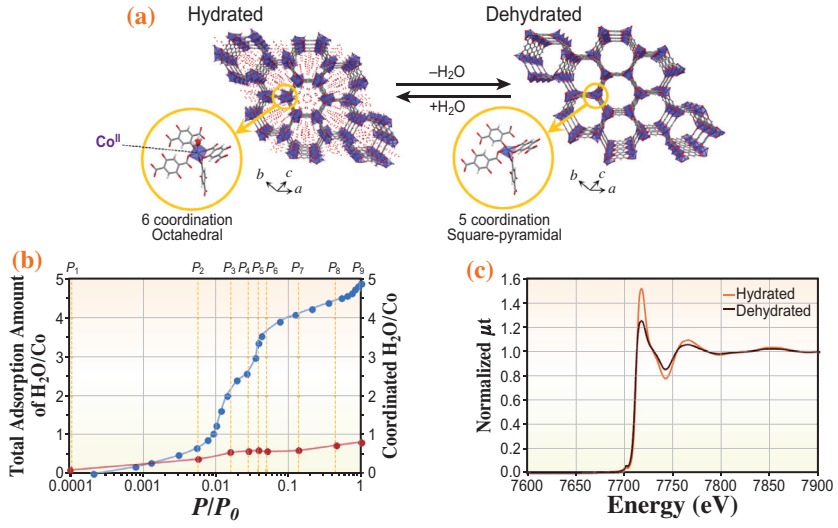

Fig. 1. **(a)** Crystal structures of MOF-74-Co in the hydrated and dehydrated states. **(b)** H_2O adsorption isotherms of bulk MOF-74-Co at 298 K (blue plot). P_1–P_9 on the upper axis indicate the relative pressures at which the XAFS-CT measurements were carried out. The red plot is the coordination adsorption isotherm of the Co ion, derived from XAFS-CT analyses. **(c)** Co *K*-edge XAFS spectra of MOF-74-Co in the hydrated and dehydrated states. [2]

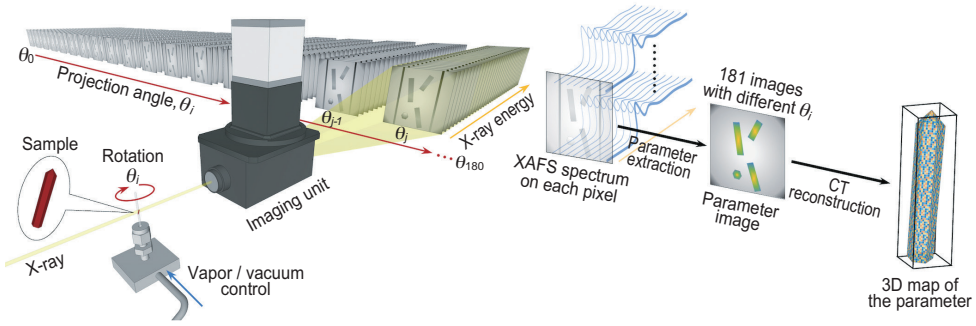

Fig. 2. Schematic illustration of the XAFS-CT method to obtain three-dimensional spatial distributions of adsorption states in a single crystalline particle. [2]

appeared entirely blue, indicating minimal hydration. At P_2, water molecules began coordinating with Co, significantly changing the hydration distribution. By P_3, red regions emerged at the center. From P_4 to P_7, hydration distribution stabilized, and near saturation pressure, the particle turned red or pale pink, indicating saturation at exposed Co sites. The histograms quantitatively illustrate H_2O coordination within the particle. The mean hydration ratio across voxels represents the average H_2O coordinatively adsorbed per Co ion. Plotted with the bulk isotherm (Fig. 1(b)), it revealed competition between coordination and non-coordination adsorption. Between P_1 and P_4, coordinated H_2O increased gradually but remained at 0.5 H_2O/Co by P_3, even as total adsorption reached 2.0 H_2O/Co. From P_4 to P_7, bulk adsorption rose rapidly to 4.0 H_2O/Co, driven by H_2O–H_2O interactions, while coordination adsorption stayed constant. Eventually, both coordination and physisorption saturated, completing hydration.

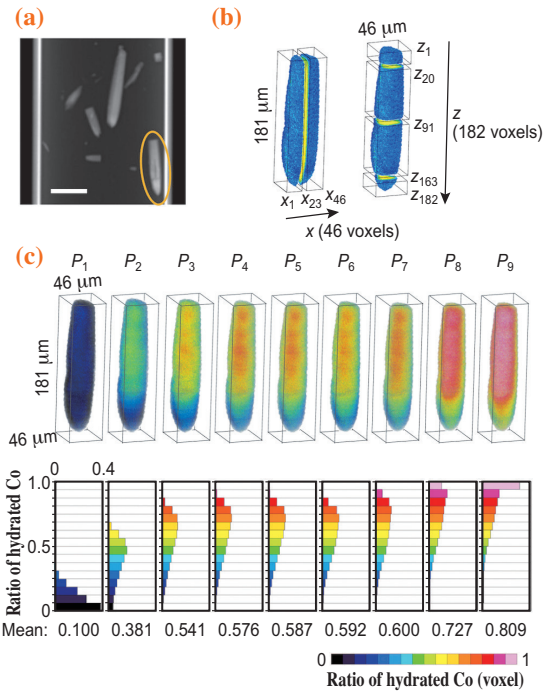

Fig. 3. **(a)** X-ray absorbance image of MOF-74-Co crystals in a capillary with a 100 μm scale bar. **(b)** 3D reconstructed image of Co density of the particle, showing the voxel coordinates and the cross sections of interest. **(c)** 3D distribution map of the Co hydration ratio with voxel transparency of 75%. Below are the histograms of relative frequencies of the voxels classified with the Co hydration ratio in each voxel. The values in the histograms are the mean values of the Co hydration ratio. [2]

Microbeam X-ray diffraction at SPring-8 **BL40XU** confirmed single crystallinity throughout the particle, with consistent lattice parameters matching reported MOF-74-Co structures. However, diffraction spots at the edges were broader than those at the center, indicating reduced crystallinity and increased orientational disorder. The mosaicity parameter at the edge was larger than at the edge, highlighting significant local differences while preserving the overall structure.

In conclusion, 3D visualization of Co hydration revealed heterogeneous H_2O affinity within MOF-74-Co crystals, particularly at the edges where reduced crystallinity affected adsorption. These findings emphasize the importance of local crystallinity in determining adsorption properties. While ideal particles exhibit uniform adsorption, XAFS-CT imaging and microbeam diffraction captured true heterogeneities, offering critical insights for optimizing MOFs as functional materials.

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