Insights on new gas sorbents from in situ X-ray scattering and density functional theory

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By combining in situ scattering measurements at the Advanced Photon Source (APS), [1] namely microstructural characterization using ultra-small-angle and small-angle X-ray scattering (USAXS, SAXS) and structural characterization using wide-angle X-ray scattering (WAXS) including X-ray diffraction (XRD), all under various gas/pressure/temperature conditions, with density functional theory (DFT) calculations, key insights were drawn for CO_2 sorption behaviour in a 1-dimensional (1D) porous coordination polymer (PCP): catena-bis(dibenzoylmethanato)-(4,4'-bipyridyl)nickel(II), denoted NiDBM-Bpy. It was shown that the 1D NiDBM-Bpy chains are held together by van der Waals forces and sorbed guest molecules preferentially occupy the spaces between the chains. The flexible structure variation was measured as a function of gas pressure, composition, and temperature, with both mixed gas flow and supercritical CO_2 regimes explored experimentally. It was further shown, when the precise structure varies with guest sorbate molecules, and may not even be fully known, DFT models of energy level can be used to predict gas sorption effects and structure changes indicated by XRD pattern variation. By comparing XRD pattern predictions with the corresponding experimental results, different scenarios could be selected or ruled out, thus providing insights on structures not available directly from single-crystal XRD studies under gas pressure conditions of interest. Meanwhile, corresponding USAXS/SAXS studies revealed microstructure motifs associated with organization of adsorbed CO_2 molecules within void spaces of the NiDBM-Bpy structure over extended length scales.

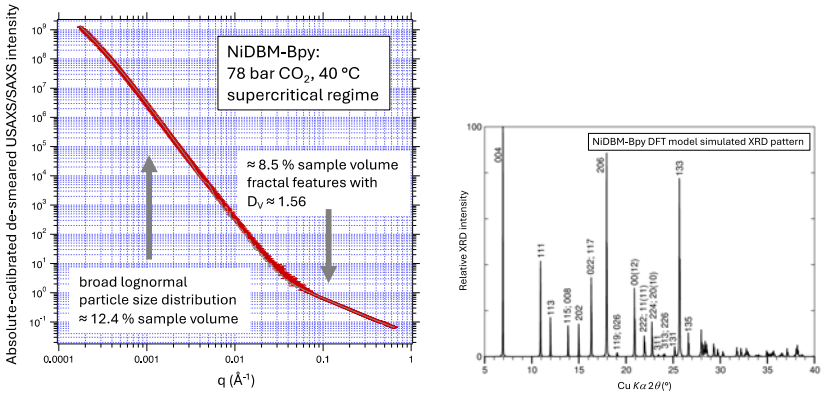

Figure 1. (a) USAXS/SAXS data with microstructural motifs. (b) Simulated XRD of DFT structure model with excellent fit to data.

These studies build on previous work on this and simpler, related materials [2-5], but now show potential for supporting optimized materials design for new sorbents using artificial intelligence (AI) approaches by providing critical "learning" datasets for connecting structure to gas sorption performance.

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