Structural basis of CO_2 adsorption in a porous metal-organic framework material

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There is continued and sustained research interest in developing a better understanding of the properties of flexible porous coordination polymer (PCP) or flexible metal-organic framework (MOF) materials, especially those relevant to their selective gas adsorption capabilities [1]. Such interest is based on the potential of PCPs or MOFs to address commercial needs for molecular sorption and sensing, enhanced gas recovery, carbon mitigation, and other gas storage applications. While many MOFs are not found to change in structure significantly when guest solvent or gas molecules are adsorbed or desorbed, several porous flexible MOFs have been discovered that exhibit reversible structural transitions between nanoscale low-porosity and high-porosity states during the adsorption and desorption of gases. Such structurally-dynamic flexible MOFs can show adsorption isotherms characterized by step-shape features where the pore system opens to accommodate the guest molecule. Below the step, little adsorption occurs, while the physical process at the step can be described to as a "gate opening" event [2]. Another important aspect of the sorption isotherms is that the desorption branch frequently exhibits hysteresis with respect to the adsorption branch of the isotherm. The temperature and pressure conditions that lead to gate opening can vary significantly for different guest molecules. In soft porous crystals, it is also possible to have behavior that is far more complex than a simple guest-induced gate opening, such as "breathing" effects with multiple steps in the adsorption and/or desorption branches of the isotherm. Meanwhile, the frequently observed hysteresis in the isotherm curve can be exploited as a basis for separating different gas species having different adsorption or desorption threshold pressures.

Using a representative porous, flexible, metal-organic framework (MOF) material, Ni(1,2-bis(4-pyridyl)ethylene)[$Ni(CN)_4$] (NiBpene or PICNIC-60) as a model system, we describe the structural basis for its CO_2 adsorption. NiBpene exhibits a CO_2 sorption isotherm with characteristic hysteresis and features on the desorption branch that can be associated with discrete structural changes [3,4]. Various gas adsorption effects on the structure can be demonstrated for CO_2 with respect to N_2, CH_4 and H_2 under static and flowing gas pressure conditions. We used a combination of crystal structure determination and density functional theory (DFT) to investigate the structural transitions during adsorption and desorption. Possible enhancements of CO_2 gas adsorption under supercritical pressure conditions are also presented, together with the implications for future exploitation. *In situ operando* small-angle neutron and X-ray scattering (SANS and SAXS), neutron diffraction (ND), X-ray diffraction (XRD) and wide-angle X-ray scattering (WAXS), under relevant gas pressure and flow conditions, are discussed with respect to previous studies [4,5,6], including *ex situ*, *a priori* single-crystal XRD structure determination. The results show how this porous, flexible MOF material responds structurally during CO_2 adsorption, single or dual gas flow results for structural change remain similar to the static (Sieverts) adsorption case, and supercritical CO_2 adsorption results in enhanced gas uptake. Insights are drawn for this representative flexible MOF with implications for future porous, flexible MOF sorbent design [7].

References

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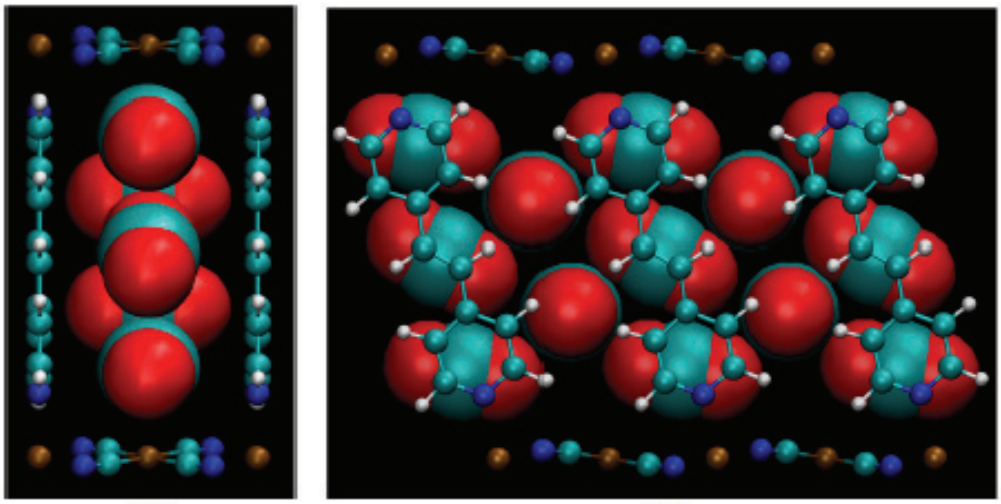

Figure 1. Predicted geometry of CO_2 and pore morphology at loading of 5 CO_2 per Bpene, projected along (a) the ab plane; (b) the ca plane. CO_2 molecules magnified for clarity. Element key: gold = Ni, white = H, blue = N, green = C, red = O.