ESRF report for experiment CH3368 at Beamline ID31

Gas-Induced Structural Transitions in Metal-Organic Frameworks

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Introduction.

One of our principal areas of research focuses on the capture and removal of carbon dioxide (CO_2) and sulphur dioxide (SO_2) by recently developed porous metal-organic frameworks (MOFs).[1] MOF materials are porous frameworks constructed from metal ions or clusters bridged by functional organic ligands. Capture and storage of CO_2 in MOFs is potentially of great significance in the development of the "Low-Carbon Economy" and thereby in the mitigation of global warming. However, the CO_2 adsorption capacities in MOFs under dynamic conditions have remained insufficient for practical applications, and strategies to enhance CO_2/host interaction and hence adsorption capacity are required.

In this study, we have investigated factors which control the capture capacity of CO_2 and SO_2 from gas mixtures under dynamic conditions and studied framework phase changes under different sample environments. We had previously established the crystal structures of two solvated framework materials (SOF-2 and NOTT-203) from single-crystal diffraction methods, and these materials show highly unusual gas uptakes with stepwise adsorption and hysteretic desorption isotherms. However, it is only by carrying out *in situ* powder X-ray diffraction measurements at ESRF Beamline ID31 that we have been able to probe the interaction between adsorbed gas molecules and framework material and to study changes in the local framework structure upon guest inclusion.

Experiment.

Monochromatic beam (λ = 0.495809 Å), high resolution detector, Cryostream cooler, *in situ* sample cell, gas loading/controlling system, data collection in capillary mode

Results and discussion.

Part I. *In-situ* PXRD study of the microporous supramolecular framework SOF-2

We recently synthesised a new hydrogen-bonded organic framework material (denoted as SOF-2) from a polyamine-functionalised ligand. The solvated crystal structure (Fig. 1) has been determined by single crystal methods. The ligand co-crystallises with the solvent molecules *via* hydrogen bonding, forming a three-dimensional extended framework structure which incorporates large structural voids. Significantly, the desolvated material is stable upon removal of guest solvent molecules as suggested by the TGA and PXRD, and therefore generates permanent micropores which have the potential to capture gas molecules.

The CO_2 adsorption isotherm at 196 K exhibits two steps coupled with a small degree of hysteresis upon desorption. At high temperatures (273 K and 283 K), the adsorption/desorption hysteresis loop shifts to a high pressure region (10-16 bar), but with similar uptake capacity. The CO_2 gas-specific isothermal sorption profiles observed at 196 K suggest the presence of a breathing process featuring a structural phase transition between two forms of this material, namely a narrow pore (***np***) form and a large pore (***lp***) form. The additional uptake of CO_2 is, therefore, due to the gas-specific framework breathing from ***np*** to ***lp*** to provide additional accessible pore volume. This phase change is triggered by a specific CO_2 gas uptake of ~1.5 mmol/g.

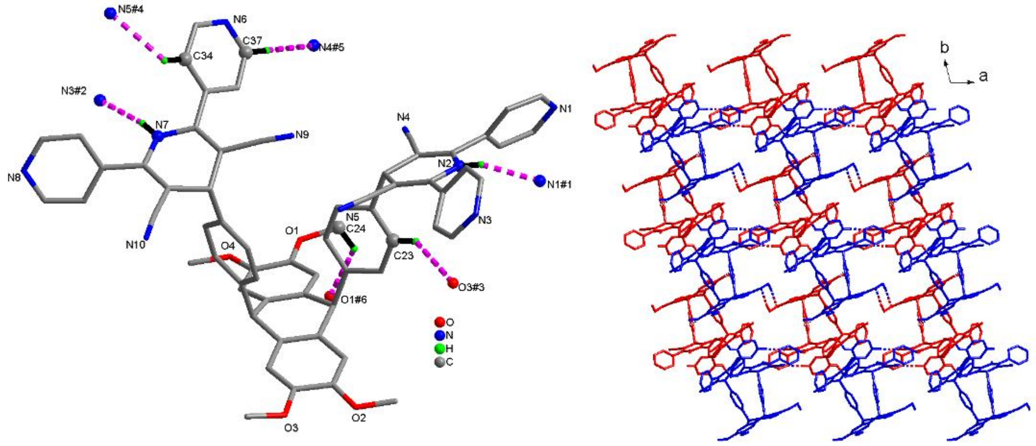

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Figure. 1 Views of the X-ray crystal structure of SOF-2. (a) View of the asymmetric unit for SOF-2; (b) view of the framework structure along the crystallographic *c*-axis.

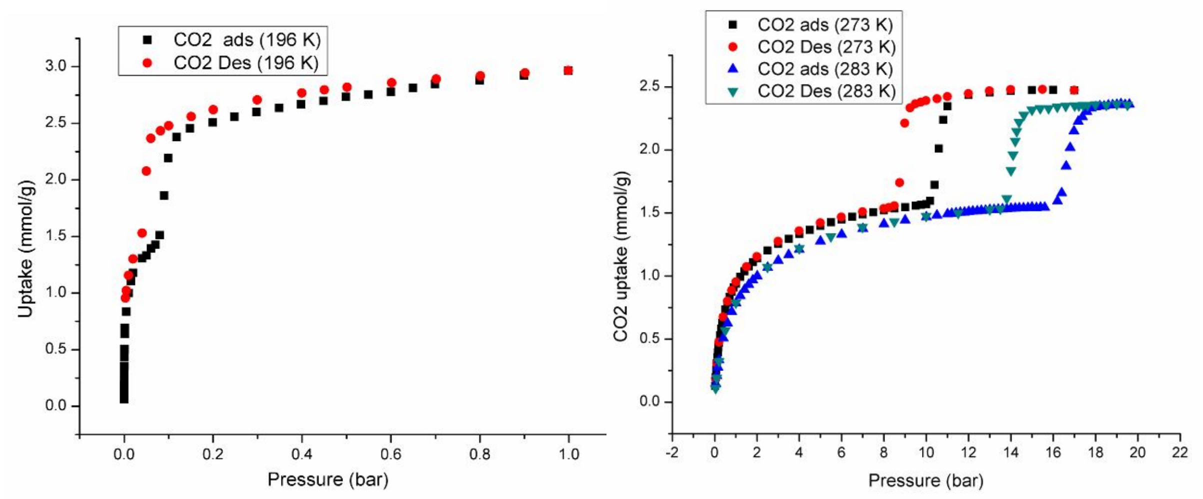

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Figure. 2 CO_2 isotherms at 196 K (a) 273 and 283 K (b) for desolvated SOF-2.

To further understand the mechanism of the phase transition, we carried out an *in-situ* PXRD study of this material on Beamline ID31 at ESRF. *In-situ* powder diffraction studies at various CO_2 pressures (0-20 bar) were carried out at 195 K to track the framework breathing behaviour during the adsorption/desorption process. The powder patterns of solvated SOF-2 and *in-situ*-desolvated SOF-2 were recorded at 273 K at 0, 4, 10, 14, 20, and 25 bar of CO_2 adsorption loadings and at 9 and 4 bar of CO_2 desorption loadings (Fig. 3). Powder diffraction patterns from the bare material (0 bar) confirms that the framework remains intact after degassing, and no apparent peak change was observed at 10 bar CO_2 loadings, confirming retention of the original ***np*** phase at low pressure. At CO_2 pressure of 14 bar and above, shifting and splitting of peaks were observed in the diffractograms, confirming a structural change and the presence of the ***lp*** phase at high pressures. The powder pattern for the final degassed material confirms the disappearance of these new peaks and shows the presence of the original ***np*** phase, confirming the reversibility of this breathing process. These results are entirely consistent with the CO_2 isotherms at 273 K and thermodynamic analysis, strongly supporting the proposed gas-specific change on pore structure.

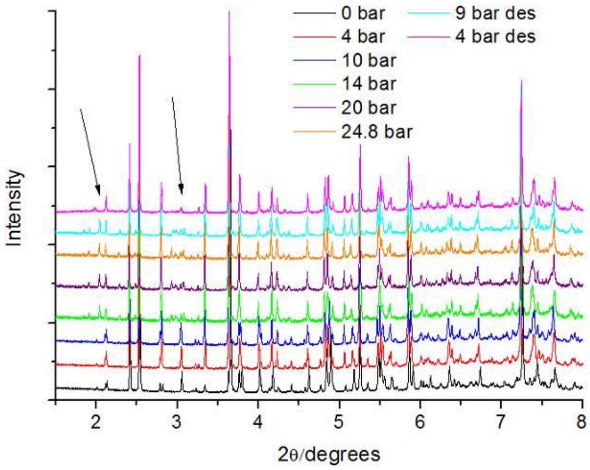

Figure 3. High pressure *in-situ* PXRD patterns for SOF-2 at 273 K.

Part II. SO_2-induced framework breathing behaviour in the flexible MOF NOTT-203

We have synthesised an indium-carboxylate MOF material (denoted as NOTT-203). The crystal structure for the as-synthesised material has been determined by single crystal diffraction methods. It shows a (4,4)-connected 3D framework structure with pore diameter of 1.5 nm (Fig. 4). The as-synthesised material undergoes a framework phase transition upon desolvation, and the crystal structure of the desolvated material has also been obtained by single crystal diffraction methods, confirming the flexibility of this MOF material.

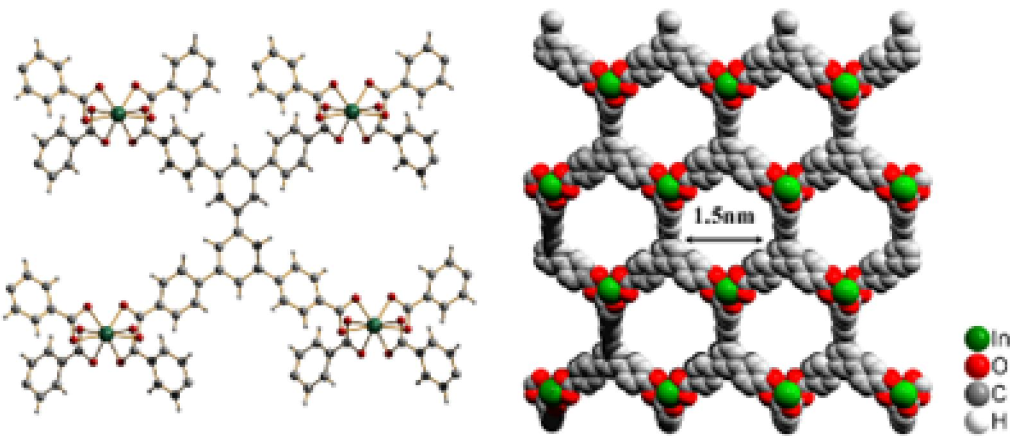

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Figure 4. Views of (a) the coordination environment of the $[In(O_2CR)_4]$ node; (b) the (4,4)-connected diamondoid network for NOTT-203.

The desolvated material shows interesting SO_2 sorption isotherms with two-adsorption steps and a broad hysteretic desorption loop (Fig. 5a). Between 268 and 283 K, NOTT-203 gives type-IV isotherms with apparent adsorption/desorption hysteresis loops. A maximum uptake of 13.6 mmol g^{-1} (86.9 wt%) was recorded at 268 K and 1.0 bar. At low SO_2 pressure (below 0.1 bar), narrow hysteresis loops between SO_2 uptake of 0 and ~7 mmol g^{-1} were observed at all three temperatures. At higher temperatures of 293-303 K, the hysteresis loops at high SO_2 pressure disappear and corresponding desorption isotherms give good reversibility. However, the hysteresis loops at low SO_2 pressure (below 0.15 bar) are still present but much narrower than those at low temperatures. Interestingly, NOTT-203 show similar uptake capacities of SO_2 at 1.0 bar for all three temperatures (293, 298 and 303 K), suggesting that similar SO_2-host systems are achieved at 1.0 bar for all three temperatures (Fig. 5a). This observation is unusual for physisorption in which the uptake capacity is driven by the temperature of the system. Comparison of the SO_2 adsorption isotherms at all six temperatures (Fig. 5a) indicates that at low pressures the uptake capacities decrease gradually with increasing temperature. At increased pressure, adsorption of SO_2 at 293, 298 and 303 K reaches saturation at similar uptake capacities of ~8 mmol g^{-1} at 1.0 bar. In contrast, adsorption isotherm of SO_2 at 293 K, 298 K and 303 K show inflection points above the saturated uptake of ~8 mmol g^{-1} at 0.35 bar, 0.45 bar and 0.75 bar, respectively, and a further 2-6 mmol g^{-1} of SO_2 are adsorbed at 1.0 bar, indicating the pore structure expands to allow additional SO_2 uptakes under these conditions. These results suggest that NOTT-203 has excellent capacity and ability for SO_2 capture.

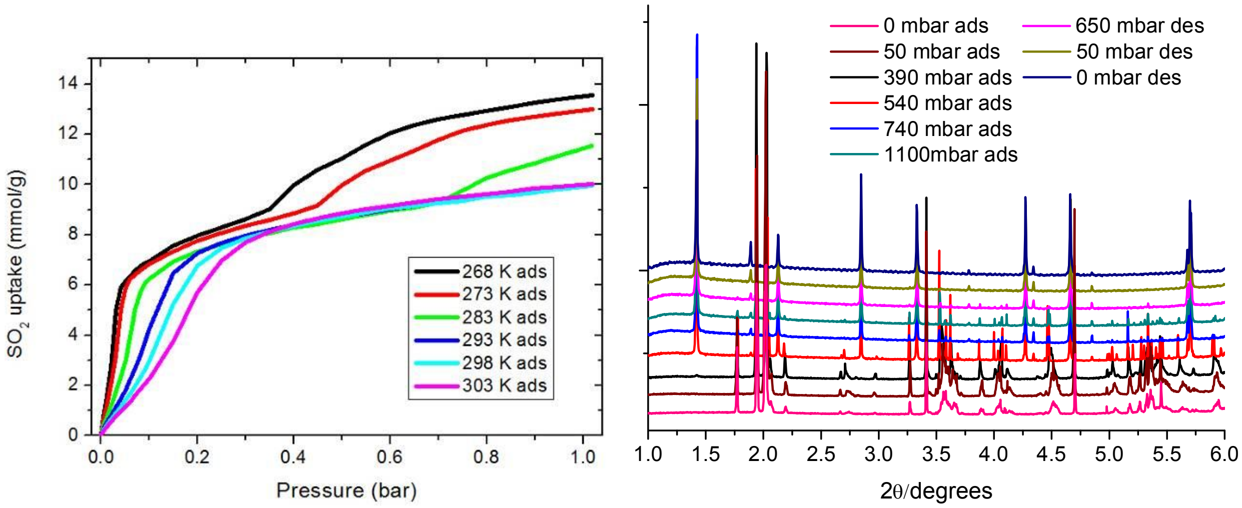

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Figure. 5 (a) SO_2 sorption isotherms for NOTT-203 at 268—303 K; (b) *in-situ* PXRD patterns for NOTT-203 at 273 K.

We then measured the *in-situ* PXRD for the desolvated material at different SO_2 loadings at 273 K to track the framework phase change during the sorption process (Fig. 5b). A dramatic change on the powder diffraction patterns was observed upon SO_2 inclusion at a particular pressure (540 mbar), and the framework phase change is irreversible upon removal of SO_2 molecules (see 0 mbar des). The shift of the diffraction peaks to lower 2θ angle indicates an expansion of the unit cell, consistent with the larger pore phase suggested from the sorption isotherm results. The powder pattern at the final stage (after adsorption and desorption of SO_2) can be indexed to a trigonal cell: the two possible unit cells found are summarised in Table 1. Structure determinations using both these unit cell assignments for this phase are currently under investigation.

Table 1. Comparison of unit cell parameters for as-synthesised, desolvated, and SO_2-loaded samples.

	As-synthesised	Desolvated	SO_2-loaded[a]	SO_2-loaded[b]
Space group	*F*222	*C*2/c	*R*3	*R*3
a (Å)	16.512	19.814	26.6307	30.1057
b (Å)	25.952	28.330	26.6307	30.1057
c (Å)	30.569	26.219	39.6372	31.0791
α (°)	90	90	90	90
β (°)	90	97.866	90	90
γ (°)	90	90	120	120
V (Å^3)	13100	14580	24344.378	24394.802

[a,b] Two possible solutions were obtained from indexing of the powder pattern, and initial refinements suggested both of them fit the experimental PXRD data. Further investigation is currently underway.

Conclusions.

We were able to confirm the framework phase change of a supramolecular framework SOF-2 as a function of CO_2 pressure, and convincingly explain the details of the framework breathing from ***np*** form to ***lp*** form. We were also able to confirm, for the first time, the SO_2-induced framework transition in the indium-based MOF NOTT-203. This helped us to understand its unusual gas adsorption capacity and selectivity at a molecular basis.

Reference:

1. J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1201-1507.