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Direct visualisation of carbon dioxide adsorption in
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The crystal structures of zeolitic imidazolate framework 7 (ZIF-7) under various CO₂ pressures were studied by high-resolution neutron powder diffraction. CO₂ adsorption in ZIF-7 is visualised and demonstrated to be primarily controlled by the benzimidazolate ligands via a gate-opening mechanism. Our results highlight the importance of pressure on the CO₂ adsorption and the related structural framework responses in ZIF-7.

Zeolitic imidazolate frameworks (ZIFs) are important members of the family of metal organic framework (MOF) materials. They can act as host frameworks for CO₂ adsorption, with important potential applications in low-temperature CO₂ separation and sequestration technology. ZIFs are so-called because of their zeolite-like structures, but instead of aluminosilicate frameworks they are composed of transition metal cations coordinated by imidazolate ligands. There has been considerable interest in ZIFs' structure–property relations and the influences of modifications of its zeolite-like structures. ZIF-7 (Zn(PhIm)₂, PhIm = benzimidazolate) is a typical ZIF with sodalite (SOD) framework topology.^{1,2} Due to the phenyl group in its benzimidazolate ligands, the structure and properties of ZIF-7 are distinct from its more commonly-considered cousin, ZIF-8 (ref. 1 and 3–10) and aluminosilicate sodalites which share similar cubic crystalline topology. ZIF-7 has previously been shown to

exhibit gate-opening behaviour during CO₂ sorption.^{11,12} Its framework flexibility was shown to be related to a reversible structural phase transition upon loading and unloading of CO₂ guest molecules into the nanoporous host structure.¹³ Theoretical calculations indicate that the benzimidazolate ligands in ZIF-7 may be the key to its framework flexibility and related unique CO₂ sorption behaviour.^{11,12,14}

If we are to develop a better understanding of the CO₂ adsorption process in ZIF-7 and the functionality of the benzimidazolate ligands, it is necessary to elucidate the guest molecular configurations and framework response of ZIF-7 during CO₂ incorporation, ideally by direct crystal structural study. To this end, we have employed high-resolution neutron powder diffraction to monitor the structural effects associated with CO₂ adsorption in ZIF-7 under industrial CO₂ pressures. Our results show the dominant role of benzimidazolate ligands in the CO₂ adsorption process in ZIF-7. They also reveal the importance of gas loading pressure on the guest–host relationships in the ZIF-7 (CO₂) system.

Deuterated ZIF-7 (D-ZIF-7) powder (0.14 g) was prepared based on the procedure described previously, but employing deuterated benzimidazole as reagent.¹² The sample was placed into an aluminium can with gas loading system. Neutron powder diffraction measurements were performed under *p*CO₂ = 0, 50, 100, 200 kPa at 300 K using high-resolution neutron powder diffractometer D2B at the Institut Laue-Langevin. Before data collection, in order to remove all possible residing guest molecules, the sample was heated from 300 to 393 K at a rate of 1 K min⁻¹ under vacuum; the temperature was then kept at 393 K for 2 hours before cooling to 300 K (1 K min⁻¹) for neutron diffraction measurements. The crystal structure of guest-free D-ZIF-7 was refined by the Rietveld method^{15,16} using Topas 4.1,¹⁷ using the hydrogenated ZIF-7 structure given by Yaghi *et al.* as the starting model.¹ The determination of the location of CO₂ molecules in the D-ZIF-7 (CO₂) structure under *p*CO₂ = 50 kPa was carried out using Fourier difference maps generated by GSAS.^{18,19} Further input from DFT calculation indicated that two CO₂ adsorption sites are most reasonable for

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[†] Electronic supplementary information (ESI) available: Synthesis and characterisation of D-ZIF-7 sample, neutron powder diffraction details, structure refinement methods and illustrations of D-ZIF-7 (CO₂) structures. CCDC 973356–973359. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ta13981f

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Rietveld refinement of the internal structure of D-ZIF-7 (CO₂) under $p\text{CO}_2 = 50, 100, 200$ kPa. In particular, the modelling of D-ZIF-7 (CO₂) structure ($p\text{CO}_2 = 100$ kPa) was carried out by combined-Rietveld refinement on two neutron diffraction datasets obtained using different incident beam wavelengths $\lambda = 1.5946$ and 2.3909 Å. Further experimental details are provided in the ESI.†

Both CO₂ adsorption sites reside in the small cavities formed by the benzimidazolate ligands in the six-membered rings of zinc atoms (Fig. 1). They are designated A and B according to their host cavity features. Cavity A has the largest void in ZIF-7 and has previously been proposed as the primary gas adsorption site.¹¹ Its zinc ring plane is perpendicular to the 3-fold rotoinversion axis and the benzimidazolates point towards the axis to form a rhombohedral cage. Cavity B, on the other hand, has lower point symmetry and is open. Comparing it with Cavity A, one notes that the two opposing benzimidazolates in Cavity B point away from the cavity axis and the six-membered ring formed by the zinc atoms is distorted. The Wyckoff multiplicities of cavities A and B in ZIF-7 structure are 6 and 18, respectively. There is no significant CO₂ adsorption either around zinc four-membered rings or in the topological beta-cage of ZIF-7. The CO₂ adsorption sites in ZIF-7 share certain similarities with those in ZIF-8: the dominant gas adsorption sites in ZIF-8 are in a Cavity A type pores formed by methylimidazolates.^{20–23} In ZIF-7 the benzimidazolate ligand the controlling factor on CO₂ adsorption.

CO₂ adsorption site preferences revealed by our experimental data are in excellent agreement with recent simulation results from *Morris et al.*¹⁴ Simulated binding energies indicate Cavity B is more energetically preferable than Cavity A for CO₂ adsorption. Experimental CO₂ occupancies (Table 1) confirm this adsorption preference. This is due to the geometry differences between the two cavities. Since Cavity B is relatively open, it accommodates guest incorporation and transportation more readily. While one might anticipate small differences between the behaviour of hydrogenous ZIF-7 and deuterated ZIF-7, due to mass differences, the correspondence of our results with those of *Morris et al.*¹⁴ indicates that such differences are not significant within the framework of this study.

In guest-free D-ZIF-7, the diameter of the largest guest-accessible window in Cavity A is ~ 3 Å. Considering the Lennard-Jones

Table 1 Physical data of D-ZIF-7 (CO₂) structures under various CO₂ pressures. (space group: $R\bar{3}$)

$p\text{CO}_2$ [kPa]	0	50	100	200
CO ₂ occupancy	A	0	0.35	0.26
	B	0	0.53	0.68
Calculated total CO ₂ uptake [mmol g ⁻¹]	0	2.60	2.76	2.73
$a = b$ [Å]	22.94	23.00	22.88	22.95
c [Å]	15.75	15.76	15.66	15.71
V [Å ³]	7178	7224	7098	7165

collision diameter of CO₂ (4.05 Å),²⁴ it is very difficult for CO₂ to enter into Cavity A *via* this window if the structure is static. The rotational freedom of the benzimidazolate ligands plays an important role in accommodating guest molecule transport and dynamics.¹¹ There are a number of examples from the literature showing that the static crystal structure and dynamic radii of guest molecules do not always match.^{25–29} Thus, it is reasonable that Cavity A has some adsorption capacity. Cavity B, on the other hand, has much larger guest accessibility than Cavity A. The benzimidazolates with phenyl group pointing away from the cavity axis open up to form a large channel (diameter ~ 5 – 6 Å) for CO₂ adsorption. The topological beta-cage of ZIF-7 plays little part in CO₂ incorporation from both theoretical and experimental aspects; we attribute this to the strong steric effect from phenyl rings. It is worth noting that along with the increase of pressure, CO₂ molecules tend to aggregate in Cavity B while leaving Cavity A relatively empty. This phenomenon is of interest for further investigation on the CO₂ transportation in ZIF-7; the direct CO₂ transport route from Cavity A to B is *via* the beta-cage, however, CO₂ transport barriers from Cavity A and B into beta-cage are very high, therefore the actual CO₂ transport route is uncertain and expected to be influenced by the benzimidazolate ligands.

A CO₂-induced gate-opening process in D-ZIF-7 is indicated by our experimental results. Compared with the previous experimental CO₂ adsorption isotherms,^{13,14} the calculated total CO₂ uptake in our D-ZIF-7 (CO₂) structures (Table 1) suggests that at $p\text{CO}_2 = 50$ kPa the D-ZIF-7 sample is nearly fully saturated with CO₂. Examining our D-ZIF-7 structural results we notice that the unit cell expands when CO₂ pressure increases from 0 to 50 kPa. The benzimidazolate ligands of both Cavity A and B rotate to open up those cavities for CO₂ adsorption (Fig. 2). When the CO₂ pressure increases from 50 to 100 kPa, the total amount of CO₂ adsorbed increases. At this stage, although CO₂ begins to flow into Cavity B, the benzimidazolates at Cavity A continue to rotate to increase the accommodation space for more CO₂ molecules to enter. Meanwhile, at Cavity B, the zinc six-membered ring becomes more distorted due to the movement of the ligands for gate-opening. It seems that the ligand movement in Cavity B induces an electrostatic field change in the cavity itself which helps to increase the affinity of CO₂. The distortion of the zinc six-membered ring may be responsible for the subtle shrinkage in the unit cell dimensions.

At higher external CO₂ pressure, from $p\text{CO}_2 = 100$ to 200 kPa, the influence of external pressure on the CO₂ adsorption and structural behaviour of ZIF-7 becomes crucial. Fig. 2c clearly

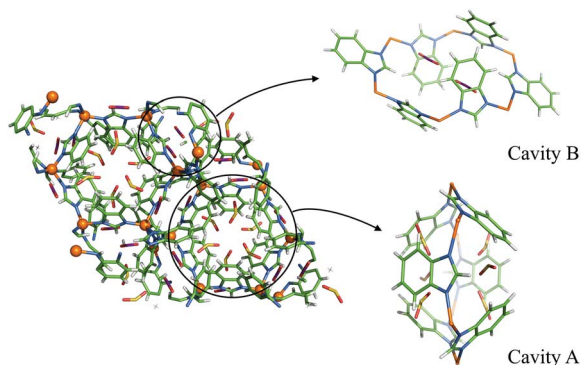


Fig. 1 D-ZIF-7 (CO₂) structure, $p\text{CO}_2 = 50$ kPa. Zn: orange, C: cyan, N: blue, H/D: silver. CO₂: C in Cavity A yellow, in Cavity B purple; O, red.



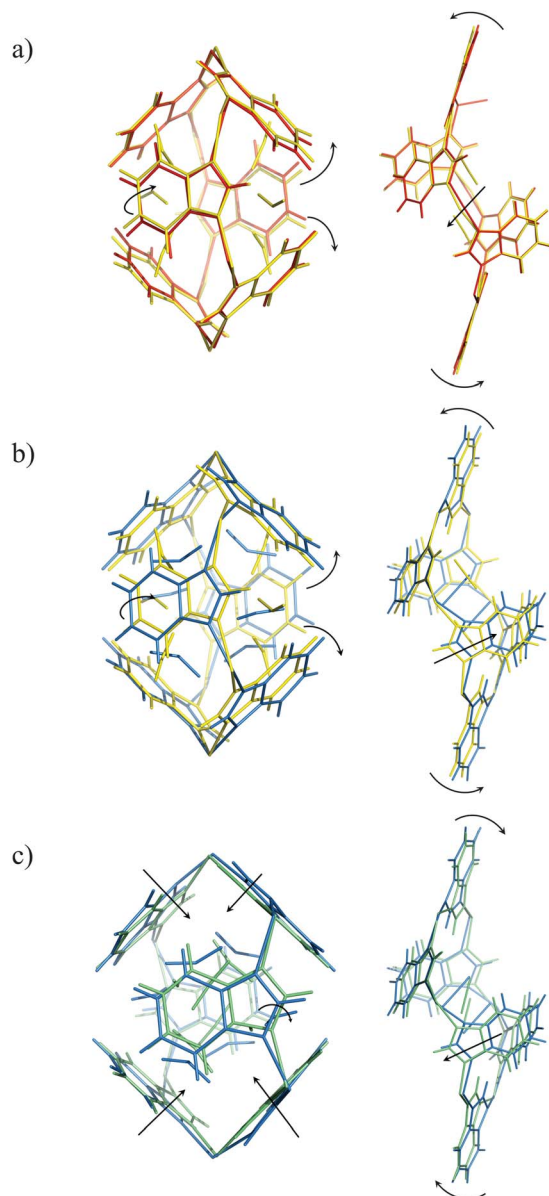


Fig. 2 Dynamic structural behaviours of Cavity A (left) and B (right) at $p\text{CO}_2 =$ (a) 0 (red) to 50 (yellow) kPa; (b) 50 to 100 (blue) kPa; 100 to 200 (cyan) kPa.

shows that Cavity A is squeezed by the external pressure instead of continuing to open up for internal CO_2 adsorption in this pressure regime. At Cavity B, the zinc six-membered ring becomes less distorted and ligands move in the opposite sense compared to that seen upon pressure change from 50 to 100 kPa. This ligand movement induces anomalous unit cell expansion. For CO_2 pressures from 100 to 200 kPa the total CO_2 uptake and CO_2 occupancy hardly increase any further. This suggests that the extrusion of Cavity A by increasing pressure inhibits further CO_2 adsorption and transportation to Cavity B. The effect of external vs. internal pressure also influences the CO_2 locations as a function of $p\text{CO}_2$. This is illustrated in Fig. 3, where both CO_2 adsorption sites are seen to move into the centre of Cavity A and B upon increasing $p\text{CO}_2$.

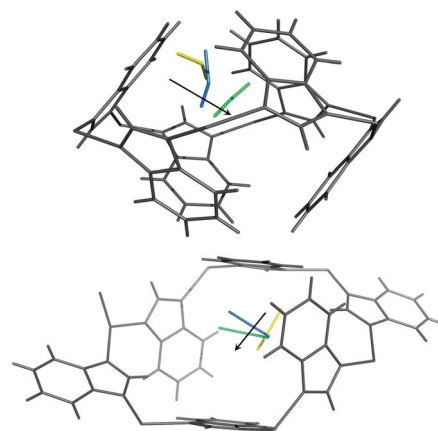


Fig. 3 The CO_2 adsorption site at Cavity A (upper figure) and B (lower figure) at $p\text{CO}_2 =$ 50 (yellow), 100 (blue), 200 (cyan) kPa.

Conclusions

In summary, using high-resolution neutron powder diffraction, we have determined the CO_2 adsorption geometry and site preference in ZIF-7. The results illustrate the importance of the benzimidazolate ligands in controlling the CO_2 affinity and structural flexibility of ZIF-7. They also reveal the influence of pressure in the CO_2 adsorption process in ZIF-7. This is of most importance in understanding the potential of these materials in gas storage and separation in industrial processes. We find that the gas adsorption properties of ZIF-7 depend upon a balance between the internal pressure of the guest molecule and the external gas pressure imposed at the higher range of pressures applied. We will explore the role of the latter in future studies of the structural response of ZIF-7 under different imposed pressures with a variety of guest molecules.

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